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asymmetric supercapacitors	Journal of Materials Science	2019/02	曾珍	17023110	5
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LED 封装硅胶增黏剂的合成及黏接性能研究	南昌航空大学学报: 自然科学版	2020/09	游文	15023225	2
加成型液体硅橡胶增粘剂研究概述	当代化工研究	2020/06	游文	15023225	2
季戊四醇四苯甲酰甲酸酯的合成及光引发性能	应用化学	2018/06	周玉炳	13023230	5

Preparation and Characterization of a Novel Terbium Complex Coordinated with 10-Undecenoic Acid for UV-Cured Coatings	International Journal of Polymer Science	2020/02	章红飞	13023226	4
Low-crystalline Ni/Co-oxyhydroxides nanoarrays on carbon cloth with high mass loading and hierarchical structure as cathode for supercapacitors	Electrochimica Acta	2020/08	郭瑶	17023105	5

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Molten NaCl-induced MOF-derived carbon-polyhedron decorated carbon-nanosheet with high defects and high N-doping for boosting the removal of carbamazepine from water†

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The efficient removal of endocrine-disrupting pollutants (EDCs) from water is a crucial issue for improving the quality of drinking water. Herein, hierarchically structured carbon composites (HCCs) composed of carbon-polyhedron decorated carbon nanosheets were fabricated using the zeolite imidazole framework-8 (ZIF-8) as the precursor in the presence of molten NaCl. The as-prepared hierarchical carbon composites showed higher specific surface areas, more defects, high N-doping, and hydrophilicity compared with the NaCl-free ZIF-8-derived carbon polyhedrons (CPs). In addition, the as-prepared HCCs exhibited boosted adsorption performances for the removal of the model EDC, namely carbamazepine (CBZ), surpassing CPs and commercial powdered activated carbon (AC). The adsorption kinetics showed that HCCs possessed a higher sorption rate as compared to CPs and AC. In the initial 5 min, the adsorption amount of CBZ on HCCs reached 94.9% of the adsorption quantity at equilibrium. Furthermore, the maximum adsorption capacity of CBZ on HCCs is 248.7 mg g⁻¹, which is superior to that of CPs and AC. X-ray photoelectron spectroscopy characterizations indicated that the predominant factors for controlling the adsorption of CBZ on HCCs are π - π electron donor-acceptor interactions and hydrogen bonding, although, some of the adsorbed CBZ molecules were decomposed by oxidation. Finally, a fixed-bed experiment demonstrated that the HCCs have great potential as a filler for the purification of tap water.

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Environmental significance

Endocrine-disrupting chemicals (EDCs) can cause adverse effects on the nervous, immune, and reproductive systems of humans and animals, even at low concentrations. EDCs can be found in a variety of sources such as pesticides, children's products, food-contact materials, and personal care products. Food and water are the main ways of contracting EDCs. Therefore, it is vital to remove EDCs from food and drinking water. Carbamazepine is a typical EDC that is widely used in the treatment of epilepsy to control seizures and as an analgesic for trigeminal neuralgia and mental disorders. In this study, we have developed a facile method to prepare hierarchical-structured carbon composites from porous coordination polymers for the removal of EDCs from water.

1. Introduction

In recent years, increasing number endocrine-disrupting chemicals (EDCs) have been detected in drinking water. EDCs can cause adverse effects on the nervous, immune, and

reproductive systems of humans and animals, even at concentrations as low as 1–10 ng L⁻¹.^{1–4} Carbamazepine (CBZ) is one of the typical EDCs and is widely used in the treatment of epilepsy to control certain types of seizures and as an analgesic for trigeminal neuralgia and mental disorders.^{5,6} Because of its poor biodegradability, the removal efficiency of CBZ from water is less than 10% by conventional treatment methods,⁶ resulting in the ubiquitous presence of CBZ in surface water and tap water. Therefore, it is vital to remove these EDCs to improve the quality of water.

In general, the techniques and methods for the removal of EDCs from water include advanced oxidation, membrane bioreactors, and ozonolysis. Among these, physical adsorption is one of the most competitive approaches owing

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to its high efficiency, low cost, and simplicity of operation at ambient temperature. In order to completely remove EDCs, a sorbent with high adsorptive capacity, fast adsorption rate, and easy regeneration is highly desired. Activated carbon (AC) has been widely used as a sorbent in domestic water purification devices for the removal of EDCs from tap water. However, commercial AC has been found to possess several disadvantages, such as low adsorption capacity, slow adsorption rate, and low efficiency for the removal of EDCs, particularly in the treatment of complicated water systems. Consequently, it is urgent to develop a highly efficient sorbent to replace commercial AC to improve water quality.

Metal-organic framework (MOF)-derived porous carbon materials have demonstrated excellent adsorption performance for removing EDCs from water owing to their high specific surface area, high porosity, hierarchical pores, and heteroatom doping.^{7–19} ZIF-8-derived porous carbon possesses high adsorption capacities of 320 mg g^{−1} and 400 mg g^{−1} for ibuprofen and diclofenac from water, respectively.¹¹ Moreover, ZIF-8-derived porous carbon has been used to remove ciprofloxacin from water with a high adsorption capacity of 416.7 mg g^{−1}, which is much higher than that of commercial AC.¹⁶ Bio-MOF-1-derived porous carbon shows high adsorption capacities for both the acidic clofibric acid (540 mg g^{−1}) and the basic atenolol (552 mg g^{−1}).¹² ZIF-67-derived porous carbon demonstrated high adsorption performance for the removal of aromatic compounds.¹³ Although these MOF-derived porous carbon materials demonstrate high adsorption capacities for EDCs in water, the removal efficiency of EDCs is still low, especially the adsorption kinetics, making it difficult to meet the demand for the purification of domestic tap water.

Recently, modifiers, such as KOH,¹⁰ (NH₄)₂WS₄,²⁰ and KCl/LiCl,²¹ were used to tune the microstructures and improve the corresponding performance of MOF-derived porous carbon materials. For example, the use of KOH not only effectively enhanced the surface area and pore volume of MOF-derived carbon but also stimulated the transformation of the initial morphologies of MOF-derived carbon (such as from polyhedrons and rods to honeycomb and ribbons, respectively).^{10,22} Furthermore, guests like (NH₄)₂WS₄ or (NH₄)₂WS₄ in MOFs can transform the common HKUST-1-type MOFs into complex porous carbon with hierarchical structures through high-temperature MOF-guest interactions.²⁰ Moreover, molten salts, including KCl, LiCl, and NaCl, can transform MOF nanoparticles into carbon nanosheets,²¹ 3D nanosheet-linked-polyhedron carbon,²³ and web-like interconnected carbon networks.²⁴ These MOF-derived porous carbons have exhibited enhanced performance in energy storage and catalysis due to their high surface area and pore volume, as well as their hierarchical structures. We speculate that these porous carbon materials with hierarchical structures are excellent sorbent candidates for the removal of EDCs from water.

Herein, porous carbon materials with hierarchical structures (HCCs) have been fabricated in the presence of molten NaCl

using ZIF-8 as the precursor. The resulting as-prepared HCCs are composed of carbon-polyhedrons and carbon nanosheets and possess a much higher specific surface area than that of ZIF-8-derived carbon polyhedrons (CPs). CBZ was used as a model EDC pollutant to compare the adsorption performances of HCCs, CPs, and commercial powdered AC to evaluate their adsorption capacities, removal efficiencies, and removal rates. Furthermore, the effects of water temperature, pH, and other factors on the adsorption performances were also investigated, and the adsorption interactions between HCCs and target pollutants were clarified. Finally, the feasibility of using HCCs as a filler for domestic water purifiers was evaluated using a fixed-bed system.

2. Experimental

2.1 Materials and reagents

2-Methylimidazole (HMIM) and carbamazepine (CBZ) were purchased from Aladdin (Shanghai, China). Methanol was purchased from Damao Chemical Reagent Factory (Tianjin, China). NaCl, Zn(NO₃)₂·6H₂O, HCl (37 wt%), NaOH were purchased from Xilong Scientific Co., Ltd. (Guangdong, China). Powdered AC was purchased from Macklin (Shanghai, China). All reagents were AR grade and were used without further purification.

2.2 Synthesis of HCCs and CPs

Firstly, ZIF-8 nanoparticles were prepared as follows: 2.947 g of Zn(NO₃)₂·6H₂O and 6.551 g of HMIM were separately dissolved in 500 mL of methanol. Then, the methanol solution with Zn(NO₃)₂·6H₂O was added dropwise into the methanol solution of HMIM under stirring for 24 h. The obtained ZIF-8 nanoparticles were collected by centrifugation, washed with methanol and dried at 60 °C for 12 h. Second, 200 mg of ZIF-8 nanoparticles were suspended in 10 mL of aqueous solution containing 600 mg of NaCl. The resulting mixture was dried at 80 °C, then the obtained ZIF-8/NaCl powder was placed in a porcelain boat and transferred to a tube furnace and calcined under N₂ atmosphere at 900 °C for 2 h with the heating rate of 2 °C min^{−1}. The resulting black sample was washed with 10 wt% HCl to remove any inorganic impurities, and then washed thoroughly using distilled water to pH = 7 and dried at 80 °C for 24 h to give the as-prepared HCCs product. Carbon polyhedrons (CPs) were prepared by the calcination of ZIF-8 nanoparticles using the above heat-treatment process in the absence of NaCl.

2.3 Characterization

The phases of the samples were characterized by X-ray diffraction (XRD) on a D8 Advance X-ray diffractometer (Bruker) with Cu Kα radiation ($\lambda = 1.5406 \text{ \AA}$) at a scan rate of 4° min^{−1}. The pore structure of the samples was analysed by N₂ adsorption-desorption isotherms on a TriStar II 3020 surface area & pore size analyser (Micromeritics). The defects of the samples were characterized by Raman spectroscopy on

a Lab RAM HR800 Laser Raman spectrometer (HORIBA Jobin Yvon) using a 647 nm argon-ion laser. The morphologies and microstructures of the samples were observed using a Quanta 450 scanning electron microscope (SEM) and Talos F200X transmission electron microscope (TEM) (FEI), respectively. The elements and corresponding chemical states in the surface of the samples were analysed by X-ray photoelectron spectroscopy (XPS) on an Axis Ultra (Kratos) XPS spectrometer. The surface zeta potentials of the samples were determined using a Zetasizer Nano-ZS90 particle size/potential analyser (Malvern). The wettability of HCCs, CPs, and AC tablets, which were prepared using a tableting machine under 10 MPa, was measured on an optical contact angle meter (DSA 20, Krüss, Germany). UV-vis absorption spectroscopy was used to calculate the residual concentration of CBZ in solution.

2.4 Sorption experiments

2.4.1 Batch adsorption. All isothermal adsorption experiments were performed in a gas-bath oscillator at 180 rpm with a pre-set temperature. Sorbent (20 mg) was added to the conical flasks containing 50 mL of target pollutant aqueous solution (DI water) with the concentration (C_0) ranging from 10–100 mg L⁻¹. To evaluate the effect of solution pH, the initial pH of the CBZ solution (pH = 2–12) was adjusted with 1 M HCl or 1 M NaOH solution. After the adsorption reached equilibrium, the sorbent was immediately removed through filtration using 0.45 µm Millipore membrane filters. Tap water was used to further assess the effects of the components in the water on the adsorption capacities of the as-prepared sorbents. The quantity of CBZ adsorbed per unit mass of sorbent was calculated using eqn (1).

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where C_0 (mg L⁻¹) and C_e (mg L⁻¹) correspond to the initial concentration of CBZ and the concentration at the equilibrium of CBZ, respectively, V (L) is the volume of solution and m (g) is the mass of sorbent.

2.4.2 Adsorption kinetics. The sorbent (200 mg) was added to 500 mL of the target pollution solution (100 mg L⁻¹) with constant vibration at a rate of 180 rpm. At the predetermined time, 1.5 mL of solution was collected and immediately filtered to remove suspended sorbent through 0.45 µm membrane filters.

2.4.3 Fixed-bed application. Fixed-bed columns are generally used to continuously remove contaminants. The sorbents that are close to the inlet are first saturated through adsorption. As the process continues, the target contaminant concentration at the outlet of the column is higher than the setting concentration ($C/C_0 = 0.1$, $C/C_0 = 0.5$), called the breakdown point.²⁵ The ratio of solution volume to sorbent volume (bed volume, BV) and residual (C_e/C_0) were used to plot a curve called the breakthrough curve, and this curve was used to describe the working process of the fixed-bed

column. In the fixed-bed tests, columns were packed with HCCs, CPs, and ACs, respectively. The column has a bed depth of 0.5 cm (~0.2 g of sorbent) and a diameter of 1.3 cm. The breakthrough curves of HCCs, CPs, and AC for the removal of CBZ from tap water were studied in a continuous-flow fixed-bed column at a flow rate of 3 mL min⁻¹, and the initial target pollutant concentration was 10 mg L⁻¹. At given time intervals, the CBZ solutions from the outlet of the column were collected, and the concentrations were determined and analysed using UV-vis spectrophotometry. To evaluate the reusability of the HCCs in the fixed-bed column, 1 L of NaOH solution (0.5 mol L⁻¹) and 500 mL of methanol were used to wash CBZ in the HCCs columns at the flow rates of 3 and 4 mL min⁻¹, respectively. In addition, the HCCs were also regenerated by heat-treatment at 600 °C for 30 min with a heating rate of 5 °C min⁻¹ under N₂. The recycled HCCs columns were reused to continuously remove target pollutants from tap water.

3. Results and discussion

3.1 Characterization

Fig. 1 depicts the synthesis procedure of the HCCs. Firstly, the ZIF-8/NaCl hybrid powder (simply mixed with ZIF-8) was heated to 900 °C from room temperature and remained at 900 °C for 2 h under an N₂ atmosphere. Polyhedral ZIF-8 nanocrystals were converted to carbon polyhedrons, and some of the carbon polyhedrons were transformed into carbon nanosheets under the induction of molten NaCl. After the removal of inorganic impurities in the composites, the HCCs were successfully prepared.

Fig. S1† shows the XRD patterns of the as-prepared ZIF-8 nanoparticles and ZIF-8/NaCl hybrids. For the as-prepared ZIF-8 nanoparticles, the characteristic peaks matched very well with the simulated pattern. After physically mixing with NaCl, there were no obvious changes in the diffraction peaks of ZIF-8, and the sharp peaks at 32°, 45°, 58°, and 68° were attributed to the NaCl (PDF #05-0628). This indicates that the mixing of NaCl and ZIF-8 does not affect the crystal structure of ZIF-8. Fig. 2a shows the XRD patterns of the as-prepared HCCs and CPs from the calcination of the ZIF-8/NaCl hybrids and ZIF-8 nanoparticles, respectively. The XRD patterns of HCCs and CPs

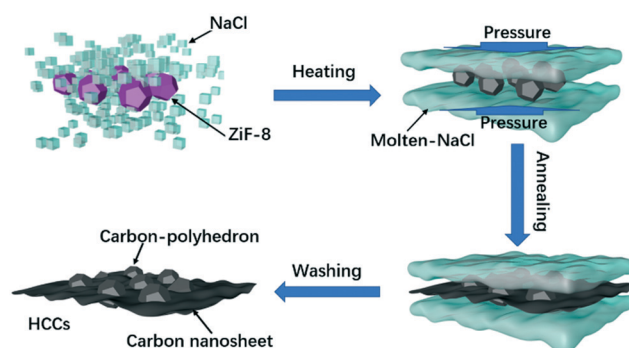


Fig. 1 Schematic showing the preparation of ZIF-8-derived HCCs.

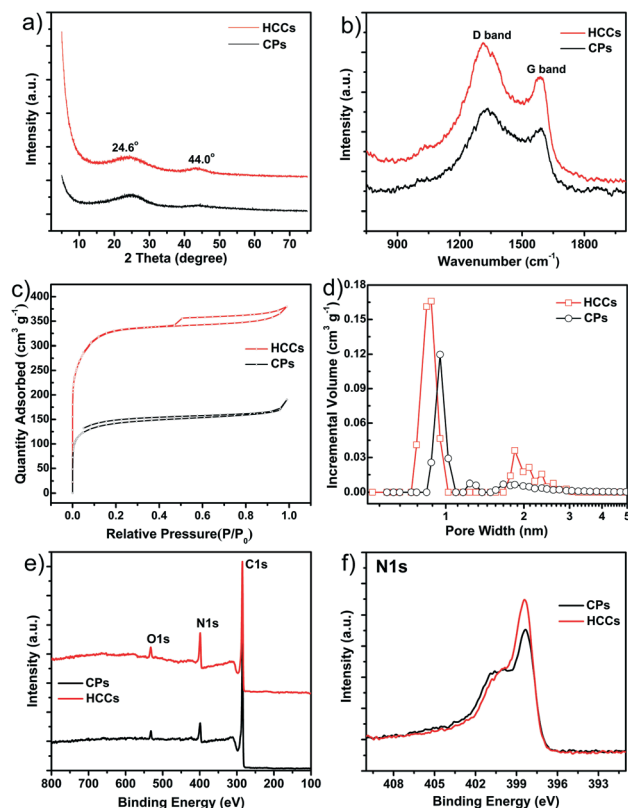


Fig. 2 a) XRD patterns, b) Raman spectra, c) nitrogen adsorption-desorption isotherms, d) pore size distribution curves, e) XPS survey scan and f) N1s spectra of CPs and HCCs.

are completely consistent with the typical amorphous pyrolytic porous carbon materials.¹⁵ In the low-angle region, the relatively high diffraction intensities indicate that there are abundant micropores in both HCCs and CPs.²⁶ Meanwhile, the obvious increase in the low-angle scattering from HCCs suggests the presence of a high density of pores. In addition, two diffuse scattering peaks at about $2\theta = 24.6$ and 44.0° are broad, suggesting that both HCCs and CPs are amorphous.²⁷ Raman spectroscopy was used to observe the defects of the as-prepared HCCs and CPs. Two characterization bands at around 1320 cm^{-1} (D band) and 1580 cm^{-1} (G band) can be observed in the Raman spectra (Fig. 2b) of HCCs and CPs. The band corresponds to the defects and disorder-induced mode in carbon materials. The G-band represents the graphitic mode for $\text{sp}^2\text{-C}$ domains.²⁸ Generally, the defects of carbon materials are evaluated by the intensity ratio of the D-band to the G-band (I_D/I_G), and a higher I_D/I_G represents more defects. The intensity ratios of I_D/I_G for HCCs and CPs were 1.15 and 1.08, respectively. This indicates that the molten NaCl increases the defects in HCCs, which may improve the adsorption of pollutants on the surface.²⁹

Fig. 2c shows the N_2 adsorption-desorption isotherms of HCCs and CPs. It can be clearly seen that CPs exhibit an ideal type I isotherm based on the IUPAC classification, while the hysteresis loop can be ignored, indicating the micropores in CPs. Meanwhile, the N_2 adsorption isotherm of HCCs

presents a quasi-type I isothermal plot, and a hysteresis loop (type 4) occurs in the P/P_0 range of 0.5–1.0, suggesting the co-presence of micropores and mesopores in the HCCs samples. The type 4 hysteresis loop indicates that there are slit-type pores and it is a layered structure, which suggests that the mesopores may not be generated from inside the particles; instead, they are between particles. The specific surface area (S_{BET}) of HCCs and CPs calculated from the Brunauer-Emmett-Teller (BET) method are listed in Table S1.† The S_{BET} of HCCs is much higher than that of CPs, indicating that the molten NaCl improves the pore structure of the ZIF-8-derived carbon materials. The higher S_{BET} of HCCs provides more active sites for the adsorption of target pollutant molecules as compared to that of CPs. Fig. 2d shows the pore-size distribution of HCCs and CPs calculated by the Tarazona non-local density functional theory (NLDFT) model (cylindrical pores). The pore-size distribution curve of CPs indicates that there are only micropores and almost no mesopores in CPs. However, HCCs possess micropores and mesopores. Most of the micropores fall within the size range of 0.88–1.02 nm, while the mesopores are mainly distributed in the range of 2–3 nm. The above results confirmed that the use of molten NaCl favours the introduction of mesopores and thus increases the pore volume of HCCs. The larger surface area, higher pore volume, and more mesopores provide faster mass transfer and higher adsorption capacity for the removal of target pollutant molecules from water,^{30,31} implying that HCCs may have a faster adsorption rate and higher adsorption capacity as compared to CPs.

XPS spectroscopy was used to analyse the chemical components and their corresponding chemical states of CPs and HCCs. Fig. 2e shows the XPS survey scan spectra of CPs and HCCs. From the spectra, three sharp peaks, C1s, O1s, and N1s, located at 285, 399, and 532 eV, respectively, indicate that the main chemical components in the CPs and HCCs are carbon, nitrogen, and oxygen. In addition, as shown in Fig. 2f and Table S2,† it is remarkable that the N atomic conc% in CPs (9.41%) is lower than that in HCCs (12.45%), suggesting that the molten NaCl effectively holds the N species in the confinement pyrolysis process of ZIF-8. Previous reports have also indicated that the molten salt can effectively help the reserve of N species during the molten salt-confinement pyrolysis process of MOF, organic matter and biomass.^{23,32,33} Our previous work reported that the N-doping could improve the adsorption capacity of CBZ on the surface of porous carbons because of the π - π electron donor-acceptor (EDA) interaction.²⁷ Therefore, the increased N content in HCCs may effectively increase the adsorption capacity of CBZ.

Fig. 3a and b show the typical SEM images of CPs and HCCs, respectively. As illustrated in Fig. 3a, ZIF-8-derived CPs exhibit a polyhedron morphology with a diameter of ~ 100 nm, retaining the initial morphology of ZIF-8 (Fig. S2†). In addition, most CPs are stuck together, which blocks the pores and causes deterioration of the adsorption performance. However, the SEM images of the ZIF-8/NaCl hybrids-derived HCCs (Fig. 3b) illustrate that the carbon

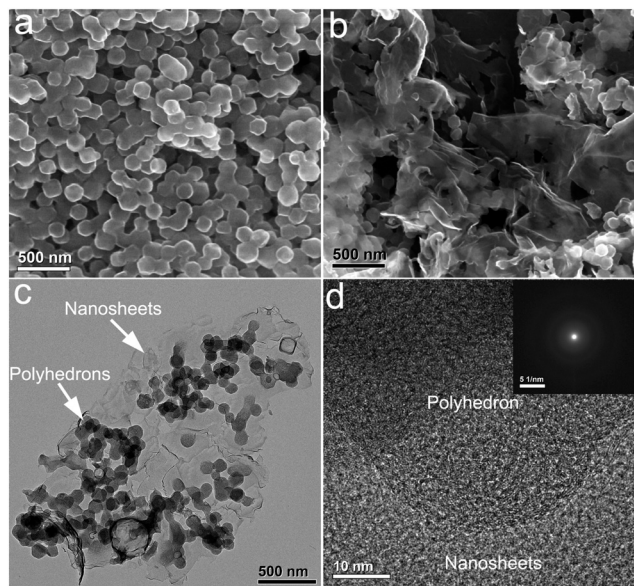


Fig. 3 Typical SEM images of a) CPs and b) HCCs. c) TEM image, d) HRTEM image and SAED pattern (inset) of HCCs.

polyhedrons are decorated on the surface of the carbon nanosheets, suggesting that the molten NaCl induced carbon nanosheet formation from the ZIF-8 precursor, which is similar to previous reports.^{23,34,35} This is thought to be mainly due to the precipitation/dissolution process during the carbon structure growth in the molten salt³⁴ and the confinement effect in NaCl-sealed reactors.²³ Besides, these carbon nanosheets were intertwined to form hierarchical structures, and macropores can be observed in the HCCs. The presence of macropores minimizes the diffusive resistance to facilitate mass transport,^{36,37} which would accelerate the adsorption of target pollutant molecules or ions to the active sites dispersed over the micro and/or mesopores in HCCs. The microstructures of HCCs were further characterized by TEM. Fig. 3c shows the typical TEM image of HCCs. The carbon polyhedrons were connected to each other and anchored to the surface of graphene-like carbon nanosheets. The HRTEM image (Fig. 3d) of HCCs shows no observable lattice fringe in either carbon polyhedrons and carbon nanosheets. Also, the selected area electron diffraction pattern (inset in Fig. 3d) implies that both the carbon polyhedrons and the carbon nanosheets in HCCs are amorphous.

3.2 Adsorption properties

3.2.1 Adsorption kinetics. CBZ was used as the target pollutant to compare the adsorption properties of HCCs, CPs, and commercial powdered AC ($S_{\text{BET}} = 866.9 \text{ m}^2 \text{ g}^{-1}$, pore volume = $0.751 \text{ cm}^3 \text{ g}^{-1}$; please see Fig. S3 and Table S1†). Fig. 4a displays the adsorption kinetics of CBZ on HCCs, CPs, and AC. In the initial stage (5 min), the amount of adsorbed CBZ on the three adsorbents increased quickly and then slowed down until the adsorption equilibrium was reached. The high adsorption rate in the initial stage is

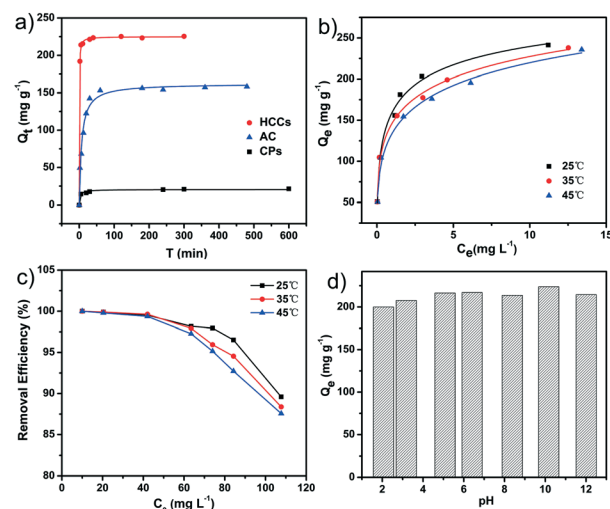


Fig. 4 a) Effects of contact time on the adsorbed amount of CBZ on HCCs, CPs, and AC. b) Adsorption isotherms of CBZ on HCCs and c) the corresponding removal efficiency at different temperatures. d) The effect of pH on the adsorption capacity of CBZ on HCCs.

mainly due to a large number of adsorption sites available on the surface of the adsorbent.³⁸ As shown in Fig. 4a, the required time for the CBZ adsorption equilibrium on HCCs is less than AC and CPs. In the initial 5 min, the adsorption of CBZ on HCCs reached 94.9%, while only reaching 65.6% and 40% for AC and CPs, respectively. The adsorption capacities of CBZ on HCCs, AC, and CPs were calculated to be 225.4, 158.4 and 21.3 mg g^{-1} , respectively. To further understand the adsorption kinetics of CBZ, the pseudo-first-order and pseudo-second-order kinetic models (see section S1†) were used to fit the experimental data. The obtained results are summarized in Table S3.† According to the values of the correlation coefficients (R^2), the pseudo-second-order kinetic model is more suitable for the adsorption of CBZ on HCCs, AC, and CPs, suggesting that the adsorption of CBZ on HCCs, AC and CPs may not be determined by a single factor. To better analyse their adsorption kinetics, the time required to go from the adsorption start to 90% of the maximum adsorption capacity and the corresponding adsorption amount of CBZ were used to evaluate the adsorption rates (see section S2†) the results are summarized in Table S4.† It is obvious that HCCs possess a faster adsorption rate compared to AC, CPs, as well as other reported sorbents for the removal of CBZ.

3.2.2 Adsorption isotherms. From the adsorption isotherms of CBZ on HCCs at different temperatures, as shown in Fig. 4b, it can be clearly observed that the adsorption capacities of CBZ on HCCs decrease with increasing temperature. This indicates that the adsorption of CBZ on HCCs is an exothermic process, which matches well with the results of the thermodynamic studies listed in Table S5.† Furthermore, the increasing initial concentration of CBZ gradually increased the adsorption capacity of CBZ until equilibrium was reached. The corresponding residual amounts of CBZ are shown in Fig. 4c. It was observed that

the removal efficiency of CBZ from water decreased with the increase in the initial concentration. When the initial concentration of the target pollutant was lower than 60 mg L⁻¹, the CBZ removal efficiency of HCCs was higher than 97.2%. To describe the interaction between adsorbates and sorbents, both Langmuir and Freundlich models (see section S3†) were used to fit the experimental data. Table S6† shows the detailed parameters calculated from the two models, and the Langmuir model indicates a better fit of the adsorption data than the Freundlich model, confirming that monolayer adsorption is the main type of adsorption of CBZ on the surface of HCCs. The calculated maximum adsorption capacity of CBZ on HCCs was 248.7 mg g⁻¹ at 25 °C.

3.2.3 Effect of solution pH. Fig. 4d illustrates the effects of solution pH on the adsorption capacity of CBZ. Our previous studies demonstrated that CBZ is very stable under both strong acid and alkali conditions.³⁹ It was observed that the adsorption capacity of CBZ on HCCs increased slightly with the increase in pH (pH < 5) and it was relatively stable when the pH was between 5 and 12. In a wide pH range, 2–12, the HCCs retained high adsorption capacities (>200 mg g⁻¹).

3.2.4 Adsorption mechanisms. The possible adsorption mechanisms between HCCs and CBZ were analysed as follows. First, the ζ potential of HCCs, are presented in Fig. S4† and the isoelectric point of HCCs is 4.89, which indicates that the surface charge of HCCs is positive at pH < 4.89, and negative at pH > 4.89. However, the pK_a value of CBZ is 13.9, suggesting that CBZ is mainly present in its molecular form in the pH range of 2–12. Therefore, the electrostatic interaction between CBZ and HCCs is not the dominant force. Second, log *K*_{ow} of CBZ is 2.45, implying that the adsorption of CBZ on HCCs was mainly controlled by the hydrophobic interaction. However, like the other porous carbon materials, there are O/N containing groups on the surface of the HCCs, which improve the hydrophilicity of HCCs. As shown in Fig. 5, a water droplet completely spread out on the surface of the HCCs tablet after 2 seconds, indicating that HCCs are more hydrophilic than AC and CPs. Therefore, the high adsorption capacity of CBZ on HCCs suggests that the hydrophobic interaction is not the leading role.

Moreover, functional groups, including –COOH, –OH, on the surface of HCCs and –NH₂ in CBZ molecules may form hydrogen bonds, resulting in enhanced adsorption. With the increase in the solution pH, the hydrogen bonding between CBZ and HCCs was largely enhanced. As shown in Fig. 4d,

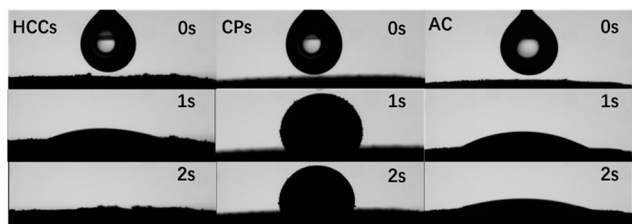


Fig. 5 Dynamic water contact angle measurement for the HCCs, CPs, and AC.

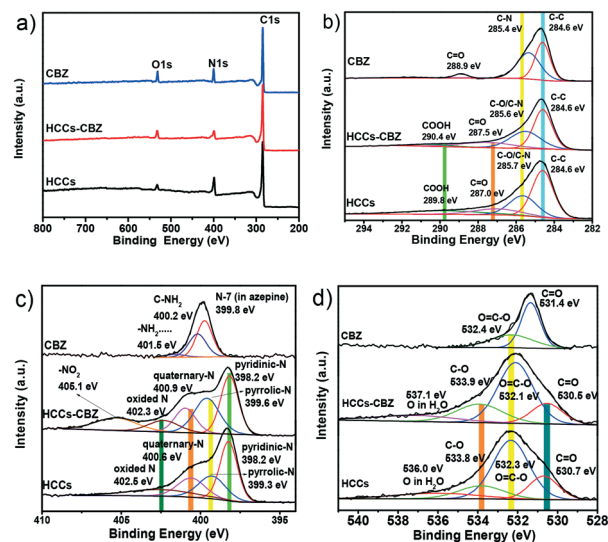


Fig. 6 XPS spectra of CBZ, HCCs and HCCs-CBZ: a) scan survey, b) C1s, c) N1s and d) O1s spectra.

with increasing solution pH, the adsorption capacity of CBZ on HCCs increased and then stabilized in an alkaline environment, which suggests that hydrogen bonding may exist in the adsorption of CBZ on HCCs.

Finally, the π - π electron donor-acceptor (EDA) interaction, which widely exists between aromatic compounds and carbon materials,^{27,40–43} maybe the major surface interaction between CBZ and HCCs. In this respect, the surface chemical environment of HCCs will change before and after the adsorption of CBZ, which can be characterized by XPS analyses. Fig. 6 shows the XPS spectra of CBZ, HCCs prior to adsorption, and HCCs after adsorption of CBZ (HCCs-CBZ), respectively. The spectra (Fig. 6a) show that the main peaks are C1s, N1s, and O1s in CBZ, HCCs, and HCCs-CBZ. The N1s content (Table S2†) on the surface of HCCs was slightly reduced after adsorbing CBZ due to the low N element content in CBZ and the decomposition of CBZ.⁴⁴ Fig. 6b depicts the high-resolution C1s spectra of CBZ, HCCs, and HCCs-CBZ. For CBZ, the C1s spectra can be fitted with three peaks at 284.6, 285.4, and 288.9 eV, which correspond to C–C, C–N, and C=O, respectively, in the CBZ molecule. Because of the electron-withdrawing capability of the amide group, CBZ can act as a π -electron acceptor.⁴⁵ For HCCs, the C1s spectrum can be deconvoluted into four peaks at 284.6, 285.7, 287.0, and 289.8 eV, which were assigned to C–C, C–O/C–N, C=O, and COOH, respectively. These O-containing groups on the surface of HCCs are electron-rich. Both the electron-rich groups and the aromatic benzene rings on the surface of HCCs are electron donor groups; as such the HCCs can be considered as strong π -electron donors. Therefore, we speculate that the adsorption of CBZ onto HCCs is mainly controlled by π - π electron donor-acceptor (EDA) interaction. After the adsorption of CBZ, the C1s of HCCs-CBZ was fitted with four peaks, which were attributed to C–C (284.6 eV), C–O/C–N (285.6 eV), C=O (287.5 eV), and COOH (290.4 eV).

According to the π - π electron donor-acceptor (EDA) interaction, the electron density of the atoms on the surface of HCCs decreased, resulting in the increased binding energy between carbon atoms and oxygen atoms in C=O and COOH. The reduced binding energy of carbon in C-O/C-N groups of HCCs-CBZ may be attributed to the interference of C-N from adsorbed CBZ molecule. The same trend was seen in the XPS spectra of O1s and N1s. Fig. 6c shows the N1s XPS spectra of CBZ, HCCs, and HCCs-CBZ. The N1s XPS spectra of CBZ were fitted to three peaks, corresponding to -N-C in azepine (N-7, 399.8 eV), C-NH₂ (400.2 eV), and -NH₂ (401.5 eV) in CBZ. For HCCs, the N1s XPS spectra could also be deconvoluted into four peaks at 398.2, 399.3, 400.6, and 402.5 eV, which were assigned to the pyridinic N, pyrrolic N, quaternary N, and oxidized N, respectively. After the adsorption of CBZ, four peaks, corresponding to the pyridinic N, pyrrolic N, quaternary N, and oxidized N could still be observed from the N1s spectra of HCCs-CBZ. However, the binding energies of pyrrolic N and quaternary N increased by 0.3 eV over those of HCCs. This implies that the pyrrolic N and quaternary N on the surface of HCCs were involved in the EDA interaction between π -electron donor HCCs and π -electron acceptor CBZ, which further confirmed that CBZ molecules were successfully adsorbed onto the surface of HCCs. Furthermore, in the XPS N1s spectra of HCCs-CBZ, we observed a new peak at 405.1 eV (-NO₂), which can be attributed to the formed superoxide ions on the surface of HCCs leading to the oxidation of CBZ.⁴⁴ Fig. 6d shows the O1s XPS spectra of CBZ, HCCs, and HCCs-CBZ. Two peaks at 531.4 and 532.4 eV in the O1s spectra of CBZ were assigned to O=C and O=C-O, respectively. For HCCs, the O1s spectra were deconvoluted to four peaks at 530.7, 532.3, 533.8, and 536.0 eV, corresponding to C=O in the ketone (lactone) and carbonyl, O=C-O in the carboxyl/carbonyl, C-O-C in the epoxy and ether, and the O in H₂O, respectively. After the adsorption of CBZ on HCCs, the binding energies of C=O and O=C-O were reduced because of the hydrogen bonding between CBZ and HCCs. In contrast, the increased binding energy for C-O-C in the epoxy or ether could be attributed to their reduced electron density in the π - π electron donor-

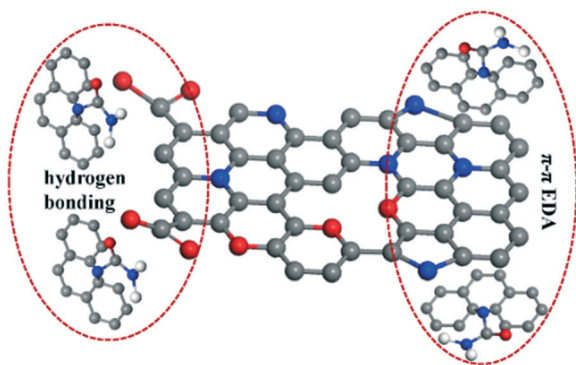


Fig. 7 Schematic illustration of the adsorption mechanism of CBZ on HCCs.

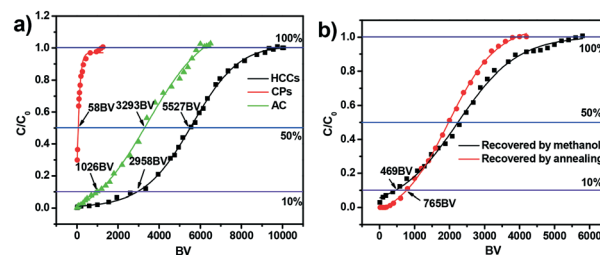


Fig. 8 a) CBZ breakthrough curves through the column filled with HCCs, CPs, and AC, respectively. b) CBZ breakthrough curve through the column filled with recovered HCCs.

acceptor (EDA) interaction. The schematic illustration of the adsorption mechanism is shown in Fig. 7.

3.2.5 Removal of CBZ using a fixed-bed reactor. To explore the practical application of HCCs as a sorbent to remove CBZ from domestic tap water, fixed-bed column tests were performed using tap water containing CBZ at a concentration of 10 mg L⁻¹; the flow rate was set at 3 mL min⁻¹. The CBZ adsorption amounts in DI water and tap water are presented in Fig. S5.† The compositions of the tap water are summarized in Table S7.† Because of the effect of the ionic strength in the tap water, the adsorption capacity of CBZ on HCCs in the tap water is slightly lower than that in DI water. Fig. 8a shows the CBZ breakthrough curve through the columns filled with HCCs, CPs, and AC, respectively. The residual CBZ in the front part of the whole curve increased very slowly because the active sites on the sorbents were almost empty, and the adsorption rate was extremely fast. The residual CBZ amount after passing through the column then showed a linear increase because the active sites were gradually filled until saturation. The 10% breakthrough volumes ($C_0/C_t = 0.1$) of HCCs, CPs, and AC were 2958, 1026, and 0 bed volume (BV), respectively. The 50% breakthrough volumes ($C_0/C_t = 0.5$) of HCCs, CPs, and AC were 5527, 3293 and 58 BV, respectively. This indicated that HCCs can be used as a sorbent for the effective removal of CBZ from tap water. Furthermore, the reusability of the fixed-bed column filled with HCCs was evaluated using solvent elution and heat-treatment, respectively. Fig. 8b shows the CBZ breakthrough curve through the fixed-bed column after recovery. The 10% breakthrough volumes ($C_0/C_t = 0.1$) of the recycled HCCs were reduced to 469 BV and 765 BV by the methanol elution method and calcination, respectively. This indicates that it is difficult to elute the adsorbed CBZ on the surface of HCCs completely, suggesting that the adsorption interaction between CBZ and HCCs is strong. The calcination method can carbonize all the CBZ to liberate the adsorption sites but the produced carbon remained in the pores, reducing the adsorption capacity of the recycled HCCs.

Conclusions

In conclusion, molten NaCl was used to direct the growth of MOF-derived porous carbon materials to enhance their adsorption performance toward EDCs. The as-prepared

hierarchical carbon composites (HCCs) showed a much higher specific surface area, higher N-doping, more defects and hydrophilicity than the NaCl-free ZIF-8-derived carbon polyhedrons (CPs). The batch adsorption results showed that the HCCs possessed greater adsorption capacity, higher removal efficiency, and a faster rate as compared to CPs and commercial powdered AC for the removal of CBZ from water. Furthermore, the effects of solution temperature, pH, and components in tap water indicated that the adsorption of CBZ on HCCs is an exothermic process, and the adsorption capacity of CBZ on HCCs could be increased with the increase in the solution pH, and then stabilized under alkaline conditions. Also, the components in the tap water did not significantly reduce the adsorption capacity of CBZ on HCCs. The adsorption of CBZ on HCCs was mainly controlled by the π - π electron donor-acceptor (EDA) interactions and hydrogen bonding. Finally, the great adsorption performance of HCCs was further confirmed by a fixed-bed adsorption experiment. The impressive results indicate that the introduction of chemical guests into the carbonization of MOFs can effectively improve the morphology, microstructure and surface chemical environment of MOFs-derived porous carbons, resulting in their excellent adsorption performance for the removal of EDCs from water.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

- 1 S. Álvarez-Torrellas, J. A. Peres, V. Gil-Álvarez, G. Ovejero and J. García, Effective adsorption of non-biodegradable pharmaceuticals from hospital wastewater with different carbon materials, *Chem. Eng. J.*, 2017, **320**, 319–329.
- 2 X. Yi, N. H. Tran, T. Yin, Y. He and K. Y.-H. Gin, Removal of selected PPCPs, EDCs, and antibiotic resistance genes in landfill leachate by a full-scale constructed wetlands system, *Water Res.*, 2017, **121**, 46–60.
- 3 E. Archer, B. Petrie, B. Kasprzyk-Hordern and G. M. Wolfaardt, The fate of pharmaceuticals and personal care products (PPCPs), endocrine disrupting contaminants (EDCs), metabolites and illicit drugs in a WWTW and environmental waters, *Chemosphere*, 2017, **174**, 437–446.
- 4 J. M. Braun, Early-life exposure to EDCs: role in childhood obesity and neurodevelopment, *Nat. Rev. Endocrinol.*, 2016, **13**, 161.
- 5 J. M. Monteagudo, A. Durán, R. González and A. J. Expósito, In situ chemical oxidation of carbamazepine solutions using persulfate simultaneously activated by heat energy, UV light, Fe^{2+} ions, and H_2O_2 , *Appl. Catal., B*, 2015, **176–177**, 120–129.
- 6 I. A. Appavoo, J. Hu, Y. Huang, S. F. Y. Li and S. L. Ong, Response surface modeling of Carbamazepine (CBZ) removal by Graphene-P25 nanocomposites/UVA process using central composite design, *Water Res.*, 2014, **57**, 270–279.
- 7 N. L. Torad, M. Hu, S. Ishihara, H. Sukegawa, A. A. Belik, M. Imura, K. Ariga, Y. Sakka and Y. Yamauchi, Direct Synthesis of MOF-Derived Nanoporous Carbon with Magnetic Co Nanoparticles toward Efficient Water Treatment, *Small*, 2014, **10**, 2096–2107.
- 8 J. Y. Song, B. N. Bhadra, N. A. Khan and S. H. Jhung, Adsorptive removal of artificial sweeteners from water using porous carbons derived from metal azolate framework-6, *Microporous Mesoporous Mater.*, 2018, **260**, 1–8.
- 9 M. Sarker, I. Ahmed and S. H. Jhung, Adsorptive removal of herbicides from water over nitrogen-doped carbon obtained from ionic liquid@ZIF-8, *Chem. Eng. J.*, 2017, **323**, 203–211.
- 10 H. J. An, B. N. Bhadra, N. A. Khan and S. H. Jhung, Adsorptive removal of wide range of pharmaceutical and personal care products from water by using metal azolate framework-6-derived porous carbon, *Chem. Eng. J.*, 2018, **343**, 447–454.
- 11 B. N. Bhadra, I. Ahmed, S. Kim and S. H. Jhung, Adsorptive removal of ibuprofen and diclofenac from water using metal-organic framework-derived porous carbon, *Chem. Eng. J.*, 2017, **314**, 50–58.
- 12 B. N. Bhadra and S. H. Jhung, Adsorptive removal of wide range of pharmaceuticals and personal care products from water using bio-MOF-1 derived porous carbon, *Microporous Mesoporous Mater.*, 2018, **270**, 102–108.
- 13 X. Liu, C. Wang, Q. Wu and Z. Wang, Metal-organic framework-templated synthesis of magnetic nanoporous carbon as an efficient adsorbent for enrichment of phenylurea herbicides, *Anal. Chim. Acta*, 2015, **870**, 67–74.
- 14 B. N. Bhadra, J. K. Lee, C.-W. Cho and S. H. Jhung, Remarkably efficient adsorbent for the removal of bisphenol A from water: Bio-MOF-1-derived porous carbon, *Chem. Eng. J.*, 2018, **343**, 225–234.
- 15 X. Li, H. Yuan, X. Quan, S. Chen and S. You, Effective adsorption of sulfamethoxazole, bisphenol A and methyl orange on nanoporous carbon derived from metal-organic frameworks, *J. Environ. Sci.*, 2018, **63**, 250–259.
- 16 S. Li, X. Zhang and Y. Huang, Zeolitic imidazolate framework-8 derived nanoporous carbon as an effective and recyclable adsorbent for removal of ciprofloxacin antibiotics from water, *J. Hazard. Mater.*, 2017, **321**, 711–719.
- 17 B. N. Bhadra, A. Vinu, C. Serre and S. H. Jhung, MOF-derived carbonaceous materials enriched with nitrogen: Preparation and applications in adsorption and catalysis, *Mater. Today*, 2019, **25**, 88–111.
- 18 R. Gusain, N. Kumar and S. S. Ray, Recent advances in carbon nanomaterial-based adsorbents for water purification, *Coord. Chem. Rev.*, 2020, **405**, 213111.

- 19 W. Yang, X. Li, Y. Li, R. Zhu and H. Pang, Applications of Metal–Organic-Framework-Derived Carbon Materials, *Adv. Mater.*, 2019, **31**, 1804740.
- 20 T. Wang, H.-K. Kim, Y. Liu, W. Li, J. T. Griffiths, Y. Wu, S. Laha, K. D. Fong, F. Podjaski, C. Yun, R. V. Kumar, B. V. Lotsch, A. K. Cheetham and S. K. Smoukov, Bottom-up Formation of Carbon-Based Structures with Multilevel Hierarchy from MOF–Guest Polyhedra, *J. Am. Chem. Soc.*, 2018, **140**, 6130–6136.
- 21 Z. Yu, X. Wang, Y.-N. Hou, X. Pan, Z. Zhao and J. Qiu, Nitrogen-doped mesoporous carbon nanosheets derived from metal-organic frameworks in a molten salt medium for efficient desulfurization, *Carbon*, 2017, **117**, 376–382.
- 22 P. Pachfule, D. Shinde, M. Majumder and Q. Xu, Fabrication of carbon nanorods and graphene nanoribbons from a metal–organic framework, *Nat. Chem.*, 2016, **8**, 718.
- 23 Y. Wang, L. Tao, Z. Xiao, R. Chen, Z. Jiang and S. Wang, 3D Carbon Electrocatalysts In Situ Constructed by Defect-Rich Nanosheets and Polyhedrons from NaCl-Sealed Zeolitic Imidazolate Frameworks, *Adv. Funct. Mater.*, 2018, **28**, 1705356.
- 24 Y. Qian, T. An, K. E. Birgersson, Z. Liu and D. Zhao, Web-Like Interconnected Carbon Networks from NaCl-Assisted Pyrolysis of ZIF-8 for Highly Efficient Oxygen Reduction Catalysis, *Small*, 2018, **14**, 1704169.
- 25 X. Peng, F. Hu, T. Zhang, F. Qiu and H. Dai, Amine-functionalized magnetic bamboo-based activated carbon adsorptive removal of ciprofloxacin and norfloxacin: A batch and fixed-bed column study, *Bioresour. Technol.*, 2018, **249**, 924–934.
- 26 Y. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach and R. S. Ruoff, Carbon-Based Supercapacitors Produced by Activation of Graphene, *Science*, 2011, **332**, 1537–1541.
- 27 D. Chen, S. Xie, C. Chen, H. Quan, L. Hua, X. Luo and L. Guo, Activated biochar derived from pomelo peel as a high-capacity sorbent for removal of carbamazepine from aqueous solution, *RSC Adv.*, 2017, **7**, 54969–54979.
- 28 W. Wang, H. Quan, W. Gao, R. Zou, D. Chen, Y. Dong and L. Guo, N-Doped hierarchical porous carbon from waste boat-fruited sterculia seed for high performance supercapacitors, *RSC Adv.*, 2017, **7**, 16678–16687.
- 29 Y.-h. Shih and M.-s. Li, Adsorption of selected volatile organic vapors on multiwall carbon nanotubes, *J. Hazard. Mater.*, 2008, **154**, 21–28.
- 30 R. Kaiser, A. Kulczyk, D. Rich, R. J. Willey, J. Minicucci and B. MacIver, Effect of Pore Size Distribution of Commercial Activated Carbon Fabrics on the Adsorption of CWA Simulants from the Liquid Phase, *Ind. Eng. Chem. Res.*, 2007, **46**, 6126–6132.
- 31 Z. Chang, J. Dai, A. Xie, J. He, R. Zhang, S. Tian, Y. Yan, C. Li, W. Xu and R. Shao, From Lignin to Three-Dimensional Interconnected Hierarchically Porous Carbon with High Surface Area for Fast and Superhigh-Efficiency Adsorption of Sulfamethazine, *Ind. Eng. Chem. Res.*, 2017, **56**, 9367–9375.
- 32 T. Ouyang, K. Cheng, Y. Gao, S. Kong, K. Ye, G. Wang and D. Cao, Molten salt synthesis of nitrogen doped porous carbon: a new preparation methodology for high-volumetric capacitance electrode materials, *J. Mater. Chem. A*, 2016, **4**, 9832–9843.
- 33 X. Deng, B. Zhao, L. Zhu and Z. Shao, Molten salt synthesis of nitrogen-doped carbon with hierarchical pore structures for use as high-performance electrodes in supercapacitors, *Carbon*, 2015, **93**, 48–58.
- 34 X. Liu and M. Antonietti, Molten salt activation for synthesis of porous carbon nanostructures and carbon sheets, *Carbon*, 2014, **69**, 460–466.
- 35 X. Liu and M. Antonietti, Moderating Black Powder Chemistry for the Synthesis of Doped and Highly Porous Graphene Nanoplatelets and Their Use in Electrocatalysis, *Adv. Mater.*, 2013, **25**, 6284–6290.
- 36 M.-H. Sun, S.-Z. Huang, L.-H. Chen, Y. Li, X.-Y. Yang, Z.-Y. Yuan and B.-L. Su, Applications of hierarchically structured porous materials from energy storage and conversion, catalysis, photocatalysis, adsorption, separation, and sensing to biomedicine, *Chem. Soc. Rev.*, 2016, **45**, 3479–3563.
- 37 X. Liu, C. Giordano and M. Antonietti, A Facile Molten-Salt Route to Graphene Synthesis, *Small*, 2014, **10**, 193–200.
- 38 X. Xin, Q. Wei, J. Yang, L. Yan, R. Feng, G. Chen, B. Du and H. Li, Highly efficient removal of heavy metal ions by amine-functionalized mesoporous Fe₃O₄ nanoparticles, *Chem. Eng. J.*, 2012, **184**, 132–140.
- 39 C. Chen, D. Chen, S. Xie, H. Quan, X. Luo and L. Guo, Adsorption Behaviors of Organic Micropollutants on Zirconium Metal–Organic Framework UiO-66: Analysis of Surface Interactions, *ACS Appl. Mater. Interfaces*, 2017, **9**, 41043–41054.
- 40 L. Jiang, Y. Liu, S. Liu, G. Zeng, X. Hu, X. Hu, Z. Guo, X. Tan, L. Wang and Z. Wu, Adsorption of Estrogen Contaminants by Graphene Nanomaterials under Natural Organic Matter Preloading: Comparison to Carbon Nanotube, Biochar, and Activated Carbon, *Environ. Sci. Technol.*, 2017, **51**, 6352–6359.
- 41 C. R. Minitha, M. Lalitha, Y. L. Jeyachandran, L. Senthilkumar and R. T. Rajendra Kumar, Adsorption behaviour of reduced graphene oxide towards cationic and anionic dyes: Co-action of electrostatic and $\pi - \pi$ interactions, *Mater. Chem. Phys.*, 2017, **194**, 243–252.
- 42 O. G. Apul, Q. Wang, Y. Zhou and T. Karanfil, Adsorption of aromatic organic contaminants by graphene nanosheets: Comparison with carbon nanotubes and activated carbon, *Water Res.*, 2013, **47**, 1648–1654.
- 43 F. Gao, X. Chen, K. Yin, S. Dong, Z. Ren, F. Yuan, T. Yu, Z. Zou and J.-M. Liu, Visible-Light Photocatalytic Properties of Weak Magnetic BiFeO₃ Nanoparticles, *Adv. Mater.*, 2007, **19**, 2889–2892.
- 44 L. Nielsen, M. J. Biggs, W. Skinner and T. J. Bandosz, The effects of activated carbon surface features on the reactive adsorption of carbamazepine and sulfamethoxazole, *Carbon*, 2014, **80**, 419–432.
- 45 N. Cai and P. Larese-Casanova, Sorption of carbamazepine by commercial graphene oxides: A comparative study with granular activated carbon and multiwalled carbon nanotubes, *J. Colloid Interface Sci.*, 2014, **426**, 152–161.

Research Article

Preparation and Characterization of a Novel Terbium Complex Coordinated with 10-Undecenoic Acid for UV-Cured Coatings

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A UV-cured composite containing a rare earth complex was prepared for this study. First, the photoluminescent terbium complex was synthesized with a long-chain unsaturated fatty acid (10-Undecenoic acid) by a solution precipitation method, resulting in the 10-UA-Tb(III) complex. Its structure was proven by FTIR, elemental analysis, XRD, and TGA. The results indicated that the organic acid ligand successfully coordinated with the Tb^{3+} ion and that the complex had a chelate bidentate structure. The emission spectrum of the 10-UA-Tb(III) complex indicated that the complex can emit a bright green light with the unique luminescence of the Tb^{3+} ion. Furthermore, the luminescence properties of complexes with different ratios of Tb^{3+} and ligand were studied, and the ratio of Tb^{3+} and the ligand had an obvious impact on the luminescence intensity of the 10-UA-Tb(III) complex. Subsequently, the prepared rare earth complex was doped into a UV-cured coating in different proportions to obtain a UV-cured composite. The morphology of the rare earth UV-cured composite was observed by SEM. The images showed that the rare earth complex was dispersed uniformly in the polymer matrix. Moreover, the composites could emit fluorescence. Additionally, it has good thermal stability and compatibility with the resin. Therefore, these composites should have potential applications in UV curable materials, such as luminescence coatings.

1. Introduction

Lanthanide elements have excellent features that are unique to 4f electronic structures, such as abundant energy level transitions, large atomic magnetic moments, and strong spin coupling [1]. Moreover, when rare earth elements combine with other elements to form rare earth complexes, the crystal structure of the rare earth complexes will be diversified due to the coordination number being varied from three to twelve [2]. Therefore, rare earth elements and complexes are endowed with unique electrical, optical, magnetic, and thermal properties that have attracted widespread attention [3, 4]. In particular, the luminescence properties of rare earth ions have many applications, such as luminescent probes [5] and sensitizers for electroluminescent devices [6]. However, due to the weak light emitted from lanthanide ions themselves, they need suitable ligands to absorb ultraviolet light and then transmit the energy to the lanthanide ions to emit luminescence. The ability of organic ligands to sensitize rare earth ions is called the “antenna effect” [7]. Hence, organic

ligands need to meet the following requirements: good ultraviolet absorbance, highly efficient energy transfer, acceptable energy in the launching state, and a moderate lifetime [8]. Rare earth organic ligands fall into three major categories: β -diketones [9], organic carboxylic acids [10], and supramolecular macrocycles [11]. Among them, the coordination ability between rare earth ions and organic carboxylic acids is strong because rare earth ions are hard acids, and oxygen atoms in carboxylic acids are hard bases whose coordination is in accordance with the affinity principle of acids and bases [12]. Furthermore, the coordination between carboxylate oxygen ions and lanthanide ions can be of various forms, such as a chelated bidentate, bridged bidentate, and monodentate; as a result, rare earth carboxylic acid complexes have numerous special structures, such as lamellar, catenulate, and reticular, which are relatively stable [13].

UV-curing technology is a green technology that is considered a “5E” technology due to many advantages, including high efficiency, wide adaptability, low cost, low energy cost, and environmental friendliness [14]. Moreover, UV-curing

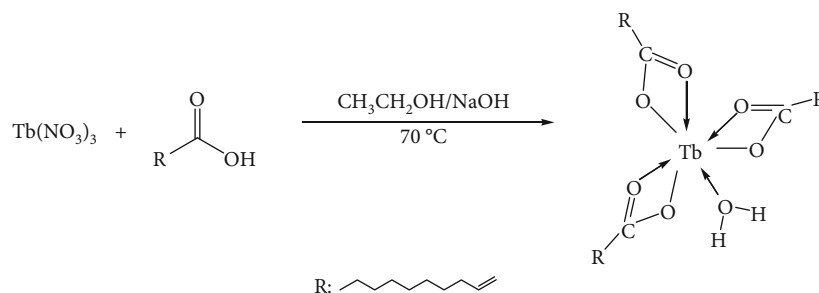


FIGURE 1: The synthetic route of the 10-UA-Tb(III) complex.

technology possesses other advantages, such as having simple operating conditions, requiring low equipment investment and being a relatively mature technology [15]. Thus, UV-curing technology has a wide range of applications as a coating [16] and adhesive [17] and in 3D printing [18]. In recent years, organic-inorganic hybrid materials have also received extensive attention because the utilization of nanosized inorganic particles is capable of improving the properties of polymers [19, 20]. It has been reported that nanoparticulate SiO_2 [21], TiO_2 [22], ZnO [23], and polyhedral oligomeric silsesquioxanes (POSS) [24, 25] have been introduced into UV-cured systems and have shown improved properties. However, studies on the introduction of rare earth complexes into UV-cured systems have rarely been reported [26, 27]. In this work, the rare earth complexes were synthesized by solution precipitation, after which the rare earth complexes were doped into UV-cured systems form rare earth polymer composites. In order to obtain the desirable luminescent properties of UV curable materials, we dope fluorescent terbium complex into the UV curable system. And the composites will be new potential applications in the UV-curing fields.

Most rare earth complexes select aromatic cyclic carboxylic acids as ligands because they contain conjugate double bonds and rigid plane structures that have good absorption in the ultraviolet region [28–31]. Nevertheless, this study selected unsaturated fatty acids called 10-Undecenoic acids to coordinate with terbium ions that can emit a bright pure green light. The double bond and long chain of 10-Undecenoic acid could improve the compatibility of the rare earth complexes in the polymer matrix. The structural characterization of rare earth complexes was investigated by FTIR, XRD, and elemental analysis. The morphology of rare earth complexes and rare earth UV-cured composite was observed by SEM. Their luminescence properties and thermal stability were tested by a fluorescence spectrometer and TGA, respectively. The mechanical properties of the composite films were tested, including pencil hardness, adhesion, and flexibility.

2. Experimental Section

2.1. Materials and Instruments. Tb_4O_7 (99.99%) was purchased from Ganzhou Zhanhai Industrial and Trading Co., Ltd.; 10-Undecenoic acid (10-UA, AR) was obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China); B-369 urethane acrylate, Irgacure 1173 photoinitiator, and reactive

diluent TMPTA were all industry grade and were bought from Guangdong Boxing New Material Technology Co., Ltd. Other chemicals were supplied by Xilong Scientific Co., Ltd. and used without further purification.

The instruments used in this work included a Magna 380 infrared spectrometer (Nicolet Company, USA), F-7000 fluorescence spectrometer (Hitachi Co., Ltd., Japan), TG-209 thermogravimetric analyzer (Netzsch Company, Germany), Nova Nano SEM 450 field emission scanning electron microscope (FEI Company, USA), Flash EA1112 elemental analyzer (Thermo Company, USA), D8 ADVANCE X-ray diffractometer (Bruker Company, Germany), ST 1KW 230MM 220V UV-curing machine (Dongguan Ergu Photoelectric Technology Co., Ltd., China), and QHQ-A Portable Pencil Scratch Tester and QFH film masker (Tianjin Yonglida Material Testing Machine Co., Ltd.).

2.2. Synthesis of 10-UA-Tb(III) Complex. The synthetic route of the 10-UA-Tb(III) complex is shown in Figure 1. Tb_4O_7 (0.5 mmol, 0.374 g) was dissolved in a mixed solution containing excess concentrated nitric acid and 10% hydrogen peroxide, and the mixture was heated to make the solution transparent. Then, the solution heating continued to remove excess nitric acid until it appeared as a white solid, resulting in $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. After cooling, the $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL anhydrous ethanol. The 10-Undecenoic acid (10-UA) ligand dissolved in 50 mL anhydrous ethanol was added in a three-necked flask equipped with a thermometer, condenser tube, and dropping funnel (note that the molar ratio of the ligand 10-UA to Tb^{3+} ion was 3 : 1). Subsequently, the prepared ethanol solution of terbium(III) nitrate was dripped slowly into a three-necked flask, and the pH of the solution was adjusted to 6-7 with a 1 mol/L NaOH solution until a large amount of precipitation was separated. Next, the coordination reaction was continued for 2 h at 70°C with magnetic stirring. After heating, the solution was allowed to stand overnight to precipitate completely. The product was filtered and washed with anhydrous ethanol and deionized water several times. The product was kept in a vacuum oven at 60°C for 24 h to obtain the white powder (1.058 g) that was the 10-UA-Tb(III) complex, and the yield was 72.8%. The elemental calculation resulted in 54.53% C, 8.20% H (C/H 6.65), and 15.40% O. The actual results were 53.60% C, 8.02% H (C/H 6.68), and 15.09% O. By changing the molar ratio of the ligand to the Tb^{3+} ion, other 10-UA-Tb(III) complexes were prepared based on the above process.

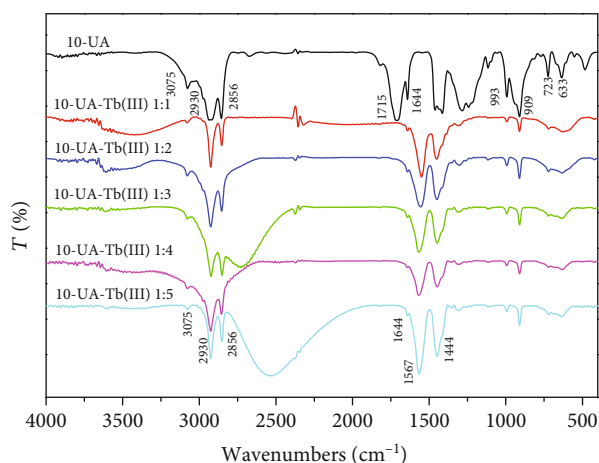


FIGURE 2: FTIR spectra of 10-UA and 10-UA-Tb(III) complexes.

2.3. Preparation of UV-Cured Film with 10-UA-Tb(III) Complex. 80% of B-369 aliphatic urethane acrylate, 15% of TMPTA reactive diluent, and 5% of photoinitiator 1173 were successively added to the plastic beaker, after which it was mixed well and stirred in an ultrasonic cleaner for 5 minutes. Subsequently, a certain amount of 10-UA-Tb(III) complexes was doped into the formulation coating and uniformly dispersed for 20 minutes. The mixed coating stood for 10 minutes and was evenly coated on a glass substrate with a thickness of 20 μm . The films were cured under a high-pressure mercury lamp (1000 W) with a UV radiation intensity of 36 mJ/cm^2 and a main wavelength of 365 nm. Finally, rare earth UV-cured composites were produced.

2.4. Measurement and Characterization

2.4.1. FTIR Spectra. The Fourier-transform infrared (FTIR) spectra of the samples were collected using a USA Nicolet Magna 380 infrared spectrometer through KBr tablets for wavenumbers of 400–4000 cm^{-1} .

2.4.2. XRD Spectra. X-ray diffraction with Cu-K α radiation was carried out to characterize the crystal phase of the sample at 40 kV and 40 mA. The 2θ angle was collected from 3° to 80°.

2.4.3. Field Emission Scanning Electron Microscope (FESEM). FESEM images of the 10-UA-Tb(III) complex and UV-cured film doped with the 10-UA-Tb(III) complex were collected using a Nova SEM450 field emission scanning electron microscope. The specimens were prepared by smearing the test samples on a conductive adhesive and then depositing gold on the surface.

2.4.4. Fluorescence Spectra. The luminescence excitation and emission spectra of 10-UA-Tb(III) complexes were performed with an F-7000 fluorescence spectrometer. The sample powder was added into a sample pool. The width of the excitation and emission slits was both 2.5 nm, and the voltage was 400 v. The scanning speed was 1200 nm/min. For the rare earth UV-cured films, the width of excitation and emission was adjusted to 5.0 nm.

2.4.5. Thermogravimetric Analysis. The thermal stability of the samples was collected with a TG-209 thermogravimetric analyzer. The temperature range was 50–1000°C, and the heating rate was 10°C/min. The atmosphere was nitrogen with a gas flow rate of 100 mL/min. The data were recorded every 0.5 s.

2.4.6. Mechanical Property Tests. The mechanical properties of the rare earth UV-cured films were investigated using pencil hardness, adhesion, and flexibility tests. The pencil hardness test was conducted according to the ASTM D3363-05 standard. The adhesion was conducted according to ASTM D3002 (0B-5B). The flexibility of the coatings was measured by the T-Bend test according to ASTM D4145-10. The cured coating films were tested water resistance, solvent resistance, acid resistance (0.1 mol/L HCl), and alkali resistance (0.1 mol/L NaOH).

3. Results and Discussion

3.1. Infrared Spectra. The FTIR spectra of the 10-UA-Tb(III) complexes with different ratios (Tb^{3+} :10-UA) and the organic ligand 10-UA are shown in Figure 2. According to Figure 2, the spectral bands of these complexes were roughly consistent. The band owing to $\nu(\text{C}=\text{O})$ of the carboxylic group in 10-UA at 1715 cm^{-1} disappeared and split into two new peaks at 1567 cm^{-1} and 1444 cm^{-1} , which corresponded to asymmetric vibration absorption and symmetric vibration absorption of the carboxylate ion (COO^-), respectively. This result indicated that rare earth Tb(III) ions successfully coordinated with carboxyl acid ligands. Moreover, the $\Delta\nu(\nu_{\text{as}}-\nu_{\text{s}})$ values of all complexes were approximately 123 cm^{-1} , which is less than 200 cm^{-1} , indicating that the Tb(III) ion and ligands were in the form of chelate bidentate coordination [30, 32]. There were two absorption peaks from the ethylenic bond at 3075 cm^{-1} and 1644 cm^{-1} , which were assigned to ν_{CH} and $\nu_{\text{C}=\text{C}}$, respectively. The bands at 2930 cm^{-1} and 2856 cm^{-1} were attributed to the asymmetric vibration absorption and symmetric vibration absorption of methylene, respectively. In addition, the in-plane rocking vibration of $-\text{CH}_2$ was at approximately 723 cm^{-1} . In comparison, there was a broad absorption band at approximately 3434 cm^{-1} due to asymmetric vibration absorption of $-\text{OH}$ in the 10-UA-Tb(III) complexes.

3.2. XRD Spectra. As shown in Figure 3, the phase structure of the 10-UA-Tb(III) complex with a ratio of 1:3 (Tb^{3+} :ligand) was revealed by XRD. There were two sharp X-ray diffraction peaks at $2\theta = 3.81^\circ$ and $2\theta = 29.46^\circ$. The strong and sharp peak at $2\theta = 29.46^\circ$ belongs to the (111) reflection of Tb-10-UA. In addition, there was a weak diffuse reflection at $2\theta = 6.75^\circ$. These data confirmed the existence of a crystal structure, and a characteristic peak of Tb_4O_7 appeared at 29.46°, which proved that the terbium ion successfully coordinated with the 10-Undecenoic acid ligand.

3.3. Morphology Analysis. With a cotton swab, the powder sample was smeared on a conductive adhesive. The surface of the sample was sprayed with gold and then tested. The SEM images of the 10-UA-Tb(III) complex are presented in

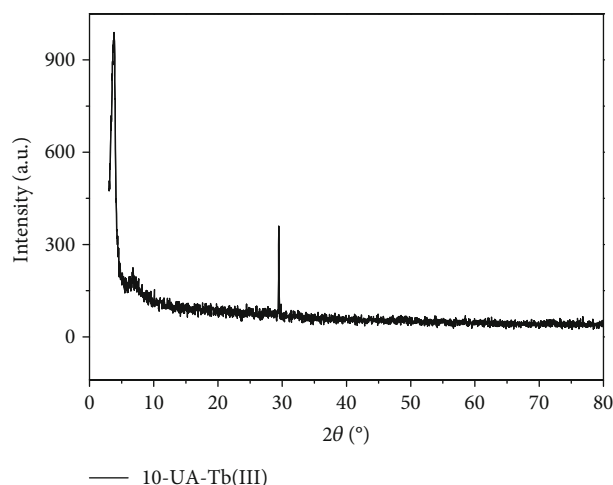


FIGURE 3: XRD curve of the 10-UA-Tb(III) complex.

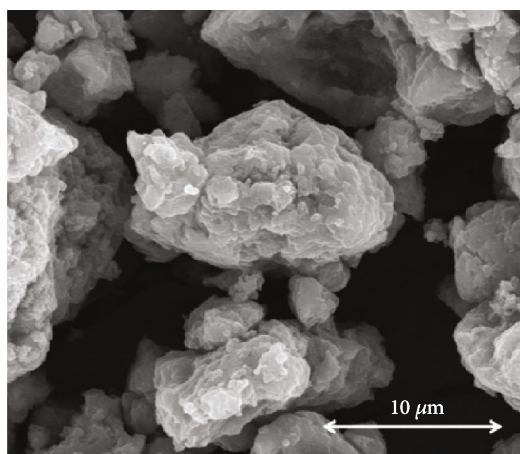


FIGURE 4: SEM image of the 10-UA-Tb(III) complex.

Figure 4. The result showed that the 10-UA-Tb(III) complex had a rough rock structure with a size belonging in the microscopic regime. Its edge line was clear. There was an agglomeration phenomenon that resulted in the appearance of large particles.

The morphology of the rare earth UV-cured film containing 2.0% of the 10-UA-Tb(III) complex was studied by SEM. Figure 5(a) shows the surface morphology of the rare earth polymer film, and Figure 5(b) shows the cross-section morphology of the rare earth polymer film. It is shown that the Tb-UA complex cannot be dissolved in the polymer matrix. The rare earth UV-cured composite exhibited a heterogeneous morphology. There were discrete particles of the 10-UA-Tb(III) complex mixed uniformly in the polymer matrix, and they were evenly dispersed, although they appeared aggregated.

3.4. Luminescence Testing. The excitation spectra and the emission spectra of 10-UA-Tb(III) complexes with different ligand contents are shown in Figures 6(a) and 6(b), respectively. As shown in Figure 6(a), the 10-UA-Tb(III) complexes had a wide absorption range from 270 nm to 400 nm. Among

them, the maximum excitation wavelength of all complexes was 273 nm. Selecting 273 nm as the excitation wavelength to excite samples, the emission spectra are measured in Figure 6(b). From the emission spectra, the emission peaks from the 10-UA-Tb(III) complexes with different ligand contents were similar. The emission peaks from the rare earth complexes were at 491, 548, 586, and 623 nm, which belonged to the characteristic peaks of the Tb^{3+} ions. The first was attributed to the transition of $^5D_4 \rightarrow ^7F_6$, the second to the transition of $^5D_4 \rightarrow ^7F_5$, the third to the transition of $^5D_4 \rightarrow ^7F_4$, and the fourth to the transition of $^5D_4 \rightarrow ^7F_3$. Among these transitions, the highest fluorescence intensity emission peak was the $^5D_4 \rightarrow ^7F_5$ transition at 548 nm, which resulted in a green emission. The emission bands were narrow, and the peak shapes were sharp, which indicated that the 10-UA-Tb(III) complexes possessed good monochromatic properties. Furthermore, the proportion of ligands had a significant impact on fluorescence intensity. From Figure 6(b), the fluorescence intensity of the 10-UA-Tb(III) complex with a ratio of 1:4 (Tb^{3+} :10-UA) was the strongest. It is possible that when the organic ligand content increases, more ultraviolet light is absorbed to transfer energy to the Tb^{3+} ion, and the Tb^{3+} ion radiated more energy through the f-f energy level transition. Moreover, the triplet energy level of the 10-UA was better matched with the f energy level of the terbium(III) ion, which could be sensitized effectively. However, the fluorescence intensity decreased when the ratio was 1:5. This phenomenon was caused by the concentration quenching effect. That is, the proportion of ligands had a significant impact on fluorescence intensity. At first, the increase of fluorescence intensity follows with the increase of the ligand number. The fluorescence intensity will decrease when the ligand number reached a number.

Different amounts of 10-UA-Tb(III) complexes were doped into the as-prepared UV-cured coatings to obtain rare earth polymer composite coatings; the thin doped films were coated on glass slides and cured under a 1000 W UV-curing machine. The luminescence of the composites containing 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 wt % of 10-UA-Tb(III) complexes was investigated, as shown in Figure 7. According to Figure 7(a), there were two obvious excitation peaks at 272 nm and 306 nm in all of the UV-cured composites. Selecting 272 nm as the maximum excitation wavelength to excite the sample, the emission spectra of the rare earth polymer composites are shown in Figure 7(b). The films doped with different amounts of the rare earth complex all radiated the characteristic emission peaks of terbium ions, which are located at 492 nm, 547 nm, and 588 nm. Moreover, the concentration was too low to emit strong fluorescence. When the content of the 10-UA-Tb(III) complex in the UV-cured film increased gradually, the fluorescence intensity was enhanced correspondingly.

3.5. Thermal Stability. Figure 8 shows the thermal stability of the 10-UA-Tb(III) complex. The decomposition process of the 10-UA-Tb(III) complex from 50°C to 1000°C was roughly divided into the following stages: 50~200°C, 200~499.7°C, and 499.7~1000°C. There was a low weight loss of approximately 2.20% within 50~200°C due to the trace

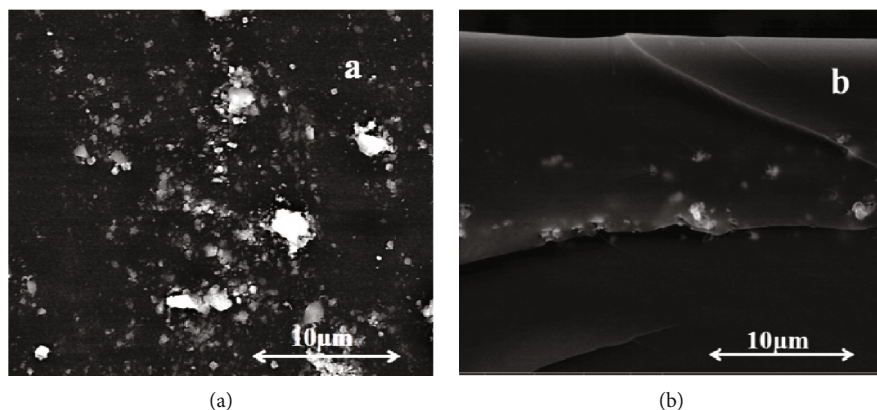


FIGURE 5: SEM images of rare earth UV-cured composite: (a) surface morphology and (b) section morphology.

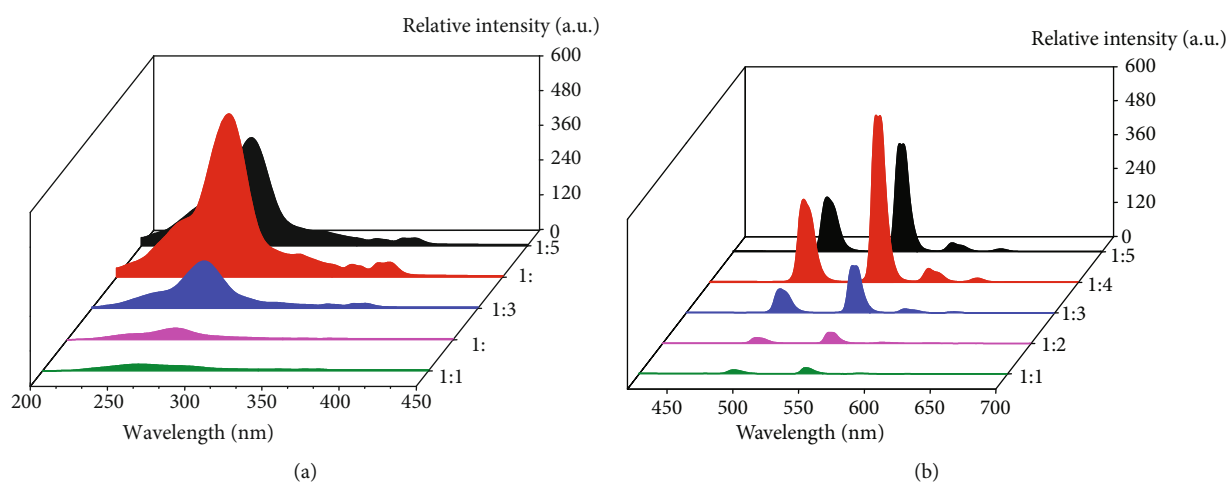


FIGURE 6: Excitation spectra (a) and emission spectra (b) of the 10-UA-Tb(III) complex.

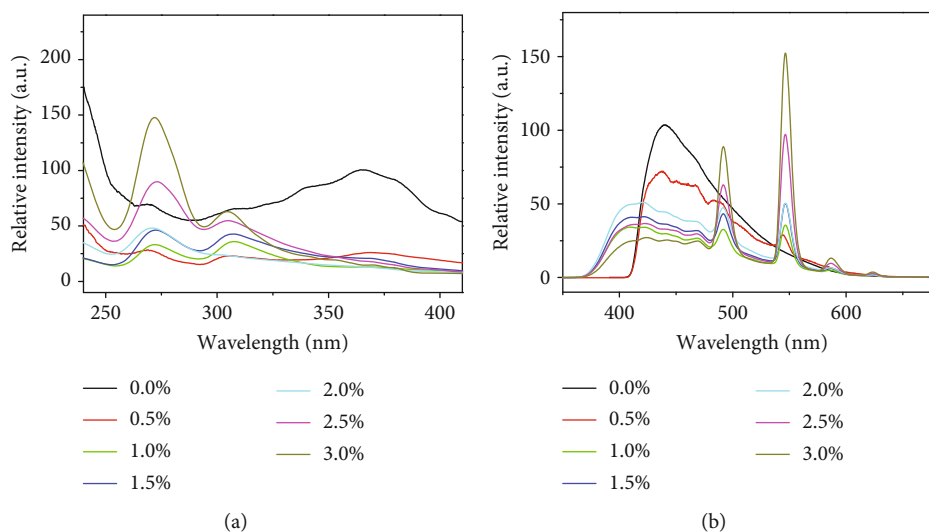


FIGURE 7: Luminescence properties of rare earth UV-cured composite: (a) excitation spectra and (b) emission spectra.

amount of water removed. Subsequently, there was an evident decline from 200.0°C to 499.7°C with a total of 67.48% weight loss, which could be attributed to cracking of the 10-Undecenoic acid skeleton. There were two maximum decom-

position rates for this process at 347.8°C and 465.1°C. Then, there was a gentle incline from 499.7°C to 699.2°C, which decomposed by 6.71% and remained at approximately 23.61%. This process could be the decomposition of the

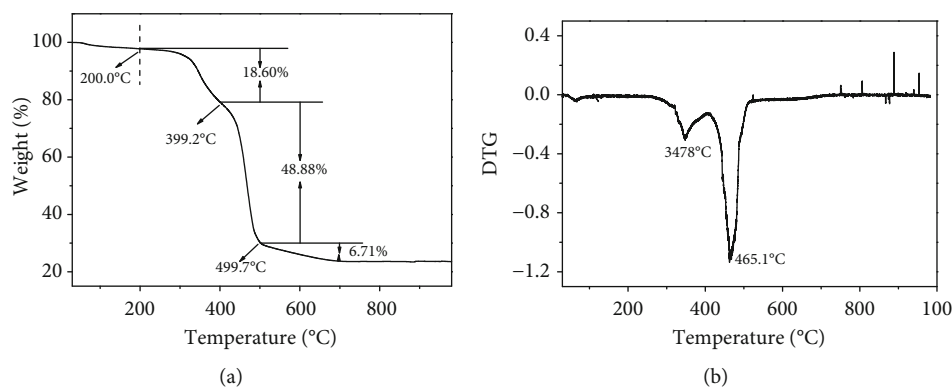


FIGURE 8: (a) TG and (b) DTG curves of the 10-UA-Tb(III) complex.

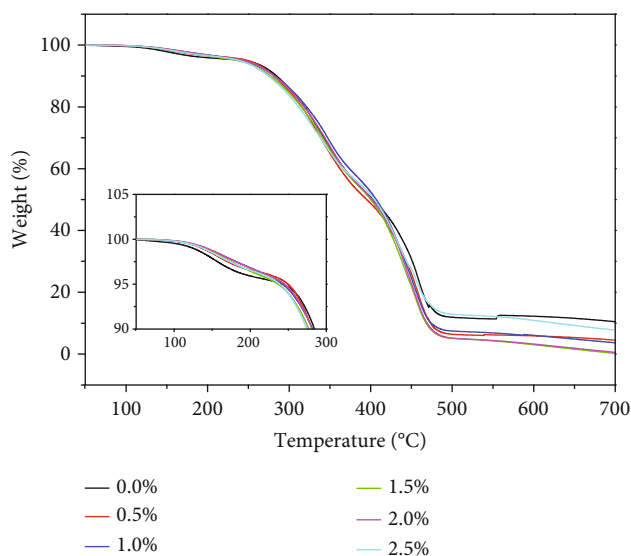


FIGURE 9: (a) TG and (b) DTG curves of the 10-UA-Tb(III) complex.

terbium hydroxide, where $\text{Tb}(\text{OH})_3$ decomposed into $\text{TbO}(\text{OH})$ and then $\text{TbO}(\text{OH})$ was transferred to Tb_2O_3 . The test result was in agreement with the speculative structure of the 10-UA-Tb(III) complex above. This proved that the 10-UA-Tb(III) complex had good thermal stability.

The stability of the UV-cured coating films doped with different contents of rare earth complexes was explored, as shown in Figure 9. According to the TG curves, the addition of the 10-UA-Tb(III) complex did not have a strong influence on the UV-cured coatings because their thermal stability was approximately the same from 50°C to 700°C. It began to slowly decompose from 100°C to 240°C. In this interval, the stability of the rare earth UV-cured composite was slightly better than that of the UV-cured coating undoped with a rare earth complex. Subsequently, it decomposed rapidly at 240°C, and the decomposition was completed at 500°C. As a whole, the addition of the 10-UA-Tb(III) complex did not have a distinct impact on the original UV-cured coating. The reason may be that the thermal properties of UV-cured film are mainly influenced from the polymer matrix. The addition of the

TABLE 1: The curing time and properties of UV-cured films.

Content (wt %)	0	1.0	3.0	5.0	10.0
Curing time (s)	28	28	24	25	21
Pencil hardness	6H	6H	6H	6H	6H
Adhesion/grade	5B	4B	3B	3B	3B
Flexibility	3T	3T	3T	3T	3T
Solvent resistance/MEK	>250	>250	>250	>250	>250

10-UA-Tb(III) complex did have a slightly influence on decomposed rate of the UV-cured films from 100°C to 240°C. The low amount of Tb-UA complex has a slight influence on the thermal properties of the UV-cured film.

3.6. Mechanical Properties of the UV-Cured Film. The photopolymerization efficiency and mechanical properties of the rare earth UV-cured composites were evaluated, including curing time, pencil hardness, adhesion, and flexibility, as shown in Table 1. The curing time of the rare earth UV-cured films was slightly shortened with an increase with the 10-UA-Tb(III) complex. A possible explanation is that the addition of rare earth complexes enhanced the ability to absorb ultraviolet light from the entire UV-cured system, which led to the promotion of the cleavage of the photoinitiator 1173. Thus, it effectively promoted cross-linking curing of the resin and monomer. The pencil hardness of all films was high at 6H. The addition of rare earth complexes had a little effect on the pencil hardness. The adhesion of the composite films decreased perhaps because the cross-linking density was reduced after curing with the addition of the rare earth complexes. However, the flexibility of the films was good. From Table 1, we can notice that the UV-cured films showed good solvent resistance for methyl ethyl ketone. It revealed that the UV-cured films had the structure of tight cross-link network. That the rare earth complexes had no effect on solvent resistance may be the 10-UA containing double bond copolymerized with the resin or reactive diluent. Moreover, the rare earth UV-cured films were soaked in 0.1 mol/L HCl, 0.1 mol/L NaOH, and water. After 48 h, the composite films were detached and wrinkled in hydrochloric acid

solution and sodium hydroxide solution, but there was no change in water.

4. Conclusions

A novel terbium complex was synthesized and coordinated with 10-Undecenoic acid via a solution precipitation method. The coordinated structure and molecular component of the 10-UA-Tb(III) complex were studied by a series of characterization methods that indicated that the 10-UA-Tb(III) complex was a chelate bidentate complex, and its molecular formula was $\text{Tb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3 \cdot \text{H}_2\text{O}$. The 10-UA-Tb(III) complex showed excellent luminescence properties. In particular, the complex with a ratio of 1:4 (Tb^{3+} :10-UA) emitted the highest fluorescence intensity. Next, the 10-UA-Tb(III) complex was doped into a UV-cured coating to prepare rare earth UV-cured composites. As a result, the composite exhibited a heterogeneous morphology, as seen in SEM images, and the composite also possessed a luminescence peculiarity that emitted a green light. For mechanical properties, the curing time slightly shortened. The hardness, adhesion, and flexibility were good. The addition of the 10-UA-Tb(III) complex did not conspicuously change the thermal stability of the UV-cured coating. In summary, this research can provide a direction to further explore rare earth organic hybrid composites that could be applied to UV-cured coatings and luminescence materials. The complex of Te-Undecenoic acid is suitable for UV-curing material. The composites of them can be cured less than 60 s and have good photoluminescent, mechanical properties after UV irradiation.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgments

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References

- [1] D. I. Alexandropoulos, L. Cunha-Silva, L. Pham, V. Bekiari, G. Christou, and T. C. Stamatatos, "Tetranuclear lanthanide(III) complexes with a zigzag topology from the use of pyridine-2,6-dimethanol: synthetic, structural, spectroscopic, magnetic and photoluminescence studies," *Inorganic Chemistry*, vol. 53, no. 6, pp. 3220–3229, 2014.
- [2] J. G. Bünzli, "Review: Lanthanide coordination chemistry: from old concepts to coordination polymers," *Journal of Coordination Chemistry*, vol. 67, no. 23–24, pp. 3706–3733, 2014.
- [3] S. Bangarigadu-Sanasy, C. R. Sankar, P. A. Dube, J. E. Greedan, and H. Kleinke, "Magnetic properties of Tl9LnTe6 , $\text{Ln} = \text{Ce}$, Pr , Tb and Sm ," *Journal of Alloys and Compounds*, vol. 589, pp. 389–392, 2014.
- [4] B. L. An, X. D. Huang, J. M. Zhang, X. Y. Zhu, and J. Q. Xu, "Synthesis and strong luminescence of water soluble lanthanide complexes sensitized by a new tridentate organic ligand," *Journal of Luminescence*, vol. 187, pp. 340–346, 2017.
- [5] H. L. Tan, J. Wu, and Y. Chen, "Terbium(III) based coordination polymer microparticles as a luminescent probe for ascorbic acid," *Microchimica Acta*, vol. 181, no. 11–12, pp. 1431–1437, 2014.
- [6] R. Z. Cui, W. Q. Liu, L. Zhou et al., "Highly efficient green phosphorescent organic electroluminescent devices with a terbium complex as the sensitizer," *Dyes and Pigments*, vol. 136, pp. 361–367, 2017.
- [7] J. Feng and H. J. Zhang, "Hybrid materials based on lanthanide organic complexes: a review," *Chemical Society Reviews*, vol. 42, no. 1, pp. 387–410, 2013.
- [8] M. Hatanaka and A. Osawa, "Computational study on the luminescence quantum yields of terbium complexes with 2,2'-bipyridine derivative ligands," *Physical Chemistry Chemical Physics*, vol. 20, no. 5, pp. 3328–3333, 2018.
- [9] K. P. Zhuravlev, V. A. Kudryashova, and V. I. Tsaryuk, "Luminescence and energy transfer processes in europium and terbium complexes with 2-substituted cycloalkanones and 1,10-phenanthroline derivatives," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 314, pp. 14–21, 2016.
- [10] K. Burek, S. Eidner, S. Kuke, and M. U. Kumke, "Intramolecular deactivation processes of electronically excited lanthanide(III) complexes with organic acids of low molecular weight," *Spectrochimica Acta A*, vol. 191, pp. 36–49, 2018.
- [11] Y. F. Geng, P. Li, J. Z. Li, X. M. Zhang, Q. D. Zeng, and C. Wang, "STM probing the supramolecular coordination chemistry on solid surface: structure, dynamic, and reactivity," *Coordination Chemistry Reviews*, vol. 337, pp. 145–177, 2017.
- [12] B. Kumar, G. Kaur, and S. B. Rai, "Acetylsalicylic acid sensitized lasing luminescence of terbium complex in PVA: a case of energy avalanche via 1, 10-phenanthroline," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 332, pp. 413–421, 2017.
- [13] M. J. Ma, C. C. Li, D. K. Shu, C. Wang, and P. Xi, "Synthesis and characterization of bright green terbium coordination complex derived from 1,4-bis(carbonylmethyl)terephthalate: structure and luminescence properties," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 190, pp. 68–75, 2017.
- [14] F. Bauer, U. Decker, S. Naumov, and C. Riedel, "Photoinitiator-free UV curing and matting of acrylate-based nanocomposite coatings: Part 3," *Progress in Organic Coatings*, vol. 77, no. 6, pp. 1085–1094, 2014.
- [15] L. Fertier, H. Koleilat, M. Stemmelen et al., "The use of renewable feedstock in UV-curable materials - A new age for polymers and green chemistry," *Progress in Polymer Science*, vol. 38, no. 6, pp. 932–962, 2013.
- [16] T. Ç. Çanak and I. E. Serhatlı, "Synthesis of fluorinated urethane acrylate based UV-curable coatings," *Progress in Organic Coating*, vol. 76, no. 2–3, pp. 388–399, 2013.
- [17] S. W. Lee, J. W. Park, C. H. Park et al., "UV-curing and thermal stability of dual curable urethane epoxy adhesives for temporary bonding in 3D multi-chip package process,"

- International Journal of Adhesion and Adhesives*, vol. 44, pp. 138–143, 2013.
- [18] D. K. Patel, A. H. Sakhaei, M. Layani, B. Zhang, Q. Ge, and S. Magdassi, “Highly stretchable and UV curable elastomers for digital light processing based 3D printing,” *Advanced Materials*, vol. 29, no. 15, p. 1606000, 2017.
- [19] M. Periolatto and F. Ferrero, “Cotton and polyester surface modification by methacrylic silane and fluorinated alkoxy silane via sol-gel and UV-curing coupled process,” *Surface and Coatings Technology*, vol. 271, pp. 165–173, 2015.
- [20] M. Mohseni, S. Bastani, and A. Jannesari, “Influence of silane structure on curing behavior and surface properties of sol-gel based UV-curable organic-inorganic hybrid coatings,” *Progress in Organic Coatings*, vol. 77, no. 7, pp. 1191–1199, 2014.
- [21] H. Xie and W. F. Shi, “Polymer/SiO₂ hybrid nanocomposites prepared through the photoinitiator-free UV curing and sol-gel processes,” *Composites Science and Technology*, vol. 93, pp. 90–96, 2014.
- [22] S. W. Lee, J. W. Park, C. H. Park et al., “Optical properties and UV-curing behaviors of optically clear PSA- TiO₂ nano-composites,” *International Journal of Adhesion and Adhesives*, vol. 44, pp. 200–208, 2013.
- [23] B. Faure, G. Salazar-Alvarez, A. Ahnizay et al., “Dispersion and surface functionalization of oxide nanoparticles for transparent photocatalytic and UV-protecting coatings and sunscreens,” *Science and Technology of Advanced Materials*, vol. 14, no. 2, pp. 023001–023304, 2013.
- [24] Y. Wang, F. Liu, and X. X. Xue, “Morphology and properties of UV-curing epoxy acrylate coatings modified with methacryl-POSS,” *Progress in Organic Coating*, vol. 78, pp. 404–410, 2015.
- [25] B. Yu, Y. J. Tao, L. Liu et al., “Thermal and flame retardant properties of transparent UV-curing epoxy acrylate coatings with POSS-based phosphonate acrylate,” *RSC Advances*, vol. 5, no. 92, pp. 75254–75262, 2015.
- [26] D. V. Lapaev, V. G. Nikiforov, G. M. Safiullin et al., “UV laser-induced enhancement of photoluminescence intensity in vitrified terbium(III) β -diketonate complex film in air,” *Journal of Luminescence*, vol. 194, pp. 407–413, 2018.
- [27] F. A. Rafiqi and K. Majid, “Synthesis, characterization, luminescence properties and thermal studies of polyaniline and polythiophene composites with rare earth terbium(III) complex,” *Synthetic Metals*, vol. 202, pp. 147–156, 2015.
- [28] B. J. Gao, W. Zhang, Z. G. Zhang, and Q. Lei, “Preparation of polymer-rare earth complex using salicylic acid-containing polystyrene and its fluorescence emission property,” *Journal of Luminescence*, vol. 132, no. 8, pp. 2005–2011, 2012.
- [29] M. Zhao, R. Tang, and S. Xua, “Investigations into the bovine serum albumin binding and fluorescence properties of Tb (III) complex of a novel 8-hydroxyquinoline ligand,” *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Q. Shen, Z. F. Yang, and R. R. Tang, Eds., vol. 135, pp. 953–958, 2015.
- [30] Y. W. Wu, H. X. Hao, Q. Y. Wu, Z. Gao, and H. Xie, “Preparation and luminescent properties of the novel polymer-rare earth complexes composed of poly(ethylene-co-acrylic acid) and europium ions,” *Optical Materials*, vol. 80, pp. 65–70, 2018.
- [31] H. N. Wanga, L. Fanga, Z. Zhang et al., “Light-induced rare earth organic complex/shape-memory polymer composites with high strength and luminescence based on hydrogen bonding,” *Composites Part A Applied Science and Manufacturing*, vol. 125, p. 105525, 2019.
- [32] B. J. Gao, L. Fang, and J. Y. Men, “Studies on preparation, structure and fluorescence emission of polymer-rare earth complexes composed of aryl carboxylic acid-functionalized polystyrene and Tb(III) ion,” *Polymer*, vol. 53, no. 21, pp. 4709–4717, 2012.



Nitrogen-doped hierarchically structured porous carbon as a bifunctional electrode material for oxygen reduction and supercapacitor

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Supercapacitor

ABSTRACT

Development of an efficient electrode material with robust porous architecture, high catalytic activity and excellent electrochemical performance toward both oxygen reduction reaction (ORR) and supercapacitor is extremely important. Herein, a facile route to fabricate nitrogen-doped hierarchical porous carbon (NHPC) materials as a bifunctional electrode material for ORR and supercapacitors is presented. The as-prepared NHPC-0.5 integrate the feature of high-level nitrogen-doping (12.1 at %), large specific surface area (up to 1798.4 m² g⁻¹) and hierarchical multi-pores of cross-linked micro and mesoporous channels. When used as ORR electrocatalyst, the NHPC-0.5 demonstrated highest selectivity (four-electron transfer process), high activity (half-wave potential 0.883 V vs. RHE, initial potential 1.004 V vs. RHE) and favorable tolerance against methanol. When tested its application in zinc-air batteries, its maximum output power density was 25.1 mW cm⁻², and delivers a superior durability of negligible potential loss after 100 cycles. When applied in supercapacitor, the NHPC-0.5 can deliver a high specific capacitance of 283.7 F g⁻¹ at current density of 1 A g⁻¹ in 1 M H₂SO₄ electrolyte, and outstanding cyclic stability (105.8% capacitance retention after 40,000 cycles). Moreover, a symmetric supercapacitor (NHPC-0.5//NHPC-0.5) can release an energy density of 11.3 W h kg⁻¹ at the power density of 502 W kg⁻¹. The encouraging results of this work may provide a new perspective to construct N-doped hierarchical porous carbon materials in energy storage devices with excellent electrochemical performance.

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1. Introduction

To meet the ever-increasing and urgent demands for sustainable and environmentally friendly alternative energy caused by excessive burning of large quantities of fossil fuels, abundant advanced materials have been investigated for energy conversion and storage system. Among the various advanced materials, hierarchical porous carbon is one of the most versatile electrode material in ORR [1–3] and supercapacitors [4–6], because of its high specific surface area, high porosity with variable pore sizes and pore structures, better

electrical conductivity and stable physicochemical properties [7–9].

Generally, several factors significantly affect the ORR and supercapacitor performances of hierarchical porous carbon, including specific surface area, controllability of pore size and electrical conductivity [10–12]. The hierarchical porosity can significantly enhance the electrochemical performances of the carbon materials. The micropores bring about large specific surface to provide effective active sites, and the mesopores/macropores served as ions reservoirs, offering convenient pathway to achieve more active sites, greatly decreasing the ionic resistance, which are crucial for the application of ORR and supercapacitors [13]. Moreover, the ORR and supercapacitors performance of hierarchical porous carbon can be significantly improved by doping of heteroatoms (P, B, S, and N, etc.) [14–17]. It has been proved that the

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heteroatoms doping, especially N atom can improve the chemical composition of the surface of materials, upgrade the hydrophilicity and electronic conductivity of carbon materials, substantially offer additional pseudocapacitance to improve the supercapacitive performance [12,18,19]. When used in electrocatalysts, the introduction of N atoms can conduct a charge delocalization in the sp^2 hybridized carbon skeleton, which is beneficial to the oxygen adsorption and reduction, bring about the considerable increasing in electrocatalysts performance [20]. In addition, N-doping can effectively enhance the wettability of the electrode materials, and endows porous carbon with additional redox reaction for pseudocapacitors [21]. Accordingly, it is extremely important to explore a facile and efficient method to prepare high-level N-doped porous carbon materials with hierarchical porous structure simultaneously for the applications of ORR and supercapacitors.

Various routes have been exploited to fabricate heteroatom-doped hierarchical porous carbon, such as, non-template method [22–24] and template method, including soft template [22,23,25,26], hard template [27] and post-activation treatment [28–32]. Among the various methods mentioned above, template method can not only greatly simplify the synthesis procedures of carbon materials, offer them with appropriate pore structure, but also dope other non-carbon elements in organic precursors simultaneously [33,34]. Despite the great achievements of previous literature reports, their ORR and supercapacitor performance usually restricted by low specific capacitance, small energy density and dissatisfied cycle stability.

Herein, N-doped hierarchical porous carbon (NHPC) was fabricated via templated polyacrylonitrile (PAN) solution by using aqueous suspension of porogenic fillers of SiO_2 and $ZnCl_2$. The obtained NHPCs possessed large specific surface area ($1798\text{ m}^2\text{ g}^{-1}$), highly nitrogen content (12.1 at.%) as well as interconnected hierarchical multi-pores structure of micropores and mesopores, demonstrated the desired features for high performance electrocatalytic and supercapacitor. As expected, the as-prepared NHPCs showed highly active for the electrocatalysis in an alkaline electrolyte. Notably, when used as cathode of zinc-air battery, the as-prepared NHPCs exhibited a maximum output power density of 25.01 mW cm^{-2} . In addition, the NHPCs displayed excellent performance in supercapacitor with a high specific capacitance (283.7 F g^{-1} at a current density of 1 A g^{-1} measured in three-electrode system), high energy density (11.3 W h kg^{-1}) and outstanding cyclic capability (capacitance retention of 99.3% after 12,000 cycles at a current density of 6.7 A g^{-1} in two-electrode system). Those outstanding performance endow the NHPCs served as promising candidate material in the application of electrocatalysis and supercapacitor.

2. Materials and methods

2.1. Preparation

Zinc chloride (98%), PAN (MW:85000), nano-size silica ($15 \pm 5\text{ nm}$), Nafion (5 wt%) solution were purchased from Shanghai Macklin. All chemicals were used as received without purification.

The hierarchical porous carbon materials were prepared according to the following procedures: a certain amount of zinc chloride ($ZnCl_2$) was dissolved in deionized water under the condition of continuous stirring to obtain an aqueous solution, and the concentration of $ZnCl_2$ in the solution was kept at 60 wt% to guarantee complete dissolution of PAN. Then PAN (0.5 g) and silica (0, 0.125, 0.25 and 0.375 g, respectively) were added to the above aqueous solution slowly by constantly stirring for at least 1 h at ambient temperature to obtain a homogenous suspension. Subsequently, the suspension was freeze-dried for 24 h. Following, in the

carbonization process, the freeze-dried products was first stabilized at $280\text{ }^\circ\text{C}$ with heating rate of $1\text{ }^\circ\text{C min}^{-1}$ for 1 h under air atmosphere, and then heated to $800\text{ }^\circ\text{C}$ at a temperature rate of $5\text{ }^\circ\text{C min}^{-1}$ under N_2 atmosphere and kept for 0.5 h. Finally, the products were leached with HF solution to etch the SiO_2 template and washed with deionized water until the pH of filtrate was close to neutral and dried overnight to obtain N-doped hierarchical porous carbon materials. The as-prepared materials were expressed as NHPC-X, where X represents the mass ratio of SiO_2 to PAN (0, 0.25, 0.5 and 0.75, respectively).

2.2. Characterization

The morphologies and structures of the as-prepared products were investigated by scanning electron microscope (FEI Quanta 250) and transmission electron microscopy (FEI Talos F200X). The crystal structure of the products was tested by X-ray powder diffractometer (Bruker, D8 Advance) using $Cu\text{ K}\alpha$ radiation with a scan range of $10\text{--}80^\circ$. The elemental composition and chemical state of the materials were characterized by an Axis Ultra X-ray photoelectron spectroscopy (Kratos). The nitrogen adsorption-desorption isotherms were recorded on a TriStar II 3020 instrument (Micromeritics) at 77 K to evaluate the pore structures of the samples. The specific surface area and pores size distributions of the samples were calculated by Brunner-Emmet-Teller (BET) method and density functional theory (DFT), respectively. The micropore surface area was determined by t-plot method.

2.3. ORR testing

The ORR performance of the NHPCs were tested by cyclic voltammogram (CV) and linear scan payment map (LSV) techniques using Shanghai Chen Hua CHI660E electrochemical workstation. The measurement was conducted in a three-electrode system, in which the Pt wire, and saturated $Ag/AgCl$ electrode were served as the counter and reference electrode, respectively. The HP-1 ring-disk electrode with a glassy carbon disk was employed as working electrode. Amounts of 5 mg NHPCs were dissolved in the solution containing $450\text{ }\mu\text{L}$ of deionized water and $50\text{ }\mu\text{L}$ of Nafion (5 wt%), the mixture was ultrasonic agitated for 1 h to gain uniform ink. Then $10\text{ }\mu\text{L}$ of the ink was dropped onto the ring-disk electrode with 0.2475 cm^2 geometrical cross section area and naturally dried to make the working electrode. All the tests were performed in 0.1 M KOH electrolyte, and the electrolyte was purged with N_2 or O_2 for 30 min before testing. All measured potentials were converted into a reversible hydrogen electrode (RHE) according to the following formula (1):

$$E_{vs\text{ RHE}} = E_{vs\text{ MP}} + 0.059pH + 0.197(V) \quad (1)$$

where $E_{vs\text{ RHE}}$ is the potential vs. reversible hydrogen electrode, $E_{vs\text{ MP}}$ is the measured potential.

The formulas for calculating the average number of electrons transferred (n) during the oxygen reduction reaction were as follows:

$$J^{-1} = J_k^{-1} + B^{-1}\omega^{-1/2} \quad (2)$$

$$B = 0.62nFA\nu^{-1/6}C_{O_2}D_{O_2}^{2/3} \quad (3)$$

where J (mA cm^{-2}) is the measured current density, J_k (mA cm^{-2}) is the kinetic current density, ω (rad s^{-1}) is the angular velocity of the electrode rotation, n is the number of electrons transferred per each O_2 molecule, A (0.2475 cm^2) is the geometric area of the electrode, F

(96485 C mol⁻¹) is the Faraday constant, and ν (cm² s⁻¹) is the viscosity of 0.1 M KOH. C_{O_2} (1.2×10^{-6} mol cm⁻³) is the concentration of O₂ in 0.1 M KOH, and D_{O_2} (1.9×10^{-5} cm² s⁻¹) is the diffusion coefficient of O₂ in 0.1 M KOH.

2.4. Zinc-air battery testing

A zinc-air battery was assembled to evaluate the ORR efficiency. The air cathode was made with 5 mg of NHPCs, 450 μ L of deionized water and 50 μ L of Nafion (5 wt%) and ultrasonicated for 1 h to obtain a homogenous ink. Then the ink was uniformly dropped onto carbon paper with an area of 1 cm² to achieve mass loading of 1 mg cm⁻². A polished zinc sheet was used as the anode. The measurement was performed in two-electrode system, cathode was the carbon paper partially coated with copper foil, anode was the zinc plate (2×1 cm), 6 M KOH solution was adopted as electrolyte. Primary Zn–air battery was measured by LSV method to obtain a polarization curve of the NHPCs. The galvanostatic discharge-charge (GCD) cycling was carried out on a LAND testing system at the current density of 20 mA cm⁻².

2.5. Supercapacitor testing

The supercapacitor performance of the NHPCs were tested using CV, GCD and the electrochemical impedance spectroscopy (EIS) in three-electrode system and two-electrode systems, respectively. The working electrode was made by mixing the NHPCs, PVDF and carbon black with a mass ratio of 8:1:1 in poly-2-methyl-pyrrolidone to obtain a homogeneous slurry, then the slurry was brushed onto a carbon cloth and naturally dried. The mass loading of NHPCs on the carbon cloth was about 3–4 mg cm⁻². A Pt foil and saturated Ag/AgCl electrodes served as the counter and the reference electrode in three-electrode system, respectively. For the two-electrode systems, two identical NHPCs electrodes with the same mass loading were pressed together using a polypropylene membrane as separator. All the measurements were performed in 1 M H₂SO₄ solution at room temperature.

The specific capacitance of the NHPCs in three-electrode system and two-electrode systems were calculated according to the formula (4), the energy density and power density of the NHPCs in two-electrode systems were calculated in accordance with the formula (5) and the formula (6), respectively.

$$C = \frac{I \times \Delta t}{m \times \Delta V} \quad (4)$$

$$E = \frac{1}{2 \times 3.6} C (\Delta V)^2 \quad (5)$$

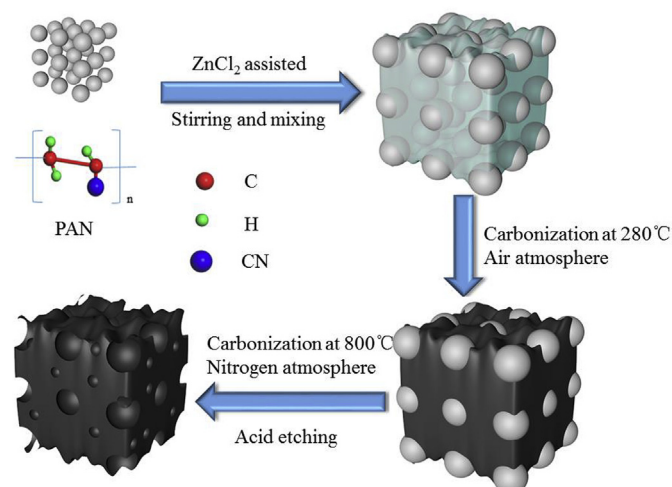
$$P = \frac{E \times 3600}{\Delta t} \quad (6)$$

where the gravimetric specific capacitance is C (F g⁻¹), the applied current is I (A), the discharge time is Δt (s), the mass of active materials in the working electrode is m (g), the working potential range is ΔV (V), the energy density is E (W h kg⁻¹); the power density is P (W kg⁻¹).

3. Results and discussion

3.1. Characterization of NHPCs

The synthesis procedure of the NHPCs is briefly illustrated in Scheme 1. PAN was a ubiquitous precursor for preparing N-doped porous carbon materials on account of its high nitrogen content and



Scheme 1. Synthesis process of N-doped hierarchical porous carbon materials.

well-established carbonization chemistry. SiO₂ nanoparticles were used as the template. After freeze-drying process, water was removed, and silica-PAN composites yielded. During the stabilization and carbonization stage, PAN can be readily converted into an N-doped porous carbon framework, the SiO₂ nanoparticles worked as a hard template for mesopores. The ZnCl₂ was not only used as pore-forming agent to produce great quantity micro/mesopores inside the carbon network, but also served the dual role of a solubility enhancing porogen to promote the co-dissolution of PAN in aqueous solution containing SiO₂. During further etching, the silica template can be easily eliminated in HF solution and obtained the NHPCs with hierarchical pore structures.

SEM analysis was employed to study the microstructure of the as-prepared NHPCs, and the results are exhibited in Fig. S1. As shown in the Figs. S1a–b, the NHPC-0.5 exhibits a three-dimensional (3D) honeycomb morphology established by loose laminated porous carbon skeletons with abundant visual pores. From the SEM image of the edge of the material, it is made up of small pieces stacked layer by layer, and the outer edge is slightly uneven in steps. Figs. S1c–d clearly demonstrated that the numerous interconnected pores possess distinguishing shapes and sizes, macropores of several hundreds of nanometers and mesopores of tens of nanometers are observed in the sample. The three-dimensional cross-linked porous structure is beneficial to the practical application in electrochemistry. More details of the pore morphology and structure were further studied by the TEM, as displayed in Fig. 1 and Fig. S2. It is confirmed from Fig. 1a that the NHPC-0.5 has a highly porous characteristic with multi-pores of interconnected meso- and micro-pores, which were formed during the process of pyrolysis and acid etching because of the volatilization of ZnCl₂ and removal of SiO₂. Fig. 1b and c showed the high-resolution TEM (HRTEM) of the selected regions in Fig. 1a, the selected area electron diffraction (SAED) pattern proved the amorphous carbon structure. The high-angle circular dark-field scanning TEM (HAADF-STEM) image (Fig. 1d) further confirmed the three-dimensional (3D) hierarchical porous structures of the sample, the corresponding energy dispersive spectrometer (EDS) element mapping images (Fig. S2) reveals the uniform dispersion of C, O, and N elements throughout the sample.

The specific surface area, pore volume and pore size distribution of the NHPCs were obtained by nitrogen adsorption-desorption measurement, the corresponding nitrogen adsorption-desorption isotherms of NHPCs is displayed in Fig. 2a. The N₂ adsorption

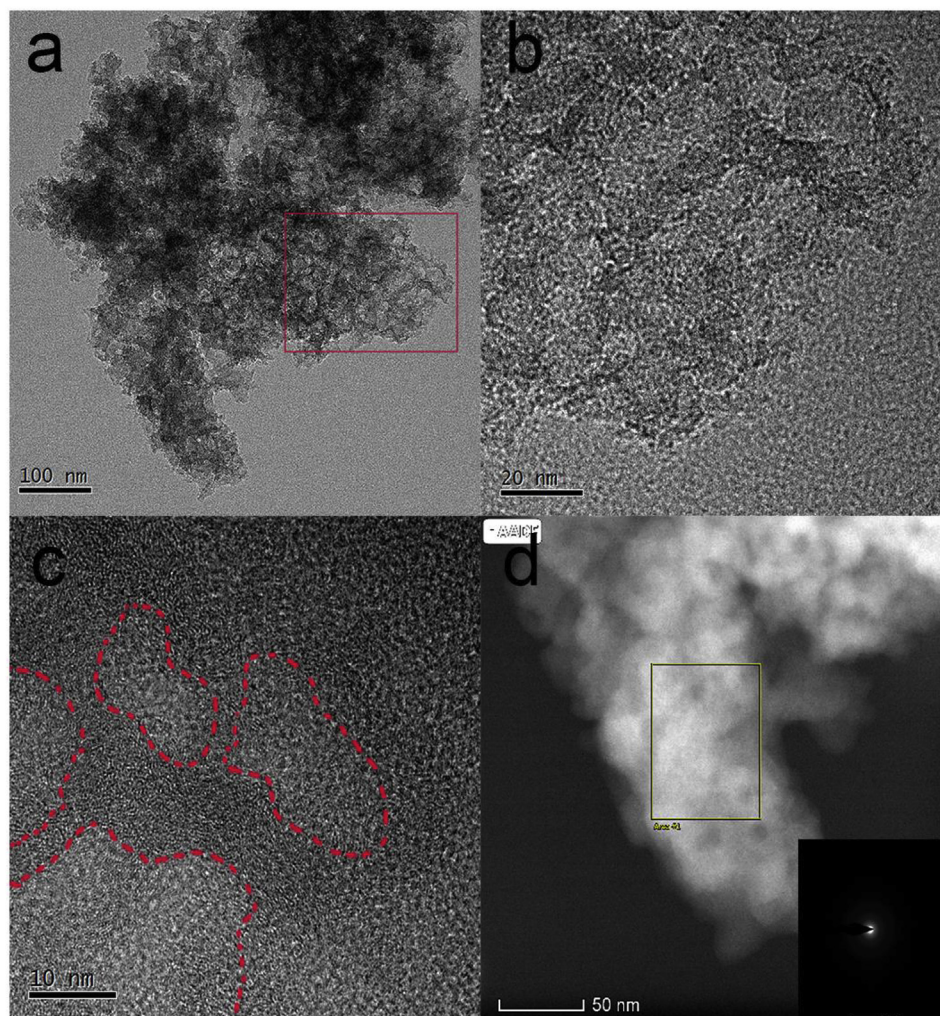


Fig. 1. a) TEM and b, c) HRTEM, d) HAADF-STEM and selected area electron diffraction pattern (inset of d) of NHPC-0.5.

isotherm of NHPCs exhibit a hybrid of type I and IV isotherms with an evident type-H4 hysteresis loop, suggesting the hierarchical porous characteristic of the NHPCs samples. The strong N_2 adsorption at relative low pressure area ($P/P_0 < 0.02$) indicates the presence of micropores, the apparent hysteresis loops at a relative pressure about 0.5–1.0 suggests the mesoporous feature of the samples, and the steep uptake at relative pressure of 0.9–1.0 implies the presence of macropore, which are in good accordance with the morphology of SEM and TEM images. The pore size distribution (Fig. 2b) further confirms the hierarchical pore architecture with dominated pore size ranging from 0.8 to 10 nm. Such a hierarchical porous structure is highly propitious to the ORR and supercapacitor performance because it can shorten the ion diffusion path and accelerate the ion transport [35]. The specific surface area and micropore surface area were calculated from the N_2 adsorption isotherms according to the BET and t-plot methods, respectively, and displayed in Table S1. The specific surface area of the NHPC-0.75 is as high as $1798 \text{ m}^2 \text{ g}^{-1}$ with total pore volume of $2.83 \text{ cm}^3 \text{ g}^{-1}$, which is much higher than previously reported N-doped hierarchical porous carbon [4,36–39]. It is noteworthy that the $S_{\text{micro}}/S_{\text{meso}}$ and $V_{\text{micro}}/V_{\text{meso}}$ fraction of NHPCs gradually reduces with the increase of mass ratio of SiO_2 to PAN (Fig. S3). Previous literature reported [20,40,41] that the optimization of micro/mesopore ratio is a key factor for the ORR and supercapacitor

performance of porous carbon. The excessive micropore hinders the ion diffusion path and delays the ion transport. Conversely, the increasing mesopore leads to the loss of active site because of the reduction of the specific surface area. Therefore, NHPC-0.5 may be a desirable candidate for ORR and supercapacitor owing to its well-developed hierarchical pore structure with optimized micro/mesopore ratio.

Fig. 2c depicted the XRD patterns of the products. The patterns of the products have two distinct diffraction peaks at 25° and 44° , which can be identified to the diffraction peaks of the (002) and (101) plane of partially graphitized amorphous carbon, respectively. The graphitization degrees of the NHPCs were researched by Raman spectroscopy analysis in depth. It can be seen from Fig. 2d, all the samples exhibit two distinct peaks, 1342 cm^{-1} (D band) and 1595 cm^{-1} (G band), respectively. The D band is attributed to the defects or the disordered carbon structure, while the G band related to the ordered graphitic sp^2 bonded carbons. Moreover, the intensity ratio of D band and G band (I_D/I_G) expresses the degree of disorder of materials. The I_D/I_G value of NHPC-0, NHPC-0.25, NHPC-0.5, NHPC-0.75 were calculated to be 1.23, 1.14, 1.15 and 1.18, respectively. The minimum I_D/I_G value of NHPC-0.25 indicates the higher degree of graphitization and the less defect in the sample. Especially, the I_D/I_G increases with the increasing of X from 0.25 to 0.75, indicating the enhanced disorder structure or defect with

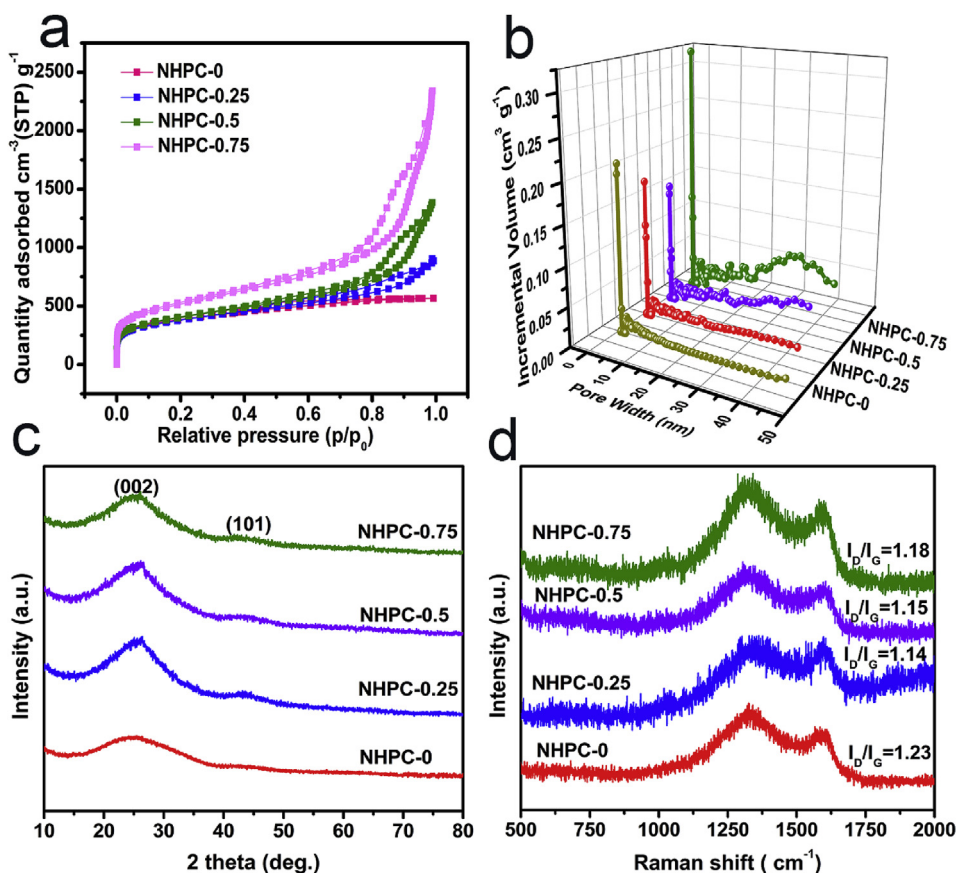


Fig. 2. a) Nitrogen adsorption–desorption isotherms and b) pore-size distribution of NHPCs; c) XRD and d) Raman spectra of NHPCs.

increasing of the mass ratio of SiO₂ to PAN.

XPS technique is employed to investigate the chemical composition and electronic state of the elements of the as-prepared NHPCs, the corresponding results are demonstrated in Fig. 3 and Fig. S4. The XPS spectra of all samples have three peaks at 284.5, 398.1 and 531.0 eV, corresponding to C 1s, N 1s and O 1s, respectively, suggest the presence of C, N, and O element (Fig. S4a). The elemental composition of all samples is presented in Fig. 3e. A relatively high-level doping of 12.1 at% for N element was obtained in NHPC-0.5, and the detailed information of C, N, O elements are displayed in Table S2. To investigate the detail of C and N configuration in the NHPCs, high-resolution C 1s and N 1s spectra of the NHPCs are plotted in Fig. S4b and Fig. 3a–d. The high-resolution C 1s spectra in Fig. S4b can be fitted into four peaks centered at nearby 284.6, 285.8 and 288.8 eV after deconvoluting, which can be assigned to the C–C, C–N/C–O and O–C=O bonding, respectively. The high-resolution N 1s spectra of the NHPCs in Fig. 3a–d can be deconvoluted into pyridine N (N-6) (398.2 eV), pyrrole N (N-5) (399.7 eV), graphitized N (N-G) (400.6 eV) and oxidized N (N–O) (403.4 eV). The pyridine N can introduce the electron donor into carbon materials by offering a pair of electrons to the π -conjugated ring, which has appreciable impact on the increased capacitance [7,42]. The pyrrole N can facilitate the electron transfer process available and import extra pseudocapacitance due to their electron-donor characteristic. In addition, the graphitized N will significantly enhance the conductivity, while N-oxides improve the wettability of carbon materials [42]. Fig. 3f and Table S3 showed the relative ratio of four types of N species. Such a N-doped hierarchical porous structure is highly desirable for ORR and supercapacitor because it can achieve rapid ion diffusion by shortening the diffusion

pathways.

3.2. ORR performance of NHPCs

Since the synthesized NHPCs combine the advantages of high-level nitrogen, large specific surface area and hierarchical porous structure, we expect it have an extraordinary ORR performance. The ORR performance of as-prepared NHPCs were tested by rotating disk electrode at a sweep speed of 5 mV s^{−1} in 0.1 M KOH solution, as illustrated in Fig. 4 and S5. Fig. 4a showed the CV curves performed in N₂ and O₂-saturated electrolyte. It can be clearly seen that the CV curves possess obvious cathode peak near 0.8 V in O₂-saturated except NHPC-0, while there is no obvious cathode peak in N₂-saturated. The cathode peaks appearing in the whole ORR process come from the response of the material to oxygen, suggesting that the as-synthesized NHPCs are promising catalysts for ORR. Remarkably, NHPC-0.5 possesses the highest peak voltage (0.8443 V) in all samples (0.8203 V for NHPC-0.25, 0.8335 V for NHPC-0.75).

LSV is another routine test method to measure the ORR performances, which can obtain the initial potential, half-wave potential and limiting current density of the material. The larger the initial potential, the more positive the half-wave potential and the greater the ultimate limiting current density, the better ORR performance of materials. The ORR performance of the as-synthesized NHPCs were further evaluated by LSV using a rotating ring-disk electrode (RRDE) at a rotating rate of 1600 rpm with a sweep speed of 5 mV s^{−1} in O₂-saturated alkaline solution, and the corresponding LSV curves are displayed in Fig. 4b. NHPC-0.5 possess a larger limiting current density (3.4682 mA cm^{−2} at 0.3 V vs RHE)

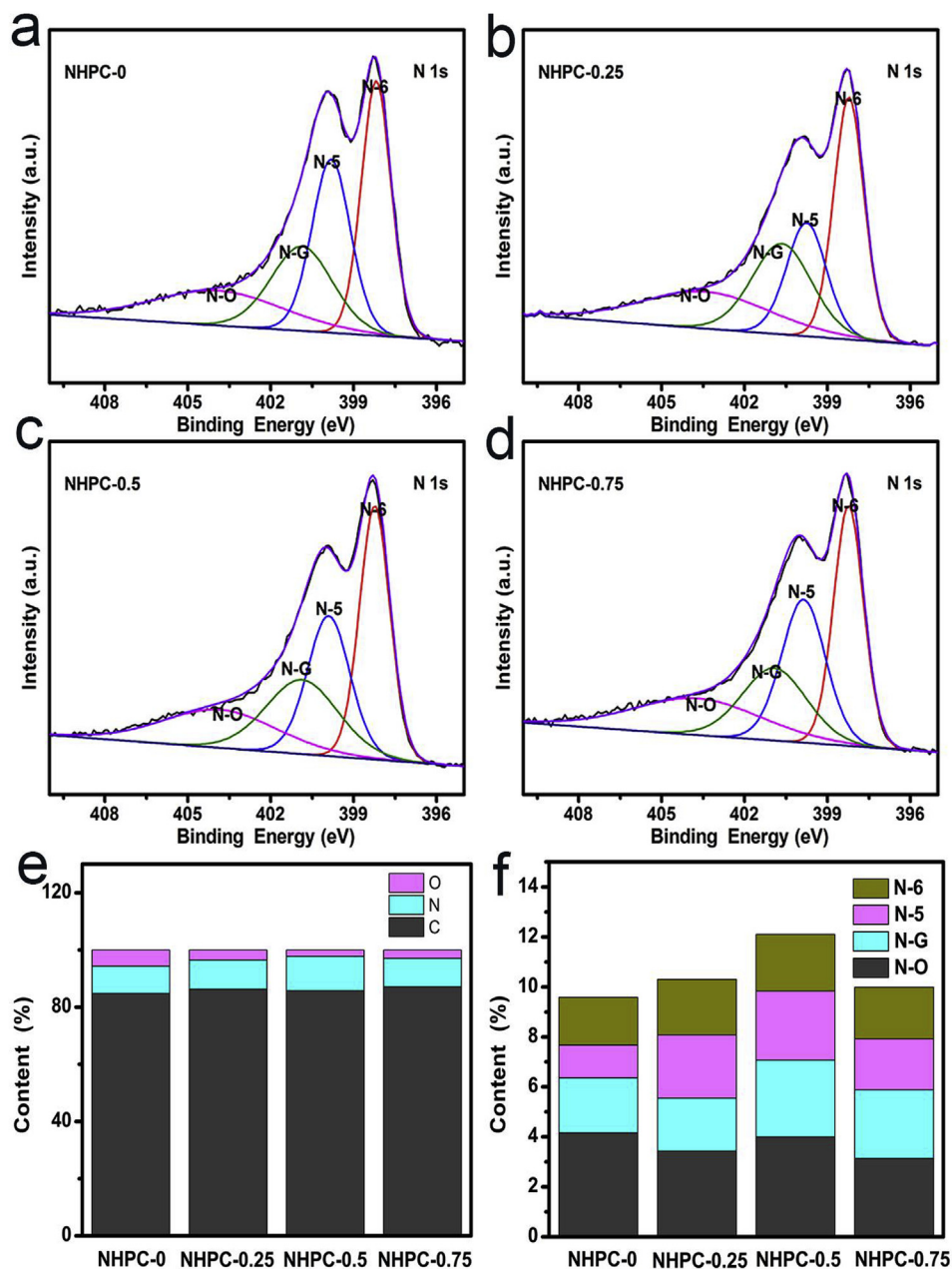


Fig. 3. a-d) N 1s of NHPCs; e) the content of C 1s, O 1s and N 1s for NHPCs; f) the content of different N including pyridinic N (N-6), pyrrolic N (N-5), graphitic N(N-G) and oxidized N(N-O) for NHPCs.

and an ideal onset potential (1.004 V vs RHE, at $j = 0.1 \text{ mA cm}^{-2}$), as well as a higher half-wave potential (0.883 V vs RHE, at $j = 1/2j_{\text{max}}$) compare with other samples (Fig. 4e), even higher than that of reference Pt/C catalyst (initial potential 1.0303 V vs RHE, half-wave potential 0.86 V vs RHE), suggesting excellent ORR activity of NHPC-0.5, which is better than those reported carbon-based materials described in Table 1 [35,43–48]. To investigate the reaction kinetics, the LSV curves of NHPC-0.5 at different rotation speeds were recorded and presented in Fig. 4c, while the LSV curves of other samples at different rotation speeds are displayed in Fig. S5. Fig. 4d and Fig. S5 showed the link between j^{-1} and $\omega^{-1/2}$ of different samples estimated from the Koutechy-Levich (K-L plot) equation through LSV curves. As shown in Fig. 4d, the K-L curve of NHPC-0.5 exhibits a good linear relationship at potential range of 0.3–0.6 V, indicating that oxygen reduction was controlled by diffusion.

The electron transfer number per oxygen molecule n is another key parameter to evaluate electrocatalysis catalytic activity. The electron transfer number n of the NHPC-0.5 was about 4.39 calculated according to the formula (2) and (3) at range of 0.3–0.6 V, indicating a direct four-electron transfer process for electrocatalysis. Within all the NHPCs samples, NHPC-0.5 delivers the superior performance in electrocatalysis activity, which can be put down to the synergistic effects of high specific surface area, the hierarchical porous structure with appropriate micro/mesopore ratio, along with high nitrogen content and species. These multi-aspect merits render the NHPC-0.5 a promising catalyst for ORR.

Furthermore, durability is one of the important factors for ORR, and the LSV curves were performed on in O_2 -saturated alkaline medium to test the stability of NHPC-0.5, the Pt/C catalyst was tested as benchmark. As shown in Figs. S6a–b, after 10,000 CV

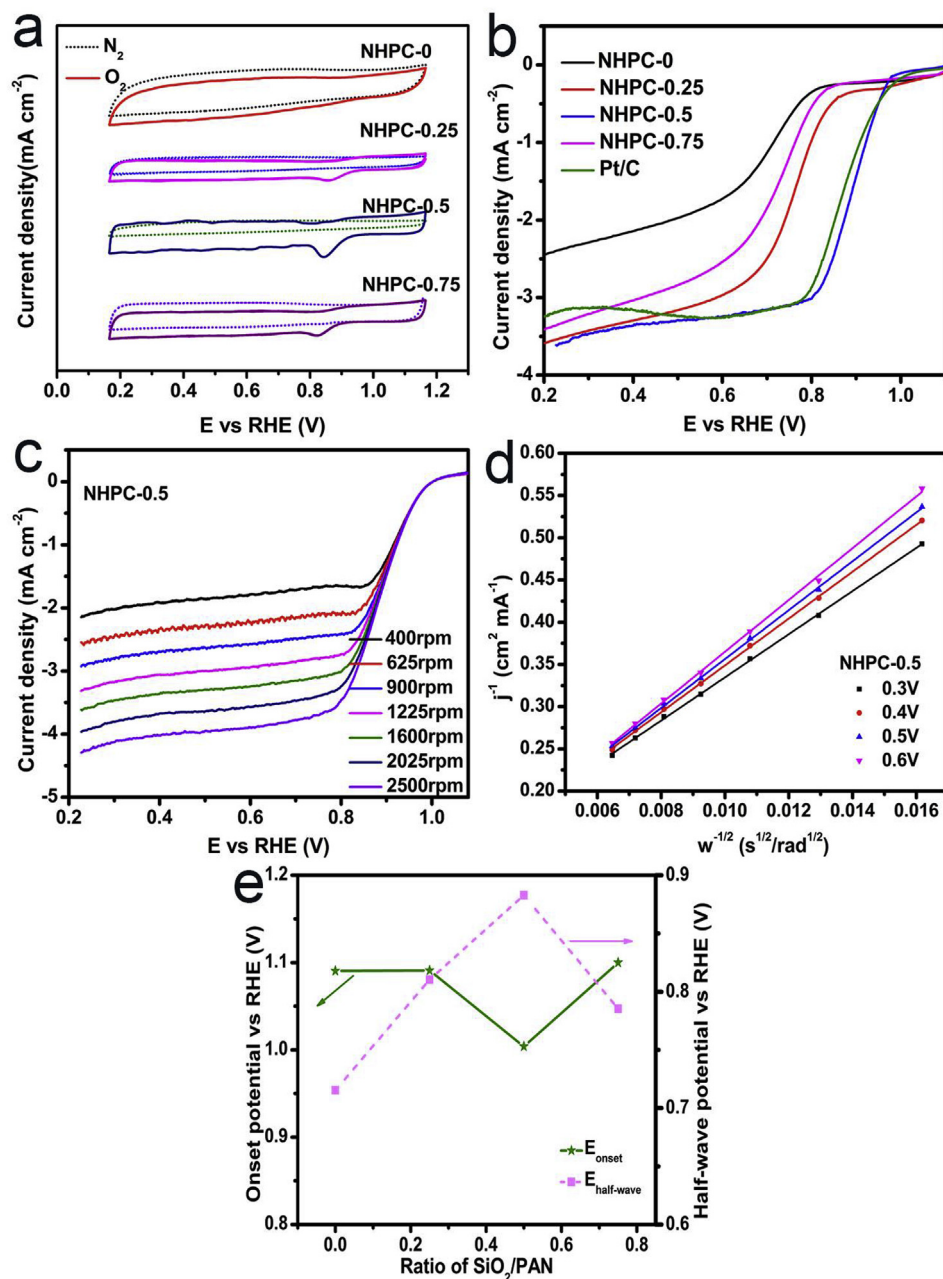


Fig. 4. Electrocatalysis performance test: a) CV in saturated nitrogen and oxygen of NHPCs, sweep rate of 5 mV s^{-1} (0.1 M KOH); b) LSV of NHPCs and Pt/C in saturated oxygen at a rotating rate of 1600 rpm, sweep rate of 5 mV s^{-1} (0.1 M KOH); c) LSV of NHPC-0.5 with different rate in saturated oxygen (0.1 M KOH); d) The dependence of j^{-1} on $\omega^{-1/2}$ of NHPC-0.5 derived from d); e) the initial and half-wave potential of NHPCs derived from b).

Table 1

ORR performance of carbon-based materials.

Samples	Measurement condition	Onset potential (V)	Half-wave potential (V)	Current density (mA cm^{-2})	Ref.
Nitrogen-doped porous carbon	0.1 M KOH, 1600 rpm, 10 mV s^{-1}	0.95 (RHE)	0.86 (RHE)	4.8 (at 0.2 V vs. RHE)	[35]
rGO/CB/Co-Bi	0.1 M KOH, 1600 rpm, 10 mV s^{-1}	0.88 (RHE)	0.7 (RHE)	5.4 (at 0.1 V vs. RHE)	[43]
Fe-N/C	0.1 M KOH, 1600 rpm, 10 mV s^{-1}	0.99 (RHE)	—	4.8 (at 0.45 V vs. RHE)	[44]
Nitrogen-doped holey graphene nanocapsules	0.1 M KOH, 1600 rpm, 5 mV s^{-1}	1.03 (RHE)	0.85 (RHE)	5.2 (at 0.5 V vs. RHE)	[45]
N-doped porous carbon spheres	0.1 M KOH, 1600 rpm, 10 mV s^{-1}	—	0.25 (SCE)	4.6 (at 0.7 V vs. SCE)	[46]
Ammonia modification of activated carbon	0.1 M KOH, 1600 rpm, 5 mV s^{-1}	0.05 (Ag/AgCl)	—	4.55 (at -1 V vs. Ag/AgCl)	[47]
N-doped hierarchically porous carbons	0.1 M KOH, 1600 rpm, 5 mV s^{-1}	0.84 (RHE)	0.85 (RHE)	4.32 (at 0.8 V vs. RHE)	[48]
NHPC-0.5	0.1 M KOH, 1600 rpm, 5 mV s^{-1}	1.004 (RHE)	0.883 (RHE)	3.47 (at 0.3 V vs. RHE)	This work

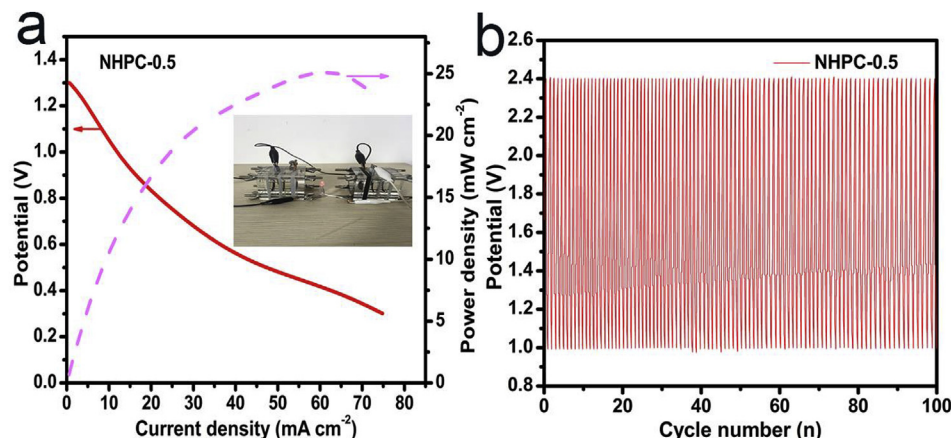


Fig. 5. Zinc-air battery test of NHPC-0.5: a) the polarization curve and output power density curve, sweep rate of 100 mV s^{-1} (6 M KOH); b) cycle stability after 100 cycles, current density of 10 mA cm^{-2} (6 M KOH).

curves cycling test at a sweep speed of 100 mV s^{-1} , negative shift in half-wave potential of NHPC-0.5 is 11 mV, which is less than half of Pt/C (27 mV). In addition, the negative shift in half-wave potential of NHPC-0.5 and Pt/C is 10 and 12 mV after the injection of 5 mL of 2 M methanol into the testing electrolyte (0.1 M KOH, 40 mL), respectively. It indicated the NHPC-0.5 exhibited superior stability and better resistance to methanol than those of the benchmark Pt/C catalyst, making it a promising cathodic catalyst for electrodes in metal-air batteries application.

Inspired by the outstanding ORR activity and durability of NHPCs in alkaline media, the performance of NHPC-0.5 catalyst was further investigated in a self-made zinc-air battery to investigate its possibility for commercial zinc-air batteries. The battery possesses an open circuit potential of 1.3 V in Fig. 5a. Fig. 5a also showed that the output power density was 25.1 mW cm^{-2} when the current density was about 5 mA cm^{-2} . This was ascribed to that NHPC-0.5 has a hierarchical porous structure, which can broaden the ion transport space and accelerate the mass transfer rate of ions. Moreover, it is also helpful to improve performance since a certain amount of nitrogen doping can endow abundant active sites for NHPC-0.5. Charging and discharging performance was also an indicator to measure the performance of the battery. Generally, the lower charging voltage and the higher discharging voltage indicated the advantage of NHPC-0.5 with relatively low energy consumption and higher power supply voltage in practical applications. A cycling durability test was carried out at the current density of 20 mA cm^{-2} (Fig. 5b). Notably, NHPC-0.5 exhibits a stable charge–discharge profile, suggesting its favorable charge–discharge ability. After 100 cycles, a negligible potential loss can be observed on both the charge and discharge curves, proving superior durability of the self-made Zn–air battery. As illustrated in the inset of Fig. 5a, two self-contained Zn–air batteries connected in series can illuminate a light, further confirmed the practical applications of NHPC-0.5 in energy storage devices.

3.3. Supercapacitor performance of NHPCs

Given the above desirable characterization and excellent ORR performance, the as-prepared NHPCs were further studied as electrode for supercapacitor, and the supercapacitor performance of the NHPCs were put into effect in a three-electrode system in 1 M H_2SO_4 electrolyte. Fig. 6a showed the CV curves of the NHPCs at a sweep speed of 10 mV s^{-1} in the potential range from -0.02 to 0.98 V (vs. RHE). The CV curves of the NHPCs electrodes exhibit a quasi-rectangular with distinct reversible hump, suggesting that

the capacitive performance of the samples derived from the combination of electric double-layer capacitance (EDLC) and pseudocapacitance owing to the presence of redox active nitrogen functional group. The NHPC-0.5 presents the larger integral area than other samples, indicating the highest capacitance can be expected. Fig. 6b and S7 presented the CV curves of NHPC-0.5 and other samples at different sweep speeds. It can be observed from Fig. 6b that the CV curves still retain the original shape even at high sweep speed of 200 mV s^{-1} , confirming the excellent rate capability. Fig. 6c and S7 displayed the GCD curves of NHPC-0.5 and other samples at different current densities from 1 to 50 A g^{-1} . The GCD curves obviously derived from linearity, illustrating the coexistence of EDLC and pseudocapacitance behavior of the NHPC-0.5, which is consistent with the CV measurement. The specific capacitances of NHPCs were calculated based on the discharge curves according to the formula (4) and presented in Fig. 6d. The specific capacitances of the as-prepared NHPCs are higher than other carbon materials ever reported and traditional commercial activated carbon material ($80\text{--}120 \text{ F g}^{-1}$) [49]. As expected, among the NHPCs, the NHPC-0.5 delivers the highest specific capacitance of 283.7 F g^{-1} at a current density of 1 A g^{-1} with capacitance retention of 84% at a high current density of 20 A g^{-1} , which is superior than those previously reported carbon-based electrodes, as shown in Table 2 [4,5,24,37,39,50–54]. The superior capacitive behavior of NHPC-0.5 mainly because of its highest amount of N functional groups offer extra pseudocapacitance and moderate surface area with proper micro/mesopore ratios render effective electrode/electrolyte interface for EDLC. Electrochemical impedance spectroscopy (EIS) is significant to clarify kinetics information of electrode, including capacitive property, electrical resistance property and electrolyte ion transport behavior. EIS of NHPCs were measured over a frequency range of $10^{-2}\text{--}10^5 \text{ Hz}$ at open circuit potential and corresponding Nyquist plots are illustrated in Fig. 6e and Fig. S8a. At high frequency, the intercept of curves at real axis (Z') represents the value of equivalent series resistance (R_s), which is the total internal resistance of electrode system. The diameter of semicircle signifies interfacial charge transfer resistance (R_{ct}) between electrolyte and electrode/electrolyte interface. As showed in Fig. 6e and S8a, NHPC-0.5 exhibit smaller R_s and lower R_{ct} value, demonstrating the low internal resistance, favorable electrical conductivity, and faint charge transfer resistance. At low frequency, almost vertical lines of NHPC-0.5 clearly showing better capacitive behaviors. Furthermore, the cycle stability was performed by repeated GCD to further examine the electrochemical stability of electrodes. Fig. 6f illustrated the capacitance retention and the

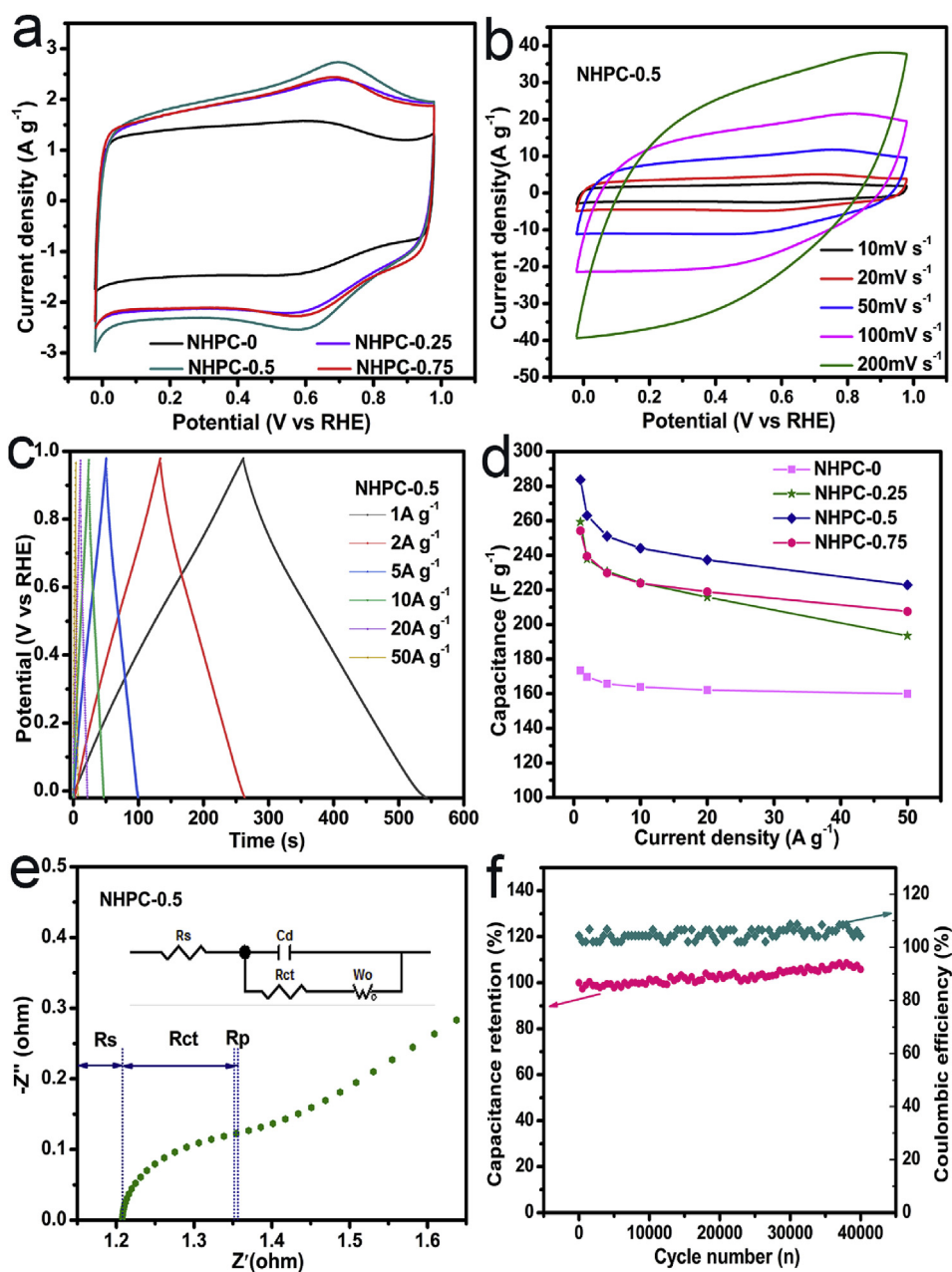


Fig. 6. Capacitance test of three-electrode system: a) CV of NHPCs with a sweep speed of 10 mV s⁻¹ (1 M H₂SO₄); b) CV of NHPC-0.5 with different scan speeds from 10 mV s⁻¹ to 200 mV s⁻¹ (1 M H₂SO₄); c) GCD curves of NHPC-0.5 with different current density from 1 A g⁻¹ to 50 A g⁻¹ (1 M H₂SO₄); d) specific capacitance change of NHPCs with different current densities; e) EIS of NHPC-0.5 (1 M H₂SO₄); f) capacitance retention and coulomb efficiency curves of NHPC-0.5 after circulating for 40,000 cycles at a current density of 4 A g⁻¹ (1 M H₂SO₄).

coulomb efficiency curve for NHPC-0.5 after circulating for 40,000 cycles at a current density of 4 A g⁻¹. The NHPC-0.5 presents a high capacitance retention of 105.8% and coulomb efficiency of 104.2% after 40,000 cycles, demonstrating the superb cycling performance of NHPC-0.5.

The NHPC-0.5 was assembled into a symmetric supercapacitor (NHPC-0.5//NHPC-0.5) device to investigate the practical device behavior of NHPCs. Fig. 7a showed the CV curve of NHPC-0.5//NHPC-0.5 at different sweep speeds. It can be observed that all the curves exhibited a regular rectangle even at a high sweep speed of 200 mV s⁻¹, indicating ideal capacitive behavior and high rate performance. The GCD curves of the NHPC-0.5//NHPC-0.5 measured at different current density of (Fig. 7b) display nearly

isosceles triangle shape, demonstrating seductive capacitive behavior. The calculated specific capacitance values of NHPC-0.5//NHPC-0.5 presented in Fig. 7c are 81.6 F g⁻¹, 80.5 F g⁻¹, 78.8 F g⁻¹, 76.8 F g⁻¹ and 73.6 F g⁻¹ at current density from 1 A g⁻¹ to 20 A g⁻¹, respectively. Even at a high current density of 20 A g⁻¹, it still maintains a high specific capacitance of 73.6 F g⁻¹ (capacitance retention of 90.2%), suggesting remarkable rate capability. The small internal resistance of NHPC-0.5//NHPC-0.5 supercapacitor, as shown in Fig. S8b, suggests that the device possess an ideal capacitance characteristic. The inset of Fig. 7c displayed the ragone plot of the energy density versus power density to further assess the energy storage performance of the NHPC-0.5//NHPC-0.5 supercapacitor. The NHPC-0.5//NHPC-0.5 supercapacitor exhibits

Table 2
Supercapacitance performance of carbon-based supercapacitors.

Samples	Measurement condition	Current density ($A g^{-1}$)	Capacitance ($F g^{-1}$)	Rate capability (%)	Cycle numbers	Capacity retention (%)	Ref.
Yolk-shelled carbon spheres	2-electrode, 6 M KOH	0.5	120	75 ($20 A g^{-1}$)	—	—	[4]
Monodisperse starburst carbon spheres	2-electrode, 1 M Na_2SO_4	0.24	60	95 ($1 A g^{-1}$)	4000	95%	[5]
N-doped ordered mesoporous carbon	3-electrode, 1 M H_2SO_4	0.25	212	79 ($20 A g^{-1}$)	—	—	[24]
Hierarchically porous carbon	3-electrode, 1 M H_2SO_4	0.1	274	59 ($20 A g^{-1}$)	5000	100	[50]
N, B co-doped hierarchically porous carbons	3-electrode, 6 M KOH	0.5	247	68 ($20 A g^{-1}$)	4000	96.2	[51]
N-doped porous monolithic carbons	3-electrode, 1 M H_2SO_4	0.2	270	72 ($100 A g^{-1}$)	5000	100	[52]
N-doped porous carbon spheres	3-electrode, 6 M KOH	1	247	64 ($30 A g^{-1}$)	5000	97	[53]
N-doped carbon aerogels	3-electrode, 6 M KOH	1	253.7	48 ($20 A g^{-1}$)	10000	94.5	[54]
N-doped porous carbon nanofibers	3-electrode, 1 M H_2SO_4	0.5	335	52 ($32 A g^{-1}$)	10000	86	[37]
Mesoporous carbon sheet-like framework	3-electrode, 6 M KOH	1	276.5	82 ($20 A g^{-1}$)	5000	91	[39]
NHPC-0.5	3-electrode, 1 M H_2SO_4	1	283.7	84 ($20 A g^{-1}$)	40000	105.8	This work
NHPC-0.5	2-electrode, 1 M H_2SO_4	1	81.6	90.2 ($20 A g^{-1}$)	12000	99.3	This work

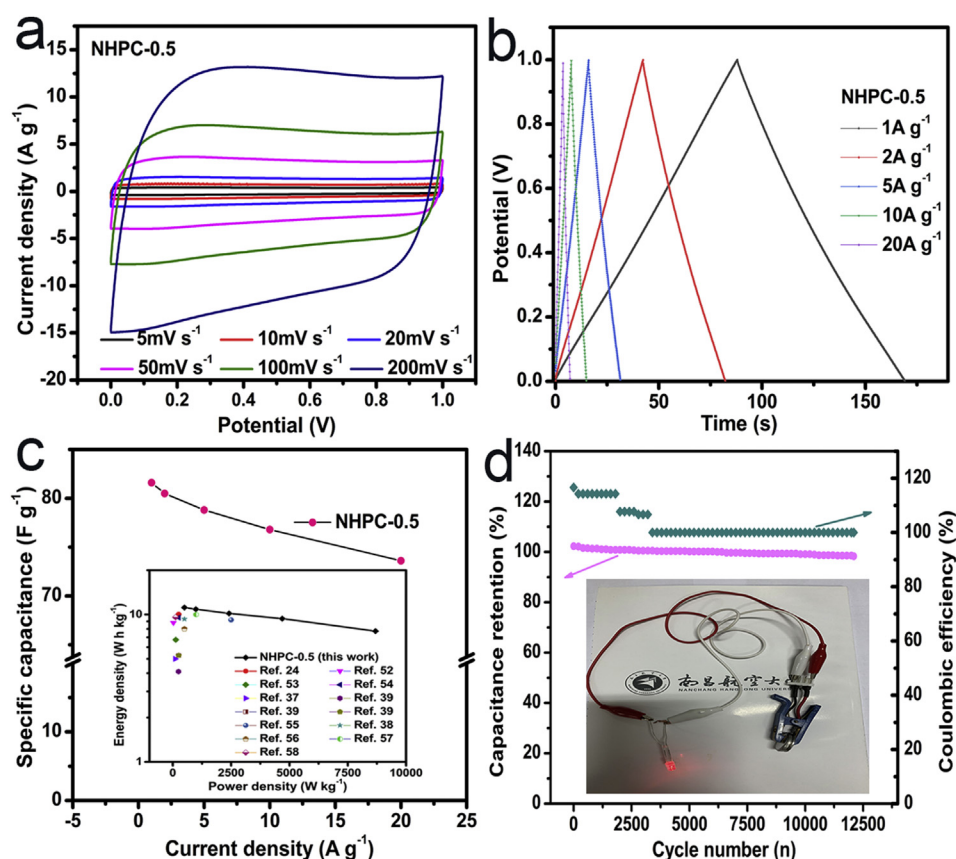


Fig. 7. a) CV of NHPC-0.5//NHPC-0.5 with different sweep speed from 5 $mV s^{-1}$ to 200 $mV s^{-1}$ (1 M H_2SO_4); b) GCD curves of NHPC-0.5//NHPC-0.5 with different current density from 1 $A g^{-1}$ to 20 $A g^{-1}$ (1 M H_2SO_4); c) specific capacitance change of NHPC-0.5//NHPC-0.5 at different current densities (the inset is Ragone plot of porous carbon materials that can be found in the previous reports and NHPCs-based supercapacitor); d) capacitance retention and coulomb efficiency curves of NHPC-0.5//NHPC-0.5 after circulating for 12,000 cycles at a current density of 6.7 $A g^{-1}$ (the inset is two button batteries connected in series can illuminate a light: the voltage of the light is 1.5 V) (1 M H_2SO_4).

an energy density of 11.3 $W h kg^{-1}$ at the power density of 502 $W kg^{-1}$. Even at a high power density of 8691 $W kg^{-1}$, the energy density can still retain 7.7 $W h kg^{-1}$, which is much higher than previously reported N-doped hierarchical porous carbon (the inset of Fig. 7c) [28,37–39,52–58]. Fig. 7d displayed the cycling stability of the NHPC-0.5//NHPC-0.5 supercapacitor tested for 12,000 cycles by GCD at a current density of 6.7 $A g^{-1}$. The NHPC-0.5//NHPC-0.5 supercapacitor exhibits good stability with almost no loss of the initial capacitance after 12,000 cycles (capacitance retention of 99.3% after 12,000 cycles). In addition, two NHPC-0.5//NHPC-0.5 supercapacitor connected in series can illuminate a light (the inset of Fig. 7d), which further demonstrates the potential of

the sample NHPC-0.5 for supercapacitor applications.

4. Conclusion

To conclude, a series of N-doped hierarchical porous carbon (NHPCs) were successfully synthesized by a simple, benign and convenient synthesis method. In this method, the utilization of $ZnCl_2$ enhancing the solubility of porogen, and enables the solubilization of PAN template as well as dispersion of porogenic particle in water, consequently enhances the surface area. The resultant NHPCs were provided with large pore volume, interconnected hierarchical porous structure, high specific surface area

and high content of nitrogen doping. Benefiting from the synergistic effect of above advantages, the as-prepared NHPCs presented excellent performance as both ORR (half-wave potential 0.883 V vs RHE, initial potential 1.004 V vs RHE, and favorable tolerance against methanol) and supercapacitor (the gravimetric specific capacitance can reach up to 283.7 F g⁻¹ at current density of 1 A g⁻¹ in 1 M H₂SO₄ electrolyte, outstanding cyclic stability of 105.8% capacitance retention after 40,000 cycles, and an energy density of 11.3 W h kg⁻¹ at the power density of 502 W kg⁻¹, even at a high power density of 8691 W kg⁻¹, the energy density can still retains 7.7 W h kg⁻¹) electrodes. The facile material synthesis and impressive performance make the NHPCs competitive for practical applications in high performance energy storage devices.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Hang Sun: Visualization, Writing - original draft, Data curation, Writing - review & editing. **Hongying Quan:** Conceptualization, Writing - review & editing. **Menghua Pan:** Investigation. **Zhiming Zhang:** Data curation. **Yong Zeng:** Data curation. **Dezhi Chen:** Conceptualization, Funding acquisition, Writing - review & editing.

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Appendix A. Supplementary data

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References

- [1] W. He, C. Jiang, J. Wang, L. Lu, High-rate oxygen electroreduction over graphitic-N species exposed on 3D hierarchically porous nitrogen-doped carbons, *Angew. Chem.* 53 (2014) 9503–9507.
- [2] G. Tao, L. Zhang, L. Chen, X. Cui, Z. Hua, M. Wang, J. Wang, Y. Chen, J. Shi, N-doped hierarchically macro/mesoporous carbon with excellent electrocatalytic activity and durability for oxygen reduction reaction, *Carbon* 86 (2015) 108–117.
- [3] Y.-L. Liu, C.-X. Shi, X.-Y. Xu, P.-C. Sun, T.-H. Chen, Nitrogen-doped hierarchically porous carbon spheres as efficient metal-free electrocatalysts for an oxygen reduction reaction, *J. Power Sources* 283 (2015) 389–396.
- [4] J. Wang, S. Feng, Y. Song, W. Li, W. Gao, A.A. Elzathary, D. Aldhayan, Y. Xia, D. Zhao, Synthesis of hierarchically porous carbon spheres with yolk-shell structure for high performance supercapacitors, *Catal. Today* 243 (2015) 199–208.
- [5] S.K. Kim, E. Jung, M.D. Goodman, K.S. Schweizer, N. Tatsuda, K. Yano, P.V. Braun, Self-assembly of monodisperse starburst carbon spheres into hierarchically organized nanostructured supercapacitor electrodes, *ACS Appl. Mater. Interfaces* 7 (2015) 9128–9133.
- [6] A.J. Amali, J.K. Sun, Q. Xu, From assembled metal-organic framework nanoparticles to hierarchically porous carbon for electrochemical energy storage, *Chem. Commun.* 50 (2014) 1519–1522.
- [7] Z. Li, X. Liu, L. Wang, F. Bu, J. Wei, D. Pan, M. Wu, Hierarchical 3D all-carbon composite structure modified with N-doped graphene quantum dots for high-performance flexible supercapacitors, *Small* 14 (2018), e1801498.
- [8] S. Yue, H. Tong, L. Lu, W. Tang, W. Bai, F. Jin, Q. Han, J. He, J. Liu, X. Zhang, Hierarchical NiCo₂O₄ nanosheets/nitrogen doped graphene/carbon nanotube film with ultrahigh capacitance and long cycle stability as a flexible binder-free electrode for supercapacitors, *J. Mater. Chem.* 5 (2017) 689–698.
- [9] J.X. Feng, H. Xu, S.H. Ye, G. Ouyang, Y.X. Tong, G.R. Li, Silica-polypyrrole hybrids as high-performance metal-free electrocatalysts for the hydrogen evolution reaction in neutral media, *Angew. Chem.* 56 (2017) 8120–8124.
- [10] Z.Y. Sui, Y.N. Meng, P.W. Xiao, Z.Q. Zhao, Z.X. Wei, B.H. Han, Nitrogen-doped graphene aerogels as efficient supercapacitor electrodes and gas adsorbents, *ACS Appl. Mater. Interfaces* 7 (2015) 1431–1438.
- [11] J. Jeong, M. Choun, J. Lee, Tree-bark-shaped N-doped porous carbon anode for hydrazine fuel cells, *Angew. Chem. Int. Ed.* 56 (2017) 13513–13516.
- [12] Y.Q. Zhao, M. Lu, P.Y. Tao, Y.J. Zhang, X.T. Gong, Z. Yang, G.Q. Zhang, H.L. Li, Hierarchically porous and heteroatom doped carbon derived from tobacco rods for supercapacitors, *J. Power Sources* 307 (2016) 391–400.
- [13] M.R. Benzigar, S.N. Talapaneni, S. Joseph, K. Ramadass, G. Singh, J. Scaranto, U. Ravon, K. Al-Bahily, A. Vinu, Recent advances in functionalized micro and mesoporous carbon materials: synthesis and applications, *Chem. Soc. Rev.* 47 (2018) 2680–2721.
- [14] W. Yang, W. Yang, L.N. Kong, A.L. Song, X.J. Qin, G.J. Shao, Phosphorus-doped 3D hierarchical porous carbon for high-performance supercapacitors: a balanced strategy for pore structure and chemical composition, *Carbon* 127 (2018) 557–567.
- [15] N. Mao, H.L. Wang, Y. Sui, Y.P. Cui, J. Pokrzywinski, J. Shi, W. Liu, S.G. Chen, X. Wang, D. Mitlin, Extremely high-rate aqueous supercapacitor fabricated using doped carbon nanoflakes with large surface area and mesopores at near-commercial mass loading, *Nano Res.* 10 (2017) 1767–1783.
- [16] K. Shen, X. Chen, J. Chen, Y. Li, Development of MOF-derived carbon-based nanomaterials for efficient catalysis, *ACS Catal.* 6 (2016) 5887–5903.
- [17] K. Yuan, C.B. Lu, S. Sfaelou, X.X. Liao, X.D. Zhuang, Y.W. Chen, U. Scherf, X.L. Feng, In situ nanoarchitecturing and active-site engineering toward highly efficient carbonaceous electrocatalysts, *Nano Energy* 59 (2019) 207–215.
- [18] Z.D. Lei, X. Long, M. Yang, D.G. Yang, H.B. Chen, H.M. Li, Nitrogen-doped porous carbon with brain-like structure derived from quaternary bipyridinium-type framework for efficient oxygen reduction electrocatalysis and supercapacitors, *Chemelectrochem* 6 (2019) 848–855.
- [19] Q.Y. Liang, H. Su, J. Yan, C. Leung, S.L. Cao, D.S. Yuan, N-doped mesoporous carbon as a bifunctional material for oxygen reduction reaction and supercapacitors, *Chin. J. Catal.* 35 (2014) 1078–1083.
- [20] C. Zhu, M. Takata, Y. Aoki, H. Habazaki, Nitrogen-doped porous carbon as mediated by a facile solution combustion synthesis for supercapacitor and oxygen reduction electrocatalyst, *Chem. Eng. J.* 350 (2018) 278–289.
- [21] M. Yang, Z. Zhou, Recent breakthroughs in supercapacitors boosted by nitrogen-rich porous carbon materials, *Adv. Sci.* 4 (2017) 1600408.
- [22] X.Y. Yang, A. Leonard, A. Lemaire, G. Tian, B.L. Su, Self-formation phenomenon to hierarchically structured porous materials: design, synthesis, formation mechanism and applications, *Chem. Commun.* 47 (2011) 2763–2786.
- [23] Z.-Y. Yuan, B.-L. Su, Insights into hierarchically meso-macroporous structured materials, *J. Mater. Chem.* 16 (2006) 663–677.
- [24] D. Liu, G. Cheng, H. Zhao, C. Zeng, D. Qu, L. Xiao, H. Tang, Z. Deng, Y. Li, B.-L. Su, Self-assembly of polyhedral oligosilsesquioxane (POSS) into hierarchically ordered mesoporous carbons with uniform microporosity and nitrogen-doping for high performance supercapacitors, *Nano Energy* 22 (2016) 255–268.
- [25] X. Meng, F. Nawaz, F.-S. Xiao, Templating route for synthesizing mesoporous zeolites with improved catalytic properties, *Nano Today* 4 (2009) 292–301.
- [26] N.D. Petkovich, A. Stein, Controlling macro- and mesostructures with hierarchical porosity through combined hard and soft templating, *Chem. Soc. Rev.* 42 (2013) 3721–3739.
- [27] J. Du, L. Liu, Y. Yu, Z. Hu, B. Liu, A. Chen, N-doped hollow carbon spheres/sheets composite for electrochemical capacitor, *ACS Appl. Mater. Interfaces* 10 (2018) 40062–40069.
- [28] W. Wang, H. Quan, W. Gao, R. Zou, D. Chen, Y. Dong, L. Guo, N-Doped hierarchical porous carbon from waste boat-fruited sterulia seed for high performance supercapacitors, *RSC Adv.* 7 (2017) 16678–16687.
- [29] A. Raza, J. Wang, S. Yang, Y. Si, B. Ding, Hierarchical porous carbon nanofibers via electrospinning, *Carbon Lett.* 15 (2014) 1–14.
- [30] C. Triantafyllidis, M.S. Elsaesser, N. Husing, Chemical phase separation strategies towards silica monoliths with hierarchical porosity, *Chem. Soc. Rev.* 42 (2013) 3833–3846.
- [31] K. Kanamori, K. Nakanishi, Controlled pore formation in organotrialkoxysilane-derived hybrids: from aerogels to hierarchically porous monoliths, *Chem. Soc. Rev.* 40 (2011) 754–770.
- [32] L. Chen, T. Ji, L. Brisbin, J. Zhu, Hierarchical porous and high surface area tubular carbon as dye adsorbent and capacitor electrode, *ACS Appl. Mater. Interfaces* 7 (2015) 12230–12237.
- [33] P. Huang, H. Li, X. Huang, D. Chen, Multiheteroatom-doped porous carbon catalyst for oxygen reduction reaction prepared using 3D network of ZIF-8/polymeric nanofiber as a facile-doping template, *ACS Appl. Mater. Interfaces* 9 (2017) 21083–21088.
- [34] Z.M. Sheng, X.J. Chang, Y.H. Chen, C.Y. Hong, N.N. Li, C.K. Chang, R.P. Jia, S. Han, Doping-template approach of porous-walled graphitic nanocages for superior performance anodes of lithium ion batteries, *RSC Adv.* 7 (2017) 42083–42087.
- [35] H.W. Liang, W. Wei, Z.S. Wu, X. Feng, K. Mullen, Mesoporous metal-nitrogen-doped carbon electrocatalysts for highly efficient oxygen reduction reaction, *J. Am. Chem. Soc.* 135 (2013) 16002–16005.
- [36] D. Nan, J.-G. Wang, Z.-H. Huang, L. Wang, W. Shen, F. Kang, Highly porous carbon nanofibers from electrospun polyimide/SiO₂ hybrids as an improved

- anode for lithium-ion batteries, *Electrochim. Commun.* 34 (2013) 52–55.
- [37] F. Miao, C. Shao, X. Li, K. Wang, Y. Liu, Flexible solid-state supercapacitors based on freestanding nitrogen-doped porous carbon nanofibers derived from electrospun polyacrylonitrile@polyaniline nanofibers, *J. Mater. Chem.* 4 (2016) 4180–4187.
- [38] Y. Cheng, Q. Zhang, C. Fang, Z. Huang, J. Chen, L. Wu, H. Wang, Synthesis of N-doped porous carbon materials derived from waste cellulose acetate fiber via urea activation and its potential application in supercapacitors, *J. Electrochem. Soc.* 166 (2019) A1231–A1238.
- [39] Q. Wang, J. Yan, T. Wei, J. Feng, Y. Ren, Z. Fan, M. Zhang, X. Jing, Two-dimensional mesoporous carbon sheet-like framework material for high-rate supercapacitors, *Carbon* 60 (2013) 481–487.
- [40] J. Yang, H. Wu, M. Zhu, W. Ren, Y. Lin, H. Chen, F. Pan, Optimized mesopores enabling enhanced rate performance in novel ultrahigh surface area meso-/microporous carbon for supercapacitors, *Nano Energy* 33 (2017) 453–461.
- [41] W. Wang, H. Quan, W. Gao, R. Zou, D. Chen, Y. Dong, L. Guo, N-Doped hierarchical porous carbon from waste boat-fruited sterulia seed for high performance supercapacitors, *RSC Adv.* 7 (2017) 16678–16687.
- [42] M. Yang, Z. Zhou, Recent breakthroughs in supercapacitors boosted by nitrogen-rich porous carbon materials, *Adv. Sci.* 4 (2017) 1600408.
- [43] J. Sun, D. Yang, S. Lowe, L. Zhang, Y. Wang, S. Zhao, P. Liu, Y. Wang, Z. Tang, H. Zhao, X. Yao, Sandwich-Like reduced graphene oxide/carbon black/amorphous cobalt borate nanocomposites as bifunctional cathode electrocatalyst in rechargeable zinc-air batteries, *Adv. Energy Mater.* 8 (2018) 1801495.
- [44] W. Niu, L. Li, X. Liu, N. Wang, J. Liu, W. Zhou, Z. Tang, S. Chen, Mesoporous N-doped carbons prepared with thermally removable nanoparticle templates: an efficient electrocatalyst for oxygen reduction reaction, *J. Am. Chem. Soc.* 137 (2015) 5555–5562.
- [45] Z. Zhang, T. Cao, S. Liu, X. Duan, L.-M. Liu, S. Wang, Y. Liu, Substrate-Induced synthesis of nitrogen-doped holey graphene nanocapsules for advanced metal-free bifunctional electrocatalysts, *Part. Part. Syst. Char.* 34 (2017).
- [46] D. Gu, R. Ma, Y. Zhou, F. Wang, K. Yan, Q. Liu, J. Wang, Synthesis of nitrogen-doped porous carbon spheres with improved porosity toward the electrocatalytic oxygen reduction, *ACS Sustain. Chem. Eng.* 5 (2017) 11105–11116.
- [47] Y. Wang, S. Zuo, Y. Liu, Ammonia modification of high-surface-area activated carbons as metal-free electrocatalysts for oxygen reduction reaction, *Electrochim. Acta* 263 (2018) 465–473.
- [48] H.W. Liang, X. Zhuang, S. Brüller, X. Feng, K. Mullen, Hierarchically porous carbons with optimized nitrogen doping as highly active electrocatalysts for oxygen reduction, *Nat. Commun.* 5 (2014) 4973.
- [49] Z. Chen, J. Wen, C. Yan, L. Rice, H. Sohn, M. Shen, M. Cai, B. Dunn, Y. Lu, High-performance supercapacitors based on hierarchically porous graphite particles, *Adv. Energy Mater.* 1 (2011) 551–556.
- [50] J. Jiang, M. Zhou, H. Chen, Z. Wang, L. Bao, S. Zhao, S. Guan, J. Chen, Hierarchically porous carbon derived from an aqueous curable composition for supercapacitors, *Electrochim. Acta* 168 (2015) 300–307.
- [51] D.-C. Guo, J. Mi, G.-P. Hao, W. Dong, G. Xiong, W.-C. Li, A.-H. Lu, Ionic liquid C16mimBF₄ assisted synthesis of poly(benzoxazine-co-resol)-based hierarchically porous carbons with superior performance in supercapacitors, *Energy Environ. Sci.* 6 (2013) 652–659.
- [52] Y. Shu, J. Maruyama, S. Iwasaki, S. Maruyama, Y. Shen, H. Uyama, Fabrication of N-doped and shape-controlled porous monolithic carbons from polyacrylonitrile for supercapacitors, *RSC Adv.* 7 (2017) 43172–43180.
- [53] X. Li, Y. Song, L. You, L. Gao, Y. Liu, W. Chen, L. Mao, Synthesis of highly uniform N-doped porous carbon spheres derived from their phenolic-resin-based analogues for high performance supercapacitors, *Ind. Eng. Chem. Res.* 58 (2019) 2933–2944.
- [54] Z. Zhang, L. Li, Y. Qing, X. Lu, Y. Wu, N. Yan, W. Yang, Hierarchically interconnected N-doped carbon aerogels derived from cellulose nanofibrils as high performance and stable electrodes for supercapacitors, *J. Phys. Chem. C* 122 (2018) 23852–23860.
- [55] Y. Zhao, Y. Zhao, X. Ma, Y. Liu, Z. Li, T. Wang, H. Chen, J. Zhou, J. Li, X. Pan, E. Xie, Ammonia-assisted thermal activation of graphene-embellished biological fiber for flexible supercapacitors, *J. Alloys Compd.* 785 (2019) 944–950.
- [56] X. Zhang, Y. Jiao, L. Sun, L. Wang, A. Wu, H. Yan, M. Meng, C. Tian, B. Jiang, H. Fu, GO-induced assembly of gelatin toward stacked layer-like porous carbon for advanced supercapacitors, *Nanoscale* 8 (2016) 2418–2427.
- [57] H. Zhu, X. Wang, F. Yang, X. Yang, Promising carbons for supercapacitors derived from fungi, *Adv. Mater.* 23 (2011) 2745–2748.
- [58] E. Raymundo-Piñero, F. Leroux, F. Béguin, A high-performance carbon for supercapacitors obtained by carbonization of a seaweed biopolymer, *Advanced materials* 18 (2006) 1877–1882.



Molten- NaNH_2 activated carbon cloth with high areal capacitance and exceptional rate stability for flexible asymmetric supercapacitors

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ABSTRACT

An effective strategy was proposed to obtain molten- NaNH_2 activated carbon cloth (MACC) for the manufacture of flexible asymmetric supercapacitors. First, the commercial carbon cloth is oxidized by wet chemical treatment and then activated in molten- NaNH_2 . The obtained MACC possess many advantages, including moderate oxygen functional groups and nitrogen heteroatoms, excellent wettability, large surface area, high conductivity and excellent mechanical strength and flexibility. As electrode, the MACC demonstrates a high areal capacitance of 744.5 mF cm^{-2} at a current density of 1 mA cm^{-2} , and 692.0 mF cm^{-2} at a high current density of 50 mA cm^{-2} with the capacitance retention as high as 92.93% in 6 M KOH. Furthermore, the flexible asymmetrical supercapacitors are fabricated based on the MACC electrode and Co(OH)_2 electrode using aqueous electrolytes. The assembled aqueous supercapacitors can release an areal capacitance of 373.9 mF cm^{-2} under the current density of 2 mA cm^{-2} , and the corresponding energy density is up to 1.49 mW cm^{-3} at the power density of 19.45 mW cm^{-3} . The impressive results reveal that the as-prepared MACC is a potential electrode for the flexible supercapacitors.

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Introduction

With the increasing demand for flexible, lightweight and wearable electronic equipment, it is urgent to develop high-performance flexible energy storage devices such as flexible supercapacitors and batteries. The design of flexible electrode material is essential for improving the electrochemical performance of flexible energy storage device [1–3]. Commercial carbon cloths (CC) are promising flexible electrode materials to construct flexible energy storage devices due to their good flexibility, unique 3D structure, reasonable chemical stability and good electrical conductivity [4–7]. However, the commercially available pristine CC only can deliver an areal capacitance less than 1 mF cm^{-2} [8]. Therefore, much effort has been devoted to increasing the areal capacitance of the CC through the modification of electrochemically active substances, such as the transition metal hydroxides [7, 9, 10]/oxides [4, 5, 11–13], transition metal sulfide [14–16] and conductive polymers [17, 18]. Our group [6] also constructed tetsubo-like $\alpha\text{-Fe}_2\text{O}_3/\text{C}$ nanoarrays on the CC as a negative electrode to construct flexible supercapacitor that possessed a good energy density of 0.56 mW cm^{-3} at the power density of 16.8 mW cm^{-3} in $\text{Na}_2\text{SO}_4/\text{CMC}$ gel electrolyte. Currently, the modified active substance on the surface of CC is less than 2 mg cm^{-1} ; the obtained areal capacitances of CC electrodes are still far from the demand of supercapacitor with high energy density. Although the increased load can improve the areal capacitance of CC electrodes, the excessively loaded active substances on the surface of CC seriously decline the charge-storage performance, especially the rate stability. It is mainly due to the moderate electrical conductivity, slow ion diffusion and poor mechanical stability of theses active materials [19]. Thus, the development of new strategy to improve the areal capacitance of the CC is still quite crucial for achieving superior energy storage and rate capabilities. Recently, numerous studies have demonstrated the activation of CC could effectively increase its areal capacitance [8, 20, 21]. Wang et al. [8] prepared electrochemically activated CC with a high areal capacitance of 756 mF cm^{-2} at a current density of 6 mA cm^{-2} because of the introduction of oxygen functional groups on the surface of the CC. However, when the charge-discharge current density was

increased from 6 to 40 mA cm^{-2} , over half of the capacitance was lost. This is mainly because the oxidized CC contains a large amount of oxygen-containing functional groups. These oxygen-containing functional groups may interfere with electrical transport, resulting in decomposition of the electrolyte caused by certain secondary actions, thereby reducing the electrochemical performance of the carbon cloth [22]. To eliminate the negative impacts of excess oxygen-containing functional groups, an electrochemical reduction in NH_4Cl aqueous solution and an annealing reduction at H_2/N_2 atmosphere were used [1, 23], respectively. The obtained activated CC showed much enhanced rate performance. Furthermore, nitrogen doping has been considered as an effective method to increase the specific capacitance and rate stability of carbon materials [24, 25]. It is believed that the pyridine and pyrrole nitrogen atoms increase the specific capacitance of the double-layer capacitor, while the graphite nitrogen enhances the conductivity of the material. Nakayama et al. [26] fabricated N-doped CC via a hydrothermal reaction in the presence of hydrazine and ammonia, and the prepared N-doped CC showed a areal capacitance of 136 mF cm^{-2} at 0.5 mA cm^{-2} in $1 \text{ M H}_2\text{SO}_4$ aqueous electrolyte. Zhang et al. [27] prepared N-doped mesoporous CC by the activation of KOH and NaN_3 assisted hydrothermal method, the N-doped CC fabricated symmetric supercapacitor can release an areal capacitance of 130 mF cm^{-2} at 1 mA cm^{-2} in LiClO_4 electrolyte.

According to the above discussion, we propose the approach composed of moderate oxidation, and N doping can effectively improve the charge-storage capability of CC, including specific capacitance and rate capability. Herein, a two-step route including the wet chemical oxidation and molten- NaNH_2 activation were used to fabricate activated CC (MACC) (see Fig. 1). First, the commercialized CC was oxidized by wet chemical treatment and then activated in molten- NaNH_2 to reduce surface oxygen functional groups and introduce nitrogen heteroatoms. The obtained MACC electrode showed a high areal capacitance and rate performance in 6 M KOH than previously reported. In addition, the enhancement mechanism of the electrochemical performance of MACC was clarified. Finally, MACC-based flexible asymmetric supercapacitors were fabricated and the electrochemical properties were investigated.

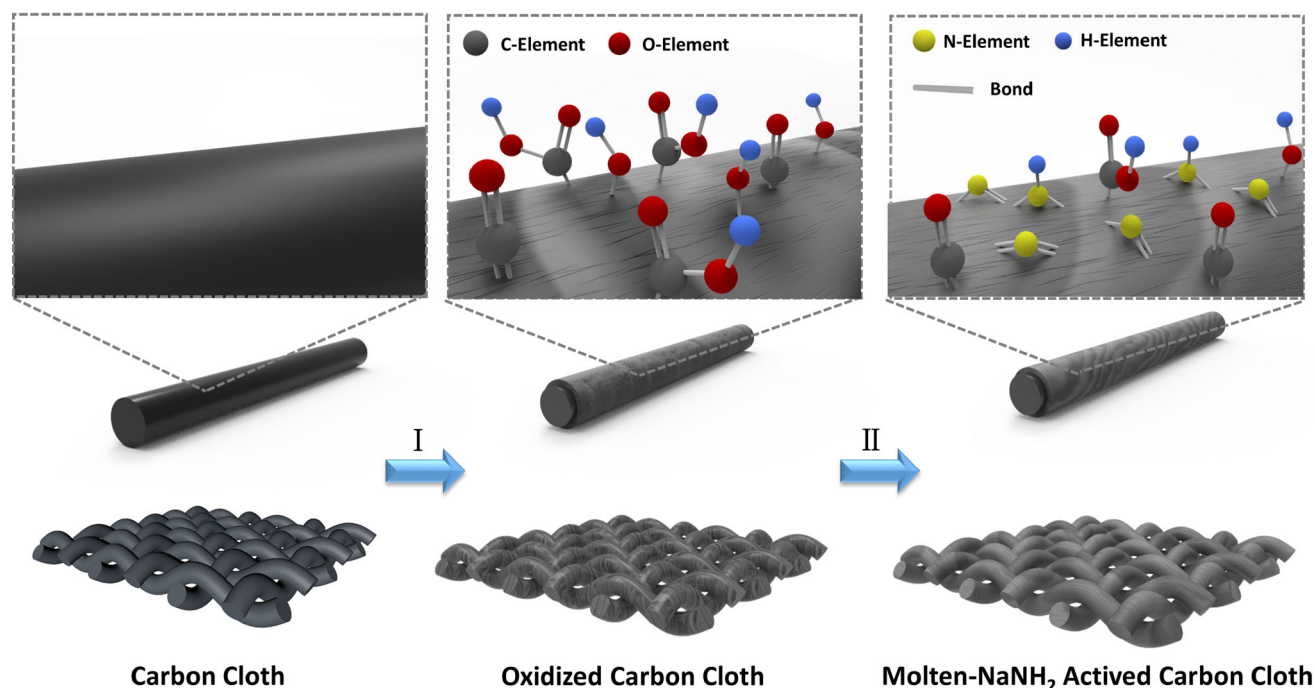


Figure 1 Schematic illustration of the preparation process of MACC.

Experimental

Synthesis of the MACC electrodes

MACC electrodes were prepared by a two-step process. Figure 1 presents the diagrammatic sketch of the preparation of MACC. The first-step was the oxidation of commercialized pristine CC (WOS1002, 12.5 mg cm⁻²). 0.5 g commercialized CC was immersed in 20 mL of H₂SO₄ (95 wt%) and 10 mL of HNO₃ (65 wt%) under an ice-water bath; then, 3 g KMnO₄ was slowly added into the above solution with continuous stirring and the temperature of the mixture was controlled below 10 °C. Soon afterward, 100 mL of deionized water was slowly added into the above solution under stirring and the temperature was kept below 25 °C. After further reaction for 6 h, a H₂O₂ aqueous solution (30 wt%) was added to the above solution to stop the oxidation process. Then the obtained oxidized CC (OCC) was washed by deionized water and dried in air. Second, the OCC and NaNH₂ with the mass ratio of 1:5 were placed in a steel crucible and then annealed in a quartz tubular furnace at 320 °C for 5 h under argon flow. The obtained MACC electrodes were washed in turn with hydrochloric acid (10 wt%) and deionized water to remove the residual NaNH₂ and then dried

in air at 60 °C for 12 h. The fabricated MACC still preserves excellent mechanical strength and flexibility (Figure S1).

Characterization

The morphology, microstructure and elemental composition of the CC, OCC and MACC were analyzed by a Quanta 450 field-emission scanning electron microscope (SEM) and a FEI Talos F200X transmission electron microscope (TEM), respectively. The phase of the CC, OCC and MACC were characterized by a D8 Advance X-ray diffractometer (XRD) with Cu K α radiation ($\lambda = 1.5406$ Å).

The graphitization degree of CC, OCC and MACC were evaluated by Raman spectroscopy, which were recorded on a Lab RAM HR800 Laser Raman spectroscopy (HORIBA) using a 647 nm argon ion laser. The specific surface area and pore size distribution of the CC, OCC and MACC were acquired on a TriStar II 3020 surface area and pore size analyzer (Micromeritics). The surface chemical state of the CC, OCC and MACC were analyzed with an Axis Ultra (Kratos) XPS spectrometer. The wettability of CC, OCC and MACC were measured on an optical contact angle meter (DSA 20, Krüss, Germany).

Electrochemical tests

The electrochemical properties of commercialized CC, OCC and MACC were analyzed on a CHI660E electrochemical workstation (Shanghai, Chen-Hua) at 25 °C using a three-electrode cell, which is constituted of working electrode ($1 \times 1 \text{ cm}^2$), counter electrode (Pt plate), reference electrode (Hg/HgO) and electrolyte (6 M KOH). To further evaluate the application of MACC, the asymmetric supercapacitors (ASCs) were fabricated by using MACC as negative electrode and Co(OH)_2 on CC as positive electrode with a filter paper between them as separator and 6 M KOH as electrolyte. The fabricated ASCs were packaged by PET film. The Co(OH)_2 on CC was fabricated by the reported method (Section S1) [4]. In order to balance the charge between the positive and negative electrodes, the area ratio of the Co(OH)_2 on CC and MACC was designed to be 5:6. The thickness of ASCs is 0.76 mm.

Calculation methods

The areal capacitances (C_a) of the electrodes were calculated from their discharge curves using the following equation.

$$C_a = \frac{I\Delta t}{S\Delta V} \quad (1)$$

The areal capacitances (C_a) and volumetric capacitance (C_v) of the supercapacitor devices could be calculated from their discharge curves using the following equations

$$C_a = \frac{I\Delta t}{S\Delta V} \quad (2)$$

$$C_v = \frac{I\Delta t}{v\Delta V} \quad (3)$$

Energy density (E) and power density (P) of the supercapacitor devices could be calculated as,

$$E = \frac{1}{2} C_v \Delta V^2 \quad (4)$$

$$P = \frac{E}{t} \quad (5)$$

where I is the discharge current, Δt is the discharge time, ΔV is the potential window during the discharge process after the removal of the voltage drop, S is the effective area of electrode or device and v is the volume of device.

Results and discussion

Characterization

To clarify the surface morphology of the CC at each stage, the pristine CC, OCC and MACC were observed by SEM. Figure 2a displays the typical SEM images of CC, revealing that the CC is consisting of carbon fibers with a smooth surface. After chemical oxidation (Fig. 2b), the surface of carbon fibers is slightly rough, suggesting that pristine surface structure of these fibers was destroyed by chemical oxidants. After further activation in molten- NaNH_2 (Fig. 2c), the carbon fibers of MACC possess a significantly rough surface, and some graphene-like sheets can be observed on the surface of carbon fibers in MACC. The rough surface suggests that the MACC should have much more active sites than the CC and OCC for the energy storage [28], which is further confirmed by their N_2 adsorption-desorption isotherms. Figure 2d displays the N_2 adsorption-desorption isotherms of CC, OCC and MACC. The N_2 gas is hardly adsorbed on the surface of the CC. The calculated specific surface area (S_{BET}) of the CC from the BET (Brunauer-Emmett-Teller) model is only $1.5 \text{ m}^2 \text{ g}^{-1}$. The N_2 adsorption-desorption isotherm of the as-prepared OCC displays a type IV characterization with H_4 hysteresis loop, indicating the porous structure. The S_{BET} of the OCC is $45.8 \text{ m}^2 \text{ g}^{-1}$. The pore volume is $0.025 \text{ m}^3 \text{ g}^{-1}$, and pore size distribution of OCC is between 1 and 5 nm (Fig. 2e), which may be mainly from the exfoliation caused by the oxidation process. After the activation using NaNH_2 , S_{BET} of the MACC increases to $136.2 \text{ m}^2 \text{ g}^{-1}$, and the pore volume raises to $0.15 \text{ m}^3 \text{ g}^{-1}$. It is clearly noticed that plentiful mesopores from 2 to 40 nm were obtained in MACC (Fig. 2e). The higher S_{BET} and pore volume indicate that the MACC has much more active sites than the CC and OCC, resulting in a higher specific capacitance for the energy storage. TEM was used to further analyze the microstructure of carbon fiber in MACC. Figure 2f, g shows the typical TEM images obtained at the edge of the MACC fiber. We can see that the MACC fiber shows a clear core-shell structure, and the thickness of activated shell is about 40 nm. The high revolution TEM image (Fig. 2h) of the activated shell showed that the activated layer is amorphous in nature, which is similar to the chemically reduced graphene oxide. Figure 2i-l demonstrates the STEM and the

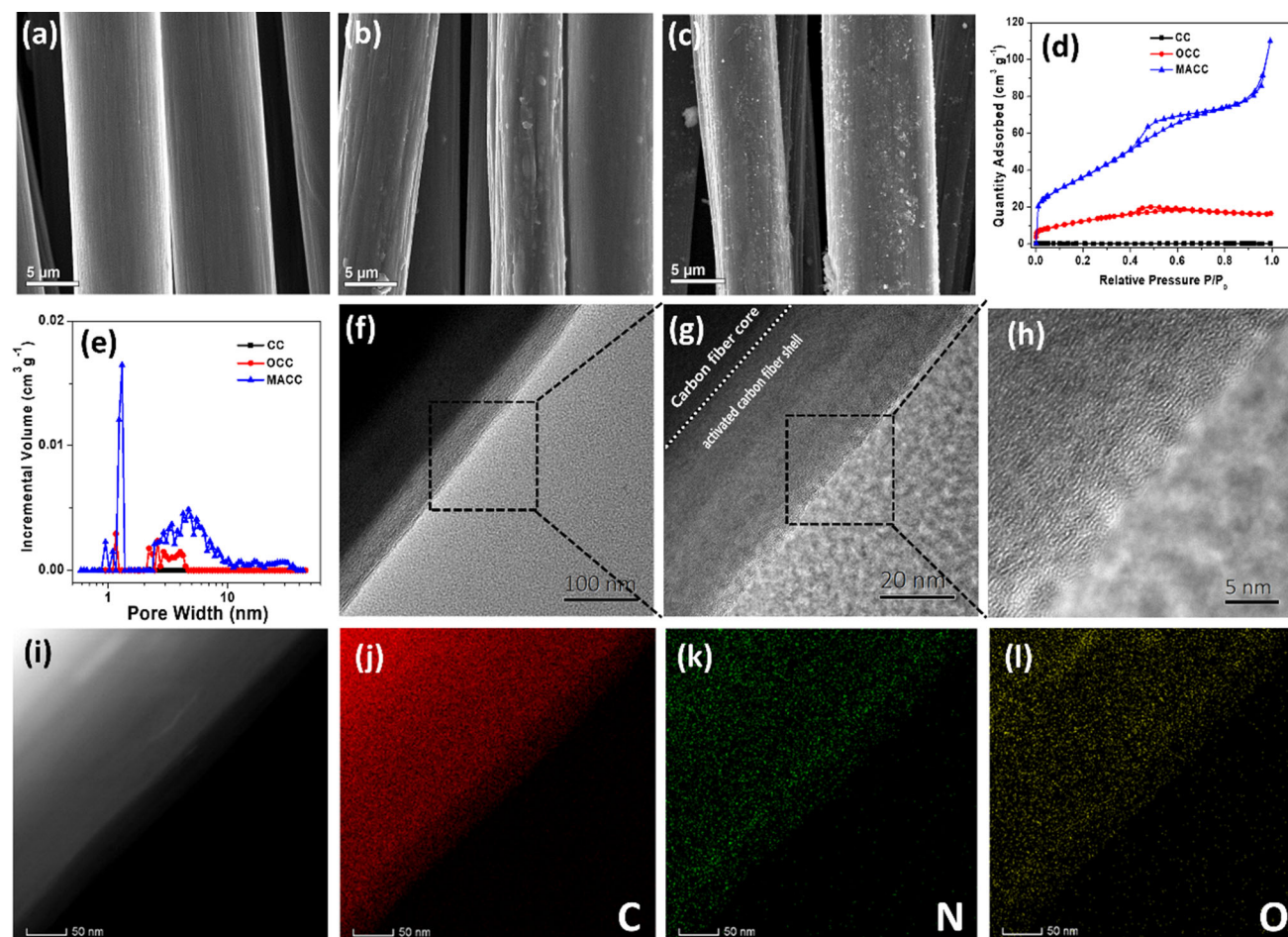


Figure 2 Typical SEM images of **a** CC, **b** OCC and **c** MACC; **d** N_2 adsorption–desorption isotherms of CC, OCC and MACC and **e** pore size distribution curves of CC, OCC and MACC; **f**–

h typical TEM images of carbon fiber in MACC, **i** STEM and **j**–**l** corresponding EDX mapping images of carbon fiber in MACC.

corresponding EDX mapping images of activated carbon fiber in MACC, which reveals the presence of nitrogen and oxygen, as well as the distribution of nitrogen and oxygen is uniform in MACC. The element percentage of MACC from the EDX spectra is listed in Table S1.

The phase of CC, OCC and MACC were tested by XRD. Figure S2 shows the XRD patterns of CC, OCC and MACC. The diffraction peaks at $2\theta = 26^\circ$ can be assigned to the (002) planes of graphite. After oxidation and activation, the half width values of (002) peak for both OCC and MACC are higher than that of CC, indicating the lower degree of graphitization of both OCC and MACC. The weak diffraction peaks at about 44° are attributed to the (101) planes of graphite. In addition, no other diffraction peak in Figure S2 indicates that no other inorganic metal oxide impurities are introduced into CC during the

oxidation and activation. Figure S3 shows the Raman spectra of CC, OCC and MACC. There are two characteristic peaks in the Raman spectra, the disorder-induced (D) band ($\sim 1350\text{ cm}^{-1}$) and graphite (G) band ($\sim 1600\text{ cm}^{-1}$). The D peak is attributed to the A_{1g} vibration mode, which represents the crystal defects and disordered structure in carbon materials. The G peak corresponds to the first-order scattering of E_{2g} modes in sp^2 C region [29, 30]. Generally, the intensity ratio of D band to G band (I_D/I_G) can be used to evaluate the graphitization degree of carbon materials. The I_D/I_G ratios of CC, OCC and MACC are 1.221, 1.384 and 1.359, respectively. The change in I_D/I_G ratio shows that the surface defects of OCC were increased after oxidation treatment, which is consistent with the observation by SEM. After molten- NaNH_2 treatment, the reduced I_D/I_G ratio indicates that the graphitization degree of MACC was

improved, which is beneficial in improving the electrical conductivity of the material.

The surface chemical state of CC, OCC and MACC were researched by XPS. Figure 3a displays the XPS survey scans of CC, OCC and MACC. A strong C1s peak and a weak O1s peak can be observed at around 284 and 532 eV, the atomic percentage of C and O in the surface of CC is 96.86 and 3.14%, respectively (Table S2). After oxidation, the intensity

of O1s peak at 532 eV is obviously increased, and the corresponding atomic percentage of O for the OCC raises to 31.12%. After activation in molten- NaNH_2 , the atomic percentage of O reduces to 9.97 at.%, and a weak N1s with 3.24 at.% at around 397 eV appears in MACC. It indicates that the activation process not only can reduce the oxygen content of OCC but also can introduce the N atoms into the surface of the carbon fibers. Figure 3b represents the C1s spectra of

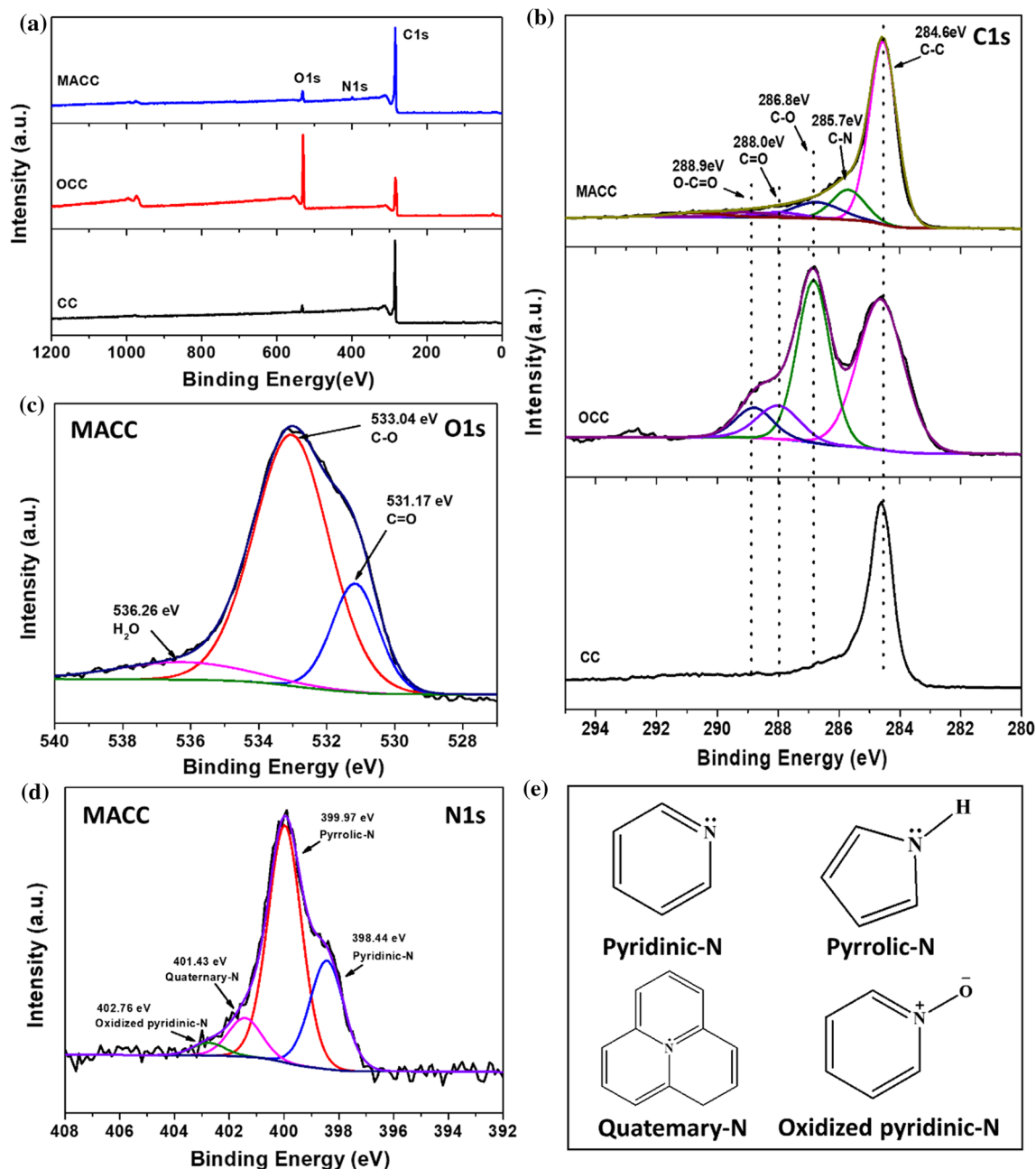


Figure 3 a XPS spectra survey scan of CC, OCC and MACC. b High resolution XPS spectra of C1s for CC, OCC and MACC, c O1s and d N1s spectra of MACC. e Location map of different N elements in MACC.

CC, OCC and MACC. A strong peak at 284.6 eV is assigned to the C–C. After oxidation, we can observe three new peaks in C1s XPS spectra of the OCC, which corresponds to the C–O (286.8 eV), C=O (288.0 eV) and O–C=O (288.9 eV). After the OCC was activated by molten- NaNH_2 , the characterization peaks of C–O and C=O reduce and the peak of C–N (285.7 eV) appears [8, 31]. The XPS spectra of O1s (Fig. 3c) and N1s (Fig. 3d) for MACC further confirm the above results. The O1s spectrum of MACC can be deconvoluted into three peaks at 531.2, 533.0 and 536.3 eV, which are corresponding to the C–O, C=O and adsorbed H_2O . The N1s spectrum of MACC is fitted into three different contributions at 402.76, 401.75, 400.24 and 398.65 eV, which are attributed to the oxidized pyridine-N (N–O), quaternary-N (N–Q), pyrrolic N (N-5) and pyridinic N (N-6) [32–34]. The N-5 and N-6 are the two major sorts of N atoms. The N-5 has good electron donor characteristics and higher charge mobility, which contributes to increase in MACC electrochemical activity. The N-6 offers a pair of electrons for conjugation with the π -conjugated rings. Therefore, it can bring in electron donor properties to MACC and has crucial effects on the improved capacitances.

In addition, the wettability is important for the capacitance of electrode materials, and the increase in the wettability of the material can effectively enhance electrochemical performance of carbon materials [35–37]. Figure S4 shows the contact angle of water on the CC, OCC and MACC. Obviously, the pristine CC is hydrophobic, which prevents water from entering the pores, thus limiting the effective surface area of the material. However, a water droplet can spread out on the surface of OCC and MACC tablets completely during one second, demonstrating that both OCC and MACC have excellent hydrophilicity. Consequently, the presence of N and O elements can improve the affinity between carbon surface and electrolyte.

Electrochemical properties

The electrochemical performance of CC, OCC and MACC electrodes were investigated using a three-electrode system in 6 M KOH. The CV curve (Fig. 4a) of MACC shows a much larger integral area than that of CC and OCC, revealing the MACC possesses a larger capacitance than that of CC and OCC. These properties indicate that the molten- NaNH_2 activation

step is critical for the improvement of electrochemical activity, which can be confirmed by the electrochemical impedance spectroscopy (EIS) analysis (Fig. 4b). We can observe one quasi-semicircle in high-frequency region and a linear part in low-frequency region in all impedance spectra. In the high-frequency region, the intersection of the curve at the real axis Z' corresponds to the bulk resistance (R_s) of electrode electrochemical system. The R_s of OCC ($\sim 2.47 \Omega$) is significantly higher than that of CC ($\sim 1.15 \Omega$) because of the introduction of many oxygen-containing groups. After activation in molten- NaNH_2 , the MACC electrode possesses a low equivalent resistance ($\sim 1.37 \Omega$) due to the reduction of O groups and the doped N atoms. In addition, the diameter of semicircle represents the charge transfer resistance (R_{ct}) of the electrodes and electrolyte interface, and obviously, the order of R_{ct} is $\text{CC} > \text{MACC} > \text{OCC}$ (Table S3). In the low frequencies, OCC exhibits higher diffusivity resistance, as seen in the higher slope, indicating that the excess oxygen-containing groups on the CC hinder the diffusion of electrolyte ions. In contrast, the diffusion resistance of the MACC electrode is much smaller, even smaller than CC, which may be due to that the continuous pores created by the molten- NaNH_2 activation process can effectively promote the rapid diffusion of the electrolyte in CC. This would improve the capacitance due to the enhanced electrolyte penetration and therefore electrochemical double-layer formation [38].

To investigate the capacitive performance at different scan rates, Fig. 4c displays the CV curves of MACC at several scan rates between 10 and 200 mV s^{-1} . It can be seen that the CV curves can retain the original shape without evident distortion even the scan rate increased to 200 mV s^{-1} , indicating the excellent capacitive properties of the MACC electrode. The galvanostatic charge–discharge (GCD) curves of the MACC electrode obtained at different current densities between 1 and 50 mA cm^{-2} are shown in Fig. 4d. We can see that these GCD curves are almost isosceles triangular shaped, which is another typical characteristic of an ideal electrode material [39], indicating excellent reversibility of MACC.

Figure 4e shows the areal capacitances (C_a) of MACC calculated from the galvanostatic discharge curves. The C_a of MACC electrode is 744.5 mF cm^{-2} at 1 mA cm^{-2} , and still retains 692.0 mF cm^{-2} at a

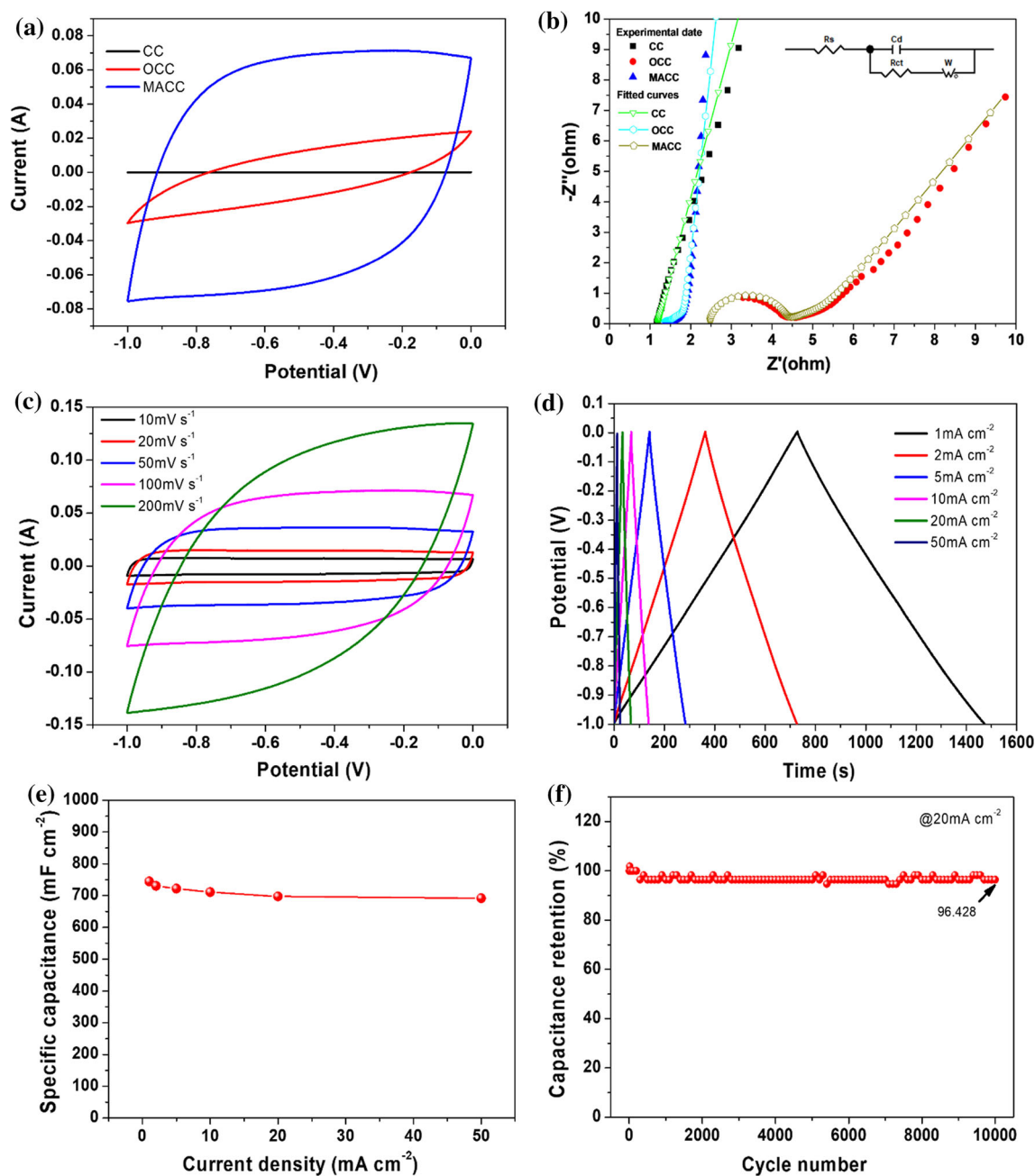


Figure 4 **a** CV curves of the CC, OCC and MACC collected at a scan rate of 100 mV s⁻¹ in 6 M KOH, **b** Nyquist plots of CC, OCC and MACC electrodes, **c** CV curves of the MACC collected at different scan rates, **d** GCD curves of the MACC obtained under

different current densities, **e** areal capacitance as a function of the current densities of the MACC electrodes, **f** stability test of the MACC via GCD cycling process at a current density of 20 mA cm⁻².

high current density of 50 mA cm⁻² with a capacitance retention of 92.93%. The electrochemical capacitance of our MACC electrode is higher than the reported activated CC [1], N-doped CC [26] and electrochemical activated CC [23]. In addition, the capacitance retention in high rate is obviously superior than the electrochemical activated CC reported

by Lu' group [8]. The detailed comparison can be found in Table 1. The cycle stability of the MACC electrode was evaluated by GCD method at 20 mA cm⁻² in 6 M KOH (Fig. 4f). The capacitance retention is about 96.4% after 10000 cycles, demonstrating the high cycle stability of MACC.

Table 1 Electrochemical performance of different CC electrodes

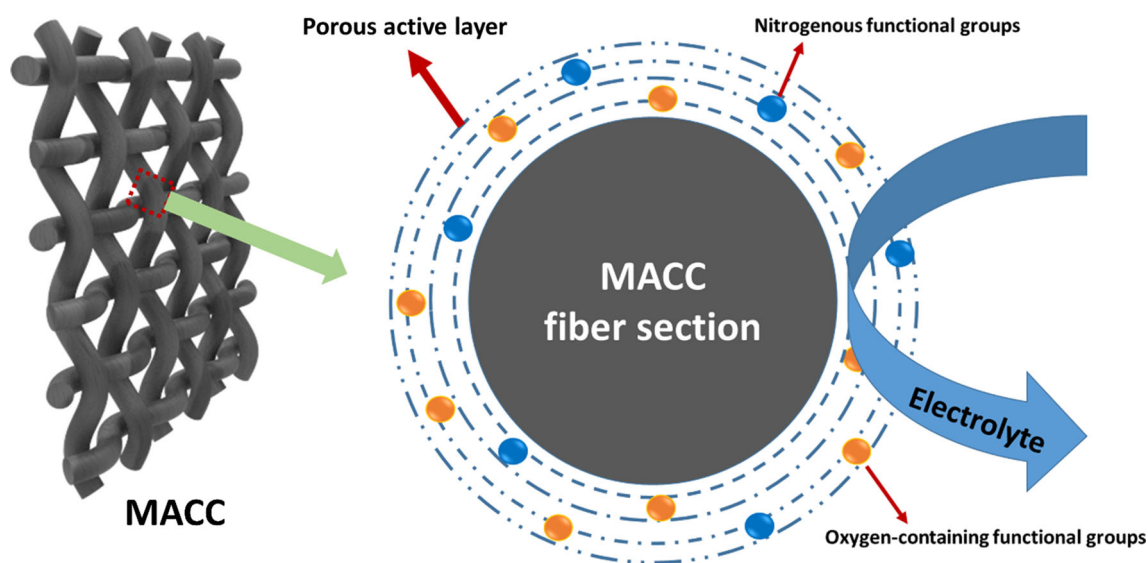
Electrode materials	Electrolyte	Potential window (V)	Specific capacitance (mF cm ⁻²)	Capacitance retention (%)	Stability (%)	Refs.
MACC	6 M KOH	(-1)-0	744.6 (1 mA cm ⁻²)	96.23 (50 mA cm ⁻²)	96.4% (10000)	This work
Activated CC	1 M H ₂ SO ₄	0-1	485.6 (2 mA cm ⁻²)	89.7 (60 mA cm ⁻²)	129% (30000)	[1]
Activated CC	1 M H ₂ SO ₄	0-1	88 (10 mV s ⁻¹)	80 (20 mA cm ⁻²)	97% (20000)	[31]
Nitrogen-doped CC	1 M H ₂ SO ₄	0-1	136 (0.5 mA cm ⁻²)	83 (15 mA cm ⁻²)	N/A	[26]
Electrochemical activated CC	1 M H ₂ SO ₄	(-0.2)-0.8	505 (6 mA cm ⁻²)	88 (48 mA cm ⁻²)	97% (10000)	[23]
Electrochemical activated CC	5.0 M LiCl	(-1)-0	756 (6 mA cm ⁻²)	65.2 (20 mA cm ⁻²)	~ 110% (30000)	[8]

The excellent electrochemical performance of the MACC electrode can be summarized for the following reasons (Fig. 5). First, the MACC has a high specific surface area, a high pore volume and rich pore structure, which can improve the contact between the electrolyte and the electrode, accelerate the diffusion of electrolyte and promote the utilization of active substances [23]. Second, the rough surface of MACC could improve the electric charge storage because of the confinement effect unique for corrugated surfaces [28, 40]. Third, the nitrogen doping and oxygen-containing groups also can improve the wettability of MACC for the increase the utilization of the carbon material and provide an

additional active sites because they are electron-rich and can attract protons to the electrode surface [35]. Finally, the introduction of nitrogen effectively enhances the conductivity of the MACC and reduces the internal resistance of the electrode [24].

Electrochemical properties of MACC//Co(OH)₂ ASCs

To further evaluate the feasibility of the MACC as negative electrode for ASCs, the aqueous ASCs were assembled using MACC as negative electrode, Co(OH)₂ on CC as positive electrode and 6 M KOH solution as electrolyte (Fig. 6a, denoted as MACC//

**Figure 5** Schematic illustration for the enhanced mechanism of the MACC electrode.

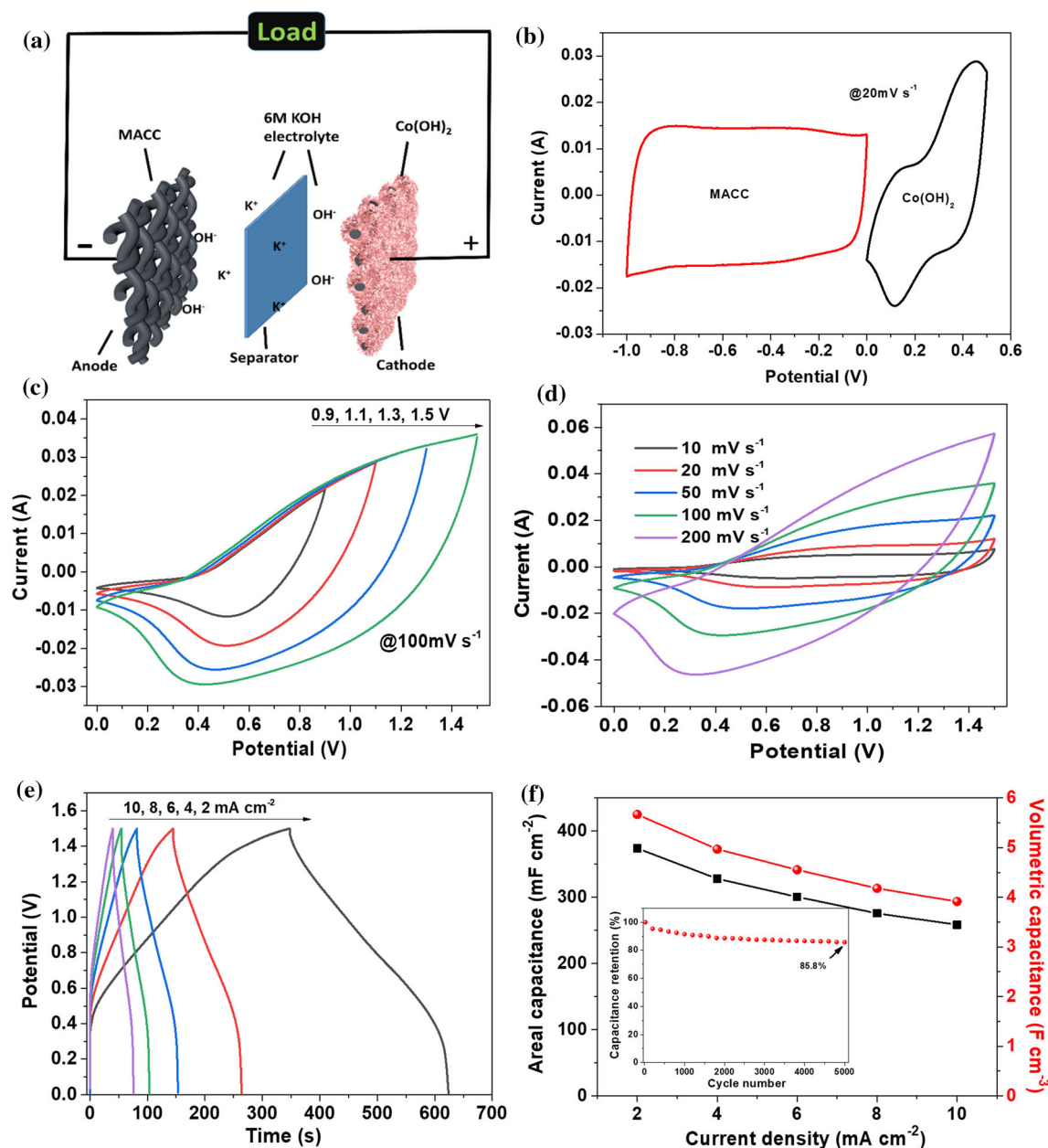


Figure 6 **a** Schematic diagram of ASCs fabricated by MACC and Co(OH)₂ on CC. **b** CV curves of MACC//Co(OH)₂ ASCs under a scan rate of 20 mV s⁻¹. **c** CV curves of the ASCs in different potential windows at a scan rate of 100 mV s⁻¹. **d** CV curves of the ASCs at different scan rates. **e** GCD curves of ASCs collected

Co(OH)₂. Typical SEM images of the Co(OH)₂ are presented in Figure S5, and the Co(OH)₂ nanoparticles are densely dispersed on the surface of carbon fibers. Meanwhile, the XRD pattern shown in Figure S6 verifies that the phase of these nanoparticles on CC is Co(OH)₂. Figure S7 displays the electrochemical properties of the Co(OH)₂ electrode using a three-electrode system with 6 M KOH as electrolyte under a

at different current densities. **f** Specific capacitances of ASCs calculated from the discharge curves as a function of current density and cycle stability of the ASCs (inset) measured at a current density of 10 mA cm⁻².

potential window of 0–0.5 V (vs Hg/HgO). CV (Figure S7a) and GCD (Figure S7b) curves indicate that the prepared Co(OH)₂ electrode shows superior electrochemical capability with an area capacitance of 961 mF cm⁻² at 1 mA cm⁻² (Figure S7c). According to the discharge curves (Fig. 6b) of the Co(OH)₂ and MACC electrodes at 20 mA cm⁻², the optimal area ratio between the Co(OH)₂ and MACC is about 5:6.

Figure 6c shows the CV curves of the MACC//Co(OH)₂ ASCs collected at different potential windows between 0.9 and 1.5 V at 100 mV s⁻¹. It can be clearly watched that the CV curves of the ASCs are the combination of those of the MACC and Co(OH)₂ electrodes, suggesting that capacitance of the ASCs is composed of the electric double-layer capacitance of MACC and the pseudocapacitive of Co(OH)₂. In addition, the shape of CV curves (Fig. 6d) retains well even if the scan rates increased to 200 mV s⁻¹, demonstrating its outstanding capacitive behavior. Moreover, the obtained CV curves (Figure S8) of ASCs at different bending angles reveal similar capacitive performance, indicating outstanding electrochemical and mechanical stability. Figure 6e displays the GCD curves of the prepared MACC//Co(OH)₂ ASCs at several current densities between 2 and 10 mA cm⁻². The areal capacitance of the ASCs (Fig. 6f) calculated from the corresponding discharge curves (Fig. 6e) is 373.9 mF cm⁻² under 2 mA cm⁻². When the current density was enhanced to 10 mA cm⁻², the ASCs still deliver 258.4 mF cm⁻² with a high capacitance retention of 69.1%. Long-time GCD cycle test was used to assess the electrochemical stability of ASCs. The obtained result indicates that MACC//Co(OH)₂ ASCs possesses good cycle stability with 85.8% capacitance retention at 10 mA cm⁻² for 5000 cycles (inset of Fig. 6f).

Figure 7a illustrates the Ragone plot of the energy density versus power density for our fabricated ASCs. It can be clearly observed that the highest energy density of aqueous MACC//Co(OH)₂ ASCs

can reach up to 1.49 mW cm⁻³ at the power density of 19.45 mW. This value is higher than those of recently reported ASCs, such as CoP/CC//MnO₂ ASCs [41], MnO₂/CC//PPy/FCC ASCs [17], α -Fe₂O₃@PANI//PANI ASCs [42], CoO@PPy//AC solid ASCs [43], MnO₂//Fe₂O₃/PPy solid ASCs [4] and activated CC solid SSCs [1]. Two series-connected ASCs devices can easily light a red LED (Fig. 7b), which indicates that the prepared MACC electrodes have great potential for high-performance supercapacitors.

Conclusions

In conclusion, MACC with high areal specific capacitance and excellent rate performance was successfully prepared by a two-step method. The obtained MACC can deliver a high specific capacitance of 744.5 mF cm⁻² at the current density of 1 mA cm⁻² in 6 M KOH, and retained 692.0 mF cm⁻² at 50 mA cm⁻², which is higher than the reported results for carbon cloth. The remarkable electrochemical performance is primary attributed to its advantages including the rough surface, high specific area, high pore volume, good mechanical stability, appropriate oxygen and nitrogen doping, and good wettability. Furthermore, the fabricated asymmetric supercapacitors exhibited higher capacitive performance with a maximum areal capacitance of 373.9 mF cm⁻² at the current density of 2 mA cm⁻² and the energy density up to 1.49 mW cm⁻³ at the power

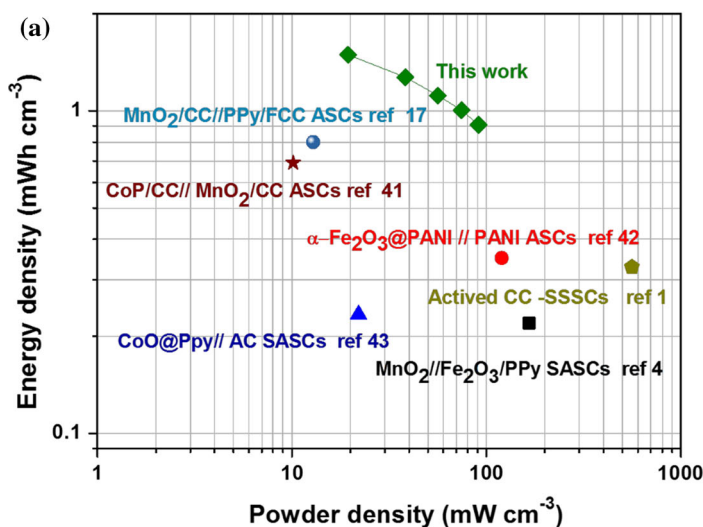


Figure 7 **a** Ragone plot of the MACC//Co(OH)₂ ASCs. **b** Two series-connected ASCs devices light a red LED.

density of 19.45 mW cm^{-3} . The obtained results indicate that the obtained MACC is a promising electrode for the high-performance flexible energy storage devices.

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References

- [1] Jiang SL, Shi TL, Zhan XB, Long H, Xi S, Hu H, Tang ZR (2014) High-performance all-solid-state flexible supercapacitors based on two-step activated carbon cloth. *J Power Sources* 272:16–23
- [2] Jost K, Perez CR, McDonough JK, Presser V, Heon M, Dion G, Gogotsi Y (2011) Carbon coated textiles for flexible energy storage. *Energy Environ Sci* 4:5060–5067
- [3] Ko Y, Kwon M, Bae WK, Lee B, Lee SW, Cho J (2017) Flexible supercapacitor electrodes based on real metal-like cellulose papers. *Nat Commun* 8:536
- [4] Wang L, Yang H, Liu X, Zeng R, Li M, Huang Y, Hu X (2017) Constructing hierarchical tectorum-like $\alpha\text{-Fe}_2\text{O}_3$ /PPy nanoarrays on carbon cloth for solid-state asymmetric supercapacitors. *Angew Chem Int Ed* 56:1105–1110
- [5] Song Y, Liu TY, Yao B, Kou TY, Feng DY, Liu XX, Li Y (2017) Amorphous mixed-valence vanadium oxide/exfoliated carbon cloth structure shows a record high cycling stability. *Small* 13:1700067
- [6] Chen D, Zhou S, Quan H, Zou R, Gao W, Luo X, Guo L (2018) Tetsubo-like $\alpha\text{-Fe}_2\text{O}_3$ /C nanoarrays on carbon cloth as negative electrode for high-performance asymmetric supercapacitors. *Chem Eng J* 341:102–111
- [7] Sekhar SC, Nagaraju G, Yu JS (2017) Conductive silver nanowires-fenced carbon cloth fibers-supported layered double hydroxide nanosheets as a flexible and binder-free electrode for high-performance asymmetric supercapacitors. *Nano Energy* 36:58–67
- [8] Wang W, Liu W, Zeng Y, Han Y, Yu M, Lu X, Tong Y (2015) A novel exfoliation strategy to significantly boost the energy storage capability of commercial carbon cloth. *Adv Mater* 27:3572–3578
- [9] Zhang YD, Hu ZA, An YF, Guo BS, An N, Liang YR, Wu HY (2016) High-performance symmetric supercapacitor based on manganese oxyhydroxide nanosheets on carbon cloth as binder-free electrodes. *J Power Sources* 311:121–129
- [10] Chen LF, Yu ZY, Wang JJ, Li QX, Tan ZQ, Zhu YW, Yu SH (2015) Metal-like fluorine-doped beta-FeOOH nanorods grown on carbon cloth for scalable high-performance supercapacitors. *Nano Energy* 11:119–128
- [11] Saray MT, Hosseini H (2016) Mesoporous MnNiCoO_4 @ MnO_2 core-shell nanowire/nanosheet arrays on flexible carbon cloth for high-performance supercapacitors. *Electrochim Acta* 222:505–517
- [12] Yu Z-Y, Chen L-F, Yu S-H (2014) Growth of NiFe_2O_4 nanoparticles on carbon cloth for high performance flexible supercapacitors. *J Mater Chem A* 2:10889–10894
- [13] Guo D, Luo YZ, Yu XZ, Li QH, Wang TH (2014) High performance NiMoO_4 nanowires supported on carbon cloth as advanced electrodes for symmetric supercapacitors. *Nano Energy* 8:174–182
- [14] Xu J, Wang QF, Wang XW, Xiang QY, Hang B, Chen D, Shen GZ (2013) Flexible asymmetric supercapacitors based upon Co_9S_8 nanorod/ Co_3O_4 @ RuO_2 nanosheet arrays on carbon cloth. *ACS Nano* 7:5453–5462
- [15] Su C, Xiang JY, Wen FS, Song LZ, Mu CP, Xu DY, Hao CX, Liu ZY (2016) Microwave synthesized three-dimensional hierarchical nanostructure CoS_2 /MoS₂ growth on carbon fiber cloth: a bifunctional electrode for hydrogen evolution reaction and supercapacitor. *Electrochim Acta* 212:941–949
- [16] Ding R, Gao H, Zhang MY, Zhang J, Zhang XT (2015) Controllable synthesis of $\text{Ni}_{3-x}\text{Co}_x\text{S}_4$ nanotube arrays with different aspect ratios grown on carbon cloth for high-capacity supercapacitors. *RSC Adv* 5:48631–48637
- [17] Feng DY, Song Y, Huang ZH, Xu XX, Liu XX (2016) Rate capability improvement of polypyrrole via integration with functionalized commercial carbon cloth for pseudocapacitor. *J Power Sources* 324:788–797
- [18] Hsu YK, Chen YC, Lin YG, Chen LC, Chen KH (2013) Direct-growth of poly(3,4-ethylenedioxythiophene) nanowires/carbon cloth as hierarchical supercapacitor electrode in neutral aqueous solution. *J Power Sources* 242:718–724
- [19] Huang ZH, Song Y, Feng DY, Sun Z, Sun X, Liu XX (2018) High mass loading MnO_2 with hierarchical nanostructures for supercapacitors. *ACS Nano* 12:3557–3567

- [20] Gu Y-J, Wen W, Wu J-M (2018) Simple air calcination affords commercial carbon cloth with high areal specific capacitance for symmetrical supercapacitors. *J Mater Chem A* 6:21078–21086
- [21] Wang H, Deng J, Xu C, Chen Y, Xu F, Wang J, Wang Y (2017) Ultramicroporous carbon cloth for flexible energy storage with high areal capacitance. *Energy Storage Mater* 7:216–221
- [22] Gao SN, Zhu LL, Liu LB, Gao AM, Liao F, Shao MW (2016) Improved energy storage performance based on gamma-ray irradiated activated carbon cloth. *Electrochim Acta* 191:908–915
- [23] Ye D, Yu Y, Tang J, Liu L, Wu Y (2016) Electrochemical activation of carbon cloth in aqueous inorganic salt solution for superior capacitive performance. *Nanoscale* 8:10406–10414
- [24] Lin S, Zhang C, Wang Z, Dai S, Jin X (2017) Molten- NaNH_2 densified graphene with in-plane nanopores and N-doping for compact capacitive energy storage. *Adv Energy Mater* 7:1700766
- [25] Wang H, Maiyalagan T, Wang X (2012) Review on recent progress in nitrogen-doped graphene: synthesis, characterization, and its potential applications. *ACS Catal* 2:781–794
- [26] Nakayama M, Komine K, Inohara D (2016) Nitrogen-doped carbon cloth for supercapacitors prepared via a hydrothermal process. *J Electrochem Soc* 163:A2428–A2434
- [27] Zhang Q, Wang N, Zhao P, Yao MQ, Hu WC (2017) Azide-assisted hydrothermal synthesis of N-doped mesoporous carbon cloth for high-performance symmetric supercapacitor employing LiClO_4 as electrolyte. *Compos Part A Appl Sci Manuf* 98:58–65
- [28] Bo Z, Li C, Yang H, Ostrikov K, Yan J, Cen K (2018) Design of supercapacitor electrodes using molecular dynamics simulations. *Nano Micro Lett* 10:33
- [29] Zhou J, Lian J, Hou L, Zhang J, Gou H, Xia M, Zhao Y, Strobel TA, Tao L, Gao F (2015) Ultrahigh volumetric capacitance and cyclic stability of fluorine and nitrogen co-doped carbon microspheres. *Nat Commun* 6:8503
- [30] Wang W, Quan H, Gao W, Zou R, Chen D, Dong Y, Guo L (2017) N-doped hierarchical porous carbon from waste boat-fruited sterculia seed for high performance supercapacitors. *RSC Adv* 7:16678–16687
- [31] Wang G, Wang H, Lu X, Ling Y, Yu M, Zhai T, Tong Y, Li Y (2014) Solid-state supercapacitor based on activated carbon cloths exhibits excellent rate capability. *Adv Mater* 26(17):2676–2682
- [32] Lin T, Chen W, Liu F, Yang C, Bi H, Xu F, Huang F (2015) Nitrogen-doped mesoporous carbon of extraordinary capacitance for electrochemical energy storage. *Science* 350:1508–1513
- [33] Sun MH, Huang SZ, Chen LH, Li Y, Yang XY, Yuan ZY, Su BL (2016) Applications of hierarchically structured porous materials from energy storage and conversion, catalysis, photocatalysis, adsorption, separation, and sensing to biomedicine. *Chem Soc Rev* 45:3479–3563
- [34] Chen XY, Chen C, Zhang ZJ, Xie DH, Deng X, Liu JW (2013) Nitrogen-doped porous carbon for supercapacitor with long-term electrochemical stability. *J Power Sources* 230:50–58
- [35] Zhao J, Lai H, Lyu Z, Jiang Y, Xie K, Wang X, Wu Q, Yang L, Jin Z, Ma Y, Liu J, Hu Z (2015) Hydrophilic hierarchical nitrogen-doped carbon nanocages for ultrahigh supercapacitive performance. *Adv Mater* 27:3541–3545
- [36] Milczarek G, Ciszewski A, Stepniak I (2011) Oxygen-doped activated carbon fiber cloth as electrode material for electrochemical capacitor. *J Power Sources* 196:7882–7885
- [37] Xiao K, Ding LX, Liu G, Chen H, Wang S, Wang H (2016) Freestanding, hydrophilic nitrogen-doped carbon foams for highly compressible all solid-state supercapacitors. *Adv Mater* 28:5997–6002
- [38] Cheng Q, Tang J, Ma J, Zhang H, Shinya N, Qin LC (2011) Graphene and carbon nanotube composite electrodes for supercapacitors with ultra-high energy density. *Phys Chem Chem Phys* 13:17615–17624
- [39] Yan J, Wei T, Shao B, Ma F, Fan Z, Zhang M, Zheng C, Shang Y, Qian W, Wei F (2010) Electrochemical properties of graphene nanosheet/carbon black composites as electrodes for supercapacitors. *Carbon* 48:1731–1737
- [40] Vatamanu J, Cao L, Borodin O, Bedrov D, Smith GD (2011) On the influence of surface topography on the electric double layer structure and differential capacitance of graphite/ionic liquid interfaces. *J Phys Chem Lett* 2:2267–2272
- [41] Zheng Z, Retana M, Hu XB, Luna R, Ikumura YH, Zhou WL (2017) Three-dimensional cobalt phosphide nanowire arrays as negative electrode material for flexible solid-state asymmetric supercapacitors. *ACS Appl Mater Interfaces* 9:16987–16995
- [42] Lu XF, Chen XY, Zhou W, Tong YX, Li GR (2015) $\alpha\text{-Fe}_2\text{O}_3$ @PANI-core shell nanowire arrays as negative electrodes for asymmetric supercapacitors. *ACS Appl Mater Interfaces* 7:14843–14850
- [43] Zhou C, Zhang Y, Li Y, Liu J (2013) Construction of high-capacitance 3D CoO @polypyrrole nanowire array electrode for aqueous asymmetric supercapacitor. *Nano Lett* 13:2078–2085

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Note

Low-crystalline Ni/Co-oxyhydroxides nanoarrays on carbon cloth with high mass loading and hierarchical structure as cathode for supercapacitors



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ABSTRACT

Compared with the crystalline transition metal oxyhydroxide, low-crystalline structure is conducive to high electrochemical performance due to its more grain boundaries and ion diffusion channels. However, the manufacture of low-crystalline oxyhydroxides remains challenging, especially those with multiple transition metals. Herein, high mass loading ($\sim 9 \text{ mg cm}^{-2}$) and low-crystalline Ni/Co-oxyhydroxides nanoarrays on carbon cloth (CC) were prepared by electrochemical reconstruction. The low-crystalline Ni/Co-oxyhydroxides nanoarrays possessed a hierarchical structure, which were consist of flake-like $(\text{Co}_{0.25}, \text{Ni}_{0.75})\text{O}(\text{OH})$ single-crystals and needle-like Ni-doped $\text{CoO}(\text{OH})$ polycrystalline. Both single crystal nanoflakes and polycrystalline nanoneedles contained a lot of defects. Owing to the unique structure, the mutual doping of Ni and Co atoms, and the abundant defects, the nanoarrays of Ni/Co-3500 showed excellent electrochemical performance with a high specific capacitance of 8.87 F cm^{-2} at 5 mA cm^{-2} and a high rate retention of 69.33% at 50 mA cm^{-2} , as well as a high cycle stability remaining 91.6% of initial capacitance after 2000 galvanostatic charge–discharge cycles at a current density of 20 mA cm^{-2} . Furthermore, the assembled asymmetric supercapacitor of Ni/Co-3500/oxidized CC delivered a high areal capacitance of 1.48 F cm^{-2} and a volumetric capacitance of 14.8 F cm^{-3} at 8 mA cm^{-2} , as well as 1.11 F cm^{-2} (11.1 F cm^{-3}) even at 50 mA cm^{-2} . The energy density of Ni/Co-3500/oxidized CC device was up to 4.35 mWh cm^{-3} at the powder density of 60.1 mW cm^{-3} . It indicates that the as-prepared low-crystalline Ni/Co-oxyhydroxides arrays on CC is a promising electrode for high energy density supercapacitors.

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1. Introduction

The rapid growth of energy consumption and the instability of renewable energy sources have highlighted an urge to develop efficient, high-performance energy storage system. Supercapacitors, also known as electrochemical capacitors, have stimulated considerable attention for their splendid electrochemical properties including fast charging/discharging process, excellent rate performance, long cycle lifetime, high power density, and low maintenance costs [1,2]. Considering the charge storage mechanism, the electrode materials of supercapacitors can be grouped into two categories [3], one is electrical double-layer capacitive materials,

such as carbon nanotubes [4], activated carbon [5], graphene [6–8], and the other is pseudocapacitive materials, such as transition metal oxides [9], sulfides [10], hydroxides [11] and conductive polymer [12]. The previous researches have demonstrated that the character of electrode materials exert an obvious influence on the electrochemical performance of supercapacitors [13–16]. Unlike the conventional electronic double layer capacitors (EDLCs) based on carbon materials, pseudocapacitor can deliver much higher special capacitance and energy density through fast redox reactions [17].

Among numerous pseudocapacitive materials, transition metal oxides/hydroxides, especially nickel oxides/hydroxide and cobalt oxides/hydroxide have drawn intensive attention due to their advantages of multiple oxidation states and easy preparation [18–20]. Most of the previous studies of transition metal hydroxides focused on crystalline materials [21–23]. Recent works [24,25] on low-crystalline or amorphous cobalt oxides/hydroxide corroborated that the low-crystalline hydroxides are able to deliver

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better performance than their high-crystalline counterparts, since they possessed more structure defects and disorder, suggesting low-crystalline or amorphous phase material is a promising candidate materials for supercapacitor with excellent electrochemical performance. Li et al. [24,25] synthesized amorphous $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ by electrochemical methods, which have high charge storage capacitance and cycle stability. Chen and his collaborators [26] reported that the amorphization hybridization of nickel hydroxide/carbon nanotubes/conducting polymers was characterized by high energy density, good rate performance, and long cycle life. Although some profound achievements have been made on low-crystalline or amorphous transition metal hydroxides, there is still a tremendous challenge to obtain low-crystalline transition metal oxyhydroxides with high capacitance, good rate capability and excellent cycling stability. Since that the addition of the conductive additive and polymer binder on current collector introduced the so-called "dead volume", which has unfavorable impact on the diffusion of the electrolyte into the electrode material and the transport of electrons in the electrode, leading to their lower contribution to the total capacitance [27]. To ensure the efficient electrode/electrolyte contact areas and fast ion diffusion, an elaborate design of electrode materials with unique structures is desirable. Furthermore, the mass loading of active material on electrodes have a crucial influence on the practical application of the electrode materials for high performance supercapacitor [28,29]. First, mass loading materials directly determine the total capacitance and amount of energy stored of electrode [29,30]. Generally speaking, active material mass loading of $8\text{--}10\text{ mg cm}^{-2}$ is required to offer sufficient energy for commercial energy storage devices [31]. However, on account of the moderate conductivity, slow ion diffusion, and poor mechanical stability of the active material, the increasing of the mass load will give rise to a sharp decline in specific capacitance, and which consequently bring about the inferior of specific capacitance and rate capability. Therefore, it is a great challenge for supercapacitors to remain excellent electrochemical performance at high mass loading of active material. One of the available approach to improve the electrochemical performance of active material with high mass loading is to construct three-dimensional (3D) hierarchical nanoarrays on conductive substrate directly [22,32]. The properly designed 3D hierarchical nanoarrays can not only accelerate the transport of charge and mass in the electrodes but also effectively relieve the generated strain during charge/discharge cycling to ensure the long cycle stability [31]. Therefore, it would be of great significance to achieve a high specific capacitance at a high mass loading of active material without using of conductive additives and polymer binders. Among the various commercial conductive substrates, CC was an excellent current collector because of its advantages of light weight, flexibility, easy processing and high stability [33,34]. Importantly, CC was widely recognized as a foldable, lightweight substrate in the manufacture of flexible portable devices [35]. Inspired by the previous reports, we expect that low-crystalline and 3D hierarchical arrays on CC would be beneficial to the electrochemical performance of transition metal oxyhydroxides, so that the high mass loading can be achieved without the sacrifice of special capacitance.

Herein, we reported a simple electrochemical reconstruction strategy to fabricate low-crystallinity Ni/Co-oxyhydroxides nanoarrays with hierarchical structure and high mass loading directly on CC. CC served as a conductive skeleton for nanoarrays growth and ensures the high conductivity as well as satisfied bonding between active material and substrate. The as-prepared low-crystallinity Ni/Co-oxyhydroxides nanoarrays electrode exhibited extraordinary areal capacitance of 8.87 F cm^{-2} at 5 mA cm^{-2} , which is among the highest areal capacitance reported for transition metal oxyhydroxides at a high mass loading $\sim 9\text{ mg cm}^{-2}$ in aqueous electrolytes. The as-prepared electrode also showed high rate capa-

bility (69.3% retention at 50 mA cm^{-2}) and cycle stability (91.6% retention after 2000 charge-discharge cycles at a current density of 20 mA cm^{-2}), which is excelled or comparable to that of low mass loading transition metal oxyhydroxides electrodes. Furthermore, the asymmetric supercapacitors (ASCs) based on the low-crystallinity Ni/Co-oxyhydroxides nanoarrays electrode as positive electrode and oxidized CC (OCC) as negative electrode were developed to achieve high energy and power densities. The assembled ASC of Ni/Co-3500//OCC exhibit extremely high energy density up to 4.35 mWh cm^{-3} at the powder density of 60.1 mW cm^{-3} . The elaborate design of intricate transition metal hydroxides with hierarchical architecture greatly creates new opportunities for the fabrication of electrode materials for high-performance supercapacitors.

2. Experimental

2.1. Preparation of Ni/Co hierarchical precursors

All the reagents were analytically pure and used without further purification. Prior to the preparation, a piece of CC ($4\text{ cm} \times 4\text{ cm}$) was consecutively cleaned with acetone, ethanol and deionized water for 15 min under ultrasonication to remove the impurities, respectively. The Ni/Co hierarchical precursors were grown onto the CC by two-steps hydrothermal method. Firstly, 2.85 g nickel chloride hexahydrate, 2.88 g urea and 0.89 g ammonium fluoride were dissolved in 80 mL deionized water and the mixed solution was constantly stirring for 0.5 h until the solution becoming uniform. Then the above solution was transferred into 100 mL Teflon-lined stainless-steel autoclave. The cleaned CC was immersed into the precursor solution. The autoclave was then sealed and maintained at $120\text{ }^\circ\text{C}$ for 6 h . After the samples were cooled to room temperature, the CC coated with green products was washed with deionized water and anhydrous ethanol several times and dried in an oven at $60\text{ }^\circ\text{C}$ for 6 h . Then, 1.75 g cobalt nitrate hexahydrate, 1.80 g urea and 0.56 g ammonium fluoride were mixed in 80 mL deionized water followed by stirring for 0.5 h to dissolve sufficiently, then the obtained solution was transferred to 100 mL Teflon-lined stainless-steel autoclave, and the as-prepared CC coated with green products was immersed into the solution. The autoclave was then sealed and maintained at $120\text{ }^\circ\text{C}$ for 9 h . After cooled to room temperature naturally, the CC coated with pink products was picked out and rinsed with deionized water and absolute ethanol to remove the residues. Finally, the obtained CC was dried at $60\text{ }^\circ\text{C}$ for 6 h to get the Ni/Co precursors.

2.2. Preparation of Ni/Co-oxyhydroxides hierarchical nanoarrays

To prepare the low crystallinity Ni/Co oxyhydroxides hierarchical nanoarrays, the obtained Ni/Co hierarchical precursors on CC ($1\text{ cm} \times 1\text{ cm}$) were treated by electrochemical reconstruction method. The electrochemical reconstruction of Ni/Co hierarchical precursors was carried out in a conventional three-electrode system using a CHI 760E electrochemical workstation (Chenhua, Shanghai) through cyclic voltammetry (CV) process. A platinum plate ($1\text{ cm} \times 1\text{ cm}$) and a Hg/HgO electrode were served as the counter and reference electrodes, respectively. The CV was performed at a potential window of $0\text{--}0.6\text{ V}$ at scan rate of 50 mV s^{-1} in 6 M KOH solution. In order to investigate the influence of electrochemical reconstitution time on materials, the Ni/Co hierarchical precursors were treated with different CV cycles, four low-crystallinity Ni/Co-oxyhydroxides hierarchical nanoarrays were obtained after 2500, 3000, 3500 and 4000 CV cycles, the corresponding cycle times were 16.7, 20.0, 23.3 and 26.7 h, and denoted as Ni/Co-2500, Ni/Co-3000, Ni/Co-3500 and Ni/Co-4000, respectively. Ni/Co hierarchical precursors were denoted as Ni/Co-0. The

mass loading of the products on CC was estimated gravimetrically by measuring the weight of pristine CC and Ni/Co-oxyhydroxides nanoarrays coated CC using a Sartorius BS124S Micro Balance. The mass loading of Ni/Co-0, Ni/Co-2500, Ni/Co-3000, Ni/Co-3500 and Ni/Co-4000 on CC were 8.5, 8.5, 9.0, 9.0 and 9.0 mg cm⁻², respectively.

2.3. Characterizations

The phase of the as-prepared samples was measured by powder X-ray diffraction (XRD, Bruker D8 Advance, Cu K_α radiation λ = 1.5406 Å) on an XRD diffractometer. The morphology and structure the as-prepared samples were analyzed by scanning electron microscopy (SEM, FEI Quanta 250) and transmission electron microscopy (TEM, FEI Talos F200X) equipped with an energy-dispersive X-ray spectroscopy detector (EDS). The elemental composition and chemical state of the as-prepared samples was determined by X-ray photoelectron spectroscopy (XPS, Kratos). Electron paramagnetic resonance (EPR) spectra were collected on a Bruker A300 EPR spectrometer operating at room temperature using the same mass of samples from surface of CC.

2.4. Electrochemical measurements

Electrochemical properties of the low crystallinity Ni/Co-oxyhydroxides hierarchical nanoarrays were investigated on a CHI760e electrochemical workstation using three-electrode system in 6 M KOH aqueous solution at room temperature (25 ± 2 °C). Here, platinum plate (1 cm × 1 cm) and Hg/HgO electrode was used as the counter electrode and the reference electrode, respectively. The samples were measured by the electrochemical testing methods including CV, galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS).

The areal special capacitance (C_{as}) and the mass special capacitance (C_{ms}) of the low-crystallinity Ni/Co oxyhydroxides hierarchical nanoarrays in three-electrode system were calculated according to Eqs. (1) and (2), respectively.

$$C_{as} = \frac{I \times \Delta t}{S \times \Delta V} \quad (1)$$

$$C_{ms} = \frac{I \times \Delta t}{m \times \Delta V} \quad (2)$$

Where I (A) is the applied current, Δt (s) is the discharge time, S (cm²) is the effective area of the working electrode, ΔV (V) is the working potential range, m is the mass loading of the active material.

In addition, the supercapacitor devices were assembled using the low crystallinity Ni/Co-oxyhydroxides hierarchical nanoarrays on CC as cathode, the oxidized CC (Section S1) as anode, a piece of filter paper as separator, 6 M KOH aqueous solution as electrolyte. The devices were sealed by PVC film, and the thickness was 1.0 mm. Electrochemical properties of the devices were assessed on a CHI760e electrochemical workstation and a CT2001A supercapacitance test system at room temperature (25 ± 2 °C). The energy density and power density of devices was calculated through the following Eqs. (3) and (4), respectively.

$$E = \frac{1}{2 \times 3.6} C_v (\Delta V)^2 \quad (3)$$

$$P = \frac{E \times 3600}{\Delta t} \quad (4)$$

where E is the energy density (mWh cm⁻³), C is volumetric capacitance (F cm⁻³), Δt is discharge time (s), P is the power density (mW cm⁻³, and ΔV (V) is discharge potential window of the ASCs.

3. Results and discussion

3.1. Characterization

Fig. 1 presents the schematic illustration of the procedure used to prepare the Ni/Co-oxyhydroxides hierarchical nanoarrays with low-crystallinity and high mass loading on CC. The homogeneous green Ni precursors were grown on the CC after the first hydrothermal process. The obvious diffraction peaks in the XRD patterns (Fig. 2) of Ni precursors match well with the standard Ni(OH)₂·0.75H₂O (PDF No.38-0715), indicating the as-prepared Ni precursors are nickel hydroxide. After the second hydrothermal process, the pink Co precursors were fabricated uniformly on the nickel hydroxide nanoflakes (Fig. 2). XRD patterns of the Ni/Co precursors nanoarrays show several obvious diffraction peaks located at 2θ = 17.512°, 33.823°, 35.480° and 39.527°, which can be identified as (020), (220), (040) and (231) planes of Co₂(CO₃)(OH)₂nH₂O (PDF No. 48-0083). The complete disappear of all nickel hydroxide peaks may be attributed to its reduced crystallinity degree

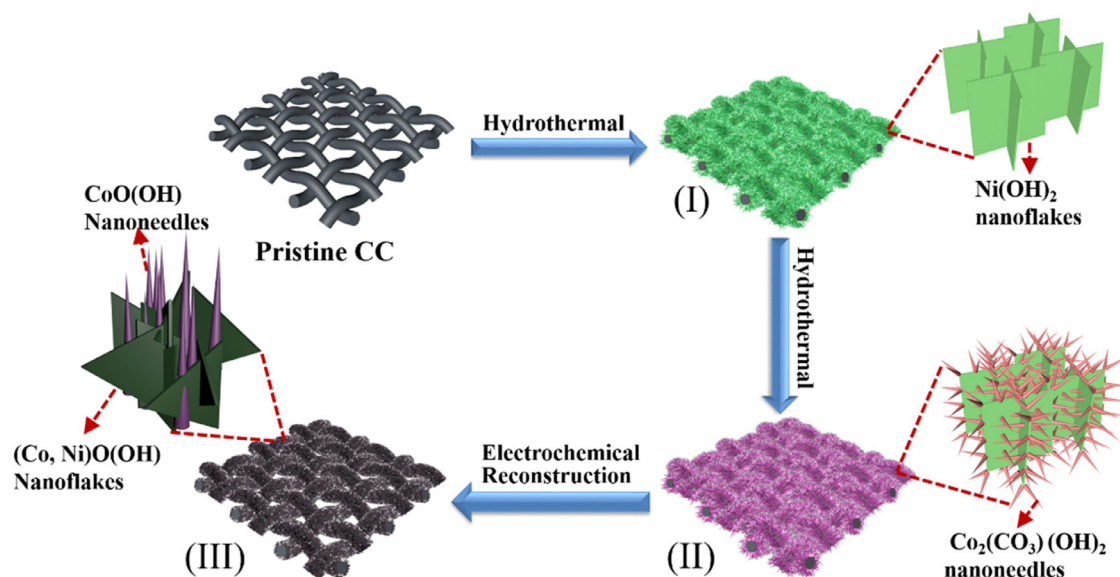


Fig. 1. Schematic illustration for the preparation of low-crystallinity Ni/Co-oxyhydroxides nanoarrays on CC.

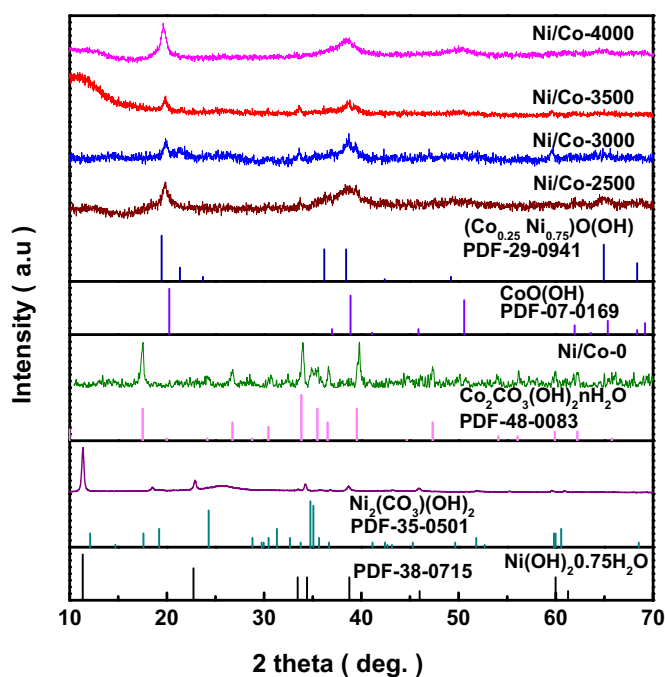


Fig. 2. XRD patterns of the Ni/Co precursors and Ni/Co-oxyhydroxides nanoarrays.

or the covered $\text{Co}_2(\text{CO}_3)(\text{OH})_2\text{nH}_2\text{O}$. Finally, Ni/Co-oxyhydroxides nanoarrays with low-crystallinity and high-mass loading were obtained through electrochemical reconstruction in alkaline solution using CV cycle method. XRD patterns in Fig. 2 show that the diffraction peaks of $\text{Co}_2(\text{CO}_3)(\text{OH})_2\text{nH}_2\text{O}$ gradually disappeared after CV cycles, and the peaks at $2\theta=20.24^\circ$, 38.89° and 50.58° can be indexed to the (012) and (015) planes of Co-oxyhydroxides

($\text{CoO}(\text{OH})$, PDF No. 07-0169), and the peaks at $2\theta=19.45^\circ$, 38.44° can be indexed to the planes of Ni/Co-oxyhydroxides ($(\text{Co}_{0.25}\text{Ni}_{0.75})\text{OOH}$, PDF No. 29-0491), resulting the formation of the Ni/Co-oxyhydroxides nanoarrays. The conversion of $\text{Co}(\text{II})/\text{Ni}(\text{II})$ to $\text{Co}(\text{III})/\text{Ni}(\text{III})$ compound could be put down to the redox reaction between $\text{Co}(\text{II})/\text{Ni}(\text{II})$ ions and dissolved oxygen in the solution [36,37]. In addition, the crystallinity of the samples decreases with the increasing of the CV cycles. When the CV cycles increase to 3500, the crystallinity of the sample appeared to be lowest, as indicated by the lowest intensity of diffraction peaks. However, as the CV cycles increase to 4000, the intensity of diffraction peaks increased, suggesting that the number of CV cycle can affect the crystallinity of the as-prepared samples.

To confirm the morphology and microstructure evolutions during the process of two-step hydrothermal and electrochemical reconstruction, the morphology of the samples was characterized by scanning electron microscopy (SEM), as shown in Fig. 3. It can be seen from Fig. 3a, the prepared $\text{Ni}(\text{OH})_2$ is flake-like, and these $\text{Ni}(\text{OH})_2$ nanoflakes are interconnected with each other and mostly perpendicular to the CC. Fig. 3b shows that the as-prepared needle-like $\text{Co}(\text{CO}_3)(\text{OH})_2\text{nH}_2\text{O}$ are grown on the surface of $\text{Ni}(\text{OH})_2$ to form hierarchical structure (Fig. 3b). After electrochemical reconstruction through 2500 CV cycles, the pristine structure of $\text{Ni}(\text{OH})_2/\text{Co}_2(\text{CO}_3)(\text{OH})_2\text{nH}_2\text{O}$ nanoarrays was still well maintained, only the $\text{Co}_2(\text{CO}_3)(\text{OH})_2\text{nH}_2\text{O}$ nanoneedles became thick and rough (Fig. 3c). As the CV cycles increased to 3000, some wispy layers appeared between the neighboring nanoneedles (Fig. 3d), and the Co-based nanoneedles remained stable on the nanoflakes when the CV cycles was increased to 3500 (Fig. 3e). Continue to increase the number of CV cycles to 4000, the nanoneedles began to agglomerate and the hierarchical structure gradually collapsed, which may lead to the decrease of active sites and deterioration electrochemical performance.

The detailed microstructure of the Ni/Co-oxyhydroxides nanoarray was further tested using TEM, taking Ni/Co-3500 as an

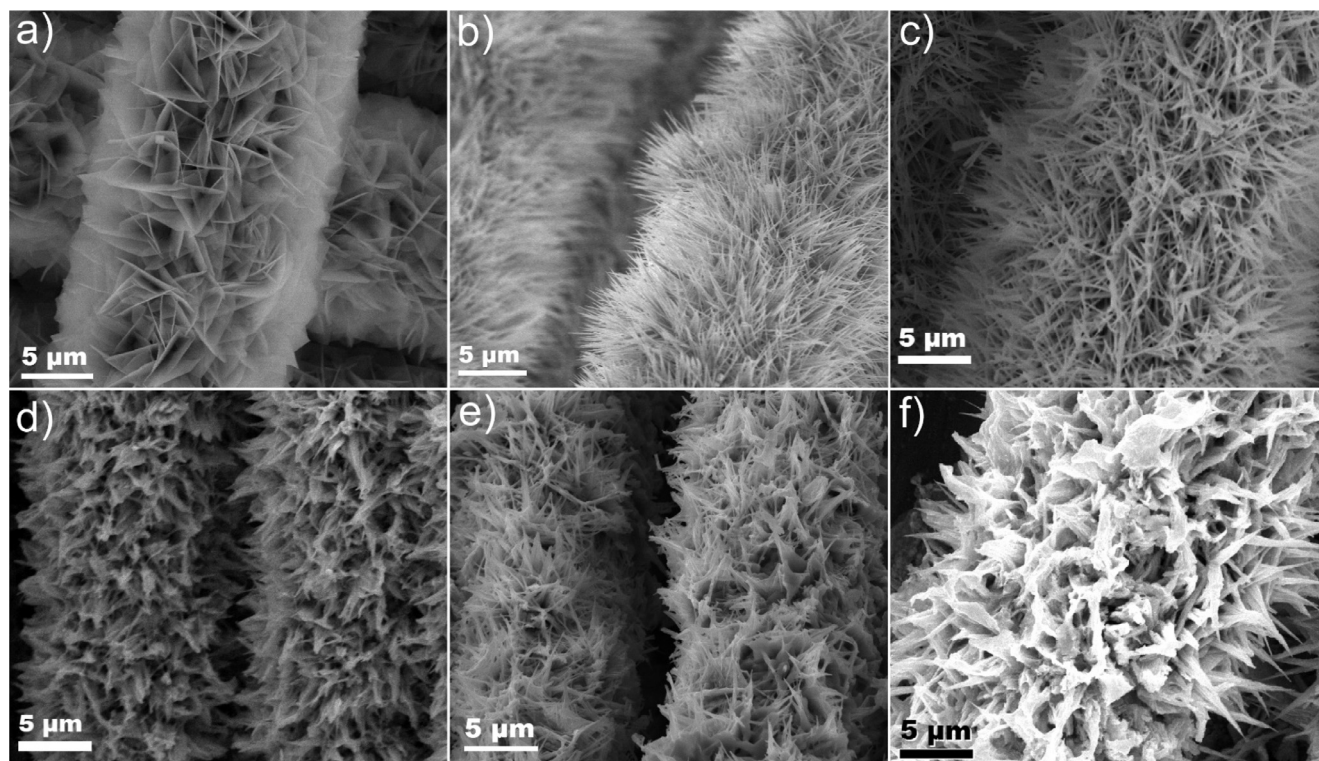


Fig. 3. SEM images of a) Ni precursors, b) Ni/Co precursors (Ni/Co-0) and Ni/Co-oxyhydroxides nanoarrays, c) Ni/Co-2500, d) Ni/Co-3000, e) Ni/Co-3500, and f) Ni/Co-4000.

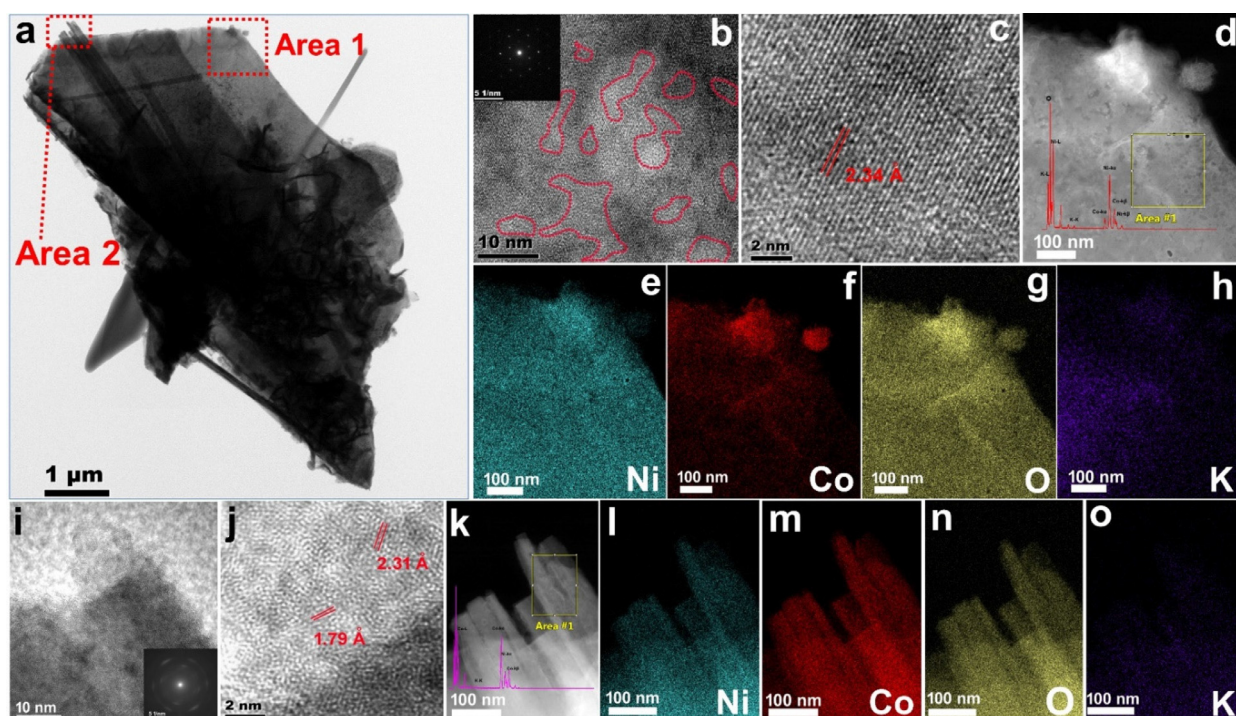


Fig. 4. a) TEM image of Ni/Co-oxyhydroxides nanoarrays, b) HRTEM image of the nanoflake (Area 1) and the corresponding SAED pattern (inset), c) magnified HRTEM image of the nanoflake, d) HAADF image of the nanoflake, EDS spectra (inset) and the corresponding EDS mapping images of e) Ni, f) Co, g) O, h) K; i) HRTEM images of the nanoneedle (Area 2) and the corresponding SAED pattern (inset), j) magnified HRTEM image of the nanoneedle, k) HAADF image of the nanoneedle, EDS spectra (inset) and the corresponding EDS mapping images l) Ni, m) Co, n) O, o) K.

example. Fig. 4a shows the typical TEM images of Ni/Co-3500 nanoarray dropped from CC. We can clearly observe that nanoneedles grew on nanoflakes to form a hierarchical structure. Fig. 4b displays the HRTEM image of the nanoflakes (Area 1 in Fig. 4a), it was found that the nanoflakes obtained by electrochemical reconstitution have abundant defect sites (red labeled area), and the corresponding selective region electron diffraction (SAED) pattern (inset of Fig. 4b) shows a lattice structure indicating that they are single crystal. In addition, the lattice spacing of 2.34 Å in magnified HRTEM image of nanoflakes (Fig. 4c) corresponds to the plane of $(\text{Co}_{0.25}\text{Ni}_{0.75})\text{O}(\text{OH})$ (PDF No. 29-0491). It indicates that both Ni and Co elements undergo phase transformation during the formation of $(\text{Co}_{0.25}\text{Ni}_{0.75})\text{O}(\text{OH})$ by electrochemical reconstruction. The high-angle annular dark field (HAADF) image of nanoflakes region is shown in Fig. 4d, and the EDS spectra for the select area in Fig. 4d shows that there are Ni, Co, O and K elements in the nanoflakes. The present K element is derived from the KOH electrolyte during electrochemical reconstitution. The corresponding EDS mapping images (Fig. 4e–h) indicate that the Ni, Co, O and K elements are dispersed uniformly in the nanoflake (Area 1 in Fig. 4a) of the Ni/Co-3500 sample. Fig. 4i shows the HRTEM image of nanoneedles (Area 2 in Fig. 4a), and these ambiguous stripes contain many disorder and defects, indicating a low-crystallinity characteristic of the nanoneedles. The diffraction rings presented in the corresponding SAED pattern (inset of Fig. 4i) suggests that nanoneedles are polycrystalline. In addition, the lattice spacing of 2.31 Å and 1.79 Å in HRTEM images of Ni/Co-3500 (Fig. 4j) match well with the (015), (012) planes of $\text{CoO}(\text{OH})$ (PDF No. 07-0169), respectively. Fig. 4k shows the HAADF image of the nanoneedle, and the EDS spectra of the select area in Fig. 4k indicate Ni, Co, O and K elements in the nanoneedle, and the corresponding EDS mapping images (Fig. 4l–o) show that the Ni, Co, O and K elements were dispersed homogeneously in the nanoneedle, suggesting the Ni atoms were doped into the $\text{CoO}(\text{OH})$ crystals.

The elemental composition and chemical bond state of the sample surface were investigated by X-ray electron spectroscopy (XPS). Fig. S1 presents the complete survey XPS spectra of the Ni/Co-0 and Ni/Co-3500. There are four peaks, C1s, O1s, Co2p and Ni2p in the spectrum of Ni/Co-0, while another K2s was found in the sample Ni/Co-3500, indicating the K element was introduced in Ni/Co-oxyhydroxides nanoarrays during electrochemical reconstruction. The high resolution XPS spectra of Ni2p, Co2p, O1s and C1s of the Ni/Co-0 and Ni/Co-3500 were shown in Fig. 5, respectively. Ni2p XPS spectra (Fig. 5a) shows two kind of nickel species: $\text{Ni}2\text{p}_{1/2}$ (871–876 eV) and $\text{Ni}2\text{p}_{3/2}$ (852–858 eV), with two satellite peaks at 876–884 and 858–864 eV, respectively [38]. For Ni/Co-0 sample, the two binding energies of $\text{Ni}2\text{p}_{1/2}$ and $\text{Ni}2\text{p}_{3/2}$ peaks located at 873.90 eV and 855.96 eV, the spin-energy separation of 17.9 eV is also the characteristic of Ni(II) hydroxides [39]. For Ni/Co-3500 sample after the electrochemical recombination through 3500 CV cycles, the binding energy pair at 872.9 and 855.5 eV correspond to $\text{Ni}2\text{p}_{1/2}$ and $\text{Ni}2\text{p}_{3/2}$ signals of Ni^{3+} , while the binding energy pair at 878.3 and 860.5 eV can be ascribed to $\text{Ni}2\text{p}_{1/2}$ and $\text{Ni}2\text{p}_{3/2}$ signals of Ni^{2+} , confirming the presence of $\text{Ni}(\text{OH})_2$ and $\text{NiO}(\text{OH})$. In the high resolution XPS spectrum of Co2p (Fig. 5b) for Ni/Co-0 sample, two groups peaks centered at 797.5 eV/804.7 eV and 781.2 eV/784.5 eV with associated Co^{2+} satellite peaks at 804.2 eV and 787.2 eV are attributed to the $\text{Co}2\text{p}_{1/2}$ and $\text{Co}2\text{p}_{3/2}$ respectively, indicating the presence of Co hydroxide and carbonate [40]. For Ni/Co-3500 sample, two major peaks at 779.9 eV and 794.9 eV and two satellite peaks at 789.3 eV and 804.7 eV can be assigned to $\text{Co}2\text{p}_{3/2}$ and $\text{Co}2\text{p}_{1/2}$ of Co^{3+} , respectively [41,42]. Meanwhile, another pair of binding energies at 782.3 eV and 797.2 eV belongs to the $\text{Co}2\text{p}_{3/2}$ and $\text{Co}2\text{p}_{1/2}$ signals of Co^{2+} [42]. It indicates the existence of $\text{Co}(\text{OH})_2$ and $\text{CoO}(\text{OH})$. Fig. 5c shows the high-resolution spectrum of O1s, for Ni/Co-0, the fitted peak at 532.7 eV is usually associated with oxygen in metal hydroxide, and the peak at 531.3 eV is typical of oxygen in metal carbonate. For Ni/Co-3500,

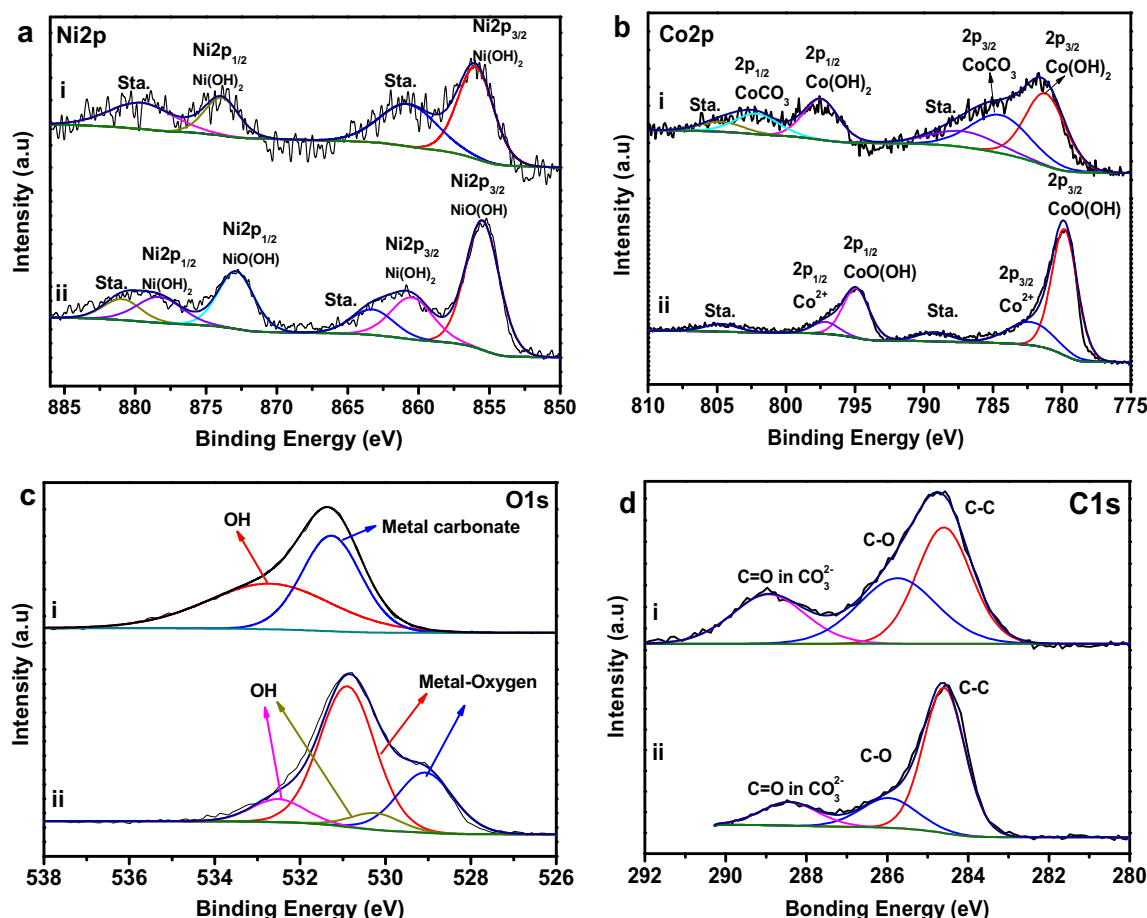
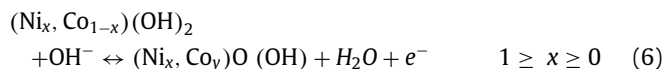
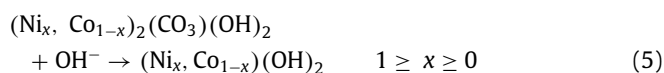


Fig. 5. XPS spectra of the Ni/Co-O (i) and Ni/Co-3500 (ii). a) Ni2p, b) Co2p, c) O1s and d) C1s.

the peaks at 529.1 eV and 530.9 eV can be attributed to metal oxygen bonds contributed by CoO(OH) and NiO(OH) [43], while peaks at 530.3 and 532.5 belong to OH groups contributed by Co(OH)_2 and Ni(OH)_2 [44]. As for the C1s spectra in Fig. 5d, the peak value of 284.6 eV can be attributed to graphite-C in CC, while the characteristic peak at 285.8 eV and 288.9 eV corresponds to the C-O and C=O in CO_3^{2-} [45]. After treated by 3500 CV cycles, the intensity of the peaks at 285.8 eV and 288.9 eV was obviously weakened, suggesting the phase transfer in the process of electrochemical reconstruction. In brief, XPS results indicate the existence of Ni^{2+} and Ni^{3+} , Co^{2+} and Co^{3+} , O (OH and metal oxygen bond), which further verifies the formation of Ni/Co oxyhydroxides.

According to the above results, we speculated that the electrochemical reconstruction contained two steps. One step is that the precursors of Ni/Co carbonate hydroxide were alkalinized to Ni/Co hydroxide as following Eq. (3), and another step is that the Ni/Co hydroxides were transformed to Ni/Co-oxyhydroxides (Eq. (4)). The two steps may happen at the same time. During the electrochemical reconstruction, the crystallinity degree reduced, and the defect increased gradually. The electron paramagnetic resonance (EPR) spectra (Figure S2) of Ni/Co-oxyhydroxides show a signal at $g = 2.002$, which corresponds to the oxygen vacancy [46,47], and the increasing intensity indicates that the number of oxygen vacancy was increased after electrochemical reconstruction. In addition, the hierarchical structure composed of nanoflakes and nanoneedle almost remained. It can be expected that the hierarchical structure will not only be propitious to the adequate utilization of active material, but also facilitate the supply of abundant surface-active sites to enhance capacitance performance. Fur-

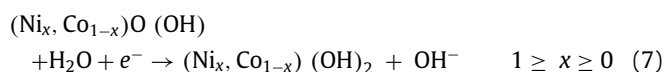
thermore, the mutual doping of Ni and Co atoms in nanoflakes and nanoneedles also effectively improved the activity of Ni/Co-oxyhydroxides nanoarrays.



3.2. Electrochemical properties of electrodes

The electrochemical properties of the as-prepared electrodes were conducted in a three-electrode cell using 6 M KOH electrolyte, and the results are presented in Fig. 6. As shown in Fig. 6a, the CV curves of all the as-prepared electrodes were completely different from of the ideal double-layer capacitors and displayed two distinct pair of redox peaks during the potential window of 0–0.6 V, which reveals the pseudocapacitive characteristics of the as-prepared electrodes. The possible pseudocapacitive behavior could be ascribe to the reversible reaction Eq. (5) and (6) of $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ [48–50].

Discharge process:



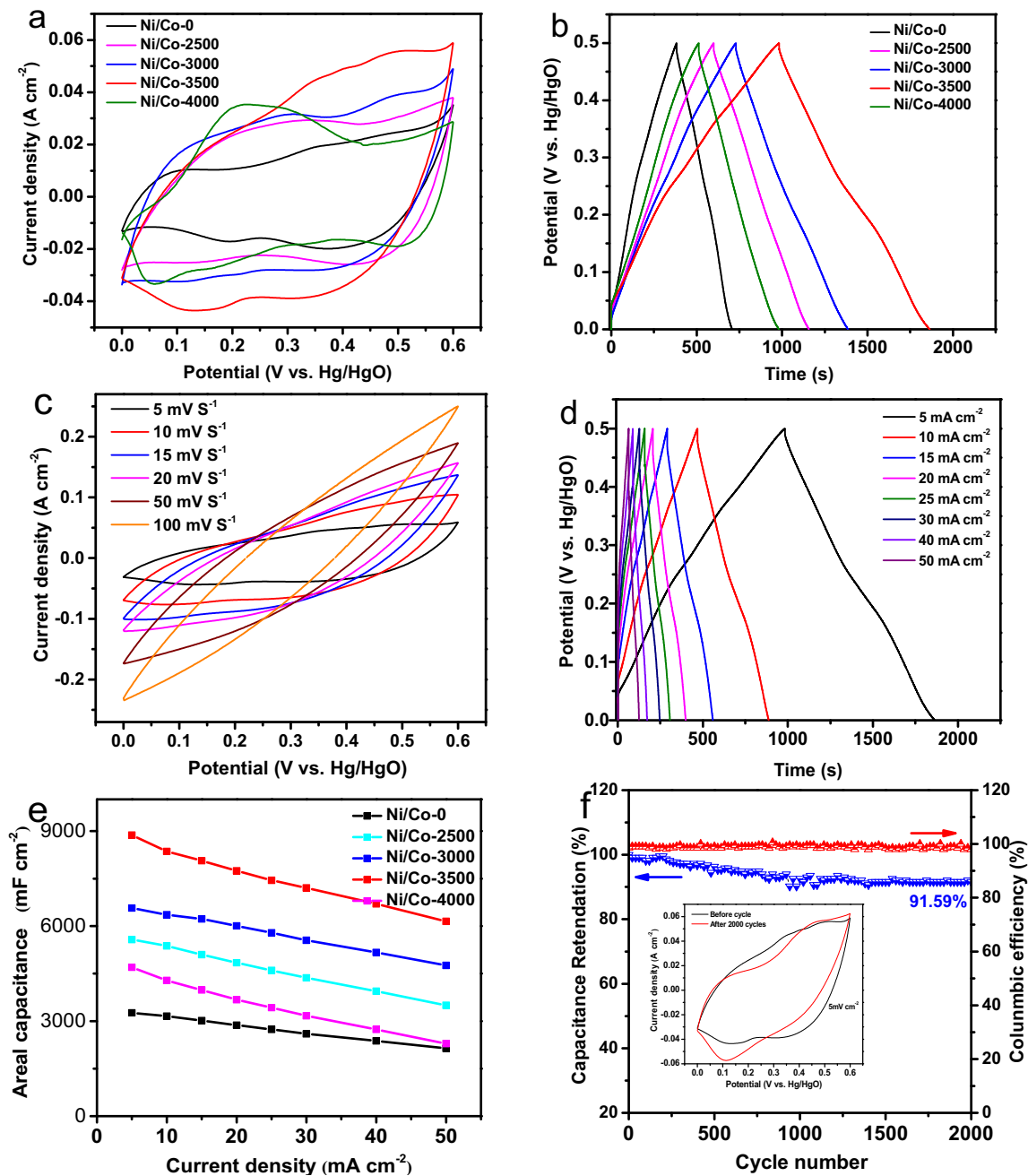
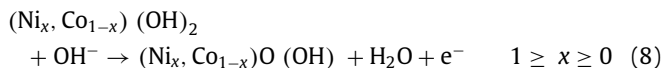


Fig. 6. a) CV curves of the as-prepared electrodes at 5 mV s^{-1} . b) GCD curves of the as-prepared electrodes at 5 mA cm^{-2} . c) CV curves of the Ni/Co-3500 electrode at different scan rates. d) GCD curves of Ni/Co-3500 electrode at different current densities. e) Areal capacitance as a function of current density for the as-prepared electrodes. f) Long-term cycling stability of the Ni/Co-3500 electrodes at 20 mA cm^{-2} .

Charge process:



Among the all as-prepared electrodes, the Ni/Co-3500 electrode exhibited larger current density at the same scan rate, suggesting higher capacitance than other electrodes. Fig. 6b shows the GCD curve at current density of 5 mA cm^{-2} in the potential range of 0–0.5 V. The shape of the GCD curves demonstrate the feature of pseudocapacitance, and the slight plateaus in the GCD curves confirm the existence of redox reaction, which is in accordance with the results of CV test. Compared with the other Ni/Co-based electrodes [21–23], our Ni/Co-oxyhydroxides showed that the redox peaks and the corresponding plateaus are inapparent,

which are possibly attributed to their low-crystallinity and abundant defects [46]. The Ni/Co-3500 electrode deliver longer charge-discharge time compared with other electrodes, indicating higher capacitance. The areal special capacitance was calculated from the discharge curves according Eq. (1), and the calculated areal special capacitance of Ni/Co-0, Ni/Co-2500, Ni/Co-3000, Ni/Co-3500 and Ni/Co-4000 electrodes are 3.26, 6.50, 6.57, 8.87 and 4.70 F cm^{-2} , respectively, which is superior than the pristine $\text{Ni}(\text{OH})_2$ (Figure S3) and $\text{Co}_2(\text{CO}_3)(\text{OH})_2$ (Figure S4) sole arrays electrodes. As expected, the areal special capacitance increases with the increasing of the number of CV cycles, and the higher areal special capacitance of Ni/Co-3500 demonstrate the advantages of the low-crystallinity materials. Moreover, the areal special capacitance of Ni/Co-4000 is inferior than other electrodes, mainly due to their

Table 1
Electrochemical properties of various Ni/Co based electrodes for supercapacitor.

Active material	Substrate	Loading mass (mg cm ⁻²)	Areal capacitance (F cm ⁻²)	Mass specific capacitance (F g ⁻¹)	Current density	Ref.
NiO@NiFe-LDH	Ni foam	2	4.5	–	4 mA cm ⁻²	[51]
Nickel nanowires@nickel–cobaltdouble hydroxide(NiNW@NiCo-DH/NF)	Ni foam	1.1–1.2	2.25	–	5 mA cm ⁻²	[21]
amorphous NiCo–OH	Ni foam	2.5	–	857	1 A g ⁻¹	[52]
Co–Ni–OH/rGO	CC	1.24	–	151.46	2.5 A g ⁻¹	[53]
Ni(OH) ₂ sheet	Ni foam	–	0.863	693	5 mA cm ⁻²	[54]
CCCH@ NiCo-LDH@Au–CuO/Cu,						
NiCo-LDH@Au–CuO/Cu	Cu fibers	1.61	1.97	1237	1.5 mA cm ⁻²	[28]
NiCo-LDH	aTC	6.72	6.37	525	8 mA cm ⁻²	[55]
G–Zn–Co@Ni–Co	Ni foam	–	7.49	–	5 mV s ⁻¹	[56]
NiCo ₂ S ₄ @Ni–Co layered double hydroxide nanotube arrays						
	Au coated cotton	–	5.68	–	2 mA cm ⁻²	[57]
ZnNiCo–P nanosheets	Ni foam	–	–	958	1 A g ⁻¹	[58]
EA–CoOOH	CFP	0.8	0.666	832	1 A g ⁻¹	[46]
Ni–Co hydroxide	CC	8.3	5.01	603	2 mA cm ⁻²	[21]
Low-crystalline Ni@Co-oxyhydroxides Arrays	CC	9.0	8.87	990	5 mA cm ⁻²	This work

'LDH' is abbreviated from layered double hydroxide.

'CCCH' is Cu-doped cobalt copper carbonate hydroxide.

'aTC' is carbonization of textile cotton cloth.

'CFP' is carbon fiber paper.

better crystallinity, which was verified by the XRD results in Fig. 2, further proved the merit of the low-crystallinity materials.

To clarify the excellent performance of Ni/Co-3500, the electrochemical properties of Ni–Co nanoarrays on CC soaked in 6 M KOH for 23.3 h without electrochemical treatment and the bare CC after electrochemical treatment (3500 CV cycles) also were investigated and shown in Fig. S5 and S6, respectively. Fig. S5a and S5b exhibit the CV and GCD curves of as-soaked Ni–Co nanoarrays. It can be observed that the capacitance properties of as-soaked Ni–Co nanoarrays without electrochemical treatment, and its specific capacitance was 3.06 F cm⁻² at a current density of 5 mA cm⁻², which is much lower than the Ni/Co-3500. It indicates that the electrochemical treatment is an effective approach to improve the capacitance performance of Ni/Co-oxyhydroxides nanoarrays on CC with high loading. In addition, the CV and GCD curves of bare CC after electrochemical treatment (as shown in Figure S6a and S6b) indicate that the bare CC has almost no contribution for the capacitance of Ni/Co-3500.

The detailed electrochemical performance of Ni/Co-3500 electrode was further investigated since Ni/Co-3500 electrode delivers superior performance. The CV curve of Ni/Co-3500 electrode performed at different scan rates, as illustrated in Fig. 6c, the weak symmetrical redox peaks with the increase of scan rate indicating that the good rate capability. In addition, the CV curves of Ni/Co-3500 electrode shows feeble distortion due to the electrode polarization generated during the charge–discharge process, which is common in pseudocapacitive materials, especially at high loading. The CV curves of other as-prepared electrodes at different scan rates are displayed in Fig. S7, which is similar with the Ni/Co-3500 electrode. Fig. 6d shows the GCD curves of Ni/Co-3500 electrode at different current densities from 5 to 50 mA cm⁻² within the potential range of 0–0.5 V. The GCD curves of the Ni/Co-3500 electrode at different current densities showed a quasi-triangular shape with slight plateaus, which is caused by the redox reaction at the electrode electrolyte interface. The GCD curves of other as-prepared electrodes at various current densities are displayed in Fig. S8. The areal specific capacitance and mass special capacitance were calculated using Eq. (1) and Eq. (2), and plotted in

Fig. 6e. Apparently, the areal capacitance of Ni/Co-3500 electrode is higher than that of other electrodes. The areal specific capacitance of Ni/Co-3500 electrode is calculated to be 8.87, 8.36, 8.06, 7.76, 7.45, 7.21, 6.70 and 6.15 F·cm⁻² at the current densities of 5, 10, 15, 20, 25, 30, 40 and 50 mA·cm⁻², respectively. Furthermore, the capacitance retention of Ni/Co-3500 electrode is up to 69.3% at 50 mA cm⁻², demonstrating good rate capability. The corresponding mass specific capacitance are 990, 933, 900, 866, 831, 804, 748 and 686 F g⁻¹ at mass loading of 9.0 mg cm⁻², respectively. To demonstrate the superiority of the low crystallinity Ni/Co-3500 electrode, we compare the areal and mass special capacitances Ni/Co-3500 electrode with other free-standing electrodes, and the detailed information of the electrochemical performance compared with other electrodes were listed in Table 1. Encouragingly, the Ni/Co-3500 electrode delivered a higher capacitance than various Ni/Co hydroxides grown on the conductive substrate published recently in literature, and most noteworthy is the high mass loading (~9 mg cm⁻²) of the Ni/Co-3500 electrode, which is very important for commercial applications. Long-term cyclic stability is another important factor for supercapacitor, and the electrochemical stability of Ni/Co-3500 electrode material was evaluated by repeating the charging/discharging test at current density of 20 mA cm⁻² (Fig. 6f). The Ni/Co-3500 electrode also displays excellent long-term stability with a high capacitance retention of 91.59% after 2000 cycles, and the CV curves of Ni/Co-3500 electrode before and 2000 cycles (inset of Fig. 6f) further confirm the excellent stability.

To study its potential as a flexible capacitor electrode, the electrochemical performance of a bending Ni/Co-3500 electrode was estimated in a three-electrode battery system with 6 M KOH as the electrolyte. Fig. S9a and Figure S9b shows the photo image of upright and bending Ni/Co-3500 nanoarrays electrodes, respectively. During electrochemical tests, no surface cracks or damage were observed on the sample surface, suggesting that the electrodes have good flexibility. the electrochemical performance of a bending Ni/Co-3500 electrode. Fig. S9c shows the GCD curves (inset) measured at a current density of 20 mA cm⁻². The calculated specific capacitance of Ni/Co-3500 electrode under bending condition is almost equal to that of the upright. In addition, the CV curves

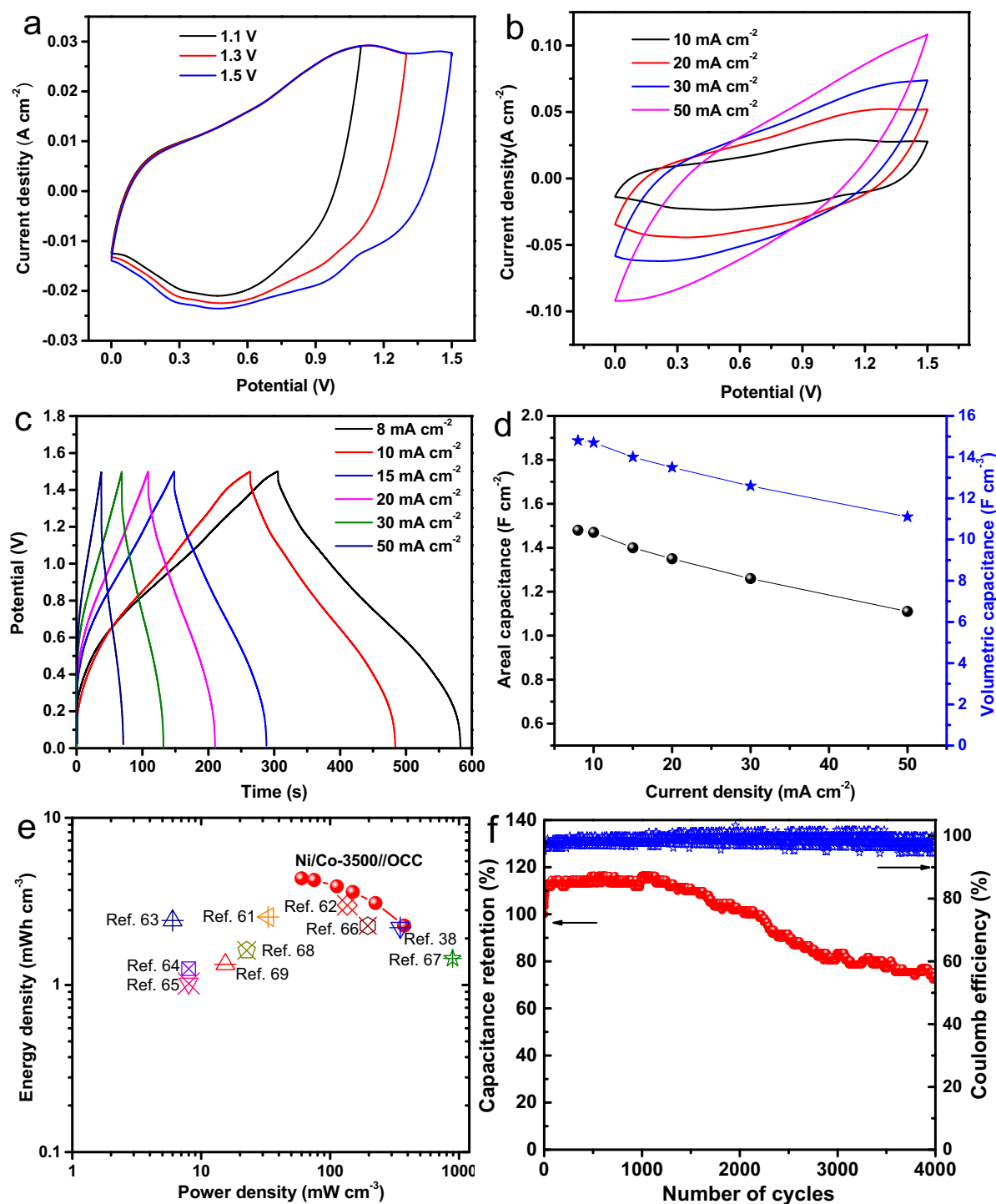


Fig. 7. a) CV curves of Ni/Co-3500//OCC ACSs at the scan rate of 10 mV s⁻¹ with the potential window of 1.1, 1.3 and 1.5 V; b) a) CV curves of Ni/Co-3500//OCC ACSs at different scan rates; c) GCD curves of Ni/Co-3500//OCC ACSs at different current densities; d) the specific capacitance of Ni/Co-3500//OCC ACSs at different current densities; e) Ragone plot of the Ni/Co-3500//OCC ACSs; f) cycle performance of Ni/Co-3500//OCC ACSs collected at 20 mA cm⁻² for 4000 cycles.

(inset of Figure S9c) of upright and bending Ni/Co-oxyhydroxides nanoarrays electrodes at a scan rate of 5 mV s⁻¹ indicate no obvious change between an upright electrode and a bending electrode, indicating that the bending did not to affect the Faraday redox reaction on the surface of Ni/Co-3500 nanoarrays. The above results confirmed the excellent flexibility of the Ni/Co-3500 nanoarrays electrodes.

The extraordinary performance of Ni/Co-oxyhydroxides nanoarrays with high mass loading is ascribed to the synergistic combi-

nation of the low crystallinity with abundant defects, the binary metal ions of Ni and Co, and hierarchical structure design. Firstly, the low-crystallinity nature of the Ni/Co-oxyhydroxides nanoarrays contribute to the superior electrochemical performance. It is reported that low-crystalline or amorphous materials had the potential to exhibit excellent electrochemical performance because of its abundant defects [52,59]. Secondly, the mutual doping of Ni and Co atoms can effectively improve capacitive performance, which has been reported in previous literature [53,60]. Thirdly, the

hierarchical structure design is an important key for remarkable capacitance. On one hand, the hierarchical structure composed with nanoflakes interconnected with nanoneedle arrays results in good electrical contact between the active material and the electrode, enable almost all the active material to participate in the electrochemical reactions, which is indispensable for good electrochemical performance. The EIS spectra (Fig. S10a) of as-prepared arrays electrodes exhibit one quasi-semicircle in high frequency region and a linear part in low frequency region. In the high frequency region (Fig. S10b), the intersection of the curve at the real axis Z' corresponds to the bulk resistance (R_s) of electrode electrochemical system, and the fitted R_s was listed in Table S1. All the bulk resistances of as-prepared hierarchical arrays electrodes were lower than $1\ \Omega$. In addition, the diameter of semicircle represents the charge-transfer resistance (R_{ct}) of the electrodes and electrolyte interface, obviously, the R_{ct} of Ni/Co-3500 is lowest in all as-prepared hierarchical arrays electrodes (Table S1). In the low frequencies (Fig. S10a), the higher slope indicates that the diffusion resistances of all electrodes are small. On the other hand, the multiple connection points in hierarchical structure create a highway for fast diffusion of electrolyte ions and the transfer of electrons. At the same time, compared with single arrays structure, the hierarchical structure in this work will not only be propitious to the adequate utilization of active material, but also provide additional active sites for electrochemical reaction. Furthermore, vertically nanoflakes offered robust support for nanoneedle, which can restrain the crumble of nanoneedle and maintained the open space among the hierarchical structure, thereby affording many pores/channels and surface-active sites to enhance the electrochemical performance.

3.2. Electrochemical properties of supercapacitor

To further evaluate the application potential of Ni/Co-3500 electrode, the asymmetrical supercapacitors were assembled using Ni/Co-3500 as cathode, oxidized CC (OCC) as anode, 6 M KOH as electrolyte and filter paper as separator. The detail synthesis process of OCC was described in the Section S1 (Supplementary Materials). Figure S11 shows the electrochemical properties of OCC. In addition of the quasi-rectangle feature of carbon materials, it can be observed a pair of redox peaks in the CV curves (Fig. S11a), which is attributed to the oxygen-containing groups on the surface of OCC. Fig. S11b displays the GCD curves of OCC, a pair of voltage platform also can be seen, and the areal capacitance of OCC calculated from the discharge curves was 4.49, 3.92, 3.56 and $3.34\ \text{F cm}^{-2}$ at the current densities of 5, 10, 15, $20\ \text{mA cm}^{-2}$, respectively. According to the specific capacitance of Ni/Co-3500 electrode and OCC, the area ratio between them is about 1:1. Fig. 7a demonstrates the CV curves of Ni/Co-3500//OCC asymmetrical supercapacitors (ASCs) in different potential windows, which indicate a stable potential window up to 1.5 V and a typical capacitive behavior for the assembled Ni/Co-3500//OCC ASCs. As shown in Fig. 7b, it is no obviously deformation in the CV curves of Ni/Co-3500//OCC ASCs with the increased scan rate from 10 to $50\ \text{mV s}^{-1}$, suggesting the good capacitance behavior of assembled ASCs. In addition, the GCD curves shown in Fig. 7c further confirm the capacitance properties of Ni/Co-3500//OCC ASCs. According to the discharge curves, the specific capacitances of Ni/Co-3500//OCC ASCs were calculated and the results are shown in Fig. 7d. Under the current density of $8\ \text{mA cm}^{-2}$, the areal capacitance and volumetric capacitance of Ni/Co-3500//OCC ASCs was $1.48\ \text{F cm}^{-2}$ and $14.8\ \text{F cm}^{-3}$, respectively. When the current density was increased to $50\ \text{mA cm}^{-2}$, the areal capacitance and volumetric capacitance of Ni/Co-3500//OCC ASCs remained $1.11\ \text{F cm}^{-2}$ and $11.1\ \text{F cm}^{-3}$, the capacitance retention was 75%. It indicated that the Ni/Co-3500//OCC ASCs exhibited high specific capacitance. The

calculated power density and energy density is listed in Fig. 7e. It can be observed that the energy density of Ni/Co-3500//OCC ASCs was $4.35\ \text{mWh cm}^{-3}$ with the power density of $60.1\ \text{mW cm}^{-3}$, and retained $2.26\ \text{mWh cm}^{-3}$ at the power density of $376\ \text{mW cm}^{-3}$, which was superior than the reported ASCs, such as $\text{ZnCo}_2\text{O}_4@\text{NiMoO}_4\cdot\text{H}_2\text{O}/\text{CNT}$ [61], $\text{Co}_3\text{O}_4/\text{NiCo}_2\text{O}_4/\text{CC}$ [62], Zn-Ni-Co TOH-130//FEG [63], NiCo-LDHs//NiCo-LDHs [64], Ni@NiO//rGO [65], $\text{NiCo}_2\text{S}_4@\text{Fe}_2\text{O}_3/\text{MnO}_2$ [66], Ni-Co hydroxide//AC [38], $\text{Co}_9\text{S}_8/\text{Co}_3\text{O}_4@\text{RuO}_2$ [67], MXene@ $\text{Fe}_2\text{O}_3/\text{MnO}_2$ [68], $\text{CN-Fe}_2\text{O}_3/\text{MnO}_2$ [69], etc. Finally, the cycling stability of Ni/Co-3500//OCC ASCs was assessed by the GCD method at the current density of $20\ \text{mA cm}^{-2}$ and shown in Fig. 7f. In the initial stage of the cycle, the capacitance retention of Ni/Co-3500//OCC ASCs was increased to about 110% and stable until 1500 cycles. After that, the capacitance retention of Ni/Co-3500//OCC ASCs was gradually decreased to 73.8% after 4000 cycles. The coulomb efficiency of Ni/Co-3500//OCC ASCs was nearly 100%.

4. Conclusion

In this work, a simple CV cycle approach was used to prepared low-crystallinity Ni/Co-oxyhydroxides nanoarrays with a high loading of $\sim 9\ \text{mg cm}^{-2}$ on flexible CC. The characterizations showed that the low-crystallinity Ni/Co-oxyhydroxides nanoarrays were derived from the phase transfer of Ni-hydroxide and Co-hydroxycarbonate by electrochemical reconstruction in KOH. The low-crystallinity Ni/Co-oxyhydroxides nanoarrays possessed advantages including the abundant defects, the mutual doping of Ni and Co atoms and the hierarchical structure, which rendered an excellent electrochemical performance to the Ni/Co-oxyhydroxides nanoarrays. Furthermore, the number of CV cycles can obviously influence the morphology, structure and electrochemical performance of Ni/Co-oxyhydroxides nanoarrays. The electrochemical reconstructed Ni/Co-3500 electrode showed the best electrochemical performance with a high area capacitance of $8.87\ \text{F cm}^{-2}$ at $5\ \text{mA cm}^{-2}$, an excellent rate performance at high current density (the capacitance retention rate was 69.33% when the current density increased from $5\ \text{mA}$ to $50\ \text{mA cm}^{-2}$) and an high cyclic stability (capacitance retention of 91.5% after 2000 cycles at $20\ \text{mA cm}^{-1}$). The assemble Ni/Co-3500//OCC ASCs delivered an energy density of $4.35\ \text{mWh cm}^{-3}$ at the power density of $60.1\ \text{mW cm}^{-3}$ and maintained $2.26\ \text{mWh cm}^{-3}$ at the power density of $376\ \text{mW cm}^{-3}$. These results indicate that the electrochemical reconstruction method can open the application of low-crystallinity transition metal oxyhydroxides in high performance supercapacitors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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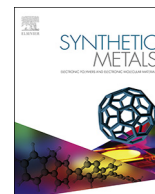
Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2020.136886.

References

- [1] T. Lin, W. Chen, F. Liu, C. Yang, H. Bi, F. Xu, F. Huang, Nitrogen-doped mesoporous carbon of extraordinary capacitance for electrochemical energy storage, *Science* 350 (2015) 1508–1513.
- [2] G. Wang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical supercapacitors, *Chem. Soc. Rev.* 41 (2012) 797–828.
- [3] M. Salanne, B. Rotenberg, K. Naoi, K. Kaneko, P.L. Taberna, C.P. Grey, B. Dunn, P. Simon, Efficient storage mechanisms for building better supercapacitors, *Nat. Energy* 1 (2016) 10.
- [4] H. Chen, Y. Ai, L. Fan, C. Xing, X. Yuan, H. Qi, W. Chi, H. Lin, H. Sheng, Carbon-coated hierarchical Ni-Mn layered double hydroxide nanoarrays on Ni foam for flexible high-capacitance supercapacitors, *Electrochim. Acta* 213 (2016) 55–65.
- [5] Z. Lu, Y. Chao, Y. Ge, J. Foroughi, Y. Zhao, C. Wang, H. Long, W. GG, High-performance hybrid carbon nanotube fibers for wearable energy storage, *Nanoscale* 9 (2017) 5063–5071.
- [6] M. Ni, Z. Huang, X. Zhang, J. Liu, L. Qiao, W. Yang, Hierarchical design of nitrogen-doped porous carbon nanorods for use in high efficiency capacitive energy storage, *RSC Adv.* 7 (2017) 22447–22453.
- [7] X. Wang, Y. Zhang, C. Zhi, X. Wang, D. Tang, Y. Xu, Q. Weng, X. Jiang, M. Mitome, D. Golberg, Y. Bando, Three-dimensional strutted graphene grown by substrate-free sugar blowing for high-power-density supercapacitors, *Nat. Comm.* 4 (2013) 2905.
- [8] L. Niu, Z. Li, W. Hong, J. Sun, Z. Wang, L. Ma, J. Wang, S. Yang, Pyrolytic synthesis of boron-doped graphene and its application as electrode material for supercapacitors, *Electrochim. Acta* 108 (2013) 666–673.
- [9] Q. Hao, X. Xia, W. Lei, W. Wang, J. Qiu, Facile synthesis of sandwich-like polyaniline/boron-doped graphene nano hybrid for supercapacitors, *Carbon N Y* 81 (2015) 552–563.
- [10] D.L. Ji, J.H. Li, L.M. Chen, D. Zhang, T. Liu, N. Zhang, R.Z. Ma, G.Z. Qiu, X.H. Liu, Needle-like CoO nanowires growing on carbon cloth for enhanced electrochemical properties in supercapacitors, *RSC Adv.* 5 (2015) 41627–41630.
- [11] M.S. Javed, J. Chen, L. Chen, Y. Xi, C. Zhang, B. Wan, C. Hu, Flexible full-solid state supercapacitors based on zinc sulfide spheres growing on carbon textile with superior charge storage, *J. Mater. Chem. A* 4 (2016) 667–674.
- [12] W.W. Li, F.X. Gao, X.Q. Wang, N. Zhang, M.M. Ma, Strong and robust polyaniline-based supramolecular hydrogels for flexible supercapacitors, *Angew. Chem. Int. Ed.* 55 (2016) 9196–9201.
- [13] L.L. Zhang, X.S. Zhao, Carbon-based materials as supercapacitor electrodes, *Chem. Soc. Rev.* 38 (2009) 2520.
- [14] Hao Jiang, P. See Lee, Chunzhong Li, 3D carbon based nanostructures for advanced supercapacitors, *Energy Environ. Sci.* 6 (2012) 41–53.
- [15] Q. Lu, J.G. Chen, J.Q. Xiao, Nanostructured electrodes for high-performance pseudocapacitors, *Angew. Chem. Int. Ed.* 52 (2013) 1882–1889.
- [16] V. Augustyn, P. Simon, B. Dunn, Pseudocapacitive oxide materials for high-rate electrochemical energy storage, *Energy Environ. Sci.* 7 (2014) 1597.
- [17] V. Augustyn, J. Come, M.A. Lowe, J.W. Kim, P.-L. Taberna, S.H. Tolbert, H.D. Abruna, P. Simon, B. Dunn, High-rate electrochemical energy storage through Li^+ intercalation pseudocapacitance, *Nat. Mater.* 12 (2013) 518–522.
- [18] R.S. Kate, S.A. Khalate, R.J. Deokate, Overview of nanostructured metal oxides and pure nickel oxide (NiO) electrodes for supercapacitors: a review, *J. Alloy. Compd.* 734 (2018) 89–111.
- [19] R.R. Salunkhe, Y.V. Kaneti, Y. Yamauchi, Metal-organic framework-derived nanoporous metal oxides toward supercapacitor applications: progress and prospects, *ACS Nano* (2017) 5293–5308.
- [20] L. Zhang, D. Shi, T. Liu, M. Jaroniec, J. Yu, Nickel-based materials for supercapacitors, *Mater. Today* 25 (2019) 35–65.
- [21] L. Li, X. Liu, C. Liu, H. Wan, J. Zhang, P. Liang, H. Wang, H. Wang, Ultra-long life nickel nanowires@nickel-cobalt hydroxide nanoarrays composite pseudocapacitive electrode: construction and activation mechanism, *Electrochim. Acta* 259 (2018) 303–312.
- [22] Y. Liu, N.Q. Fu, G.G. Zhang, M. Xu, W. Lu, L.M. Zhou, H.T. Huang, Design of hierarchical Ni-Co@Ni-Co layered double hydroxide core-shell structured nanotube array for high-performance flexible all-solid-state battery-type supercapacitors, *Adv. Funct. Mater.* 27 (2017) 1605307.
- [23] J. Yang, C. Yu, C. Hu, M. Wang, S.F. Li, H.W. Huang, K. Bustillo, X.T. Han, C.T. Zhao, W. Guo, Z.Y. Zeng, H.M. Zheng, J.S. Qiu, Surface-confined fabrication of ultrathin nickel cobalt-layered double hydroxide nanosheets for high-performance supercapacitors, *Adv. Funct. Mater.* 28 (2018) 1803272.
- [24] H.B. Li, M.H. Yu, F.X. Wang, P. Liu, Y. Liang, J. Xiao, C.X. Wang, Y.X. Tong, G.W. Yang, Amorphous nickel hydroxide nanospheres with ultrahigh capacitance and energy density as electrochemical pseudocapacitor materials, *Nat. Comm.* 4 (2013) 1894.
- [25] H.B. Li, M.H. Yu, X.H. Lu, P. Liu, Y. Liang, J. Xiao, Y.X. Tong, G.W. Yang, Amorphous cobalt hydroxide with superior pseudocapacitive performance, *ACS Appl. Mater. Inter.* (2014) 745–749.
- [26] W.C. Jiang, D.S. Yu, Q. Zhang, K.L. Goh, L. Wei, Y.L. Yong, R.R. Jiang, J. Wei, Y. Chen, Ternary hybrids of amorphous nickel hydroxide-carbon nanotube-conducting polymer for supercapacitors with high energy density, excellent rate capability, and long cycle life, *Adv. Funct. Mater.* 25 (2015) 1063–1073.
- [27] K. Xu, R. Zou, W. Li, Q. Liu, X. Liu, L. An, J. Hu, Design and synthesis of 3D interconnected mesoporous $\text{NiCo}_2\text{O}_4/\text{CoNi}_x(\text{OH})_2$ core-shell nanosheet arrays with large areal capacitance and high rate performance for supercapacitors, *J. Mater. Chem. A* 2 (2014) 10090–10097.
- [28] Y. Guo, X. Hong, Y. Wang, Q. Li, J. Meng, R. Dai, X. Liu, L. He, L. Mai, Multicomponent hierarchical Cu-doped NiCo-LDH/CuO double arrays for ultralong-life hybrid fiber supercapacitor, *Adv. Funct. Mater.* 29 (2019) 1809004.
- [29] K. Tao, P. Li, L. Kang, X. Li, Q. Zhou, L. Dong, W. Liang, Facile and low-cost combustion-synthesized amorphous mesoporous NiO/carbon as high mass-loading pseudocapacitor materials, *J. Power Sources* 293 (2015) 23–32.
- [30] M. Shi, M. Cui, L. Kang, T. Li, S. Yun, J. Du, S. Xu, Y. Liu, Porous $\text{Ni}(\text{NO}_3)_2(\text{OH})_4$ nano-sheets for supercapacitors: facile synthesis and excellent rate performance at high mass loadings, *Appl. Surf. Sci.* 427 (2018) 678–686.
- [31] Z.H. Huang, Y. Song, D.Y. Feng, Z. Sun, X. Sun, X.X. Liu, High mass loading MnO_2 with hierarchical nanostructures for supercapacitors, *ACS Nano* 12 (2018) 3557–3567.
- [32] J.A. Syed, J. Ma, B.G. Zhu, S.C. Tang, X.K. Meng, Hierarchical multicomponent electrode with intercalated $\text{Ni}(\text{OH})_2$ nanoflakes wrapped zinc cobalt sulfide nanotube arrays for sustainable high-performance supercapacitors, *Adv. Energy Mater.* 7 (2017) 1701228.
- [33] D. Chen, S. Zhou, H. Quan, R. Zou, W. Gao, X. Luo, L. Guo, Tetra-sub-like $\alpha\text{-Fe}_2\text{O}_3/\text{C}$ nanoarrays on carbon cloth as negative electrode for high-performance asymmetric supercapacitors, *Chem. Eng. J.* 341 (2018) 102–111.
- [34] S. Zhou, K. Chen, H. Quan, M. Su, Z. Zeng, M. Pan, D. Chen, L. Guo, Molten- NaNH_2 activated carbon cloth with high areal capacitance and exceptional rate stability for flexible asymmetric supercapacitors, *J. Mater. Sci.* 54 (2019) 9111–9123.
- [35] D. Guo, Y.Z. Luo, X.Z. Yu, Q.H. Li, T.H. Wang, High performance NiMoO_4 nanowires supported on carbon cloth as advanced electrodes for symmetric supercapacitors, *Nano Energy* 8 (2014) 174–182.
- [36] H. Liang, J. Lin, H. Jia, S. Chen, J. Qi, J. Cao, T. Lin, W. Fei, J. Feng, Hierarchical NiCo-LDH@NiOOH core-shell heterostructure on carbon fiber cloth as battery-like electrode for supercapacitor, *J. Power Sources* 378 (2018) 248–254.
- [37] X. Zheng, H. Quan, X. Li, H. He, Q. Ye, X. Xu, F. Wang, In situ fabrication of Ni-Co (oxy)hydroxide nanowire-supported nanoflake arrays and their application in supercapacitors, *Nanoscale* 8 (2016) 17055–17063.
- [38] X.C. Shao, X.Y. Zheng, W.R. Zou, Y.L. Luo, Q.C. Cen, Q.L. Ye, X.T. Xu, F. Wang, Alkali conversion of Ni-Co nanoarrays on carbon cloth for a high-capacity supercapacitor electrode, *Electrochim. Acta* 248 (2017) 322–332.
- [39] A.N. Mansour, C.A. Melendres, Characterization of slightly hydrated $\text{Ni}(\text{OH})_2$ by XPS, *Surf. Sci. Spectra* 3 (1994) 247–254.
- [40] H. Chen, J. Jiang, L. Zhang, Y. Zhao, D. Guo, Y. Ruan, D. Xia, One-pot fabrication of layered α -phase nickel-cobalt hydroxides as advanced electrode materials for pseudocapacitors, *Chempluschem* 80 (2015) 181–187.
- [41] M. Oku, Y. Sato, In-situ X-ray photoelectron spectroscopic study of the reversible phase transition between CoO and Co_3O_4 in oxygen of 10^{-3} Pa, *Appl. Surf. Sci.* 55 (1992) 37–41.
- [42] Z. Hu, Luolu Wang, Y. Luo, Q. Wei, M. Yan, L. Zhou, L. Mai, Vanadium-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with decreased lithium/nickel disorder as high-rate and long-life lithium ion battery cathode, *Sci. Adv.* 1 (2015) 25218.
- [43] N. McIntyre, M. Cook, X-Ray Photoelectron studies on some oxides and hydroxides of cobalt, nickel, and copper, *Anal. Chem.* 47 (1975) 2208–2213.
- [44] B.J. Tufts, S.R. Lunt, G.M. Miskelly, M.J. Sailor, K.O. Hodgson, J. Tufts, B. R. Lunt, S. M. Miskelly, et al., XPS and EXAFS studies of the reactions of Co(III) ammine complexes with GaAs surfaces, *J. Am. Chem. Soc.* 112 (1990) 5123–5136.
- [45] H. Xu, J. Wu, J. Liu, Y. Chen, X. Fan, Growth of cobalt-nickel layered double hydroxide on nitrogen-doped graphene by simple co-precipitation method for supercapacitor electrodes, *J. Mater. Sci.: Mater. El.* 29 (2018) 17234–17244.
- [46] W. Guo, C. Yu, S. Li, X. Song, H. Huang, X. Han, Z. Wang, Z. Liu, J. Yu, X. Tan, J. Qiu, A Universal converse voltage process for triggering transition metal hybrids in situ phase reconstruction toward ultrahigh-rate supercapacitors, *Adv. Mater.* 31 (2019) e1901241.
- [47] C. Drouilly, J.-M. Krafft, F. Averseng, S. Casale, D. Bazer-Bachi, C. Chizallet, V. Lecocq, H. Vezin, H. Lauron-Pernot, G. Costentin, ZnO Oxygen Vacancies Formation and Filling Followed by in Situ Photoluminescence and in Situ EPR, *J. Phys. Chem. C* 116 (2012) 21297–21307.
- [48] H. Zhang, X. Deng, H. Huang, G. Li, X. Liang, W. Zhou, J. Guo, W. Wei, S. Tang, Hetero-structure arrays of NiCoO_2 nanoflakes@nanowires on 3D graphene/nickel foam for high-performance supercapacitors, *Electrochim. Acta* 289 (2018) 193–203.
- [49] J. Liang, K. Xi, G. Tan, S. Chen, T. Zhao, P.R. Coxon, H.-K. Kim, S. Ding, Y. Yang, R.V. Kumar, Sea urchin-like NiCoO_2/C nanocomposites for Li-ion batteries and supercapacitors, *Nano Energy* 27 (2016) 457–465.
- [50] G. Nagaraju, G.S.R. Raju, Y.H. Ko, J.S. Yu, Hierarchical Ni-Co layered double hydroxide nanosheets entrapped on conductive textile fibers: a cost-effective and flexible electrode for high-performance pseudocapacitors, *Nanoscale* 8 (2016) 812–825.
- [51] L. Gao, K. Cao, H. Zhang, P. Li, J. Song, J.U. Surjadi, Y. Li, D. Sun, Y. Lu, Rationally designed nickel oxide ravin@iron cobalt-hydroxides with largely enhanced capacitive performance for asymmetric supercapacitors, *J. Mater. Chem. A* 5 (2017) 16944–16952.
- [52] C. Huang, X. Song, Y. Qin, B. Xu, H.C. Chen, Cation exchange reaction derived amorphous bimetal hydroxides as advanced battery materials for hybrid supercapacitors, *J. Mater. Chem. A* 6 (2018) 21047–21055.
- [53] D. Wang, A. Wei, L. Tian, A. Mensah, D. Li, Y. Xu, Q. Wei, Nickel-cobalt layered double hydroxide nanosheets with reduced graphene oxide grown on carbon cloth for symmetric supercapacitor, *Appl. Surf. Sci.* 483 (2019) 593–600.
- [54] X. Liu, Y. Yang, X.X. Xing, T. Zou, Z.D. Wang, Y.D. Wang, From water and Ni foam to a $\text{Ni}(\text{OH})_2/\text{Ni}$ foam binder-free supercapacitor electrode: a green corrosion route, *ChemElectroChem* 5 (2018) 434–444.

- [55] L. Zhi, W. Zhang, L. Dang, J. Sun, F. Shi, H. Xu, Z. Liu, Z. Lei, Holey nickel-cobalt layered double hydroxide thin sheets with ultrahigh areal capacitance, *J. Power Sources* 387 (2018) 108–116.
- [56] D.S. Patil, S.A. Pawar, J.C. Shin, H.J. Kim, Layered double hydroxide based on ZnCo@NiCo- nano-architecture on 3D graphene scaffold as an efficient pseudocapacitor, *J. Power Sources* 435 (2019) 226812.
- [57] Y.-F. Wang, H.-T. Wang, S.-Y. Yang, Y. Yue, S.-W. Bian, Hierarchical NiCo₂S₄@nickel-cobalt layered double hydroxide nanotube arrays on metallic cotton yarns for flexible supercapacitors, *ACS Appl. Mater. Inter.* 11 (2019) 30384–30390.
- [58] J.H. Li, Z.C. Liu, Q.B. Zhang, Y. Cheng, B.T. Zhao, S.G. Dai, H.H. Wu, K.L. Zhang, D. Ding, Y.P. Wu, M.L. Liu, M.S. Wang, Anion and cation substitution in transition-metal oxides nanosheets for high-performance hybrid supercapacitors, *Nano Energy* 57 (2019) 22–33.
- [59] H.C. Chen, Y. Qin, H. Cao, X. Song, C. Huang, H. Feng, X.S. Zhao, Synthesis of amorphous nickel-cobalt-manganese hydroxides for supercapacitor-battery hybrid energy storage system, *Energy Storage Mater.* 17 (2019) 194–203.
- [60] Z. Wei, J. Yuan, S. Tang, D. Wu, L. Wu, Porous nanorods of nickel-cobalt double hydroxide prepared by electrochemical co-deposition for high-performance supercapacitors, *J. Colloid Interface Sci.* 542 (2019) 15–22.
- [61] C. Chen, S. Wang, X. Luo, W. Gao, G. Huang, Y. Zeng, Z. Zhu, Reduced ZnCo₂O₄@NiMoO₄·H₂O heterostructure electrodes with modulating oxygen vacancies for enhanced aqueous asymmetric supercapacitors, *J. Power Sources* 409 (2019) 112–122.
- [62] J.X. Hao, S.L. Peng, T.F. Qin, Z.L. Wang, Y.X. Wen, D.Y. He, J.C. Zhang, Z.Y. Zhang, X.Y. Fan, G.Z. Cao, Fabrication of hybrid Co₃O₄/NiCo₂O₄ nanosheets sandwiched by nanoneedles for high-performance supercapacitors using a novel electrochemical ion exchange, *Sci. China-Mater.* 60 (2017) 1168–1178.
- [63] Z.H. Huang, F.F. Sun, M. Batmunkh, W.H. Li, H. Li, Y. Sun, Q. Zhao, X. Liu, T.Y. Ma, Zinc-nickel-cobalt ternary hydroxide nanoarrays for high-performance supercapacitors, *J. Mater. Chem. A* 7 (2019) 11826–11835.
- [64] Y.-M. Jeong, I. Son, S.-H. Baek, Binder-free of NiCo-layered double hydroxides on Ni-coated textile for wearable and flexible supercapacitors, *Appl. Surf. Sci.* 467–468 (2019) 963–967.
- [65] M. Yu, W. Wang, C. Li, T. Zhai, X. Lu, Y. Tong, Scalable self-growth of Ni@NiO core-shell electrode with ultrahigh capacitance and super-long cyclic stability for supercapacitors, *NPG Asia Mater.* 6 (2014) e129.
- [66] R.Y. Jia, F. Zhu, S. Sun, T. Zhai, H. Xia, Dual support ensuring high-energy supercapacitors via high-performance NiCoS@FeO anode and working potential enlarged MnO cathode, *J. Power Sources* 341 (2017) 427–434.
- [67] J. Xu, Q.F. Wang, X.W. Wang, Q.Y. Xiang, B. Hang, D. Chen, G.Z. Shen, Flexible asymmetric supercapacitors based upon Co₉S₈ nanorod//Co₃O₄@RuO₂ nanosheet arrays on carbon cloth, *ACS Nano* 7 (2013) 5453–5462.
- [68] F. Li, Y.-L. Liu, G.-G. Wang, H.-Y. Zhang, B. Zhang, G.-Z. Li, Z.-P. Wu, L.-Y. Dang, J.-C. Han, Few-layered Ti₃C₂T_x MXenes coupled with Fe₂O₃ nanorod arrays grown on carbon cloth as anodes for flexible asymmetric supercapacitors, *J. Mater. Chem. A* 7 (2019) 22631–22641.
- [69] F.F. Han, J. Xu, J. Zhou, J. Tang, W.H. Tang, Oxygen vacancy-engineered Fe₂O₃ nanoarrays as free-standing electrodes for flexible asymmetric supercapacitors, *Nanoscale* 11 (2019) 12477–12483.



Optimizing F content of donor units by ternary copolymerization for effective heterojunction solar cells

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ABSTRACT

F-benzothiadiazole derivatives as acceptor monomers, and different ratios of [5, 5'-bis(trimethyltin)-2, 2'-bithiophene], [3, 4'-difluoro-5, 5'-bis(trimethyltin)-2, 2'-bithiophene] as donor units, five polymers were synthesized by random copolymerization. UV-vis absorption, Cyclic voltammetry, Thermogravimetric Analysis (TGA), Gel Permeation Chromatography (GPC) were used to characterize these five polymers, which display excellent absorption and thermal stability. Through the device test, it was successfully verified that the simultaneous introduction of F at donor unit and acceptor unit is an effective method to improve device efficiency. Simultaneously, it was also found that the photophysical properties of **P2** (the F on D unit accounted for 21% of the entire molecule F) have greatly been improved. Finally, the **P2** shows 5.57% conversion efficiency.

1. Introduction

The design of low-bandgap materials mainly involves the effective regulation of energy levels, which can effectively broaden the absorption spectrum range, and in turn promotes efficient charge transfer. Reducing Highest Occupied Molecular Orbital (HOMO) energy level of the donor material can improve the open circuit voltage of devices [1–5]. Achieving high performance polymer solar cells are tightly linked to effective migration of Lowest Unoccupied Molecular Orbital (LUMO) between donor and acceptor [6–12].

Among a variety of donor-acceptor (D-A) polymers, polymers with fluorinated structural units have recently attracted great attention because fluorinated units can effectively modulate the energy levels of the front-line orbits and optimize the morphology of the active layer. Thus, open circuit voltages and short-circuit of devices get enhanced [13–15]. Through over ten years of development, its power conversion efficiency has exceeded 10% [16]. However, the study of the fluorination in the polymer is mainly concentrated on the A unit, ignoring the effect of fluorination of D unit on photovoltaic performance.

The random 1D-2A and 2D-1A terpolymers include one D and two A units (or two D and one A unit) that can combine the advantages of 1D-1A polymer, effectively adjusted the absorption range of the material, regulate the molecular orbital level, and increase the charge-carrier mobility. It is a commonly means to achieve highly efficient organic solar cells [17–20]. Among them, it is rare to use ternary

copolymerization (2D, 1A) to study the effect of the F content of the D unit on the photovoltaic performance of the polymer.

In 2014, Jea [21] used binary copolymerization to find that the introduction of F on donor (bithiophene derivative) units can improve the efficiency of devices by introducing F atoms on (benzothiadiazole derivative) monomers. In 2015, the research group used the same molecular skeleton as a research object found that the simultaneous introduction of F on the D and A monomers can effectively improve the conversion efficiency of the device more than the introduction of F on the D unit alone.

On this basis, we directly use F-benzothiadiazole derivatives as acceptor units, **D1** [5,5'-bis(trimethyltin)-2,2'-bithiophene] and **D2** [3, 4'-difluoro-5, 5'-bis(trimethyltin)-2,2'-bithiophene] as a donor unit. Polymer **P1** (**D1:D2** = 1:0), **P2** (**D1:D2** = 3:7), **P3** (**D1:D2** = 5:5), **P4** (**D1:D2** = 7:3), **P5** (**D1:D2** = 0:1) were synthesized by a terpolymerization method and adjusting the ratio of **D1** and **D2** to verify that the introduction of F on both D and A is an effective way to improve the efficiency of the device. On this basis it is desirable to find the proper F content of D monomers to improve the power conversion efficiency of the device.

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Table 1
Molecular weights and thermal properties of different random polymers.

Polymers	$M_n(\text{kg mol}^{-1})$	$M_w(\text{kg mol}^{-1})$	PDI	$T_d(^{\circ}\text{C})$
P1	9.08	11.45	1.26	308
P2	12.88	16.63	1.30	395
P3	10.98	13.56	1.23	311
P4	9.53	12.38	1.30	350
P5	9.32	11.81	1.26	335

2. Results and discussion

2.1. Synthesis and characterization

These random copolymers show good solubility in organic solvents at room temperature. The weight-average molecular weight (M_w) and the polydispersity index ($PDI = M_w/M_n$) were measured by a gel permeation chromatography (GPC) technique using THF as the eluent and polystyrenes as the internal standards. As shown in Table 1, all polymers have a large molecular weight, around 10 kg mol^{-1} , and their polydispersity index are around 1.2. Among them, P2 has the largest molecular weight and the widest molecular weight distribution, which gives a M_n of $12.88 \text{ kg mol}^{-1}$ and a PDI of 1.3. Moreover, the resulting polymers exhibit excellent stability with the decomposition onset temperatures (T_d) (about 5% weight loss) 308 C, 395 C, 311 C, 350 C, 365 C and 335 C for P1–P5, respectively as determined by thermogravimetric analysis (TGA) in Fig. 1 and shown in Table 1. Such good thermal properties are adequate for photovoltaic and other optoelectronic devices.

2.2. Absorption spectra of random copolymers

In order to study the optical properties of the random polymer P1–P5, the UV–vis absorption spectrum was applied to investigate the spectral response range and optical band gap of the solution and film. From Fig. 2a, it can be seen that the absorption range of the polymer in the solution is approximately the same. In addition to P4, other four polymers have four characteristic peaks in the UV–vis region. In the film, the polymer shows the same phenomenon with varying degrees of red-shift. Among them, the P2 shows the largest red-shift and P5 shows the smallest red-shift. The specific data for the five polymers absorption peaks are summarized in Table 2. The absorption of P1 and P5 in the

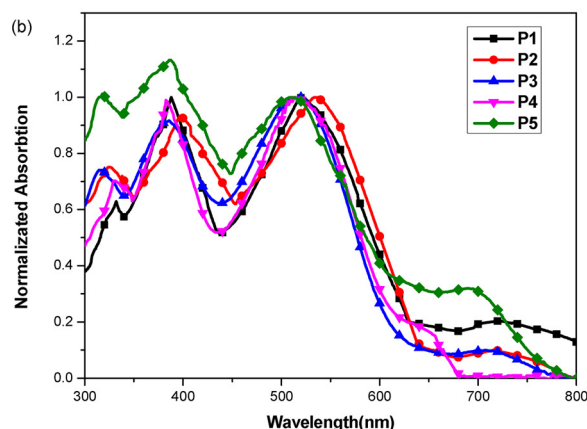
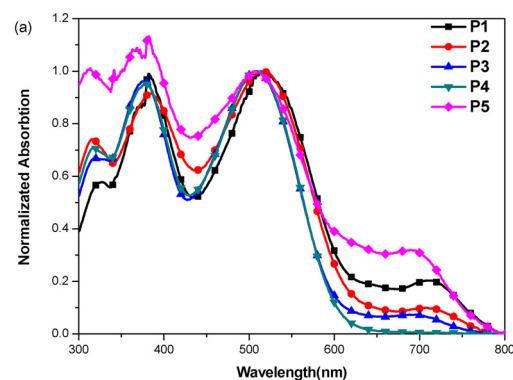


Fig. 2. Optical absorption spectra of copolymers a) in CHCl_3 solution and b) in film.

range of 650–800 nm is more than that of the other three random polymers. On the other hand, from P2 to P4, increasing the content of F-containing D units, the absorption shifts blue-shifted and the absorption in the 650–800 nm range begins to decrease. The energy band gap E_g calculated from the absorption band edges of the optical absorption spectra were about 1.58 eV, 1.60 eV, 1.61 eV, 1.62 eV and

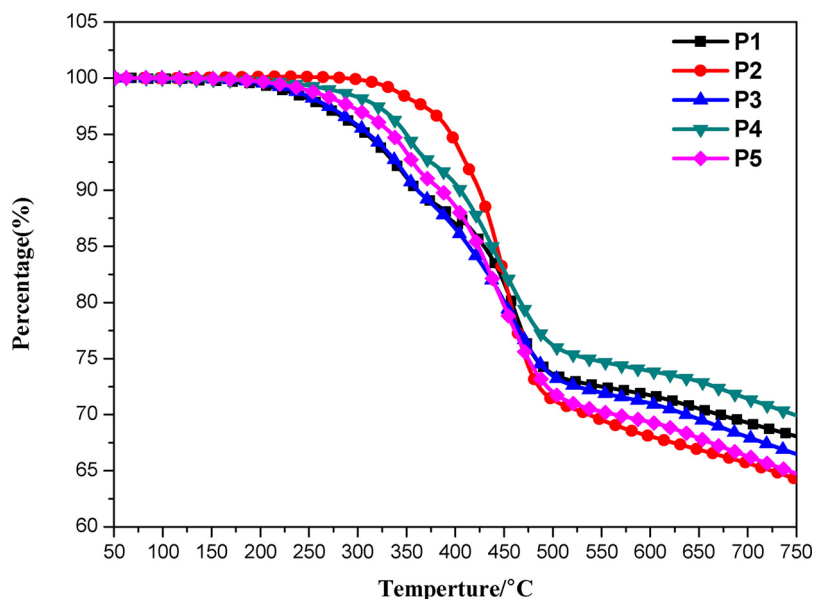


Fig. 1. TGA thermograms of polymers.

Table 2
Optical and electrochemical data of copolymers.

Polymers	HOMO ^{cv} /eV	LUMO ^b /eV	λ_{onset} /nm	E_g^{opt} /eV	$\lambda_{\text{max}}^{\text{sol}}$ /nm
P1	−5.17	−3.59	785	1.58	325, 382, 514, 710
P2	−5.26	−3.66	775	1.60	315, 385, 516, 708
P3	−5.27	−3.66	770	1.61	318, 376, 508, 695
P4	−5.31	−3.69	765	1.62	318, 379, 509
P5	−5.44	−3.83	772	1.61	313, 382, 510, 690

$$\text{LUMO}^b = E_g^{\text{opt}} + \text{HOMO}^{\text{cv}}.$$

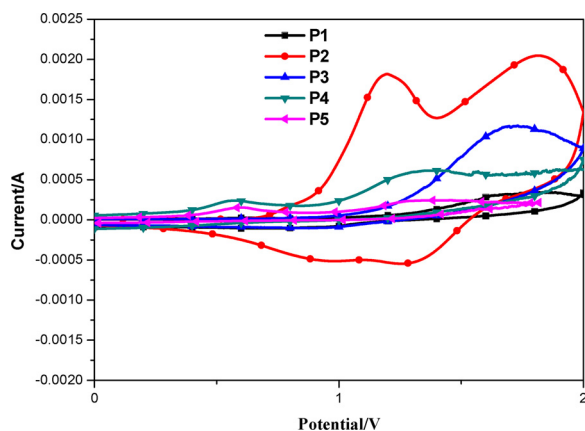


Fig. 3. Cyclic voltammetry measurements of different random polymers.

1.61 eV for P1, P2, P3, P4 and P5, respectively, according to equation $E_g = 1240/\lambda$ eV. It can be seen that with the increase of F-containing D units, the optical band gap does not change significantly, and the band gaps are all around 1.60 eV. Studies have shown that under the premise of containing F, other optical properties of the polymer can be adjusted by changing the F content without affecting the band-gap.

2.3. Electrochemical properties

The electrochemical properties of the copolymers were investigated by the Cyclic voltammetry. The energy level of the Ag/Ag⁺ reference electrode was calibrated against the FC/FC⁺ system and determined to be 4.32 eV below the vacuum level. Fig. 3 shows the cyclic voltammetry of P1–P5, which does not show the obvious reduction peak. Its bandgap

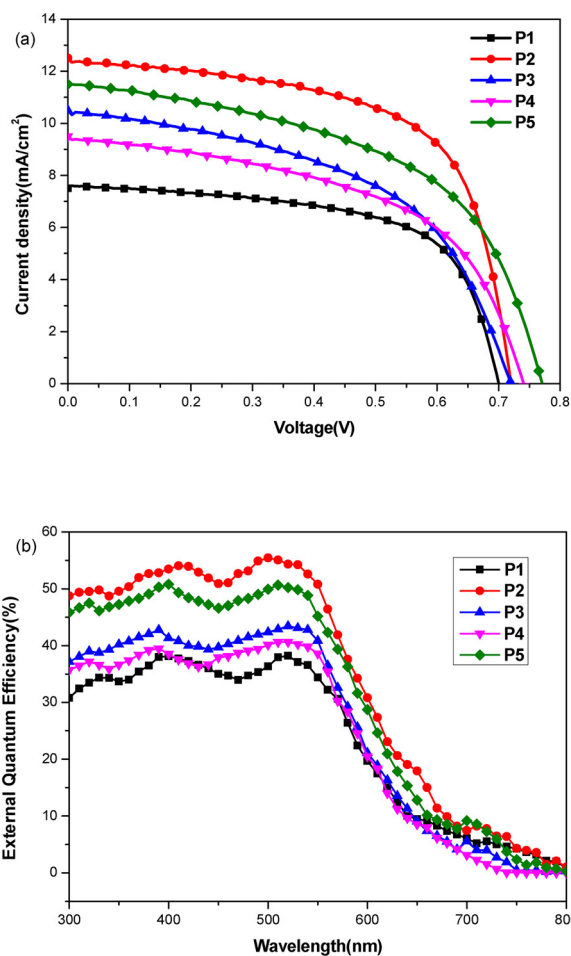


Fig. 5. a) J – V characteristic curves of Donor:PC₇₁BM in BHJ solar cell. (a) $J^{0.5}$ – V characteristics of the electron-only mobility in polymers:PC₇₁BM blend films and b) $J^{0.5}$ – V characteristics of the hole-only mobility in polymers:PC₇₁BM blend films.

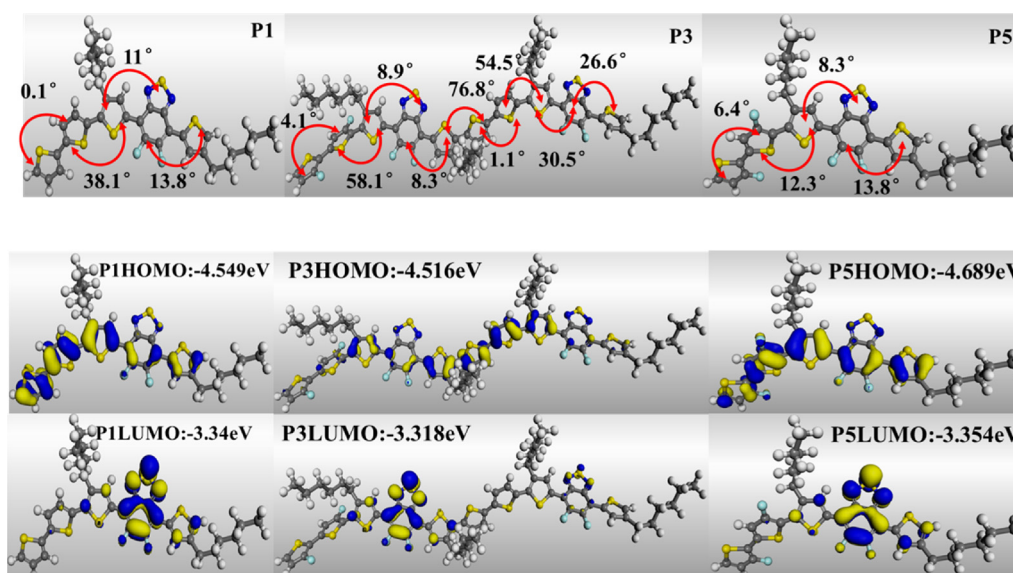


Fig. 4. Optimized geometry and molecular orbital surfaces of the HOMO and LUMO of the model compounds, obtained by the DFT/B3LYP/6-31G* method.

Table 3
Photovoltaic parameters of the HSCs based on different BHJs.

HSC	$J_{SC}/\text{mA cm}^{-2}$	V_{OC}/V	$FF\%$	$PCE\%$
P1:PC ₇₁ BM	$7.31 \pm 0.22(7.52)$	$0.69 \pm 0.01(0.70)$	$62.2 \pm 1.03(63.23)$	$3.14 \pm 0.18(3.32)$
P2:PC ₇₁ BM	$12.1 \pm 0.3(12.40)$	$0.71 \pm 0.01(0.72)$	$60.89 \pm 1(61.89)$	$5.23 \pm 0.34(5.57)$
P3:PC ₇₁ BM	$10 \pm 0.42(10.42)$	$0.71 \pm 0.01(0.72)$	$50.3 \pm 0.22(50.52)$	$3.57 \pm 0.25(3.82)$
P4:PC ₇₁ BM	$9.31 \pm 0.1(9.41)$	$0.72 \pm 0.02(0.74)$	$51.5 \pm 0.7(52.20)$	$3.45 \pm 0.22(3.67)$
P5:PC ₇₁ BM	$11.3 \pm 0.13(11.43)$	$0.75 \pm 0.02(0.77)$	$52 \pm 0.51(52.51)$	$4.41 \pm 0.24(4.65)$

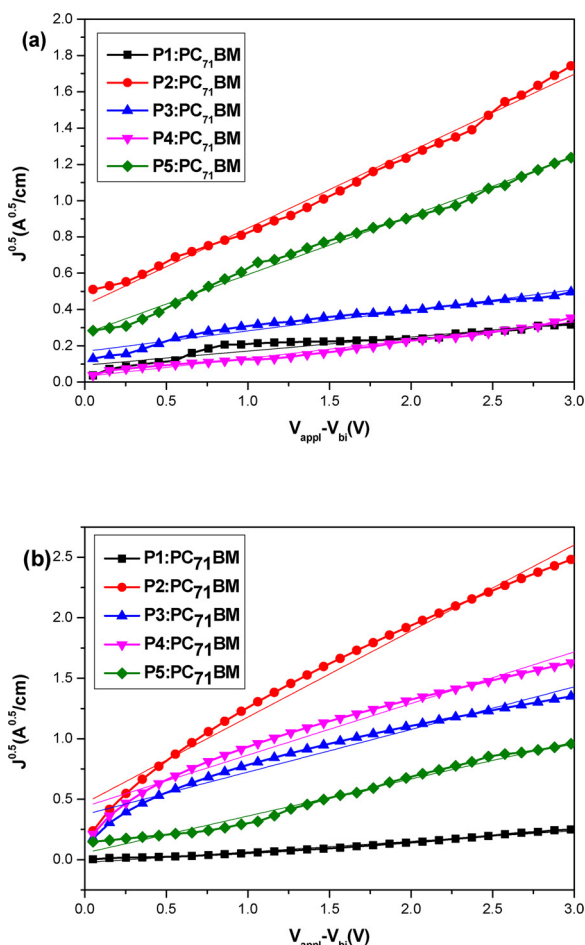


Fig. 6. Tapping-mode AFM topography images ($2 \times 2 \mu\text{m}$) of the active layers a) P1:PC₇₁BM b) P2:PC₇₁BM c) P3:PC₇₁BM d) P4:PC₇₁BM and e) P5:PC₇₁BM.

can be substituted into the calculation using the optical bandgap for the LUMO. The specific HOMO and LUMO energy levels are listed in Table 2. As the content of F-containing donor units increases, the HOMO level decreases continuously. Therefore, in theory, the open-circuit voltage will continuously increase when the above-mentioned polymer with gradually increasing F content is fabricated.

2.4. Theoretical calculations

A series of polymers, P1, P3 and P5 was systematically studied by theoretical calculations to explain the narrow band gap properties of these polymers. These optimized-polymer molecular skeletons and electron density distributions were obtained by Gaussian software based on density functional theory (DFT). In order to facilitate the calculation, P1 and P5 only calculate one duplicate D-A unit plate. P3 uses two pairs of D, A units for calculation because F-containing donors and F-free donors account for half of each. However, P2 and P4 do not perform theoretical calculations due to the need to use 4 four repeating

units and there are multiple combinations. Theoretical calculations (Fig. 4) show that the three polymers have a substantially flat state on the D unit, but the polymer P5 on D-A has a dihedral angle of 12.3° less than just the A unit. For polymer 4-P1, the overall 4-P5 has higher planarity and better conjugation. For random polymers, there is a large dihedral angle between the two different F-containing units, which is not conducive to the intramolecular transport of charge. All fluorinated polymers HOMO are distributed in thiophene and benzothiadiazole units in D and A, and the LUMO energy level is distributed on the benzothiadiazole unit. As a whole, a good push-pull mechanism has been established, which is favorable for intramolecular charge transfer.

2.5. Photovoltaic properties

In the experiment, P1–P5 was used as the electron donor, fullerene PC₇₁BM acted as acceptor, and the mass ratio was 1:1.2. A mixed solution of each group of polymers and fullerene was used to prepare the photovoltaic device. Fig. 5a shows the current density-voltage curve of the polymer and Fig. 5b shows the EQE spectra of the BHJ solar cells. The performance parameters are shown in Table 3. As the content of F-thiophenethiophene increases, the device voltage has been increased, to a degree between 0 and 0.06 V, thanks to the introduction of F atoms, resulting in a decrease in the HOMO level. It should be noted here that both P1 and P5 are synthesized from a single D monomer and A monomer, and the degree of internal molecular chaos is not as high as the P2–P4 random conjugated polymers. Taking P2, P3, and P4 as comparison objects, the short-circuit current tends to decrease as the content of F-containing D monomer increases, from 12.40 mA cm^{-2} (P2) to 9.41 mA cm^{-2} (P4). It may come from the increase of F content, which leads to the excessive aggregation of the phases and short-circuit current shows a decreasing trend. However, the short-circuit current of P5 is increased, which may be related to the low degree of internal molecular chaos. As shown in Fig. 5b, it reveals that the P2 polymer exhibits higher EQE than other polymers in the entire range of wavelengths, which is consistent with higher J_{SC} of solar cells with P2. The overall compliance with the introduction of F at both the D and A monomers is more efficient than the introduction of F at the A alone.

The electron and hole mobilities (μ_e and μ_h) of the blend films were measured by the space charge limited current (SCLC) method, which can be calculated according to the Mott–Gurney equations [22,23]

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3}$$

where J is the current density, μ is the charge mobility at zero field, ϵ_0 is the free-space dielectric constant, ϵ_r is the relative dielectric constant of the polymer blend, d is the thickness of the active layer, the thickness of the active layer for SCLC measurement is approximately 110 nm and V is the effective voltage $V_{\text{appl}} - V_{\text{bi}}$. For hole mobility a device structure of ITO/PEDTO:PSS/donor:PC₇₁BM/MoO₃/Ag was used, and for electron mobility a device structure of ITO/ZnO/donor:PC₇₁BM/LiF/Al was used. As displayed in Fig. 6, the electron mobility (μ_e) was 2.13×10^{-5} , 4.43×10^{-4} , 1.56×10^{-4} , 6.04×10^{-5} , and $4.25 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ recorded for the P1, P2, P3, P4 and P5 blends respectively. The hole mobility (μ_h) was 5.34×10^{-5} , 3.84×10^{-4} , 1.48×10^{-4} , 1.58×10^{-4} , and $8.81 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ recorded for the P1, P2, P3, P4 and P5 blends respectively. We find that introduction F to the D unit

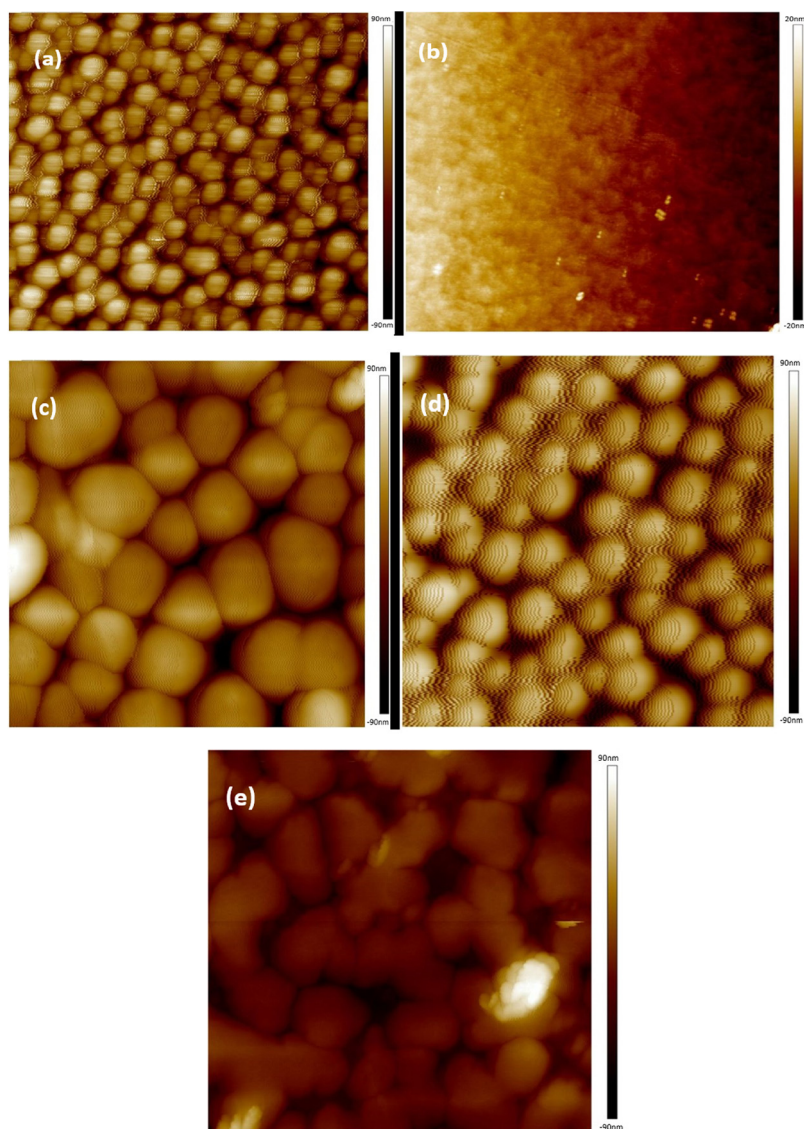


Fig. 7. Tapping-mode AFM topography images ($2 \times 2 \mu\text{m}$) of the active layers a).

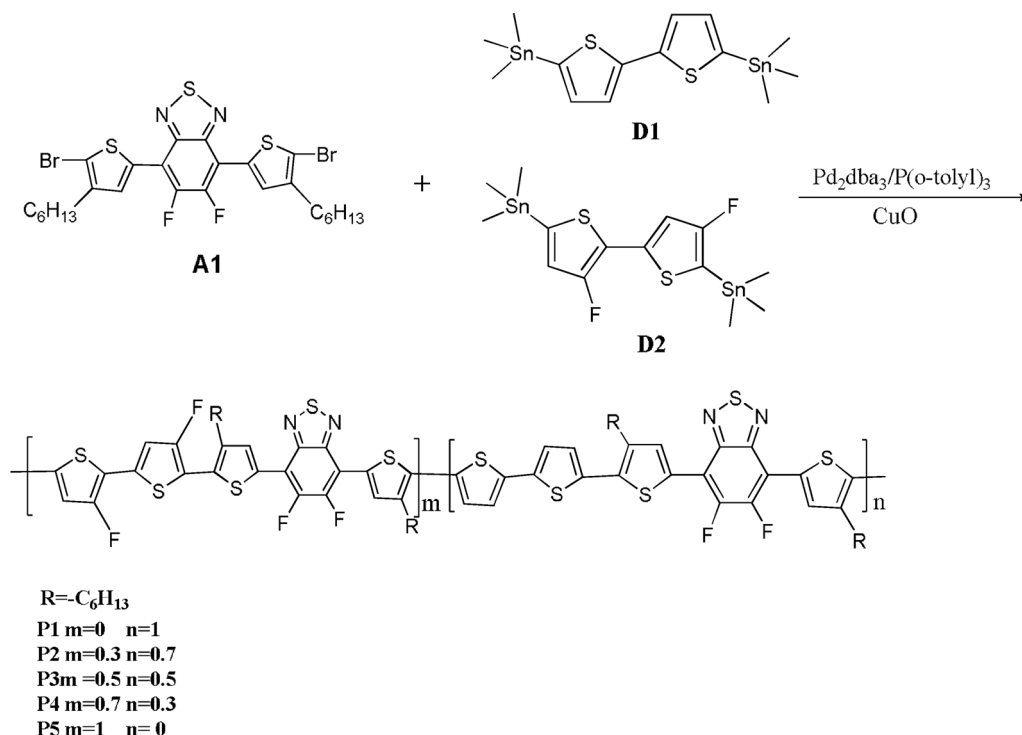
can improve electron mobility and hole mobility. The balanced electron and hole mobility contributes to a higher FF, according to the result, P2 show the best electron mobility and hole mobility, which is accord with its higher FF than other polymers.

The surface morphology of polymer/PC₇₁BM films were investigated by using tapping mode atomic force microscopy (AFM) to understand the effect of the film morphology. As show in Fig. 7, the film surface roughness of the blend film is 26.4, 1.42, 46.6, 44.0 and 45.6 nm for P1:PC₇₁BM, P2:PC₇₁BM, P3:PC₇₁BM, P4:PC₇₁BM and P5:PC₇₁BM, respectively. It has been reported a rougher surface of the active layer would facilitate the interfacial adhesion between subsequent hole extraction layer and the active layer; therefore, an improved charge transport can be anticipated, which can affect device performance. Among them, P2 show the smallest roughness, which is accord with PCE.

3. Conclusion

F-benzothiadiazole derivatives as acceptor monomers, and different ratios of D1 [5,5'-bis(trimethyltin)-2,2'-bithiophene], D2 [3,4'-difluoro-5,5'-bis(trimethyltin)-2,2'-bithiophene] as donor units, five polymers P1 (D1:D2 = 1:0), P2 (D1:D2 = 3:7), P3 (D1:D2 = 5:5), P4

(D1:D2 = 7:3), P5 (D1:D2 = 0:1) were synthesized by a terpolymerization method. After using a series of characterization methods (ultraviolet absorption, cyclic voltammetry, thermogravimetry, gel permeation chromatography) and corresponding simulation calculations, these five polymers can be used as organic solar cell donor units. And all have excellent absorption ability and thermal stability. It was demonstrated that the introduction of F at the same time as D and A is an effective way to increase the efficiency of the device through device testing. At the same time, it was found that P2 (the proportion of F in the D unit is 21% of the total molecule F) has a significant improvement in the photo-physical properties of the polymer, compared to the polymer P1 only containing F in the A monomer. The current has been greatly improved, and the short-circuit current has increased from 7.52 mA cm^{-2} to 12.40 mA cm^{-2} . Even if compared to the P5, it still achieves higher energy conversion efficiency than P5 containing F in both D and A monomer with less F content. Finally, the P2 exhibited a conversion efficiency of 5.57%.



Scheme 1. Synthesis path to polymers.

4. Experimental section

4.1. Materials and characterization

All chemical reagents were purchased from Acros, TCI and Aldrich Chemical Co. and were used as received except where stated otherwise. **D1**, **D2** and **A1** monomers required for the polymer syntheses were obtained from SunaTech Inc.

The magnetic resonance (NMR) spectra data for intermediate and target product are obtained on Bruker ARX 400 NMR spectrometer. BAS 100B instrument was used to characterize the HOMO and LUMO of polymers using cyclic voltammetry at room temperature with a scan rate of 50 mV/s. The polymers were coated on the platinum plate working electrode for experimental test. The HOMO of polymers was obtained from the onset oxidation potential according to: $HOMO = -(E_{onset}^{ox} + 4.32) eV$. The LUMO of polymers were acquired from the onset reduction potentials according to: $LUMO = -(4.32 + E_{onset}^{red}) eV$. UV–vis spectra are used to test the spectral response of the polymer on a PerkinElmer Lambda 900 UV–vis/NIR spectrometer. Thermogravimetric analyses (TGA) were performed on a TA Instruments Model TGA Q600 thermogravimetric analyzer at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 flow (100 mL min^{-1}). The photocurrent–voltage (J – V) curves of Heterojunction Solar Cells (HSCs) are recorded on Electrochemical Workstation (Xe Lamp Oriel Sol3A™ Class AAA Solar Simulators 94023 A, USA) in an ambient atmosphere. Materials Studio 7.0 is applied for DFT calculations. Gel permeation chromatography (GPC) was carried out with a Waters high-pressure infusion fluid pump 1515 and detector 2414 system in THF. AFM images were collected using a Bruker Dimension EDGE scanning probe operated in the tapping mode.

4.2. Synthesis of random D-A polymers

General procedure: In a 50 mL three-necked flask, a mixture of different molar amounts of donor units (**D1**, **D2**) and acceptor unit (**A1**) was dissolved in 15 mL of degassed toluene. Then, a corresponding amount of Pd_2dba_3 , CuO, $P(o\text{-tolyl})_3$ was added to the solution, which

was replaced with nitrogen two or three times, and the mixture was heated to $110\text{ }^{\circ}\text{C}$ for 72 h under nitrogen protection. After the reaction was completed, it was cooled to room temperature and polymer was slowly added dropwise to 300 mL of methanol. The crude copolymer was collected by filtration and purified in methanol, hexane and acetone in a Soxhlet apparatus and finally the polymer was extracted with chloroform. The chloroform solution was concentrated and slowly added to 300 mL of methanol to precipitate the co-polymer again. The solid was filtered and dried in vacuum to give a red solid with a yield of 45–75%. The synthetic route is shown in Scheme 1.

P1: **A1** (0.2 g, 0.3 mmol), **D1** (0.1483 g, 0.3 mmol) toluene (15 mL), Pd_2dba_3 (8 mg)/CuO (50 mg)/ $P(o\text{-tolyl})_3$ (10 mg) prepare **P1** according to the above procedure. 0.15 g of a red solid was obtained with a yield of 74.58%. 1H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.14(br, 1 H), 7.18(br, 1 H), 7.05(br, 1 H), 2.91(br, 2 H), 1.66–1.82(br, 6 H), 1.4–1.6(br, 22 H), 1.18–1.38(br, 72 H), 0.7–0.97 (br, 90 H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 140.0, 137.8, 134.5, 134.1, 127.9, 125.9, 124.6, 123.8, 48.6, 46.8, 41.3, 39.0, 38.7, 37.1, 35.3, 35.1, 34.6, 34.5, 33.7, 31.6, 29.7, 28.0, 27.6, 26.9, 25.8, 25.3, 22.8, 20.4, 19.4, 18.7, 14.1, 11.4.

P2: **A1** (0.2 g, 0.3 mmol), **D1** (0.0445 g, 0.09 mmol), **D2** (0.113 g, 0.21 mmol), toluene (15 mL), Pd_2dba_3 (8 mg)/CuO (50 mg)/ $P(o\text{-tolyl})_3$ (10 mg) was prepared for **P2**. This gave a yield of 78.3% of 0.16 g of a purple-red solid. 1H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.19(br, 1 H), 4.56–4.99(br, 13 H), 3.50(br, 2 H), 2.36(br, 1 H), 1.41–1.83(br, 24 H), 1.06–1.37(br, 21 H), 0.7–1.10(br, 32 H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.3, 155.0, 129.3, 100.5, 48.8, 47.3, 41.3, 38.8, 35.1, 34.7, 34.5, 33.7, 31.6, 29.4, 29.1, 28.9, 27.7, 26.9, 25.8, 25.3, 22.7, 20.7, 20.5, 19.4, 18.8, 14.0, 11.4.

P3: **A1** (0.2 g, 0.3 mmol), **D1** (0.0742 g, 0.15 mmol), **D2** (0.0795 g, 0.15 mmol), toluene (15 mL), Pd_2dba_3 (8 mg)/CuO (50 mg)/ $P(o\text{-tolyl})_3$ (10 mg) was prepared for **P3**. A 0.12 g red solid was obtained with a yield of 58.11%. 1H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.15(br, 1 H), 5.35(br, 2 H), 3.81–4.12(br, 3 H), 2.88(br, 2 H), 1.18–1.45(br, 68 H), 0.75–0.99 (br, 76 H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 163.1, 159.5, 153.7, 143.8, 139.8, 128.0, 117.6, 108.1, 41.3, 35.0, 34.6, 33.7, 31.7, 29.8, 29.1, 27.7, 27.0, 25.9, 25.2, 22.5, 20.6, 20.5, 19.3, 18.6, 14.6, 14.2, 11.5.

P4: A1 (0.2 g, 0.3 mmol), **D1** (0.1038 g, 0.21 mmol), **D2** (0.0477 g, 0.09 mmol), 15 mL toluene, Pd₂dba₃ (8 mg)/CuO (50 mg)/P (o-tolyl)₃ (10 mg), Prepare **P4**. A 0.1 g red solid yield of 47.93% was obtained. ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.06(br, 1 H), 7.73(br, 1 H), 4.69(br, 3 H), 4.08(br, 2 H), 3.71(br, 5 H), 3.39(br, 2 H), 2.80(br, 2 H), 2.38(br, 3 H), 1.51–1.58(br, 26 H), 1.15–1.32(br, 22 H), 1.18–1.38(br, 80 H), 0.72–0.95 (br, 168 H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 157.9, 148.5, 144.5, 129.9, 128.0, 100.0, 70.9, 69.0, 41.3, 38.9, 36.3, 36.1, 34.8, 33.8, 31.7, 29.7, 29.1, 27.6, 26.9, 25.93, 25.3, 22.3, 20.6, 19.3, 18.6, 14.2, 14.2, 11.5.

P5: A1 (0.2 g, 0.3 mmol), **D2** (0.1590 g, 0.3 mmol), 15 mL of toluene, Pd₂dba₃ (8 mg)/CuO (50 mg)/P (o-tolyl)₃ (10 mg), Preparation **P5**. A yield of 84.96% was obtained for a red solid of 0.18 g. ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.10(br, 1 H), 3.39(br, 2 H), 2.84(br, 3 H), 1.45–2.02(br, 14 H), 1.01–1.45(br, 32 H), 0.57–0.98 (br, 28 H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 161.0, 150.9, 146.9, 139.8, 127.7, 112.3, 100.7, 99.2, 41.2, 35.1, 34.7, 33.8, 31.7, 29.8, 29.1, 27.7, 25.0, 22.4, 20.3, 19.5, 18.8, 14.4, 13.9, 11.5.

4.3. Device fabrication

Photovoltaic devices were fabricated as follows. First, the glass/ITO substrates were cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and dried in an oven overnight at 100 °C. **PEDOT:PSS** hole transport layers were dissolved in σ -CB and spin-coated on top of the ITO a nitrogen-filled glove box. The active layer (polymer: **PC₇₁BM** = 1:1.2 wt) blend solution was spin-coated on top of **PEDOT:PSS**. The device was placed in a vacuum chamber ($< 10^{-6}$ torr), where calcium and aluminum film were thermally deposited on the active layer, producing a structure glass/ITO/PEDOT:PSS/polymer:**PC₇₁BM**/Ca/Al. The deposited Al electrode active area was 4 mm². Photovoltaic measurements were performed by using a high-quality optical fiber to guide light from the solar simulator (Xe Lamp Oriol Sol3ATM Class AAA solar Simulators). *J-V* curves were measured under AM1.5G illumination at 100 mW cm⁻², using an aperture to define the illuminated area. A thin black-plastic mask was attached to each cell for measurement of the *J-V* characteristics. Software used to perform PCE calculations is Oriol IV test station.

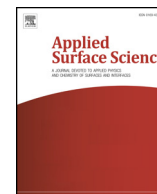
Acknowledgements

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References

- [1] Q. An, W. Gao, F. Zhang, J. Wang, M. Zhang, K. Wu, X. Ma, Z. Hu, C. Jiao, C. Yang, Energy level modulation of non-fullerene acceptors enables efficient organic solar

- cells with small energy loss, *J. Mater. Chem. A* 6 (2018) 2468–2475.
- [2] Y. Kan, C. Liu, L. Zhang, K. Gao, F. Liu, J. Chen, Y. Cao, Solution-processed small molecules with ethynylene bridges for highly efficient organic solar cells, *J. Mater. Chem. A* 4 (2016) 14720–14728.
- [3] Y. Zhang, G. Tu, J. Shi, X. He, All-thiophene-substituted N-heteroacene electron-donor materials for efficient organic solar cells, *J. Mater. Chem. A* 4 (2016) 13519–13524.
- [4] Y.-W. Su, S.-C. Lan, K.-H. Wei, Organic photovoltaics, *Mater. Today* 15 (2012) 554–562.
- [5] Y.-W. Su, Y.-C. Lin, K.-H. Wei, Evolving molecular architectures of donor–acceptor conjugated polymers for photovoltaic applications: from one-dimensional to branched to two-dimensional structures, *J. Mater. Chem. A* 5 (2017) 24051–24075.
- [6] D.P.H. Tannia Marinado, K.M.K. Kazuteru Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt, L. Sun, Tuning the HOMO and LUMO energy levels of organic chromophores for dye sensitized solar cells, *J. Org. Chem.* 72 (2007) 9550–9556.
- [7] M.D. Ganji, M. Tajbakhsh, M. Kariminasab, H. Alinezhad, Tuning the LUMO level of organic photovoltaic solar cells by conjugately fusing graphene flake: a DFT-B3LYP study, *Physica E Low. Syst. Nanostruct.* 81 (2016) 108–115.
- [8] Y. Matsuo, Design concept for High-LUMO-level fullerene electron-acceptors for organic solar cells, *Chem. Lett.* 41 (2012) 754–759.
- [9] T. Mikie, A. Saeki, N. Ikuma, K. Kokubo, S. Seki, Spiro-1,3-dioxolano fullerene with low-lying LUMO level for organic solar cells, *Chem. Lett.* 44 (2015) 282–284.
- [10] M.A. Stevens, A.C. Arango, Open-circuit voltage exceeding the outermost HOMO–LUMO offset in cascade organic solar cells, *Org. Electron.* 37 (2016) 80–84.
- [11] J.-M. Jiang, H.-C. Chen, H.-K. Lin, C.-M. Yu, S.-C. Lan, C.-M. Liu, K.-H. Wei, Conjugated random copolymers of benzodithiophene–benzooxadiazole–diketopyrrolopyrrole with full visible light absorption for bulk heterojunction solar cells, *Polym. Chem.* 4 (2013) 5321–5328.
- [12] J.-M. Jiang, M.-C. Yuan, K. Dinakaran, A. Hariharan, K.-H. Wei, Crystalline donor–Acceptor conjugated polymers for bulk heterojunction photovoltaics, *J. Mater. Chem. A* 1 (2013) 4415–4422.
- [13] J.W. Jo, J.W. Jung, E.H. Jung, H.J. Ahn, T. Shin, W.H. Jo, Fluorination on both D and A Unit in D-A Type conjugated copolymer based on difluorobithiophene and benzothiadiazole for high efficient polymer solar cells, *Energy Environ. Sci.* 8 (2015) 2427–2434.
- [14] Y. Zhang, S.C. Chien, K.S. Chen, H.L. Yip, Y. Sun, J.A. Davies, F.C. Chen, A.K. Jen, Increased open circuit voltage in fluorinated benzothiadiazole-based alternating conjugated polymers, *Chem. Commun.* 47 (2011) 11026–11028.
- [15] H. Zhou, L. Yang, A.C. Stuart, S.C. Price, S. Liu, W. You, Development of fluorinated benzothiadiazole as a structural unit for a polymer solar cell of 7 % efficiency, *Angew. Chem.* 123 (2011) 3051–3054.
- [16] S. Liu, P. You, J. Li, J. Li, C.S. Lee, B.S. Ong, C. Surya, F. Yan, Enhanced efficiency in polymer solar cells by adding a high-mobility conjugated polymer, *Energy Environ. Sci.* 8 (2015) 1463–1470.
- [17] Ö. Azeri, E. Aktas, C. Istanbuloglu, S.O. Hacıoglu, S.C. Cevher, L. Toppare, A. Cirpan, Efficient benzodithiophene and thienopyrroledione containing random polymers as components for organic solar cells, *Polymer* 133 (2017) 60–67.
- [18] J.B. Howard, B.C. Thompson, Design of random and semi-random conjugated polymers for organic solar cells, *Macromol. Chem. Phys.* 218 (2017) 1700255.
- [19] Y. Koda, T. Terashima, M. Sawamoto, Multimode self-folding polymers via reversible and thermoresponsive self-assembly of amphiphilic/fluorous random copolymers, *Macromolecules* 49 (2016) 4534–4543.
- [20] J.H. Yun, H. Ahn, P. Lee, J.K. Min, H.J. Son, Development of highly crystalline donor-acceptor-type random polymers for high performance large-area organic solar cells, *Macromolecules* (2017) 7567–7576.
- [21] J.W. Jo, S. Bae, F. Liu, T.P. Russell, W.H. Jo, Comparison of two D-A type polymers with each being fluorinated on d and a unit for high performance solar cells, *Adv. Funct. Mater.* 25 (2015) 120–125.
- [22] W. Li, Y. Qin, W. Dai, D. Zhou, Electron transport layer-free polymer solar cells show 40% higher efficiency than using ZnO transparent cathode, *J. Mater. Sci. Mater. Electron.* 29 (2018) 11296–11305.
- [23] J. Sun, F. Jin, H. Zhao, J. Yuan, W. Ma, Enhanced charge transfer, transport and photovoltaic efficiency in all-polymer organic solar cells by polymer backbone fluorination, *Chinese J. Chem.* 36 (2018) 280–286.



Full Length Article

UiO-66 derived zirconia/porous carbon nanocomposites for efficient removal of carbamazepine and adsorption mechanism

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Surface interaction

ABSTRACT

Nanoarchitecture design of metal oxides/porous carbon nanocomposites from metal-organic frameworks is attracting considerable attention. Herein, UiO-66 was used as precursor and template to fabricate zirconia/porous carbon nanocomposites with tunable specific surface area and pore volume by a two-step calcination. The results showed that the tetragonal ZrO₂ nanoparticles in carbon matrix gradually grow up and transform into monoclinic ZrO₂ and ZrO as well as escape from the porous carbon nanocubes resulting in the increase of their specific surface area and pore volume with the increase of calcination temperature. The as-prepared nanocomposites at 1200 °C (ZPCNCs-12) exhibited a high specific surface area up to 468.9 m² g⁻¹, and excellent adsorption performance with high adsorption capacity (190 mg g⁻¹), fast adsorption equilibrium (60 min) and recyclability for the removal of carbamazepine from water in a wide pH range of 2–12. FTIR spectra suggested that the adsorption of carbamazepine on ZPCNCs-12 was physical, and XPS results further confirmed that the adsorption was mainly dominated by the π - π electron donor-acceptor interaction between carbamazepine molecule and carbon nanocubes. It indicates that the two-step calcination of metal-organic frameworks is an effective approach to fabricate highly efficient sorbent for the removal of organic pollutants from water.

1. Introduction

Metal oxides/porous carbon nanocomposites have received wide spread attention in the water management, catalysis and energy storage on account of their adequate active sites, high specific surface area and excellent structure stability [1,2]. Generally, the preparation approaches of metal oxides/porous carbon nanocomposites can be classified into three categories: (1) the metal oxides grow in pre-synthesized porous carbon, such as CoO/porous carbon nanocomposites [3]; (2) pre-synthesized metal oxides nanomaterials were embedded in porous carbon precursor and then carbonized, such as SnO₂/porous carbon nanocomposites [4]; (3) pyrolysis of complexes/hybrids composed with metal ions and carbon precursors under the aid of template, such as Fe₂O₃/porous carbon nanocomposites [5]. Although lots of novel metal oxides/porous carbon nanocomposites had been synthesized and showed excellent performance, simple and controllable synthesis route of metal oxide/porous carbon nanocomposites with tunable specific surface area and pore volume still face significant challenges because traditional methods are complex and time-consuming and imprecise.

Recently, a new synthesis approach of metal oxides/porous carbon nanocomposites by direct calcination of metal-organic frameworks (MOFs), which possess many advantages including the abundant porosity, adjustable pore size, and modifiable shape as well as controllable chemical environment, in the absence of any additional carbon sources or further activation, has emerged and attracted extensive attention of researchers [6,7]. For example, MOF derived Fe₃O₄/porous carbon nanocomposite could be used as a high performance recyclable environmental super adsorbent [8], MOF-derived ZnO/porous carbon nanocomposites showed exceptional lithium anodic performance [9], and γ -Fe₂O₃/porous carbon nanocomposites exhibited excellent catalytic activity for the hydrogenation of diverse nitro compounds [10]. For adsorbent, catalyst and energy storage material, the high specific surface area is key factor because the high specific surface area can provide more active sites and high diffusion rate. Therefore, many efforts have been devoted to obtaining metal oxides/porous carbon nanocomposites with high specific surface area [3,7,9]. However, most of MOF-derived metal oxides/porous carbon nanocomposites exhibited the specific surface area below 200 m² g⁻¹ except the zinc-containing

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MOFs [7]. Because of the lower boiling point (908 °C) of Zn, zinc-containing MOFs, such as MOF-5 and ZIF-8, were the most used precursors and templates to prepare porous materials [11,12], which showed high specific surface area ($> 400 \text{ m}^2 \text{ g}^{-1}$) and wonderful performance in energy storage, catalysis, adsorption and so on [13–15]. However, it is still existing drawbacks because the released Zn vapor is harmful to environment and organism. Furthermore, the residual Zn species in porous carbon would cause secondary pollution. Therefore, to expand the application of MOFs as precursors and templates for the preparation of metal oxide/porous carbon nanocomposites, it is very urgent to investigate the heat-treatment process of other environmentally friendly MOFs in an inert atmosphere, including the morphology and structure evolution of their product.

Herein, zirconium metal-organic framework UiO-66 was used as precursor and template to prepare ZrO_x /porous carbon nanocomposites by a two-step calcination, and the morphology and structure evolution of the ZrO_x /porous carbon nanocomposites was studied in detail. Furthermore, the adsorption behaviors of carbamazepine (CBZ) on the nanocomposites were investigated and the corresponding adsorption mechanisms were clarified by FTIR and XPS spectra.

2. Experimental section

2.1. Synthesis of UiO-66

UiO-66 was synthesized using a facile one-step solvothermal method [16]. 0.053 g of ZrCl_4 (0.227 mmol) was dissolved in 24.9 g of N, N-dimethylformamide (DMF) (340 mmol) by ultrasonication for 30 min, then 0.034 g of 1,4-benzenedicarboxylic acid (H_2BDC) (0.227 mmol) was added into the above solution evenly under magnetic stirring. The reaction solution was placed in an oven at 120 °C for 24 h. White precipitation was obtained and washed by DMF for three times and then soaked by trichloromethane for 24 h with three times to remove the residual DMF. Finally, the white powder was acquired after drying at 100 °C in an oven.

2.2. Synthesis of ZrO_x /porous carbon nanocomposites

The schematic for synthesis procedure of ZrO_x /porous carbon nanocomposites is presented in Fig. 1. First, according to the TG curve (Figure S1) of UiO-66, UiO-66 powder was annealed in a tube furnace (RHTH 120-300/17) at 400 °C with a heating rate of 5° min^{-1} and maintained for 30 min (Step one) under the protection of N_2 atmosphere of $100 \text{ cm}^3 \text{ min}^{-1}$, and then the calcination temperature was raised to the set temperature (600, 800, 1000, 1200 and 1400 °C, respectively) at a heating rate of 1° min^{-1} and maintained for 2 h (Step two). After cooling to room temperature naturally, the obtained black ZrO_x /porous carbon nanocomposites (ZPCNCs) were obtained. To distinguish the samples obtained from the annealing temperature of 600, 800, 1000, 1200 and 1400 °C, the ZrO_x /porous carbon nanocomposites were abbreviated into ZPCNCs-6, ZPCNCs-8, ZPCNCs-10, ZPCNCs-12 and ZPCNCs-14, respectively.

2.3. Characterization

Thermogravimetric (TG) curve was obtained on a TG analyzer (Q600, TA Instruments) under nitrogen ($100 \text{ cm}^3 \text{ min}^{-1}$) with the temperature rate of $5^\circ \text{ C min}^{-1}$. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of ZPCNCs were acquired by a Quanta 450 SEM (FEI) and JSM 2100 TEM (JEOL), respectively. The nitrogen adsorption-desorption isotherms of ZPCNCs were obtained on a TriStar II 3020 surface area & pore size analyzer (Micromeritics). The specific surface area and pore-size distribution of ZPCNCs was calculated from the corresponding nitrogen adsorption-desorption isotherms using Brunauer-Emmett-Teller (BET) method and Tarazona non-local density functional theory (NLDFT) model

(Cylindrical pores), respectively. X-ray diffraction (XRD) patterns of ZPCNCs were obtained by D8 Advanced X-ray diffraction (Bruker) at a scan rate of 4° min^{-1} . Fourier transform infrared (FTIR) spectra of ZPCNCs were obtained on a Vertex70 FTIR spectrometer (Bruker). Raman spectra of ZPCNCs were acquired on a Lab RAM HR800 Laser Raman spectroscopy (HORIBA) using a 647 nm argon ion laser. X-ray photoelectron spectra (XPS) of ZPCNCs were recorded on an Axis Ultra XPS spectrometer (Kratos).

2.4. Adsorption experiments

2.4.1. Batch adsorption

Batch adsorption was carried using an orbital shaker at 180 rpm over 24 h under preset temperature. 10 mg of adsorbent (ZPCNCs) was added into the conical flasks containing 40 mL of CBZ with the concentration (C_0) from 10 to 100 mg L^{-1} . The initial pH of CBZ solution ($\text{pH} = 2\text{--}12$) was adjusted by adding 1 M NaOH or 1 M HCl. After adsorption equilibration, the adsorbent was removed by a $0.22 \mu\text{m}$ filters, and then the concentration of residual CBZ was analyzed by UV spectrophotometer (Hitachi U-3010/3310) at 285 nm. The quantity of organic contaminants absorbed per unit mass of ZPCNCs was calculated by the following equation:

$$Q_e = (C_0 - C_e) \frac{V}{m} \quad (1)$$

where Q_e (mg g^{-1}) is the adsorbing capacity at adsorption equilibrium, C_0 (mg L^{-1}) is the initial concentration of target contaminant, C_e (mg L^{-1}) is the concentration of target contaminant at adsorption equilibrium, V is the volume of the solution, and m is the mass of adsorbent.

2.4.2. Adsorption kinetics

100 mg ZPCNCs was added into the beaker (1 L) with 400 mL CBZ solution (100 mg L^{-1}) under constant magnetic stirring at 25 °C. Then, 1.5 mL solution sample was collected at predetermined time intervals and immediately filtered to remove the adsorbent by a $0.22 \mu\text{m}$ filters. The residual CBZ in aqueous solution was analyzed by UV spectrophotometer at 285 nm.

$$Q_t = (C_0 - C_t) \frac{V}{m} \quad (2)$$

where Q_t (mg g^{-1}) is the adsorbing capacity when the time is t , C_t (mg L^{-1}) is the concentration of target contaminant when the time is t .

3. Results and discussion

3.1. Morphology and structure

Figure S1 shows the typical SEM images of pristine UiO-66 and UiO-66 derived ZPCNCs. From the Figure S1a, the size of UiO-66 nanocubes are between 60 and 130 nm. After calcination at 600, 800 and 1000 °C, the obtained ZPCNCs-6 (Figure S1b), ZPCNCs-8 (Figure S1c) and ZPCNCs-10 (Figure S1d) possess the quasi-cubic shape with concave surfaces. It is mainly attributed to the escape of O-containing groups from UiO-66 resulting in the shrinking of the cubic framework during the pyrolysis of UiO-66. Moreover, lots of nanoparticles can be observed on the rough surfaces of these ZPCNCs, and the density of nanoparticles increases with the annealing temperature. Based on the TG curve of MOFs (Figure S2) and reported results [17–19], we believe that these nanoparticles are zirconium oxide. Figure S1e shows the typical SEM images of ZPCNCs-12, and there are some spheres with size from 50 to 400 nm besides nanocubes. According to the above analysis and the crystal growth mechanism, we speculate that these spheres are zirconium oxide grown from the nanoparticles because of the increasing temperature. As shown in Figure S1f, some polyhedral crystallites with size up to $5 \mu\text{m}$ can be observed in the ZPCNCs-14 besides nanocubes.

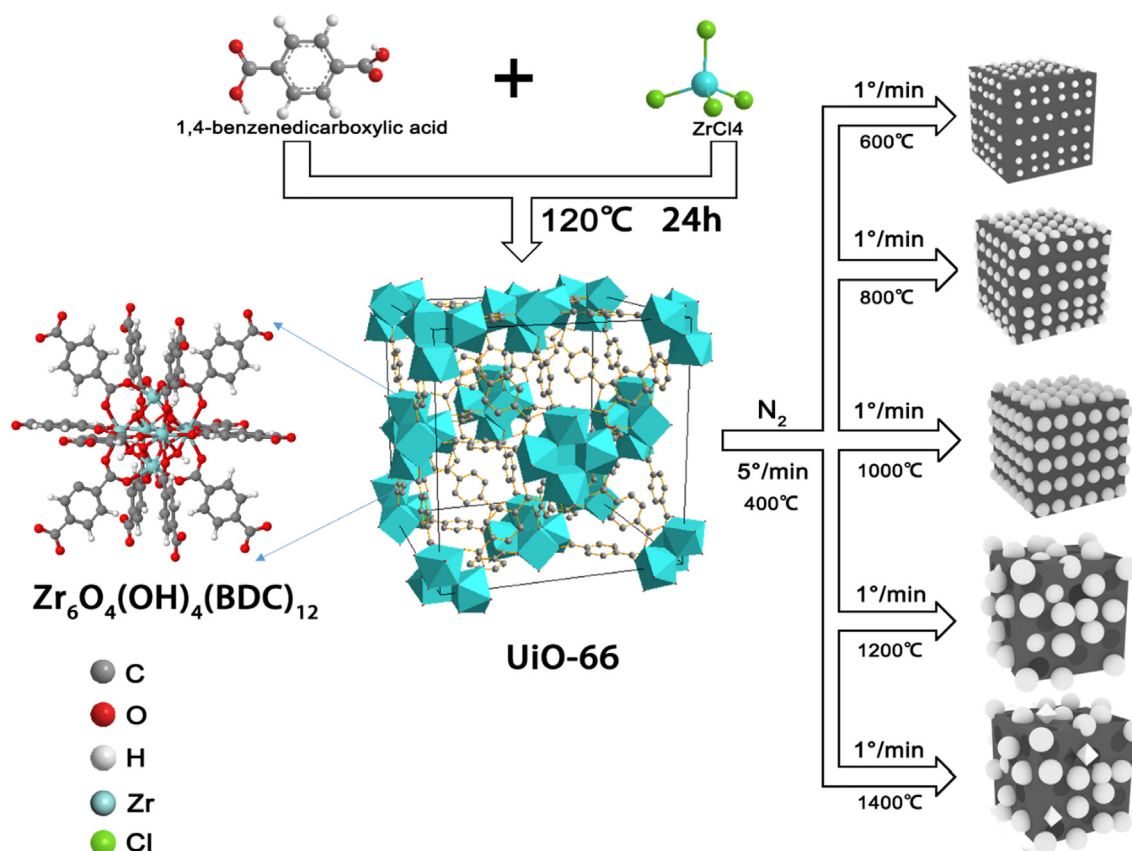


Fig. 1. Schematic illustration of the synthesis procedure of ZPCNCs.

TEM was used to further investigate the morphology and structure of ZPCNCs. Fig. 2a and 2c show the typical TEM images of ZPCNCs-6 and ZPCNC-8, respectively. It can be observed that quasi-cubic ZPCNCs-6 and ZPCNC-8 exhibit porous structure, and ZPCNCs-6 nanocubes disperse better than the ZPCNC-8. Fig. 2b and 2d show the HRTEM images of ZPCNCs-6 and ZPCNC-8, respectively. We can clearly see that nanocrystals with ordered crystal lattice stripes were encapsulated in amorphous structure, which corresponds to the UiO-66 derived zirconium oxide nanocrystals and carbon, respectively. The average size of zirconium oxide nanocrystals in ZPCNCs-6 and ZPCNC-8 is about 5 nm, which is agreement well with the XRD results. In addition, we can observe that the pores in ZPCNC-8 nanocubes is more than that of ZPCNCs-6. Fig. 2e shows the typical TEM image of ZPCNC-12, containing sphere-like crystals and porous nanocubes, which is consistent with the SEM results. The HRTEM images (Fig. 2f) of porous nanocubes in ZPCNC-12 cannot be observe evident lattice fringe in the nanocubes, which indicates that the zirconium oxide crystals escaped from the cubic carbon framework completely. Some free zirconium oxide crystals (Figure S3a) and carbon nanocubes (Figure S3b) can be observed in TEM image of ZPCNC-12. The escape of metal oxides from the carbon framework will effectively increase the porosity.

N₂ adsorption/desorption isotherms was used to further analyze the pore structure of ZPCNCs. Figure S4a shows the nitrogen adsorption-desorption isotherms of as-prepared ZPCNCs. Obviously, the isotherms of ZPCNCs-6, ZPCNCs-8 and ZPCNCs-10 are identified as typical type I isotherm (IUPAC) with prominent adsorption at low relative pressure and followed by a long horizontal plateau extending up to high relatively pressure, which is characteristic of microporous materials. The isotherms of ZPCNCs-12 and ZPCNCs-14 indicate typical type IV isotherms with a quasi-H₂ hysteresis loop, demonstrating their mesoporous characteristics. The calculated specific surface area (S_{BET}) of ZPCNCs is listed in Table 1. Clearly, the S_{BET} of ZPCNCs increases from 173 to 469 m² g⁻¹ with the increase of annealing temperature

from 600 to 1200 °C, then decreases to 327 m² g⁻¹ at 1400 °C. The higher S_{BET} of ZPCNCs with the higher annealing temperature can be attribute to that the zirconium oxide crystals escape from the carbon cubes resulting in lots of pores in the carbon cubes, which has been confirmed by SEM and TEM observation (Figure S1 and Fig. 2). The S_{BET} of ZPCNCs-12 (469 m² g⁻¹) is higher than most of reported non-zinc containing MOFs derived porous materials [7] and other UiO-66-derived porous materials [17–20]. It indicates that the two-step calcination of UiO-66 can improve effectively the porous structure of ZPCNCs. The decreased S_{BET} of ZPCNCs-1400 is mainly attributed to the collapse of partial porous structure, which is common in other reported porous materials [21]. Figure S4b shows the calculated pore-size distribution of ZPCNCs, and the corresponding pore volume and the average pore size is listed in Table 1. Obviously, the total pore volume (V_{total}) and mesoporous volume (V_{meso}) of ZPCNCs exhibits a rising trend with the increase of annealing temperature. In addition, the microporous volume (V_{micro}) of ZPCNCs gradually rises to 0.16 cm³ g⁻¹ at 1200 °C and then shows a sharp decline at 1400 °C. ZPCNCs-6, ZPCNCs-8 and ZPCNCs-10 is mainly microporous, but more mesopore in the ZPCNCs-12 and ZPCNCs-14. It indicates that the higher calcination temperature could generate more pores, especially the mesopore. The as-prepared ZPCNCs with high S_{BET} and high pore volume will exhibit high performance for adsorption and energy storage.

The phase of as-synthesized ZPCNCs was characterized by X-ray diffraction (XRD), and the obtained XRD patterns are shown in Fig. 3a. Generally, ZrO₂ has three kinds of crystal phase, including monoclinic ZrO₂ (m-ZrO₂), tetragonal ZrO₂ (t-ZrO₂), cubic ZrO₂ (c-ZrO₂). XRD patterns of ZPCNCs-6, ZPCNCs-8 and ZPCNCs-10 match well with the standard pattern of t-ZrO₂ (PDF#88-1007), and four diffraction peaks at $2\theta = 30.18, 35.14, 50.24$ and 60.20° can be assigned to the (1 0 0), (1 1 0), (1 1 2) and (2 1 1) planes of t-ZrO₂. Notably, there are no peaks of carbon in the XRD patterns of ZPCNCs, implying that the carbon in ZPCNCs is amorphous. With the increase of annealing temperature from

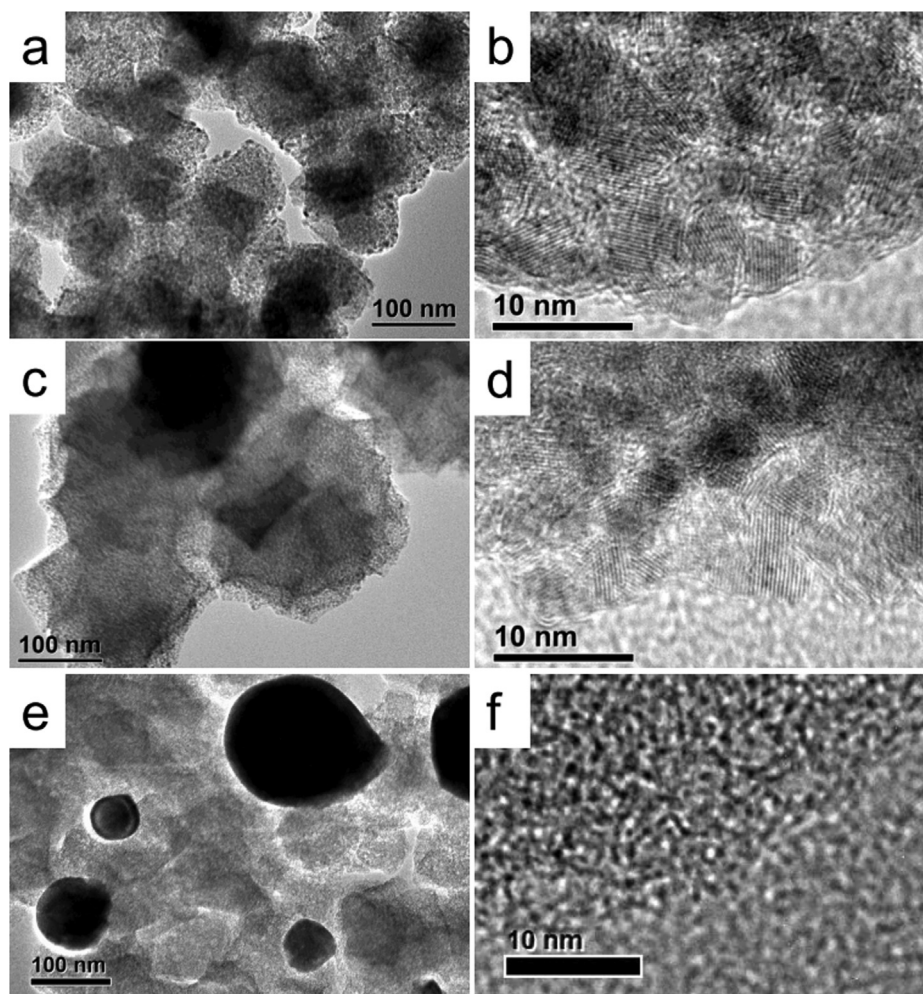


Fig. 2. Typical TEM images of (a, b) ZPCNCs-6, (c, d) ZPCNC-8 and (e, f) ZPCNC-12.

600 to 1000 °C, the diffraction peaks gradually become sharp, and other weak diffraction peaks at 34.49 and 60.22° for the (0 0 2) and (2 0 2) planes of t-ZrO₂ (PDF#88-1007) appear in ZPCNCs-10, indicating the increase of crystallinity and crystal-size of t-ZrO₂. According to the Scherrer equation, the calculated average grain size of ZrO₂ in ZPCNCs-6, ZPCNCs-8 and ZPCNCs-10 is 4.5, 4.9 and 7.9 nm, respectively. In addition, we can observe a weak diffraction peak at 28.18° in ZPCNCs-10, which belongs to the (−1 1 1) plane of m-ZrO₂ (PDF#83-0941), suggesting the phase transformation from t-ZrO₂ to m-ZrO₂ in as-prepared ZPCNCs with the increasing calcination temperature. The obtained result further confirms the reports that tetragonal phase transformed into monoclinic phase in the UiO-66 derived ZrO₂ at higher temperature, owing to the formation and growth of a monoclinic embryo during the thermal treatment [18]. XRD patterns of ZPCNCs-12 can be well-indexed to t-ZrO₂ (PDF#88-1007) and m-ZrO₂ (PDF#83-0941), and the main phase of ZPCNCs-12 is still t-ZrO₂. The sharp and distinct diffraction peaks indicate the perfect crystalline nature and

bigger size of ZrO₂. XRD pattern for ZPCNCs-14 shows two types of characteristic peaks, one is attributed to t-ZrO₂ (PDF#88-1007) and another is assigned to ZrO (PDF#89-4768) rather than ZrC (PDF#35-0784). The obtained ZrO is different from the reported results that the zirconium oxycarbide (ZrCxOy) was produced by the pyrolysis of zirconium-based MOFs under inert atmosphere [22,23]. The disappeared diffraction peaks of m-ZrO₂ in ZPCNCs-14 indicates that the m-ZrO₂ is more easily reduced to ZrO than t-ZrO₂.

The phase of carbon in ZPCNCs was analyzed by Raman spectroscopy. Fig. 3b shows the Raman spectra of all ZPCNCs samples, which demonstrate the typical characteristics of amorphous carbon. Two clear bands at around 1329 and 1590 cm^{−1} correspond to the symmetry A_{1g} mode of sp³ carbon atoms (D band) and the E_{2g} mode of sp² carbon atoms (G band), respectively [24]. Generally, the intensity ratio of D band/G band (I_{D/G}) can be used to evaluate the disorder of carbon materials [25]. It is obviously that the carbon in the as-prepared ZPCNCs is mainly amorphous, even after the heat-treatment at 1400 °C,

Table 1
Specific surface area and pore volume of ZPCNCs.

Samples	S _{BET} (m ² g ^{−1})	S _{micro} (m ² g ^{−1})	S _{meso} (m ² g ^{−1})	V _{Total} (cm ³ g ^{−1})	V _{micro} (cm ³ g ^{−1})	V _{meso} (cm ³ g ^{−1})	Average pore size (nm)
ZPCNCs-6	172	90	82	0.12	0.08	0.04	2.9
ZPCNCs-8	205	131	74	0.13	0.09	0.04	2.8
ZPCNCs-10	286	114	172	0.19	0.11	0.07	2.8
ZPCNCs-12	469	69	400	0.35	0.16	0.19	3.1
ZPCNCs-14	327	6	321	0.38	0.10	0.28	4.7

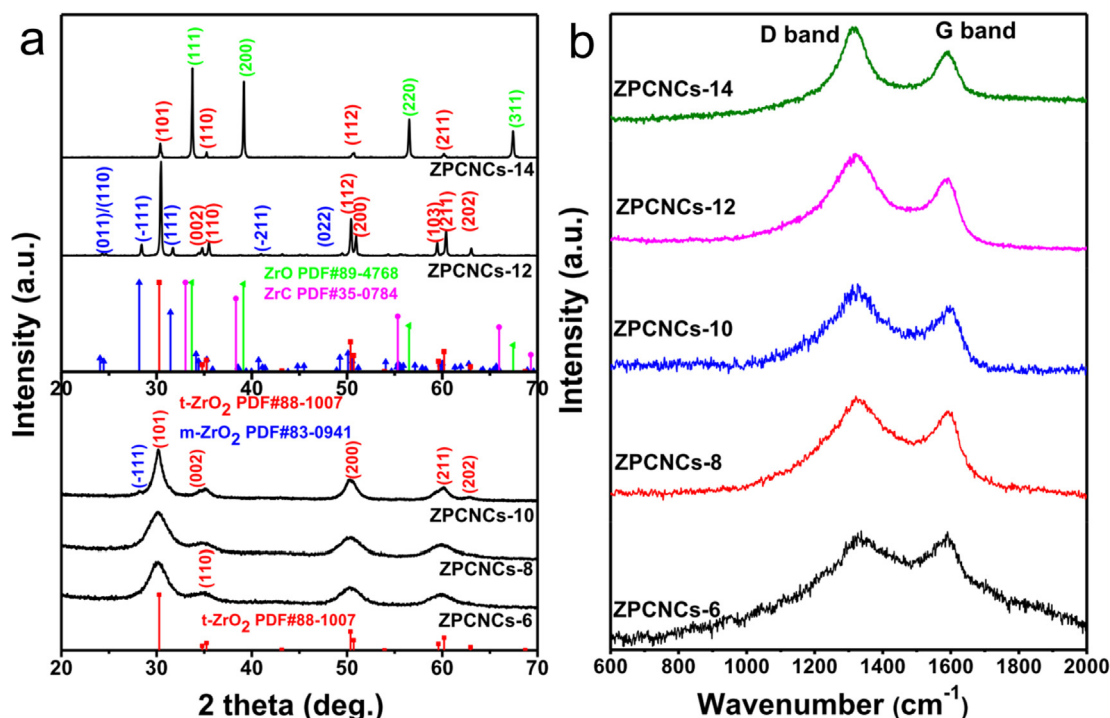


Fig. 3. (a) XRD patterns and (b) Raman spectra of ZPCNCs.

which is consistent with the XRD results.

3.2. Surface chemical state

The surface chemical state of as-prepared ZPCNCs samples was investigated by XPS. The survey scan of ZPCNCs is shown in Fig. 4a. Only zirconium, oxide and carbon present in as-prepared ZPCNCs samples, and the corresponding atomic concentration is listed Table 2. Obviously, with the increase of annealing temperature, the concentration of carbon increases, but zirconium and oxide decrease. It can be attributed that the increasing size of zirconium oxide crystals results in the decrease of the signals of zirconium and oxygen in a certain test domain ($300\ \mu\text{m} \times 700\ \mu\text{m}$, depth $< 5\ \text{nm}$). Notably, the ratio of oxygen/zirconium is higher than the stoichiometry of ZrO_2 , indicating the presence of O-containing groups on the surface of carbon materials. Fig. 4b shows the high resolution XPS of Zr 3d. Two peaks at around 185.1 and 182.7 eV ($\Delta_{\text{BE}} = 2.4\ \text{eV}$) for ZPCNCs-6 can be assigned to the Zr $3d_{3/2}$ and Zr $3d_{5/2}$ of t- ZrO_2 [26,27]. When the annealing temperature was increased to 800 and 1000 °C, the two peaks of Zr $3d_{3/2}$ and Zr $3d_{5/2}$ slightly shift to lower binding energy for ZPCNCs-8 and ZPCNCs-10, which may be attributed to the defect of oxygen atoms in t- ZrO_2 because of reduction of carbon in high temperature. For ZPCNCs-12 and ZPCNCs-14, two peaks at around 185.6 and 183.2 eV can be assigned to the Zr $3d_{3/2}$ and Zr $3d_{5/2}$ of t- ZrO_2 [28], respectively. In addition, two other peaks at 185.1 and 187.7 eV may be attributed to Zr $3d_{3/2}$ and Zr $3d_{5/2}$ of m- ZrO_2 [29], respectively. Moreover, the peak at 182.3 and 180.1 eV in ZPCNCs-14 are ascribed to the Zr $3d_{5/2}$ and Zr $3d_{3/2}$ of ZrO [28], respectively, which is from the reduction of m- ZrO_2 . In addition, no peaks below 180 eV in the Zr 3d spectra indicates no ZrC in the ZPCNCs [30]. Fig. 4c shows the O1s XPS spectra of ZPCNCs. The O1s spectra of ZPCNCs-6 can be deconvoluted into three peaks. The peak at 530.5 eV can be attributed to the Zr–O, and the peaks at 531.7 and 533.0 eV can be assigned to O–C and O=C derived from the organic ligands, respectively. For ZPCNCs-8, the O 1s spectra can be fitted to four peaks. The peaks at 530.4, 531.6 corresponds the Zr–O and O–C respectively, which is agreement well with those of ZPCNCs-6. The peaks at 532.5 and 533.8 eV can be attributed to the presence of

Zr–O–C [31]. The O1s spectra of ZPCNCs-10 is consistent with the ZPCNCs-8. For ZPCNCs-12 and ZPCNCs-14, the O1s spectra can be fitted to three peaks. The peak at 530.8/530.9 eV can be attributed to the Zr–O, and the peaks at 532.5/532.3 eV can be assigned to the presence of Zr–O–C. The C1s spectra of ZPCNCs samples is showed in Fig. 4d. It can be observed that the C1s spectra of ZPCNCs can be fitted to four peaks at 284.8, 286.1, 287.4, and 289.3 eV, which can be attributed to $\text{sp}^3\ \text{C–C}$, C–O–C, O–C–O and C=O groups. No peak of C–Zr group can be observed, indicating there is no ZrC in our as-prepared ZPCNCs samples further.

3.3. Adsorption of CBZ

3.3.1. Adsorption isotherms

Fig. 5a shows adsorption isotherms of CBZ on ZPCNCs samples, indicating that the adsorption capacity of the CBZ on ZPCNCs sharply increase with the initial concentration of CBZ from 0 to $10\ \text{mg L}^{-1}$, and then the increase tendency of adsorption capacity of CBZ slows down until adsorption equilibrium. Moreover, the equilibrium adsorption capacity of CBZ increase with the increase of calcination temperature of UiO-66 and reaches a maximum capacity $190.2\ \text{mg g}^{-1}$ at 1200 °C, which is consistent well with the specific surface area of ZPCNCs samples. It can be attributed to that the higher specific surface area of ZPCNCs-12 can possess more adsorption sites for CBZ than other ZPCNCs samples. Langmuir model and Freundlich model (see S1) was used to fit the adsorption experiment data. The obtained fitting lines and corresponding specific parameters and correlation coefficients (R^2) are shown in Figure S5 and Table 3, respectively. It indicates that the uptake profiles fit best to the Langmuir model, which means that adsorption of CBZ on ZPCNCs may a monolayer adsorption manner. In addition, the maximum theoretical adsorption capacity calculated by the Langmuir equation are 37.3, 58.4, 92.2, 210.1, $139.7\ \text{mg g}^{-1}$, respectively, which match well with the experiment values and higher than that of the pristine UiO-66 [32]. The adsorption capacity of CBZ on ZPCNCs-12 decrease with increasing temperature of solution (Figure S6), revealing the process of CBZ adsorption is exothermic reaction, which is consist with the results of thermodynamic studies

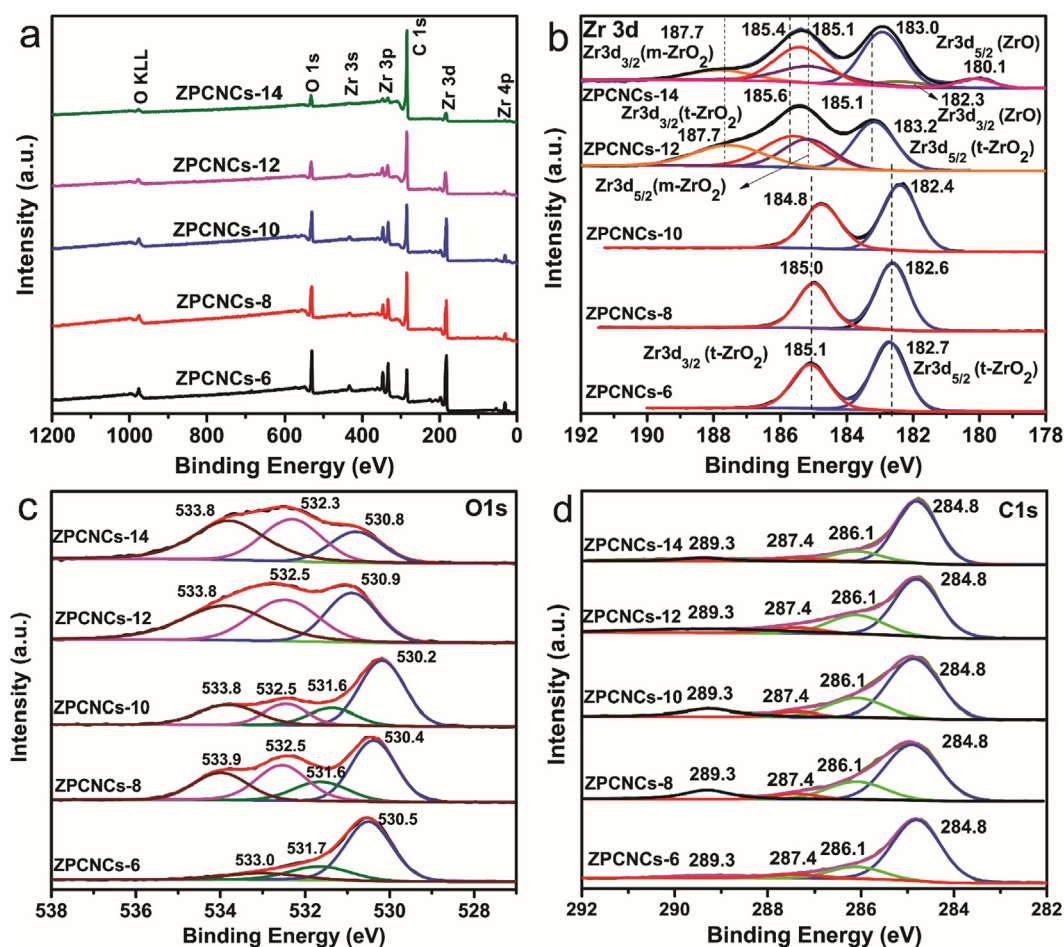


Fig. 4. XPS spectra of ZPCNCs. (a) survey scan, (b) Zr 3d, (c) O 1s, and (d) C 1s.

Table 2

Element composition of ZPCNCs from XPS spectra.

Samples	C 1s (atom %)	O 1s (atom %)	Zr 3d (atom %)	O/Zr
ZPCNCs-6	58.7	27.3	13.4	2.04
ZPCNCs-8	73.6	19.9	6.4	3.11
ZPCNCs-10	70.6	20.2	8.4	2.40
ZPCNCs-12	83.6	11.2	4.9	2.28
ZPCNCs-14	92.1	5.5	1.7	3.23

($\Delta H^\circ_{\text{CBZ}} = -66.9902 \text{ kJ}\cdot\text{mol}^{-1}$ and see S2, Figure S7 and Table S1).

3.3.2. Adsorption kinetics

The adsorption rate is a critical factor in optimizing reaction and operation conditions during the practical applications. Fig. 5b shows the adsorption kinetic of CBZ on ZPCNCs at 25 °C, it is apparently that the adsorption capacity of CBZ on ZPCNCs increase rapidly in the first 15 min and the adsorption equilibrium is reached soon after 1 h. The fast adsorption rate has a good prospect in the practical application. To gain insight into the adsorption kinetic, the pseudo-first-order and pseudo-second-order models were used to fit the kinetic data (see S3

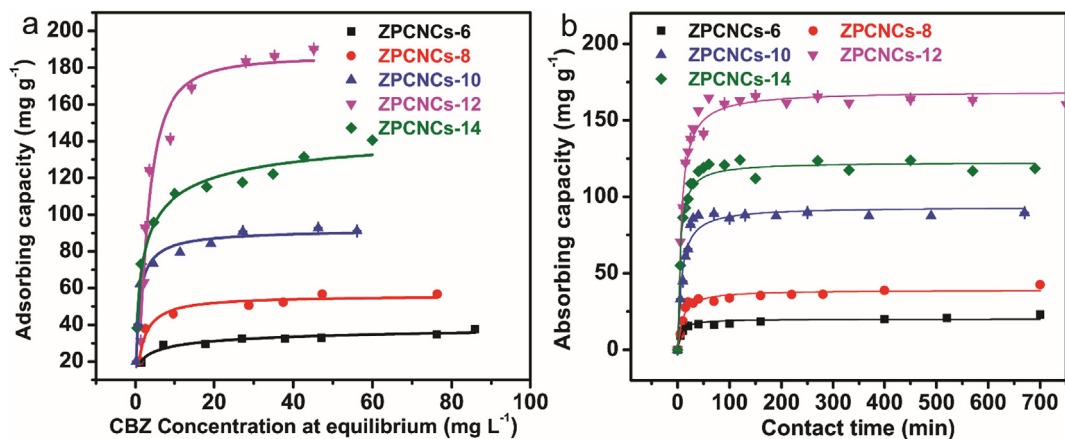


Fig. 5. (a) Adsorption isotherms and (b) adsorption kinetics of CBZ on ZPCNCs.

Table 3
Langmuir and Freundlich parameters of CBZ adsorption on ZPCNCs.

Samples	Langmuir			Freundlich		
	K_L (L mg ⁻¹)	Q_m (mg g ⁻¹)	R^2	K_f (mg ^{-1/n} L ^{1/n} g ⁻¹)	n	R^2
ZPCNCs-6	0.278	37.3	0.993	19.5	6.609	0.9129
ZPCNCs-8	0.319	58.4	0.993	25.3	4.906	0.814
ZPCNCs-10	0.942	92.2	0.998	43.0	4.537	0.819
ZPCNCs-12	0.230	210.1	0.991	49.4	2.466	0.744
ZPCNCs-14	0.388	139.7	0.991	58.7	4.420	0.901

and Figure S8), and the related adsorption kinetic parameters are listed in Table 4. The correlation coefficients of pseudo-second-order model are much higher than those of pseudo-first-order, indicating that the adsorption of CBZ on ZPCNCs fit well with the pseudo-second-order model. In addition, the theoretical maximum adsorption capacities calculated from the pseudo-second-order model agree well with the experimental values.

3.3.3. Effect of pH

As we all known, pH is a very important factor for limiting the use of adsorbents in actual wastewater treatment. Herein, because of high stability of CBZ in strong acid or alkali solution, the effect of pH on the adsorption capacity of CBZ on ZPCNCs was obtained in the pH value of 2–12. As shown in Fig. 6, there are no obvious change in the adsorption of CBZ on all five ZPCNCs during the solution pH range from 2 to 12, which indicates that the as-synthesized ZPCNCs can be used to remove CBZ from water in a wide pH range.

3.4. Adsorption interaction

The adsorption mechanisms of CBZ on ZPCNCs was studied by the characterization of ZPCNCs-12 before and after adsorption of CBZ in water. Fig. 7a shows the FTIR spectra of ZPCNCs-12, ZPCNCs-12/CBZ and pristine CBZ. For pristine ZPCNCs-12, a broad band around 540 cm⁻¹ with a pronounced shoulder near 596 cm⁻¹, which can be attributed to Zr–O stretching modes of ZrO₂ [33]. A weak band at around 740 cm⁻¹ corresponds to the Zr–O–Zr asymmetric modes of ZrO₂ [34]. Two broad bands at around 1218 and 1581 cm⁻¹ can be attributed to the stretching vibration of C–O and C=C, respectively. The weak band at 1699 cm⁻¹ can be assigned to the stretching vibration of C=O. After adsorption CBZ on ZPCNCs-12, the ratio of intensity at 540 and 596 cm⁻¹ reduces. XRD patterns (Fig. 7b) of ZPCNCs-12 and ZPCNCs-12/CBZ suggest that it is because of the reduced component of m-ZrO₂ rather than the possible interaction between ZrO₂ and CBZ. In addition, two new and weak bands at 3464 and 1678 cm⁻¹ correspond to the stretching of –N–H and –C=O in CBZ molecules, respectively. No any other new bands in the spectra of ZPCNCs-12/CBZ indicates that no new chemical bond, and the main interaction, between CBZ and ZPCNCs-12, was physical. The desorption of CBZ from ZPCNCs-12 can be easily achieved using methanol as eluent, and the recycled ZPCNCs-12 remained the high adsorption capacity even at the third cycle (Figure S9).

Table 4
Adsorption kinetic parameters of CBZ on ZPCNCs.

Samples	Pseudo-first-order				Pseudo-second-order		
	k_1 (min ⁻¹)	$Q_{e,cal}$ (mg g ⁻¹)	$q_{e,exp}$ (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	$Q_{e,cal}$ (mg g ⁻¹)	R^2
ZPCNCs-6	9.15×10^{-4}	11.8	27.5	0.654	5.24×10^{-4}	27.4	0.996
ZPCNCs-8	9.70×10^{-4}	20.9	47.5	0.800	3.15×10^{-4}	41.6	0.997
ZPCNCs-10	4.75×10^{-4}	17.9	89.7	0.232	2.39×10^{-2}	85.3	0.999
ZPCNCs-12	1.41×10^{-3}	17.6	168.1	0.264	8.03×10^{-4}	167.2	0.999
ZPCNCs-14	4.12×10^{-4}	18.6	124.1	0.051	1.48×10^{-2}	117.5	0.999

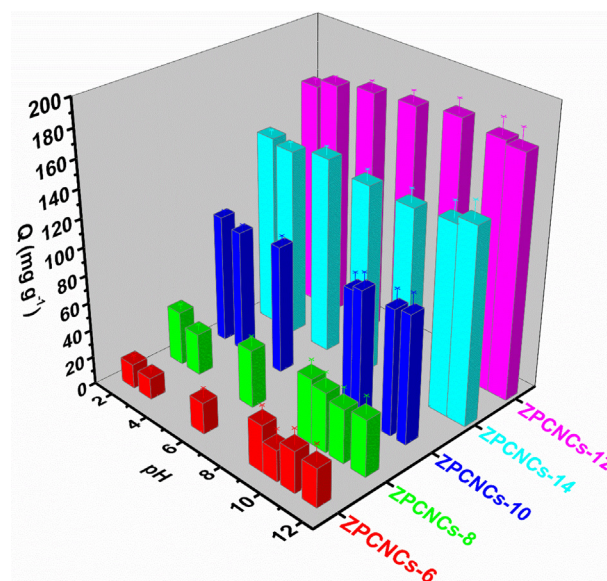


Fig. 6. pH effect of the CBZ adsorption on ZPCNCs.

Generally, the physical adsorption is dominated by intermolecular forces, including the hydrophobic interaction, hydrogen bonding, electrostatic interaction and π - π electron interaction. First, the hydrophobic interaction can be eliminated in controlling the CBZ adsorption because of the hydrophilic surface of the ZPCNCs including the ZrO₂ and oxygen-containing groups in carbon cubes. Second, hydrogen bonding is impossible the dominant adsorption interaction because of the stronger hydrogen bonding interaction between water molecules and functional groups on the surface of ZPCNCs than that of CBZ [35]. Third, zeta potential of ZPCNCs is shown in Figure S10, which indicates that the surface charge of ZPCNCs is positive at pH > the isoelectric point, but negative at pH < the isoelectric point. Meanwhile, the value of pK_a of CBZ (13.9) suggests that it is being in the form of neutral molecules between the pH of 1–13. Therefore, the electrostatic interaction is impossible to control the CBZ adsorption on ZPCNCs. Finally, carbon in ZPCNCs is a strongly π -donor because of these π -electron donor groups of the aromatic benzene rings. Meanwhile, CBZ is a π -electron acceptor because of the electron withdrawing capability of its amide group [36]. Therefore, we speculated that the π - π electron donor-acceptor (EDA) interaction should be the primary interaction for the adsorption of CBZ onto ZPCNCs. In this respect, the surface chemical environment changes of ZPCNCs-12 after adsorption of CBZ were analyzed by XPS. The N1s XPS spectra (Fig. 8a) of ZPCNCs-12/CBZ (after adsorption of CBZ) show that the N1s spectra of free CBZ can be fitted two peaks at 400.3 and 399.9 eV, which correspond to N–H and C–N, respectively. For the ZPCNCs-12/CBZ, the spectrum is deconvoluted three peaks at 401.5, 400.1 and 399.7 eV, which can be assigned to N–H, C–N and –NH₂⁺, respectively. The decreased binding energies of N–H and C–N are mainly attributed to their increased electron cloud densities from the EDA interaction between ZPCNCs-12 and CBZ. Meanwhile, it caused that the binding energies of O–C=O and

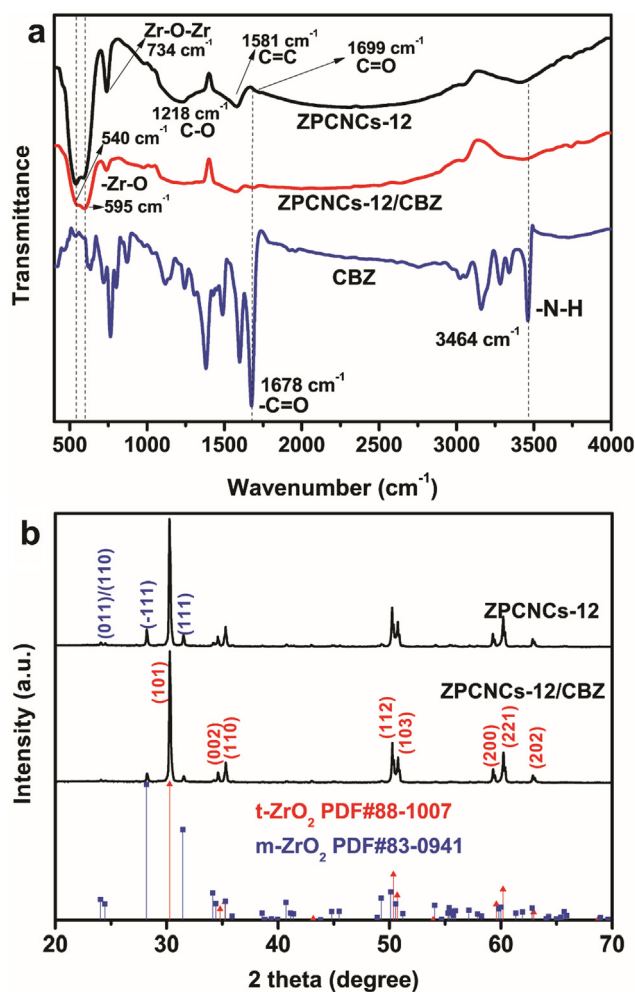


Fig. 7. (a) FTIR spectra of ZPCNCs-12, ZPCNCs-12/CBZ and CBZ. (b) XRD pattern of ZPCNCs-12, ZPCNCs-12/CBZ.

C=O, as shown in Fig. 8b, shifted up to 289.2 and 287.3 eV, respectively. Because of the existing C-N bonds in the adsorbed CBZ, the binding energy of C-O/C-N on ZPCNCs-12/CBZ stayed the same with the ZPCNCs-12.

4. Conclusion

In summary, a series of ZrO_x/porous carbon nanocomposites have been successfully synthesized via a calcination method using UiO-66 as precursor and template. The characterization results showed that the specific surface area and pore volume of the obtained nanocomposites could be effectively controlled by changing the calcination temperature. The regulatory mechanism of the specific surface area and pore volume was revealed by analyzing the morphology and structure evolution of the samples obtained at varied calcination temperature. It can be attributed to the process of growth-transformation-escape of zirconium oxide particles in carbon matrix. Finally, the as-prepared nanocomposites exhibited excellent adsorption performance for the removal of CBZ in water, and the CBZ adsorption on ZPCNCs was physical, and the dominant adsorption interaction was the EDA interaction between CBZ molecule and carbon nanocubes in ZPCNCs.

CRediT authorship contribution statement

Dezhi Chen: Conceptualization, Writing - original draft. **Xubiao Luo:** Conceptualization, Writing - review & editing. **Hang Sun:** Data curation, Writing - original draft. **Yachao Wang:** Data curation. **Zisheng Ruan:** Data curation. **Hongying Quan:** Writing - original draft. **Zhong Ren:** Writing - review & editing.

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Declaration of Competing Interest

The authors declared that there is no conflict of interest.

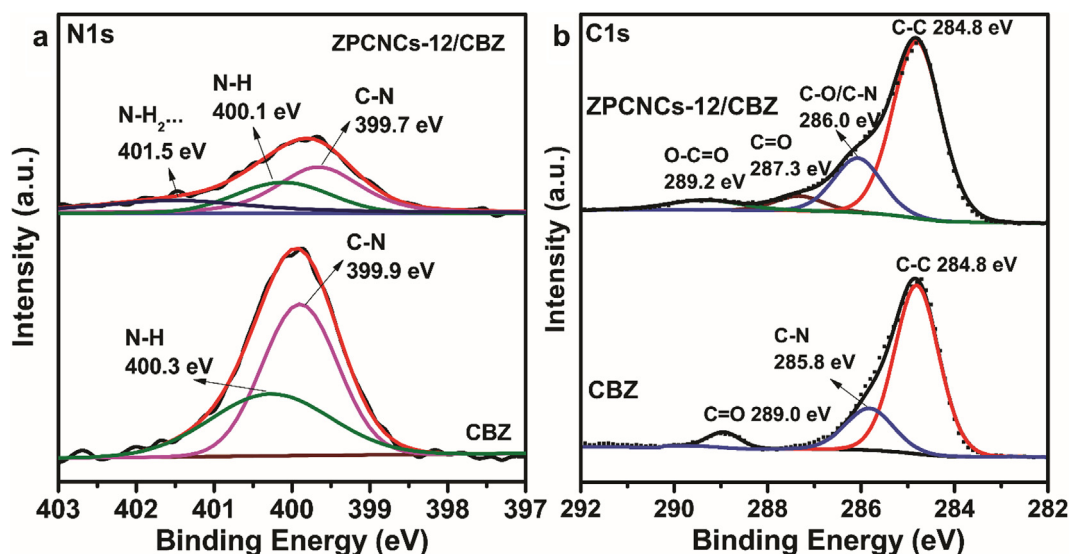


Fig. 8. XPS spectra of ZPCNCs-12/CBZ and pristine CBZ, (a) N1s and (b) C1s.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apsusc.2019.145054>.

References

- [1] S.H. Yoo, D. Jang, H.-I. Joh, S. Lee, Iron oxide/porous carbon as a heterogeneous Fenton catalyst for fast decomposition of hydrogen peroxide and efficient removal of methylene blue, *J. Mater. Chem. A* 5 (2017) 748–755.
- [2] Y. Lin, X. Wang, G. Qian, J.J. Watkins, Additive-driven self-assembly of well-ordered mesoporous carbon/iron oxide nanoparticle composites for supercapacitors, *Chem. Mater.* 26 (2014) 2128–2137.
- [3] W. Li, Z. Zhang, J. Wang, W. Qiao, D. Long, L. Ling, Low temperature catalytic combustion of ethylene over cobalt oxide supported mesoporous carbon spheres, *Chem. Eng. J.* 293 (2016) 243–251.
- [4] J. Guo, P. Li, L. Chai, Y. Su, J. Diao, X. Guo, Silica template-assisted synthesis of SnO₂@porous carbon composites as anode materials with excellent rate capability and cycling stability for lithium-ion batteries, *RSC Adv.* 7 (2017) 30070–30079.
- [5] Z. Qiang, Y.-M. Chen, B. Gurkan, Y. Guo, M. Cakmak, K.A. Cavicchi, Y. Zhu, B.D. Vogt, Cooperatively assembled, nitrogen-doped, ordered mesoporous carbon/iron oxide nanocomposites for low-cost, long cycle life sodium-ion batteries, *Carbon* 116 (2017) 286–293.
- [6] D. Chen, W. Shen, S. Wu, C. Chen, X. Luo, L. Guo, Ion exchange induced removal of Pb(II) by MOF-derived magnetic inorganic sorbents, *Nanoscale* 8 (2016) 172–179.
- [7] Y.V. Kaneti, J. Tang, R.R. Salunkhe, X. Jiang, A. Yu, K.C. Wu, Y. Yamauchi, Nanoarchitected design of porous materials and nanocomposites from metal-organic frameworks, *Adv. Mater.* (2016).
- [8] A. Banerjee, R. Gokhale, S. Bhatnagar, J. Jog, M. Bhardwaj, B. Lefez, B. Hannoyer, S. Ogale, MOF derived porous carbon-Fe₃O₄ nanocomposite as a high performance, recyclable environmental superadsorbent, *J. Mater. Chem.* 22 (2012) 19694.
- [9] S.J. Yang, S. Nam, T. Kim, J.H. Im, H. Jung, J.H. Kang, S. Wi, B. Park, C.R. Park, Preparation and exceptional lithium anodic performance of porous carbon-coated ZnO quantum dots derived from a metal-organic framework, *J. Am. Chem. Soc.* 135 (2013) 7394–7397.
- [10] Y. Li, Y.X. Zhou, X. Ma, H.L. Jiang, A metal-organic framework-templated synthesis of gamma-Fe₂O₃ nanoparticles encapsulated in porous carbon for efficient and chemoselective hydrogenation of nitro compounds, *Chem. Commun.* 52 (2016) 4199–4202.
- [11] B. Liu, H. Shioyama, H. Jiang, X. Zhang, Q. Xu, Metal-organic framework (MOF) as a template for syntheses of nanoporous carbons as electrode materials for supercapacitor, *Carbon* 48 (2010) 456–463.
- [12] B. Liu, H. Shioyama, T. Akita, Q. Xu, Metal-organic framework as a template for porous carbon synthesis, *J. Am. Chem. Soc.*, 130 (2008) 5390–+.
- [13] B. Ding, J. Wang, Z. Chang, G. Xu, X. Hao, L. Shen, H. Dou, X. Zhang, Self-sacrificial template-directed synthesis of metal-organic framework-derived porous carbon for energy-storage devices, *Chemelectrochem* 3 (2016) 668–674.
- [14] P. Zhang, F. Sun, Z. Xiang, Z. Shen, J. Yun, D. Cao, ZIF-derived in situ nitrogen-doped porous carbons as efficient metal-free electrocatalysts for oxygen reduction reaction, *Energy Environ. Sci.* 7 (2013) 442–450.
- [15] X. Li, H. Yuan, X. Quan, S. Chen, S. You, Effective adsorption of sulfamethoxazole, bisphenol A and methyl orange on nanoporous carbon derived from metal-organic frameworks, *J. Environ. Sci. (China)* 63 (2018) 250–259.
- [16] J.H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K.P. Lillerud, A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability, *J. Am. Chem. Soc.* 130 (2008) 13850–13851.
- [17] S.-C. Liu, Z.-F. Yue, Y. Liu, Mesoporous carbon–ZrO₂ composites prepared using thermolysis of zirconium based metal–organic frameworks and their adsorption properties, *J. Porous Mater.* 22 (2015) 465–471.
- [18] X. Yan, N. Lu, B. Fan, J. Bao, D. Pan, M. Wang, R. Li, Synthesis of mesoporous and tetragonal zirconia with inherited morphology from metal–organic frameworks, *CrystEngComm* 17 (2015) 6426–6433.
- [19] Z. Hasan, D.W. Cho, I.H. Nam, C.M. Chon, H. Song, Preparation of calcined zirconia-carbon composite from metal organic frameworks and its application to adsorption of crystal violet and salicylic acid, *Materials (Basel)* 9 (2016).
- [20] S. Cheng, N. Shang, X. Zhou, C. Feng, S. Gao, C. Wang, Z. Wang, High catalytic activity of a bimetallic AgPd alloy supported on UiO-66 derived porous carbon for transfer hydrogenation of nitroarenes using formic acid-formate as the hydrogen source, *New J. Chem.* 41 (2017) 9857–9865.
- [21] H.D. Wu, G. Li, Y. Li, Z.X. Geng, T.Q. Ren, T.F. Cai, Z.X. Yang, Synthesis of ZnS/C composites by metal-organic framework as high-performance lithium-ion batteries, *Cryst. Res. Technol.* 54 (2019).
- [22] J. David, G. Trolliard, C. Volkringer, T. Loiseau, A. Maître, Synthesis of zirconium oxycarbide powders using metal-organic framework (MOF) compounds as precursors, *RSC Adv.* 5 (2015) 51650–51661.
- [23] J. David, G. Trolliard, C. Volkringer, T. Loiseau, O. Masson, A. Maître, Study of the reaction mechanisms involved in the formation of zirconium oxycarbide from Metal-Organic Frameworks (MOFs) precursors, *J. Alloy. Compd.* 680 (2016) 571–585.
- [24] Y. Wang, D.C. Alsmeyer, R.L. McCreery, Raman spectroscopy of carbon materials: structural basis of observed spectra, *Chem. Mater.* 2 (1990) 557–563.
- [25] W. Wang, H. Quan, W. Gao, R. Zou, D. Chen, Y. Dong, L. Guo, N-Doped hierarchical porous carbon from waste boat-fruited sterculia seed for high performance supercapacitors, *RSC Adv.* 7 (2017) 16678–16687.
- [26] C.O. De González, E.A. García, An X-ray photoelectron spectroscopy study of the surface oxidation of zirconium, *Surf. Sci.* 193 (1988) 305–320.
- [27] S. Tsunekawa, K. Asami, S. Ito, M. Yashima, T. Sugimoto, XPS study of the phase transition in pure zirconium oxide nanocrystallites, *Appl. Surf. Sci.* 252 (2005) 1651–1656.
- [28] S. Sinha, S. Badrinarayanan, A.P.B. Sinha, Interaction of oxygen with Zr₇Fe₂₄ metglass: An X-ray photoelectron spectroscopy study, *J. Less Common Met.* 125 (1986) 85–95.
- [29] J.L. Colón, D.S. Thakur, C.-Y. Yang, A. Clearfield, C.R. Martini, X-ray photoelectron spectroscopy and catalytic activity of α-zirconium phosphate and zirconium phosphate sulfophenylphosphonate, *J. Catal.* 124 (1990) 148–159.
- [30] D.L. Cocke, M.S. Owens, XPS evidence for facile formation of surface zirconium carbides from zirconium oxide overlayer decomposition and surface carbon, *Appl. Surf. Sci.* 31 (1988) 471–476.
- [31] S.K. Dey, C.G. Wang, D. Tang, M.J. Kim, R.W. Carpenter, C. Werkhoven, E. Shero, Atomic layer chemical vapor deposition of ZrO₂-based dielectric films: Nanostructure and nanochemistry, *J. Appl. Phys.* 93 (2003) 4144–4157.
- [32] C. Chen, D. Chen, S. Xie, H. Quan, X. Luo, L. Guo, Adsorption Behaviors of Organic Micropollutants on Zirconium Metal-Organic Framework UiO-66: Analysis of Surface Interactions, *ACS Appl. Mater. Interfaces* 9 (2017) 41043–41054.
- [33] C.M. Phillippi, K.S. Mazdiyasi, Infrared and Raman Spectra of Zirconia Polymorphs, *J. Am. Ceram. Soc.* 54 (1971) 254–258.
- [34] H.R. Sahu, G.R. Rao, Characterization of combustion synthesized zirconia powder by UV-vis, IR and other techniques, *Bull. Mater. Sci.* 23 (2000) 349–354.
- [35] D. Chen, C. Chen, W. Shen, H. Quan, S. Chen, S. Xie, X. Luo, L. Guo, MOF-derived magnetic porous carbon-based sorbent: synthesis, characterization, and adsorption behavior of organic micropollutants, *Adv. Powder Technol.* 28 (2017) 1769–1779.
- [36] N. Cai, P. Larese-Casanova, Sorption of carbamazepine by commercial graphene oxides: A comparative study with granular activated carbon and multiwalled carbon nanotubes, *J. Colloid Interface Sci.* 426 (2014) 152–161.



Study on green synthesis and properties of luminescent material bis(8-hydroxyquinoline) calcium (CaQ_2)

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ABSTRACT

This work proposes a novel, effective and green synthesis method for bis(8-hydroxyquinoline) calcium (CaQ_2) that can be directly used for organic electroluminescent materials. Cycle experiment shows that the utilization of raw materials was well improved. The influence of different synthesis conditions on the crystallinity and purity of the samples was studied through X-ray diffraction spectroscopy (XRD), which indicates that the product has excellent crystallinity and high purity. EDS pattern reveals that the sample contains elements of Ca, C, N and O. The structure was investigated by Fourier transform infrared absorption spectroscopy (FTIR). Infrared absorption spectrum illustrates the Ca-O peak at 487 cm^{-1} and the existence of the quinoline ring. The crystal morphologies obtained by different synthetic conditions were detected by SEM. Since only $\text{CaQ}_2\text{-A}$ had synthesized without adding any organic solvent which had blocks with smooth surface. Luminescence properties of CaQ_2 compound were examined by fluorescence spectra at ambient temperature. The emission spectra of CaQ_2 under different synthesis conditions were obtained under the excitation of 288 nm excitation wavelength. Maximum emission wavelengths are 470 nm, 466 nm and 466 nm, respectively. The decay lifetime of CaQ_2 is 21.83 ns which was obtained at 288 nm excitation. The TG-DTA analysis shows that CaQ_2 has a high thermal stability.

1. Introduction

In recent years, OLED are highly sought after by the researchers in the monitor and lighting field. The most research focus on improving the luminescent properties of the device to seek new luminescent materials [1–5]. 8-hydroxyquinoline metal complexes have excellent electron transfer properties because of its unique intramolecular complex structure which is easy to form a stable ring structure [6]. Meanwhile, 8-hydroxyquinoline combines with different metal ions [7–9] or its derivatives combine with metal ions [10–12] can obtain different luminescent materials with the properties of photoluminescence efficiency, quantum yield, stability, light emission color, etc. At present, 8-hydroxyquinoline metal complexes are considered to be the most promising application of luminescent materials. Since 1987, Tang et al. [13] first reported that they successfully prepared the double layer organic light emitting device with green luminescent material AlQ_3 . People began to deeply research 8-hydroxyquinoline metal complexes. Tsuboi [14] et al. synthesized ZnQ_2 and MgQ_2 , observing that the emission peak was 496 and 482 nm, respectively, and the lifetime was 25 ns and 24 ns respectively. The electroluminescent properties and the blue-green light emitting mechanisms of AlQ_3 were researched by Xu [15]. Hamada [16] had studied photoluminescence and

electroluminescence properties of two valence metal ion (Be^{2+} , Mg^{2+} , Zn^{2+}) of the 8-hydroxyquinoline metal complexes. In addition, Burrows [17] discovered several green materials by discussing the photoluminescence and electroluminescence properties of trivalent metal ions (Al^{3+} , Ga^{3+} , In^{3+} , Sc^{3+}) of the 8-hydroxyquinoline metal complexes. According to the literature, most 8-hydroxyquinoline metal complexes focused on the synthesis and properties of AlQ_3 [18–23], ZnQ_2 [24–26], MgQ_2 [27] and their derivatives. In addition to researching luminescence properties of 8-hydroxyquinoline metal complexes, the exploration of synthetic conditions of 8-hydroxyquinoline metal complexes is also very important and full of great challenges, due to the inherent low yield and low purity of metal complexes by traditional ordinary liquid phase method. Duvenhage et al. [28] synthesized ZnQ_2 via co-precipitation method, while the ZnQ_2 product need to purify by recrystallization. Fukushima et al. [29] obtained three different AlQ_3 as green and blue emitting OLEDs, but the initial AlQ_3 requires purification in vacuum condition. Li et al. [30] successfully proposed two purification methods to synthesize AlQ_3 . Huo et al. [31] obtained four kinds of Zn complexes with 8-hydroxyquinoline ligands, and the average yield was about 85%. Duvenhage et al. [32] confirmed that electron donating and withdrawing groups have a big effect on the morphology of AlQ_3 . Wang et al. prepared high-purity MgQ_2 [33] via a

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facile solvothermal route, and exhibited a strong and stabilized blue-green fluorescence and linear current-voltage characteristics. Nowadays, the exploration of excellent 8-hydroxyquinoline metal complexes species and the research of their synthesis condition are very rare, therefore, it leads us to seek novel and excellent performance of the electro luminescent materials and the synthesis conditions of excellent materials. Bis(8-hydroxyquinoline) calcium had been confirmed to be a promising bluish-green fluorescent material [34] which has advantages such as comparable absolute photoluminescence efficiency to AlQ_3 and ZnQ_2 , but lack of in-depth study.

Up to now, the reports on the combination of 8-hydroxyquinoline and calcium ions are very insufficient, and the relevant research is still at an initial stage. Guerreiro [35] had mixed the acetone solution of anhydrous calcium chloride and 8-hydroxyquinoline derivative to obtain three complexes of 8-hydroxyquinoline derivative with calcium. Nagpure et al. [34] had synthesized CaQ_2 via a co-precipitation method. The currently existing synthesis method basically is chemical precipitation method, which will cause the common problems of low efficiency and low purity by adding a large number of auxiliary reagents and precipitation reagents [28,30,34], so the products obtained need further purification in order to achieve the requirements of OLED materials [28–30]. Simultaneously, the filtrate produced by ordinary chemical precipitation method cannot be recycled, it will seriously violate the concept of green and environmentally friendly. Another crucial thing is that the research of CaQ_2 is not in-depth. Some basic properties of 8-hydroxyquinoline calcium (CaQ_2) and essential optical performance parameters of CaQ_2 powder, such as fluorescence lifetime, morphology research under different preparation conditions, have not been reported by researchers.

This paper designed and synthesized high purity CaQ_2 powder via a facile and green method without adding any auxiliary reagents and precipitation reagents. As-synthesized product is high purity and has a uniform morphology. CaQ_2 emits bright blue light in the ultraviolet light irradiation and luminous performance is excellent. The influence of recycling of filtrate on yield and the morphology of CaQ_2 under different synthesized conditions was investigated. X-ray diffraction measured the molecular composition of the CaQ_2 powder. Functional groups were characterized by Fourier transform infrared spectroscopy, and the fluorescence lifetime of CaQ_2 was investigated for the first time.

2. Experimental section

CaQ_2 was synthesized at the molar ratio of calcium hydroxide: 8-hydroxyquinoline = 1:2. Took raw material of calcium hydroxide (0.4084 g, 0.0055 mol) and 8-hydroxyquinoline (1.6447 g, 0.0113 mol) into a 250 ml conical flask, injected 100 ml deionized water into the conical flask, shake gently until reagent dissolved or dispersed. Then, the color from orange red to pale yellow during the solution was stirred well at 90 °C for 4 h. After the mixture was cooled, the solid particles were filtered out, and washed 3–5 times with 85 °C deionized water. The product was then put into vacuum drying box with the condition of room temperature to 105 °C and kept the temperature for 1 hr. After cooled, get the yellow-green target product CaQ_2 -A. Filtrate reclaimed and saved until next synthesis experiment.

Synthesis of control sample: sample CaQ_2 -B was synthesized using a mixture solution of 10% anhydrous ethanol and 90% deionized water as solvent and the other conditions were same as CaQ_2 -A. In addition, CaQ_2 -C powder was synthesized by the synthetic method of literature [34] using a mixture solution of acetic acid and deionized water as solvent.

X-ray diffractions (XRD) were taken at ambient temperature in the 2 θ range of 5–70° by a Rigaku D / max 2500 X-ray diffractometer (Cu-K α radiation, λ = 1.5406 Å). Infrared spectra of the samples received in a Germany ALPHA-T infrared spectrometer with KBr disks. The photoluminescence (PL) properties of the CaQ_2 powder were measured by the equipment Hitachi F-7000 fluorospectrophotometer at room

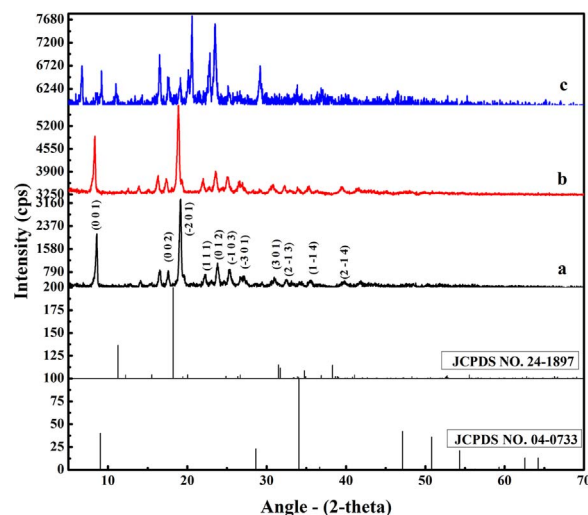


Fig. 1. XRD patterns of CaQ_2 -A (a), CaQ_2 -B (b) and CaQ_2 -C (c), the vertical lines are the standard X-ray lines for 8-hydroxyquinoline from the 24-1897 card and $\text{Ca}(\text{OH})_2$ from the 04-0733 card.

temperature with a monochromatized Xenon flash lamp 150 W as an excited source. TG-DTA analysis were acquired via an American DSC/TGA synchronous thermal equipment SDT-Q600 under dry N_2 atmosphere conditions with α -alumina (α - Al_2O_3) as a reference substance, and carried out a heating up process from ambient temperature to 900 °C, rate was 10 °C/min. The morphology of CaQ_2 was analyzed by American Nova Nano SEM 450. The elements contained in CaQ_2 were measured by British INCA 250 X-Max 50 energy disperse spectroscopy. The fluorescence lifetime decay curve was determined on a FSP980 steady-state transient fluorescence spectrometer (Edinburgh Instruments), nF920 as excitation source, and the excitation wavelength was at 288 nm.

3. Results and discussion

3.1. X-ray diffraction and X-ray energy spectrum analysis

Fig. 1 displays the X-ray diffraction (XRD) patterns of CaQ_2 -A, CaQ_2 -B and CaQ_2 -C. Through analyzing the spectrum and data, although the XRD standard card of CaQ_2 has not been reported, comparing the XRD spectra of the samples with the XRD standard card of raw material $\text{Ca}(\text{OH})_2$ (JCPDS No. 04-0733) and 8-hydroxyquinoline (JCPDS No. 24-1897), there are many new peaks have appeared, meaning the formation of new substances. The characteristic diffraction peaks of CaQ_2 -A are strong and sharp with a small amount of miscellaneous peaks, indicating that CaQ_2 -A powder has high crystallinity, large particle size and high purity. As the EDS patterns of CaQ_2 -A (a), CaQ_2 -B (b) and CaQ_2 -C (c) shows in Fig. 2, it clearly reveals that the sample CaQ_2 is composed of Ca, C, N, O (H can not be measured). Combining with the XRD spectrum analysis, we can predict the sample is CaQ_2 . More structural information will be further verified by IR. Table 1 shows the XRD peak positions and relative intensities of CaQ_2 -A, CaQ_2 -B and CaQ_2 -C. The peak numbers of CaQ_2 -A and CaQ_2 -B are almost the same, while the position of CaQ_2 -B is left shift by about 0.3° to the position of CaQ_2 -A as a whole, perhaps the reason for zero drift. In addition, the peak intensity of CaQ_2 -B is weaker than that of CaQ_2 -A. The characteristic peak intensity at the same position, CaQ_2 -C is much weaker than that of CaQ_2 -A, it shows that the addition of organic solvents will greatly affect the crystallinity of the sample. Moreover, CaQ_2 -C characteristic peaks accompany by a lot of miscellaneous peaks, perhaps because of adding organic solvents and precipitating reagents that decreases product purity. Particle size of CaQ_2 -A, CaQ_2 -B and CaQ_2 -C are given in Table 2, calculated that the average particle size of CaQ_2 -A is

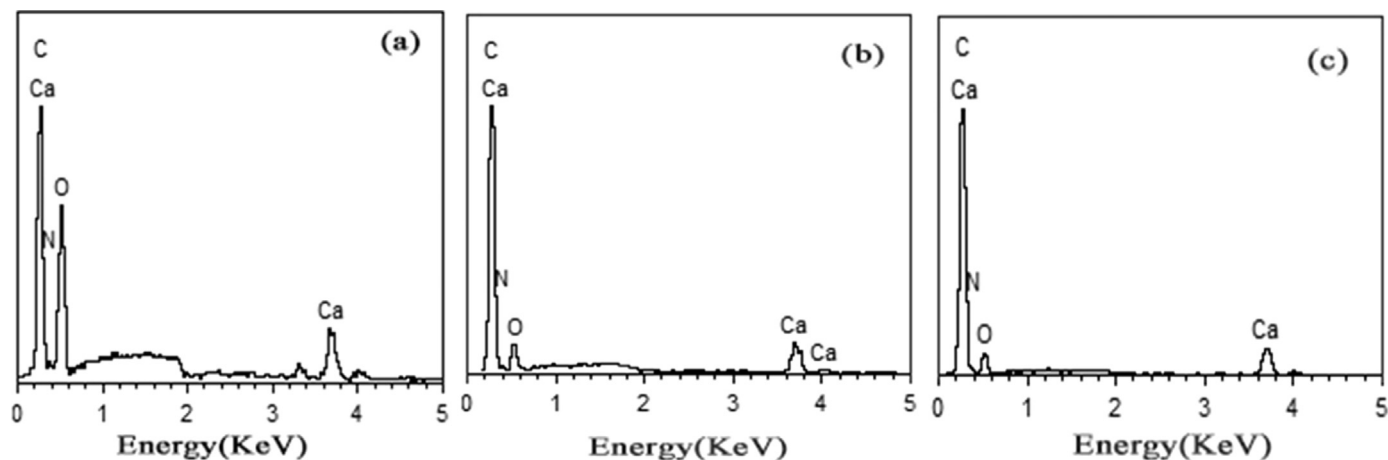


Fig. 2. EDS patterns of the CaQ₂-A (a), CaQ₂-B (b) and CaQ₂-C (c).

Table 1

XRD peak positions and relative intensities of CaQ₂-A, CaQ₂-B and CaQ₂-C.

CaQ ₂ -A		CaQ ₂ -B		CaQ ₂ -C	
Peak position (2θ)	Relative intensity (a. u.)	Peak position (2θ)	Relative intensity (a. u.)	Peak position (2θ)	Relative intensity (a. u.)
19.16	3097	18.86	2594	19.12	667
8.58	1903	8.28	1708	8.58	354
22.32	507	22.00	507	22.32	188
25.3	674	25.02	553	25.3	333
26.70	431	26.67	426	26.64	382
31.06	410	30.85	317	31	333
35.56	312	35.21	296	35.64	250

Table 2

Calculated particle size of CaQ₂-A, CaQ₂-B and CaQ₂-C using the Scherrer equation.

CaQ ₂ -A			CaQ ₂ -B			CaQ ₂ -C		
2θ(°)	β(°)	D(nm)	2θ(°)	β(°)	D(nm)	2θ(°)	β(°)	D(nm)
8.55	0.203	40.874	8.32	0.204	40.673	8.54	0.211	39.324
19.12	0.243	34.146	18.86	0.267	31.076	19.08	0.261	31.790
22.22	0.330	25.144	21.97	0.321	25.849	22.76	0.304	27.294
23.8	0.230	36.076	23.57	0.363	22.858	23.5	0.260	31.913
25.3	0.339	24.476	25.02	0.336	24.694	25.3	0.409	20.287
Dav = 32.143 nm			Dav = 29.03 nm			Dav = 30.121 nm		

slightly larger. By comparison, the crystallinity of CaQ₂-A is the best.

3.2. FTIR spectra analysis of CaQ₂

Fig. 3 shows the infrared absorption of each functional group of CaQ₂-A and CaQ₂-C clearly. The vibration absorption of Ca-O was detected at 494 cm⁻¹, and characteristic peaks of the quinolone ring were observed at 650 cm⁻¹, 734 cm⁻¹ and 792 cm⁻¹ [36]. The plane and ring deformation of the intercalated complex appeared at 561 cm⁻¹, 598 cm⁻¹ and 650 cm⁻¹. 8-hydroxyquinoline molecule stretching and ring deformation are observed at 868 cm⁻¹, 905 cm⁻¹, 1032 cm⁻¹, 1063 cm⁻¹ and 1099 cm⁻¹ [34]. The absorption bands at 650 cm⁻¹, 734 cm⁻¹, 792 cm⁻¹, 823 cm⁻¹, 868 cm⁻¹ and 905 cm⁻¹ are ascribed to C-H out of plane vibration deformation. Vibration absorption of the C=C and C=N on the pyridine ring were detected at 1601 cm⁻¹ and 1571 cm⁻¹. The C-O stretching is observed at 1032 cm⁻¹, 1063 cm⁻¹, 1099 cm⁻¹, 1234 cm⁻¹ and 1279 cm⁻¹. Characteristics absorption of the quinoline molecules were detected at 1317 cm⁻¹, 1376 cm⁻¹, 1421 cm⁻¹, 1459 cm⁻¹, 1496 cm⁻¹, 1571 cm⁻¹ and 1601 cm⁻¹ [37].

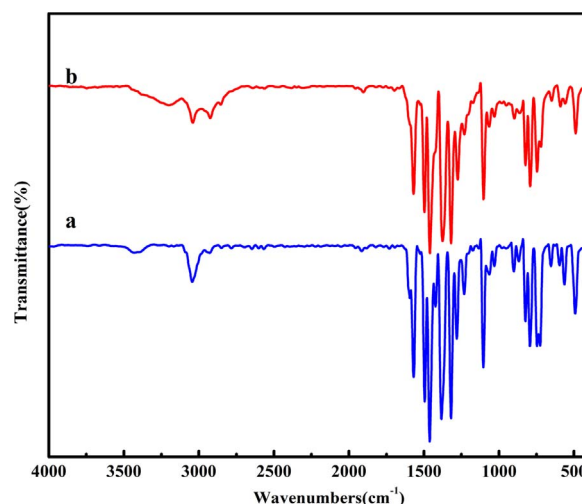


Fig. 3. FTIR spectrum of the CaQ₂-A (a) and CaQ₂-C (b).

The C-H stretching was discovered at 3045 cm⁻¹. Characteristic absorption of the phenyl or pyridine [38] is observed at 1459 cm⁻¹ and 1496 cm⁻¹. C-N stretching is observed at 1317 cm⁻¹, 1376 cm⁻¹ and 1279 cm⁻¹. The aromatic ring skeleton characteristic vibration absorption is detected at 1601 cm⁻¹, 1571 cm⁻¹, 1459 cm⁻¹ and 1496 cm⁻¹. Because it was prepared with water as solvent, the vibration absorption of the H-O appearing at 3045 cm⁻¹, indicating the existence of hydrogen bonds. Between 3045–400 wave number, the infrared vibration absorption of Fig. 3a and b are consistent, indicating the synthesis of the same substance CaQ₂. In addition, the wave number at 3418 cm⁻¹ and 3204 cm⁻¹ maybe are the absorptions of the target product, there is no clear definition now.

3.3. The influence of different synthesis methods on the morphology of CaQ₂

As shown in Fig. 4a and b describes the morphology of the CaQ₂-A powder in the low magnification and high magnification, respectively. Fig. 4a and b indicate that the CaQ₂-A powder is made up of many small particles, and part of them are agglomerated into rods. The particle shapes are consistent with the short rod shape with smooth surface. The short rod length is about 5 μm and the diameter is approximately 2 μm. Fig. 4c and d demonstrate that the CaQ₂-B powder are slender rods with rough surface. Fig. 4e–g present the morphology of the CaQ₂-C powder. 4e shows that the CaQ₂-C powder is made up of small particles with different shapes, maybe caused by impure samples. Fig. 4f and g

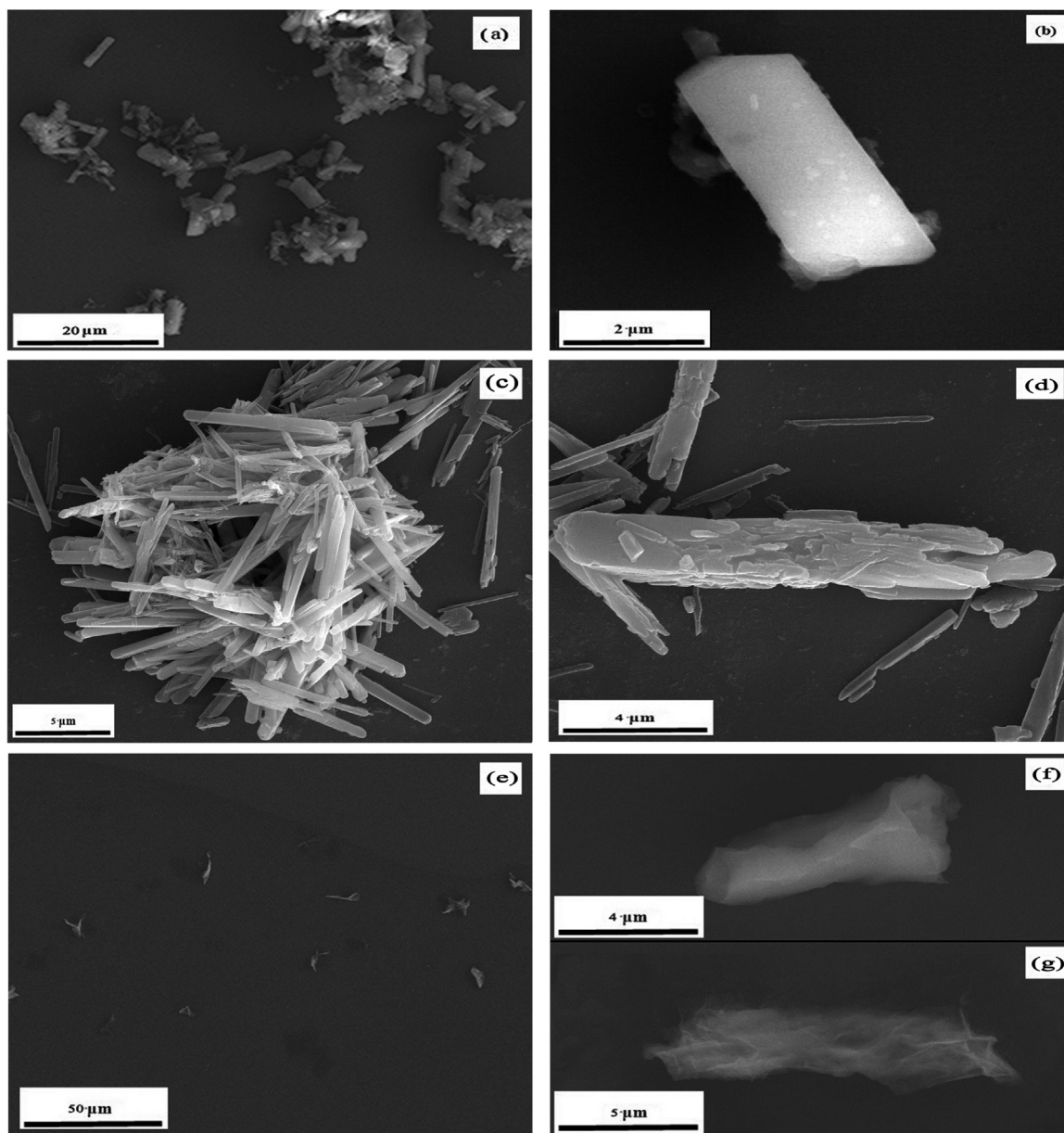


Fig. 4. a–b: SEM micrographs of CaQ₂-A, c–d: SEM micrographs of CaQ₂-B, e–g: SEM micrographs of CaQ₂-C.

indicate that shape size of the sample is varied, and the size gap is relatively larger. Furthermore, the surface of CaQ₂-B and CaQ₂-C is irregularity. By comparison, the morphology of CaQ₂-A is the best.

3.4. Luminescence analysis of CaQ₂ powder

Fig. 5 shows the excitation spectra and emission spectra of CaQ₂-A, CaQ₂-B, CaQ₂-C powder. The excitation spectra of CaQ₂ powder was obtained by scanning the full wavelength, and the maximum excitation wavelength was 288 nm. Fluorescence emission spectra was obtained under the maximum excitation wavelength of CaQ₂ powder, and the maximum emission wavelength were 470 nm, 466 nm and 466 nm, respectively, which belongs to the blue band. The fluorescence intensity of CaQ₂-A is significantly larger than that of CaQ₂-B and CaQ₂-C, indicating that the synthesis conditions have a significant effect on the fluorescence intensity. The organic solvent weakens the fluorescence intensity of CaQ₂, which is highly consistent with XRD (Fig. 1) and SEM (Fig. 4). The fluorescence spectra of CaQ₂-A shows a red shift of 4 nm with respect to the fluorescence spectra of CaQ₂-B and CaQ₂-C, it is

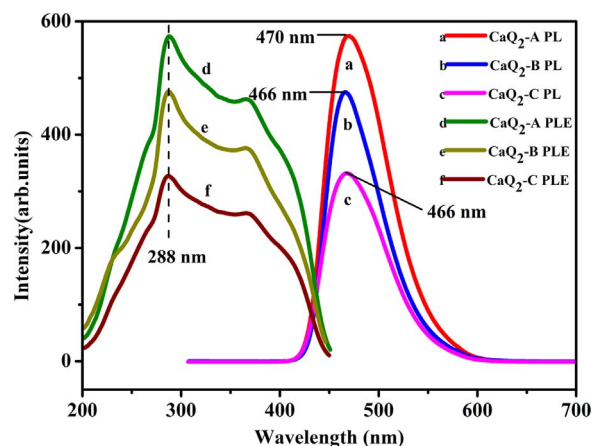


Fig. 5. PL and PLE spectra of CaQ₂-A, CaQ₂-B, CaQ₂-C.

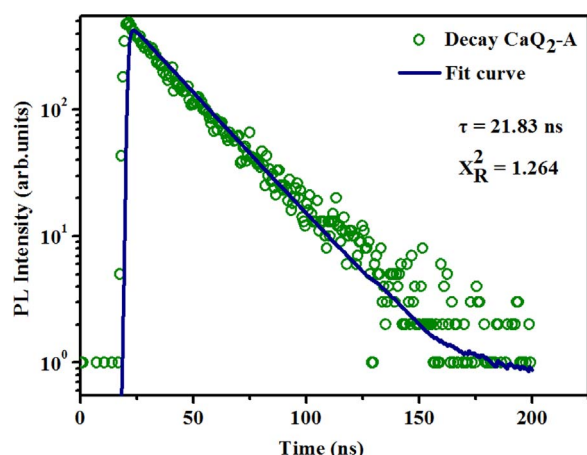


Fig. 6. Fluorescence decay and fit curve of CaQ₂-A.

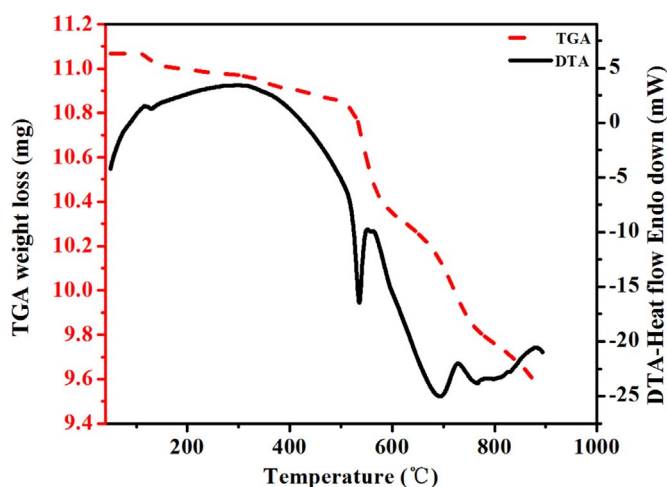


Fig. 7. TG-DTA spectrum of the CaQ₂-A powder.

attributed to a different orientation and accompanied by delocalization π - π^* transition of CaQ₂-A molecular structure.

The fluorescence lifetime decay curve of CaQ₂ powder is showed in Fig. 6. The lifetime decay data was obtained by excitation wavelength 288 nm at room temperature. Through software fitting processing, the lifetime decay curve is typical single exponential, and fit report illustrates that PL lifetime of CaQ₂ powder is 21.83 ns, longer than AlQ₃ which is well fitted with single exponential functions [39].

3.5. Thermo-gravimetric analysis of CaQ₂ powder sample

As shown in Fig. 7, in the 120–138 °C range, the TG curve exhibits an obvious weight loss (about 0.49%). In the DTA curve there have a weak endothermic peak at 127 °C due to the evaporation of water molecules. After the product dried at 105 °C, the residual water molecules decrease and the percentage of weight loss was small. In the DTA curve, at about 74 °C and 176 °C, the melting and vaporization [40] peak of 8-hydroxyquinoline did not appear, indicating that 8-hydroxyquinoline reacted completely. TG curve shows a relatively slow process of weight loss at 140–520 °C (mass lost about 1.73%), while the DTA curve without obvious endothermic peak or exothermic peak at the same position, that was attributed to dehydration of the inner layer complex combination water. A fast weightlessness process during 520–580 °C is discovered in the TG curve, and corresponding to a strong endothermic peak at 535 °C in the DTA curve, which comes down to the thermal decomposition and evaporation of the inner layer 8-hydroxyquinoline. The produced carbon dioxide would reacted with CaCO₃.

Table 3

The yield results of the filtrate cycle experiment.

Number of cycles	0	1	2	3	4	5	6	Average value
Yield / %	93.14	98.25	95.82	96.47	95.27	96.12	96.54	95.94

During 580–900 °C, TG curve had a slightly slower weight loss process with an obvious exothermic peak appearing at 729 °C. At 900 °C, the TG curve still has a downward trend, which is due to the ligand final pyrolysis, carbon was oxidized and the structure of -OH dehydroxylating, calcium carbonate decomposed to CaO.

3.6. Influence of recycling of filtrate on yield

The relationship between the number of cycles and the yield is showed in Table 3. The yield of the first reaction is 93.14%, while the first cycle is reach 98.25%, indicating that a small amount of incomplete reaction of raw materials in the next experiment to continue the reaction, well increase in atomic utilization. After multiple cycles, the yield maintain at above 95% and the average value up to 95.94%. Compare with the traditional chemical precipitation method, the disadvantage of ordinary liquid phase is low yield and low purity. According to the previous reports, the highest yield of ordinary liquid phase was below 90%, while the scheme designed in this paper has the advantages of high yield. The filtrate cycle experiment indicates that the experiment is green and environmentally friendly. The synthetic method of this paper has a great value in commerce and scientific research.

4. Conclusion

High-purity CaQ₂-A with a high intensity of blue photoluminescence were synthesized by a facile, efficient and green method without any auxiliary reagents. The addition of an organic solvent and other different synthetic conditions have a great influence on the crystallinity, purity, morphology and fluorescence properties of CaQ₂. The crystallinity of CaQ₂ obtained without organic solvent is better than that obtained by adding an organic solvent. The shape of CaQ₂-A is a short rod with smooth surface, and its morphology is more regular than CaQ₂-C. The maximum emission wavelengths are 470 nm, 466 nm and 466 nm for CaQ₂-A, CaQ₂-B and CaQ₂-C, respectively. CaQ₂-A has the maximum fluorescence intensity, indicating that the organic solvent will weaken the fluorescence intensity. The red shift by 4 nm of CaQ₂-A from the fluorescence spectra of CaQ₂-B and CaQ₂-C, which is attributed to a different orientation and accompanied by delocalization π - π^* transition of CaQ₂-A molecular structure. Fluorescence lifetime of CaQ₂ powder is 21.83 ns. CaQ₂ has high thermal stability. The result of cycle experiments shows that the method designed is green and high yield. This article provides a novel green synthetic method for the preparation of excellent performance of CaQ₂ which can be directly used for organic electroluminescent materials.

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References

- [1] L.B. Chao, H.B. Wang, N.Z. Zhuo, J. China Light Light. 103 (2015) 10–14.
- [2] R. Ballardini, G. Varani, M.T. Indelli, et al., Inorg. Chem. 25 (1986) 3858–3865.
- [3] B.S. Xu, Y.Y. Hao, H. Wang, et al., Solid State Commun. 136 (2005) 318–322.
- [4] Y.L. Sui, B. Yan, J. Photochem. Photobiol. A 182 (2006) 1–6.
- [5] L.S. Sapochak, F.E. Benincasa, R.S. Schofield, et al., J. Am. Chem. Soc. 124 (2002)

- 6119–6125.
- [6] Q.Z. Lv, J. Liaoning Teach. Coll. 10 (2008) 13–14.
- [7] O.M. Khreis, W.P. Gillin, M. Somerton, et al., *Org. Electron.* 2 (2001) 45–51.
- [8] H. Wang, W.S. Wang, H.S. Zhang, *Talanta* 53 (2001) 1015–1019.
- [9] Y.F. Xu, H.J. Zhang, H.Y. Li, et al., *Appl. Surf. Sci.* 252 (2006) 2328–2333.
- [10] M. Ghedini, M.L. Deda, I. Aiello, et al., *Synth. Met.* 138 (2003) 189–192.
- [11] M. Ghedini, M.L. Deda, I. Aiello, et al., *Inorg. Chim. Acta* 357 (2004) 33–40.
- [12] A. Mishra, P.K. Nayak, N. Periasamy, *Tetrahedron Lett.* 45 (2004) 6265–6268.
- [13] C.W. Tang, S.A. Vanslyke, *Appl. Phys. Lett.* 51 (1987) 913–915.
- [14] T. Tsuboi, Y. Nakai, Y. Torii, *Cent. Eur. J. Phys.* 10 (2012) 524–528.
- [15] X.L. Xu, Z. Xu, Y.B. Hou, et al., *J. Appl. Phys.* 89 (2001) 1082–1086.
- [16] Y. Hamada, T. Sano, M. Fujita, et al., *Jpn. J. Appl. Phys.* 32 (1993) L514–L515.
- [17] P.E. Burrows, L.S. Sapochak, D.M. McCarty, et al., *Appl. Phys. Lett.* 64 (1994) 2718–2720.
- [18] K.S. Yang, H.K. Shin, C. Kim, et al., *Synth. Met.* 152 (2005) 245–248.
- [19] X. Ma, G.K. Lim, K.D.M. Harris, et al., *Cryst. Growth Des.* 12 (2012) 5869–5872.
- [20] N. Salah, S.S. Habib, Z.H. Khan, *J. Fluoresc.* 23 (2013) 1031–1037.
- [21] J.L. Rao, K. Bhanuprakash, *J. Mol. Model.* 17 (2011) 3039–3046.
- [22] B.R. Kanchibotla, K. Garre, D. Aurongzeb, *J. Appl. Phys.* 106 (2009) 096101–096103.
- [23] H. Li, F. Zhang, Y. Wang, et al., *Mater. Sci. Eng. B* 100 (2003) 40–46.
- [24] J. Seungjun, P. Soogil, *Am. J. Infect. Control* 39 (2000) E185–E186.
- [25] M. Cho, W.J. Park, J.G. Lee, et al., *Trans. Electr. Electron. Mater.* 3 (2002) 16–19.
- [26] Y.Q. Sun, Y.L. Lei, J. Gao, et al., *Chem. Commun.* 50 (2014) 10812–10814.
- [27] C.T.R. Guerreiro, C.A. Ribeiro, M.S. Crespi, et al., *J. Therm. Anal. Calorim.* 67 (2002) 419–424.
- [28] M.M. Duvenhage, J.J. Terblans, M. Ntwaeaborwa, et al., *Physica B* 480 (2015) 141–146.
- [29] T. Fukushima, H. Kaji, *Org. Electron.* 13 (2012) 2985–2990.
- [30] H. Li, F. Zhang, Y. Wang, et al., *Mater. Sci. Eng. B* 100 (2003) 40–46.
- [31] Y. Huo, J. Lu, S. Hu, et al., *J. Mol. Struct.* 1083 (2015) 144–151.
- [32] M.M. Duvenhage, H.G. Visser, O.M. Ntwaeaborwa, et al., *Physica B* 439 (2014) 46–49.
- [33] X. Wang, M. Shao, L. Li, *Thin Solid Films* 519 (2010) 231–234.
- [34] I.M. Nagpure, M.M. Duvenhage, S.S. Pitale, et al., *J. Fluoresc.* 22 (2012) 1271–1279.
- [35] C. Guerreiro, C. Ribeiro, M. Crespi, *J. Therm. Anal. Calorim.* 70 (2002) 437–445.
- [36] J. Chen, G.Y. Liu, J.C. Deng, *J. Hubei Automot. Ind. Inst.* 24 (2010) 51–53.
- [37] R.J. Magee, L. Gordon, *Talanta* 10 (1963) 961–966.
- [38] J.E. Tackett, D.T. Sawyer, *J. Inorg. Chem.* 3 (1964) 692–696.
- [39] A.D. Walser, I. Sokolik, R. Priestley, et al., *Synth. Met.* 84 (1997) 877–878.
- [40] N. Khaorapapong, M. Ogawa, *J. Phys. Chem. Solids* 71 (2010) 1644–1650.



Nitrogen-doped hierarchically structured porous carbon as a bifunctional electrode material for oxygen reduction and supercapacitor

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ABSTRACT

Development of an efficient electrode material with robust porous architecture, high catalytic activity and excellent electrochemical performance toward both oxygen reduction reaction (ORR) and supercapacitor is extremely important. Herein, a facile route to fabricate nitrogen-doped hierarchical porous carbon (NHPC) materials as a bifunctional electrode material for ORR and supercapacitors is presented. The as-prepared NHPC-0.5 integrate the feature of high-level nitrogen-doping (12.1 at %), large specific surface area (up to 1798.4 m² g⁻¹) and hierarchical multi-pores of cross-linked micro and mesoporous channels. When used as ORR electrocatalyst, the NHPC-0.5 demonstrated highest selectivity (four-electron transfer process), high activity (half-wave potential 0.883 V vs. RHE, initial potential 1.004 V vs. RHE) and favorable tolerance against methanol. When tested its application in zinc-air batteries, its maximum output power density was 25.1 mW cm⁻², and delivers a superior durability of negligible potential loss after 100 cycles. When applied in supercapacitor, the NHPC-0.5 can deliver a high specific capacitance of 283.7 F g⁻¹ at current density of 1 A g⁻¹ in 1 M H₂SO₄ electrolyte, and outstanding cyclic stability (105.8% capacitance retention after 40,000 cycles). Moreover, a symmetric supercapacitor (NHPC-0.5//NHPC-0.5) can release an energy density of 11.3 W h kg⁻¹ at the power density of 502 W kg⁻¹. The encouraging results of this work may provide a new perspective to construct N-doped hierarchical porous carbon materials in energy storage devices with excellent electrochemical performance.

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1. Introduction

To meet the ever-increasing and urgent demands for sustainable and environmentally friendly alternative energy caused by excessive burning of large quantities of fossil fuels, abundant advanced materials have been investigated for energy conversion and storage system. Among the various advanced materials, hierarchical porous carbon is one of the most versatile electrode material in ORR [1–3] and supercapacitors [4–6], because of its high specific surface area, high porosity with variable pore sizes and pore structures, better

electrical conductivity and stable physicochemical properties [7–9].

Generally, several factors significantly affect the ORR and supercapacitor performances of hierarchical porous carbon, including specific surface area, controllability of pore size and electrical conductivity [10–12]. The hierarchal porosity can significantly enhance the electrochemical performances of the carbon materials. The micropores bring about large specific surface to provide effective active sites, and the mesopores/macropores served as ions reservoirs, offering convenient pathway to achieve more active sites, greatly decreasing the ionic resistance, which are crucial for the application of ORR and supercapacitors [13]. Moreover, the ORR and supercapacitors performance of hierarchical porous carbon can be significantly improved by doping of heteroatoms (P, B, S, and N, etc.) [14–17]. It has been proved that the

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heteroatoms doping, especially N atom can improve the chemical composition of the surface of materials, upgrade the hydrophilicity and electronic conductivity of carbon materials, substantially offer additional pseudocapacitance to improve the supercapacitive performance [12,18,19]. When used in electrocatalysts, the introduction of N atoms can conduct a charge delocalization in the sp^2 hybridized carbon skeleton, which is beneficial to the oxygen adsorption and reduction, bring about the considerable increasing in electrocatalysts performance [20]. In addition, N-doping can effectively enhance the wettability of the electrode materials, and endows porous carbon with additional redox reaction for pseudocapacitors [21]. Accordingly, it is extremely important to explore a facile and efficient method to prepare high-level N-doped porous carbon materials with hierarchical porous structure simultaneously for the applications of ORR and supercapacitors.

Various routes have been exploited to fabricate heteroatom-doped hierarchical porous carbon, such as, non-template method [22–24] and template method, including soft template [22,23,25,26], hard template [27] and post-activation treatment [28–32]. Among the various methods mentioned above, template method can not only greatly simplify the synthesis procedures of carbon materials, offer them with appropriate pore structure, but also dope other non-carbon elements in organic precursors simultaneously [33,34]. Despite the great achievements of previous literature reports, their ORR and supercapacitor performance usually restricted by low specific capacitance, small energy density and dissatisfied cycle stability.

Herein, N-doped hierarchical porous carbon (NHPC) was fabricated via templated polyacrylonitrile (PAN) solution by using aqueous suspension of porogenic fillers of SiO_2 and $ZnCl_2$. The obtained NHPCs possessed large specific surface area ($1798\text{ m}^2\text{ g}^{-1}$), highly nitrogen content (12.1 at.%) as well as interconnected hierarchical multi-pores structure of micropores and mesopores, demonstrated the desired features for high performance electrocatalytic and supercapacitor. As expected, the as-prepared NHPCs showed highly active for the electrocatalysis in an alkaline electrolyte. Notably, when used as cathode of zinc-air battery, the as-prepared NHPCs exhibited a maximum output power density of 25.01 mW cm^{-2} . In addition, the NHPCs displayed excellent performance in supercapacitor with a high specific capacitance (283.7 F g^{-1} at a current density of 1 A g^{-1} measured in three-electrode system), high energy density (11.3 W h kg^{-1}) and outstanding cyclic capability (capacitance retention of 99.3% after 12,000 cycles at a current density of 6.7 A g^{-1} in two-electrode system). Those outstanding performance endow the NHPCs served as promising candidate material in the application of electrocatalysis and supercapacitor.

2. Materials and methods

2.1. Preparation

Zinc chloride (98%), PAN (MW:85000), nano-size silica ($15 \pm 5\text{ nm}$), Nafion (5 wt%) solution were purchased from Shanghai Macklin. All chemicals were used as received without purification.

The hierarchical porous carbon materials were prepared according to the following procedures: a certain amount of zinc chloride ($ZnCl_2$) was dissolved in deionized water under the condition of continuous stirring to obtain an aqueous solution, and the concentration of $ZnCl_2$ in the solution was kept at 60 wt% to guarantee complete dissolution of PAN. Then PAN (0.5 g) and silica (0, 0.125, 0.25 and 0.375 g, respectively) were added to the above aqueous solution slowly by constantly stirring for at least 1 h at ambient temperature to obtain a homogenous suspension. Subsequently, the suspension was freeze-dried for 24 h. Following, in the

carbonization process, the freeze-dried products was first stabilized at $280\text{ }^\circ\text{C}$ with heating rate of $1\text{ }^\circ\text{C min}^{-1}$ for 1 h under air atmosphere, and then heated to $800\text{ }^\circ\text{C}$ at a temperature rate of $5\text{ }^\circ\text{C min}^{-1}$ under N_2 atmosphere and kept for 0.5 h. Finally, the products were leached with HF solution to etch the SiO_2 template and washed with deionized water until the pH of filtrate was close to neutral and dried overnight to obtain N-doped hierarchical porous carbon materials. The as-prepared materials were expressed as NHPC-X, where X represents the mass ratio of SiO_2 to PAN (0, 0.25, 0.5 and 0.75, respectively).

2.2. Characterization

The morphologies and structures of the as-prepared products were investigated by scanning electron microscope (FEI Quanta 250) and transmission electron microscopy (FEI Talos F200X). The crystal structure of the products was tested by X-ray powder diffractometer (Bruker, D8 Advance) using $Cu\text{ K}\alpha$ radiation with a scan range of $10\text{--}80^\circ$. The elemental composition and chemical state of the materials were characterized by an Axis Ultra X-ray photoelectron spectroscopy (Kratos). The nitrogen adsorption-desorption isotherms were recorded on a TriStar II 3020 instrument (Micromeritics) at 77 K to evaluate the pore structures of the samples. The specific surface area and pores size distributions of the samples were calculated by Brunner-Emmet-Teller (BET) method and density functional theory (DFT), respectively. The micropore surface area was determined by t-plot method.

2.3. ORR testing

The ORR performance of the NHPCs were tested by cyclic voltammogram (CV) and linear scan payment map (LSV) techniques using Shanghai Chen Hua CHI660E electrochemical workstation. The measurement was conducted in a three-electrode system, in which the Pt wire, and saturated Ag/AgCl electrode were served as the counter and reference electrode, respectively. The HP-1 ring-disk electrode with a glassy carbon disk was employed as working electrode. Amounts of 5 mg NHPCs were dissolved in the solution containing 450 μL of deionized water and 50 μL of Nafion (5 wt%), the mixture was ultrasonic agitated for 1 h to gain uniform ink. Then 10 μL of the ink was dropped onto the ring-disk electrode with 0.2475 cm^2 geometrical cross section area and naturally dried to make the working electrode. All the tests were performed in 0.1 M KOH electrolyte, and the electrolyte was purged with N_2 or O_2 for 30 min before testing. All measured potentials were converted into a reversible hydrogen electrode (RHE) according to the following formula (1):

$$E_{vs\text{ RHE}} = E_{vs\text{ MP}} + 0.059pH + 0.197(V) \quad (1)$$

where $E_{vs\text{ RHE}}$ is the potential vs. reversible hydrogen electrode, $E_{vs\text{ MP}}$ is the measured potential.

The formulas for calculating the average number of electrons transferred (n) during the oxygen reduction reaction were as follows:

$$J^{-1} = J_k^{-1} + B^{-1}\omega^{-1/2} \quad (2)$$

$$B = 0.62nFA\nu^{-1/6}C_{O_2}D_{O_2}^{2/3} \quad (3)$$

where J (mA cm^{-2}) is the measured current density, J_k (mA cm^{-2}) is the kinetic current density, ω (rad s^{-1}) is the angular velocity of the electrode rotation, n is the number of electrons transferred per each O_2 molecule, A (0.2475 cm^2) is the geometric area of the electrode, F

(96485 C mol⁻¹) is the Faraday constant, and ν (cm² s⁻¹) is the viscosity of 0.1 M KOH. C_{O_2} (1.2×10^{-6} mol cm⁻³) is the concentration of O₂ in 0.1 M KOH, and D_{O_2} (1.9×10^{-5} cm² s⁻¹) is the diffusion coefficient of O₂ in 0.1 M KOH.

2.4. Zinc-air battery testing

A zinc-air battery was assembled to evaluate the ORR efficiency. The air cathode was made with 5 mg of NHPCs, 450 μ L of deionized water and 50 μ L of Nafion (5 wt%) and ultrasonicated for 1 h to obtain a homogenous ink. Then the ink was uniformly dropped onto carbon paper with an area of 1 cm² to achieve mass loading of 1 mg cm⁻². A polished zinc sheet was used as the anode. The measurement was performed in two-electrode system, cathode was the carbon paper partially coated with copper foil, anode was the zinc plate (2×1 cm), 6 M KOH solution was adopted as electrolyte. Primary Zn–air battery was measured by LSV method to obtain a polarization curve of the NHPCs. The galvanostatic discharge-charge (GCD) cycling was carried out on a LAND testing system at the current density of 20 mA cm⁻².

2.5. Supercapacitor testing

The supercapacitor performance of the NHPCs were tested using CV, GCD and the electrochemical impedance spectroscopy (EIS) in three-electrode system and two-electrode systems, respectively. The working electrode was made by mixing the NHPCs, PVDF and carbon black with a mass ratio of 8:1:1 in poly-2-methyl-pyrrolidone to obtain a homogeneous slurry, then the slurry was brushed onto a carbon cloth and naturally dried. The mass loading of NHPCs on the carbon cloth was about 3–4 mg cm⁻². A Pt foil and saturated Ag/AgCl electrodes served as the counter and the reference electrode in three-electrode system, respectively. For the two-electrode systems, two identical NHPCs electrodes with the same mass loading were pressed together using a polypropylene membrane as separator. All the measurements were performed in 1 M H₂SO₄ solution at room temperature.

The specific capacitance of the NHPCs in three-electrode system and two-electrode systems were calculated according to the formula (4), the energy density and power density of the NHPCs in two-electrode systems were calculated in accordance with the formula (5) and the formula (6), respectively.

$$C = \frac{I \times \Delta t}{m \times \Delta V} \quad (4)$$

$$E = \frac{1}{2 \times 3.6} C (\Delta V)^2 \quad (5)$$

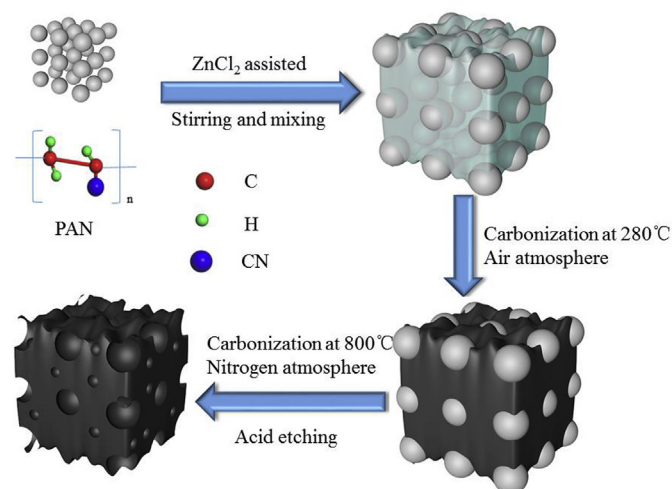
$$P = \frac{E \times 3600}{\Delta t} \quad (6)$$

where the gravimetric specific capacitance is C (F g⁻¹), the applied current is I (A), the discharge time is Δt (s), the mass of active materials in the working electrode is m (g), the working potential range is ΔV (V), the energy density is E (W h kg⁻¹); the power density is P (W kg⁻¹).

3. Results and discussion

3.1. Characterization of NHPCs

The synthesis procedure of the NHPCs is briefly illustrated in Scheme 1. PAN was a ubiquitous precursor for preparing N-doped porous carbon materials on account of its high nitrogen content and



Scheme 1. Synthesis process of N-doped hierarchical porous carbon materials.

well-established carbonization chemistry. SiO₂ nanoparticles were used as the template. After freeze-drying process, water was removed, and silica-PAN composites yielded. During the stabilization and carbonization stage, PAN can be readily converted into an N-doped porous carbon framework, the SiO₂ nanoparticles worked as a hard template for mesopores. The ZnCl₂ was not only used as pore-forming agent to produce great quantity micro/mesopores inside the carbon network, but also served the dual role of a solubility enhancing porogen to promote the co-dissolution of PAN in aqueous solution containing SiO₂. During further etching, the silica template can be easily eliminated in HF solution and obtained the NHPCs with hierarchical pore structures.

SEM analysis was employed to study the microstructure of the as-prepared NHPCs, and the results are exhibited in Fig. S1. As shown in the Figs. S1a–b, the NHPC-0.5 exhibits a three-dimensional (3D) honeycomb morphology established by loose laminated porous carbon skeletons with abundant visual pores. From the SEM image of the edge of the material, it is made up of small pieces stacked layer by layer, and the outer edge is slightly uneven in steps. Figs. S1c–d clearly demonstrated that the numerous interconnected pores possess distinguishing shapes and sizes, macropores of several hundreds of nanometers and mesopores of tens of nanometers are observed in the sample. The three-dimensional cross-linked porous structure is beneficial to the practical application in electrochemistry. More details of the pore morphology and structure were further studied by the TEM, as displayed in Fig. 1 and Fig. S2. It is confirmed from Fig. 1a that the NHPC-0.5 has a highly porous characteristic with multi-pores of interconnected meso- and micro-pores, which were formed during the process of pyrolysis and acid etching because of the volatilization of ZnCl₂ and removal of SiO₂. Fig. 1b and c showed the high-resolution TEM (HRTEM) of the selected regions in Fig. 1a, the selected area electron diffraction (SAED) pattern proved the amorphous carbon structure. The high-angle circular dark-field scanning TEM (HAADF-STEM) image (Fig. 1d) further confirmed the three-dimensional (3D) hierarchical porous structures of the sample, the corresponding energy dispersive spectrometer (EDS) element mapping images (Fig. S2) reveals the uniform dispersion of C, O, and N elements throughout the sample.

The specific surface area, pore volume and pore size distribution of the NHPCs were obtained by nitrogen adsorption-desorption measurement, the corresponding nitrogen adsorption/desorption isotherms of NHPCs is displayed in Fig. 2a. The N₂ adsorption

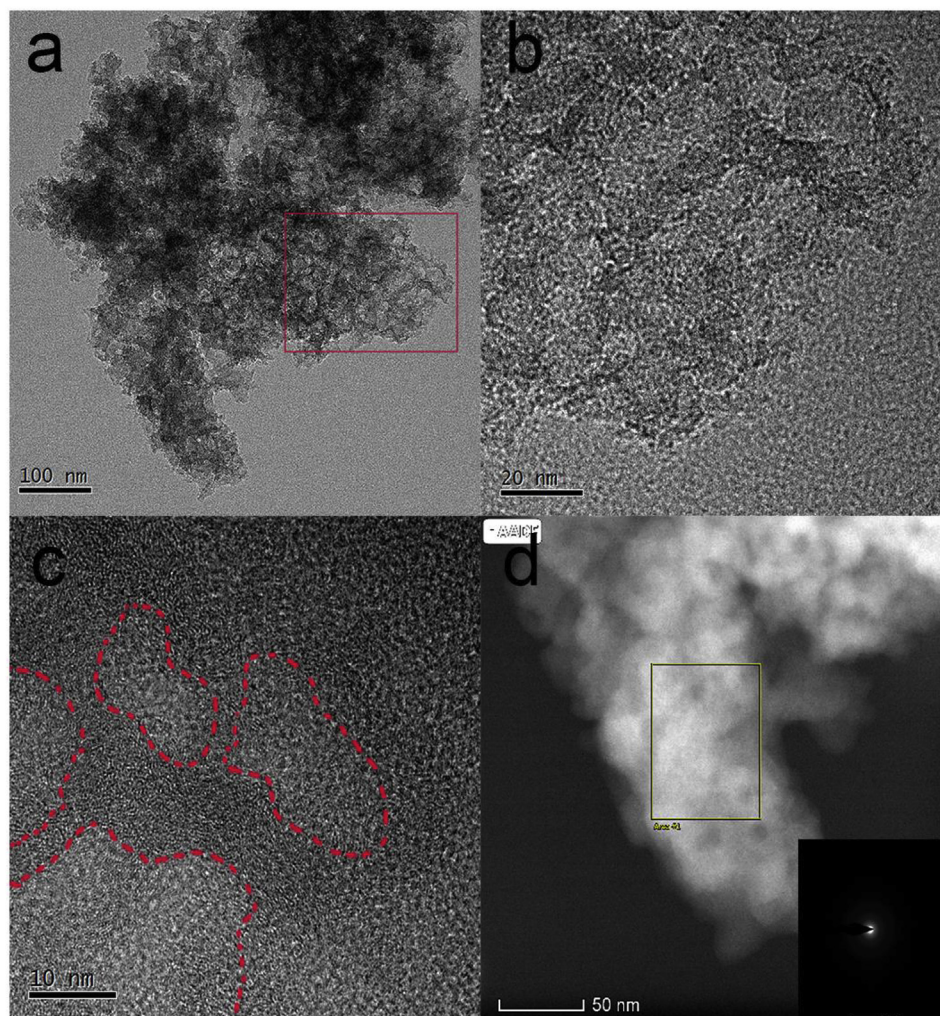


Fig. 1. a) TEM and b, c) HRTEM, d) HAADF-STEM and selected area electron diffraction pattern (inset of d) of NHPC-0.5.

isotherm of NHPCs exhibit a hybrid of type I and IV isotherms with an evident type-H4 hysteresis loop, suggesting the hierarchical porous characteristic of the NHPCs samples. The strong N_2 adsorption at relative low pressure area ($P/P_0 < 0.02$) indicates the presence of micropores, the apparent hysteresis loops at a relative pressure about 0.5–1.0 suggests the mesoporous feature of the samples, and the steep uptake at relative pressure of 0.9–1.0 implies the presence of macropore, which are in good accordance with the morphology of SEM and TEM images. The pore size distribution (Fig. 2b) further confirms the hierarchical pore architecture with dominated pore size ranging from 0.8 to 10 nm. Such a hierarchical porous structure is highly propitious to the ORR and supercapacitor performance because it can shorten the ion diffusion path and accelerate the ion transport [35]. The specific surface area and micropore surface area were calculated from the N_2 adsorption isotherms according to the BET and t-plot methods, respectively, and displayed in Table S1. The specific surface area of the NHPC-0.75 is as high as $1798 \text{ m}^2 \text{ g}^{-1}$ with total pore volume of $2.83 \text{ cm}^3 \text{ g}^{-1}$, which is much higher than previously reported N-doped hierarchical porous carbon [4,36–39]. It is noteworthy that the $S_{\text{micro}}/S_{\text{meso}}$ and $V_{\text{micro}}/V_{\text{meso}}$ fraction of NHPCs gradually reduces with the increase of mass ratio of SiO_2 to PAN (Fig. S3). Previous literature reported [20,40,41] that the optimization of micro/mesopore ratio is a key factor for the ORR and supercapacitor

performance of porous carbon. The excessive micropore hinders the ion diffusion path and delays the ion transport. Conversely, the increasing mesopore leads to the loss of active site because of the reduction of the specific surface area. Therefore, NHPC-0.5 may be a desirable candidate for ORR and supercapacitor owing to its well-developed hierarchical pore structure with optimized micro/mesopore ratio.

Fig. 2c depicted the XRD patterns of the products. The patterns of the products have two distinct diffraction peaks at 25° and 44° , which can be identified to the diffraction peaks of the (002) and (101) plane of partially graphitized amorphous carbon, respectively. The graphitization degrees of the NHPCs were researched by Raman spectroscopy analysis in depth. It can be seen from Fig. 2d, all the samples exhibit two distinct peaks, 1342 cm^{-1} (D band) and 1595 cm^{-1} (G band), respectively. The D band is attributed to the defects or the disordered carbon structure, while the G band related to the ordered graphitic sp^2 bonded carbons. Moreover, the intensity ratio of D band and G band (I_D/I_G) expresses the degree of disorder of materials. The I_D/I_G value of NHPC-0, NHPC-0.25, NHPC-0.5, NHPC-0.75 were calculated to be 1.23, 1.14, 1.15 and 1.18, respectively. The minimum I_D/I_G value of NHPC-0.25 indicates the higher degree of graphitization and the less defect in the sample. Especially, the I_D/I_G increases with the increasing of X from 0.25 to 0.75, indicating the enhanced disorder structure or defect with

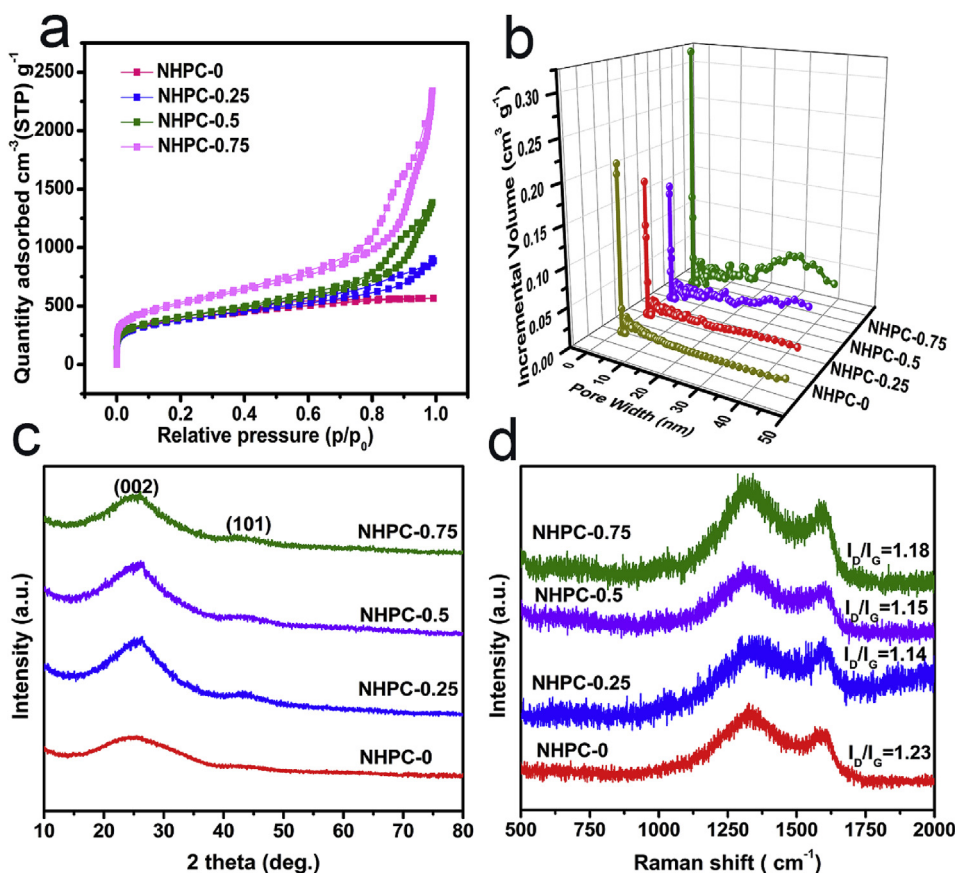


Fig. 2. a) Nitrogen adsorption–desorption isotherms and b) pore-size distribution of NHPCs; c) XRD and d) Raman spectra of NHPCs.

increasing of the mass ratio of SiO₂ to PAN.

XPS technique is employed to investigate the chemical composition and electronic state of the elements of the as-prepared NHPCs, the corresponding results are demonstrated in Fig. 3 and Fig. S4. The XPS spectra of all samples have three peaks at 284.5, 398.1 and 531.0 eV, corresponding to C 1s, N 1s and O 1s, respectively, suggest the presence of C, N, and O element (Fig. S4a). The elemental composition of all samples is presented in Fig. 3e. A relatively high-level doping of 12.1 at% for N element was obtained in NHPC-0.5, and the detailed information of C, N, O elements are displayed in Table S2. To investigate the detail of C and N configuration in the NHPCs, high-resolution C 1s and N 1s spectra of the NHPCs are plotted in Fig. S4b and Fig. 3a–d. The high-resolution C 1s spectra in Fig. S4b can be fitted into four peaks centered at nearby 284.6, 285.8 and 288.8 eV after deconvoluting, which can be assigned to the C–C, C–N/C–O and O–C=O bonding, respectively. The high-resolution N 1s spectra of the NHPCs in Fig. 3a–d can be deconvoluted into pyridine N (N-6) (398.2 eV), pyrrole N (N-5) (399.7 eV), graphitized N (N-G) (400.6 eV) and oxidized N (N–O) (403.4 eV). The pyridine N can introduce the electron donor into carbon materials by offering a pair of electrons to the π -conjugated ring, which has appreciable impact on the increased capacitance [7,42]. The pyrrole N can facilitate the electron transfer process available and import extra pseudocapacitance due to their electron-donor characteristic. In addition, the graphitized N will significantly enhance the conductivity, while N-oxides improve the wettability of carbon materials [42]. Fig. 3f and Table S3 showed the relative ratio of four types of N species. Such a N-doped hierarchical porous structure is highly desirable for ORR and supercapacitor because it can achieve rapid ion diffusion by shortening the diffusion

pathways.

3.2. ORR performance of NHPCs

Since the synthesized NHPCs combine the advantages of high-level nitrogen, large specific surface area and hierarchical porous structure, we expect it have an extraordinary ORR performance. The ORR performance of as-prepared NHPCs were tested by rotating disk electrode at a sweep speed of 5 mV s^{−1} in 0.1 M KOH solution, as illustrated in Fig. 4 and S5. Fig. 4a showed the CV curves performed in N₂ and O₂-saturated electrolyte. It can be clearly seen that the CV curves possess obvious cathode peak near 0.8 V in O₂-saturated except NHPC-0, while there is no obvious cathode peak in N₂-saturated. The cathode peaks appearing in the whole ORR process come from the response of the material to oxygen, suggesting that the as-synthesized NHPCs are promising catalysts for ORR. Remarkably, NHPC-0.5 possesses the highest peak voltage (0.8443 V) in all samples (0.8203 V for NHPC-0.25, 0.8335 V for NHPC-0.75).

LSV is another routine test method to measure the ORR performances, which can obtain the initial potential, half-wave potential and limiting current density of the material. The larger the initial potential, the more positive the half-wave potential and the greater the ultimate limiting current density, the better ORR performance of materials. The ORR performance of the as-synthesized NHPCs were further evaluated by LSV using a rotating ring-disk electrode (RRDE) at a rotating rate of 1600 rpm with a sweep speed of 5 mV s^{−1} in O₂-saturated alkaline solution, and the corresponding LSV curves are displayed in Fig. 4b. NHPC-0.5 possess a larger limiting current density (3.4682 mA cm^{−2} at 0.3 V vs RHE)

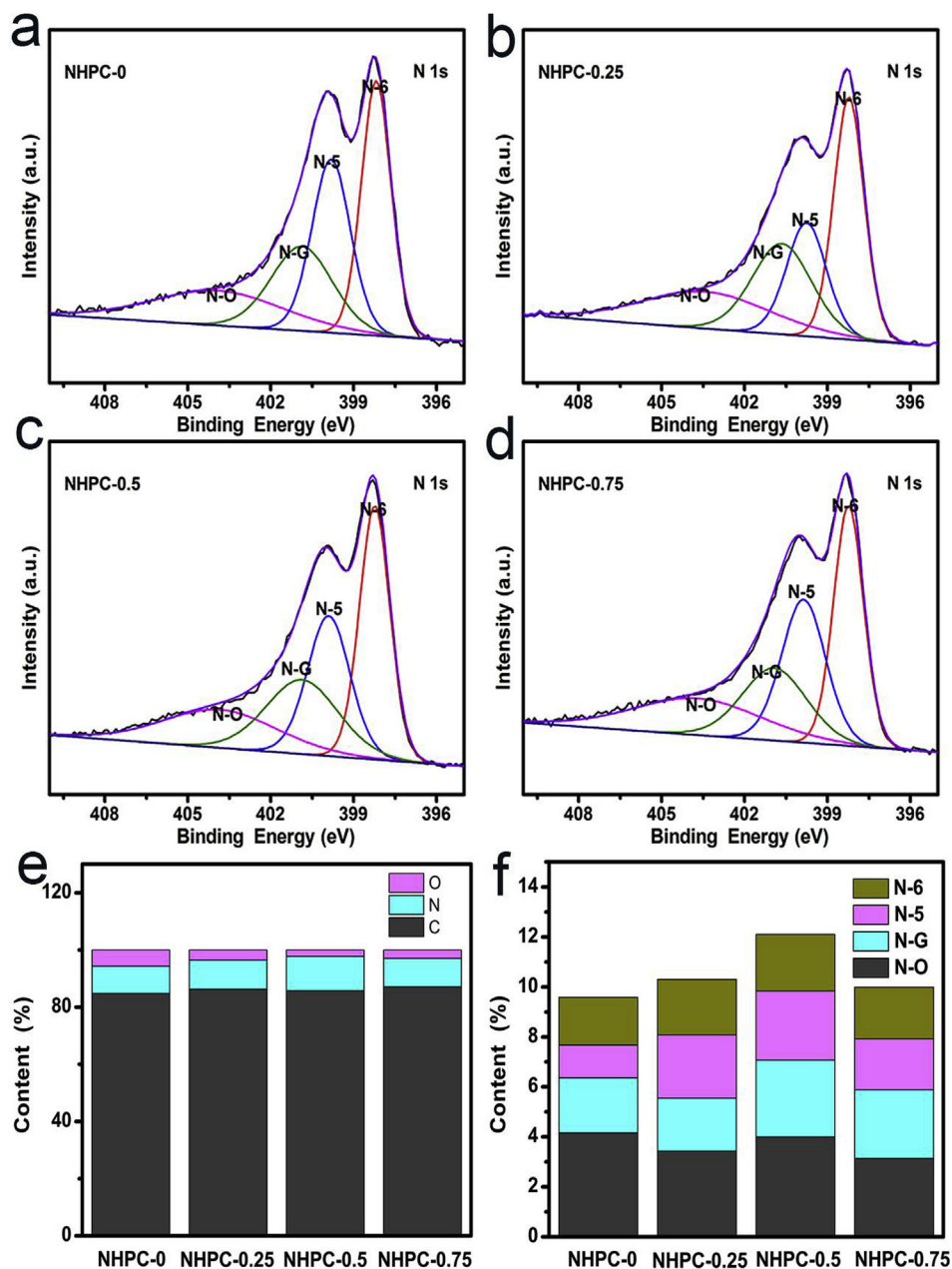


Fig. 3. a-d) N 1s of NHPCs; e) the content of C 1s, O 1s and N 1s for NHPCs; f) the content of different N including pyridinic N (N-6), pyrrolic N (N-5), graphitic N(N-G) and oxidized N(N-O) for NHPCs.

and an ideal onset potential (1.004 V vs RHE, at $j = 0.1 \text{ mA cm}^{-2}$), as well as a higher half-wave potential (0.883 V vs RHE, at $j = 1/2j_{\text{max}}$) compare with other samples (Fig. 4e), even higher than that of reference Pt/C catalyst (initial potential 1.0303 V vs RHE, half-wave potential 0.86 V vs RHE), suggesting excellent ORR activity of NHPC-0.5, which is better than those reported carbon-based materials described in Table 1 [35,43–48]. To investigate the reaction kinetics, the LSV curves of NHPC-0.5 at different rotation speeds were recorded and presented in Fig. 4c, while the LSV curves of other samples at different rotation speeds are displayed in Fig. S5. Fig. 4d and Fig. S5 showed the link between j^{-1} and $\omega^{-1/2}$ of different samples estimated from the Koutechy-Levich (K-L plot) equation through LSV curves. As shown in Fig. 4d, the K-L curve of NHPC-0.5 exhibits a good linear relationship at potential range of 0.3–0.6 V, indicating that oxygen reduction was controlled by diffusion.

The electron transfer number per oxygen molecule n is another key parameter to evaluate electrocatalysis catalytic activity. The electron transfer number n of the NHPC-0.5 was about 4.39 calculated according to the formula (2) and (3) at range of 0.3–0.6 V, indicating a direct four-electron transfer process for electrocatalysis. Within all the NHPCs samples, NHPC-0.5 delivers the superior performance in electrocatalysis activity, which can be put down to the synergistic effects of high specific surface area, the hierarchical porous structure with appropriate micro/mesopore ratio, along with high nitrogen content and species. These multi-aspect merits render the NHPC-0.5 a promising catalyst for ORR.

Furthermore, durability is one of the important factors for ORR, and the LSV curves were performed on in O_2 -saturated alkaline medium to test the stability of NHPC-0.5, the Pt/C catalyst was tested as benchmark. As shown in Figs. S6a–b, after 10,000 CV

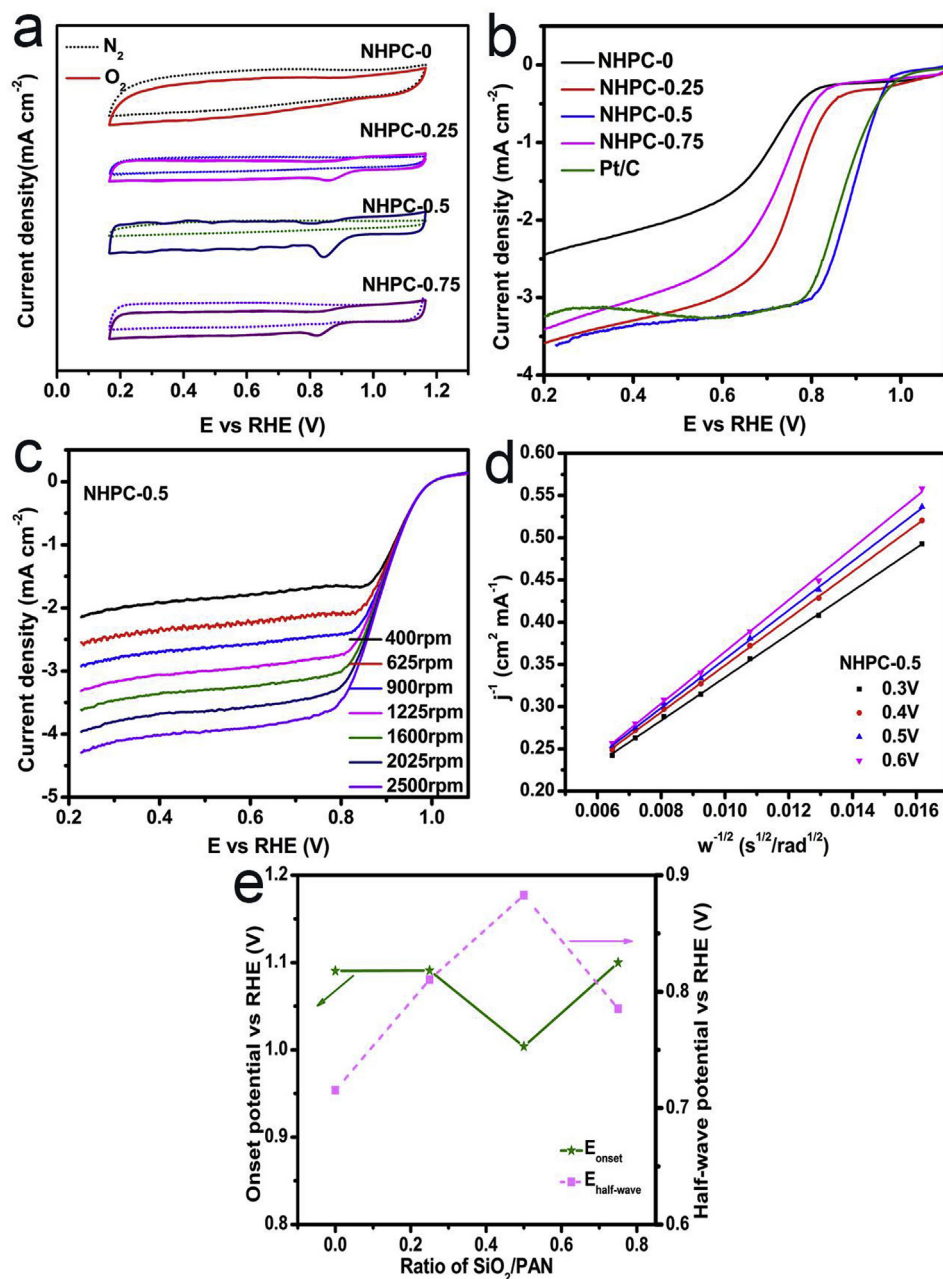


Fig. 4. Electrocatalysis performance test: a) CV in saturated nitrogen and oxygen of NHPCs, sweep rate of 5 mV s^{-1} (0.1 M KOH); b) LSV of NHPCs and Pt/C in saturated oxygen at a rotating rate of 1600 rpm, sweep rate of 5 mV s^{-1} (0.1 M KOH); c) LSV of NHPC-0.5 with different rate in saturated oxygen (0.1 M KOH); d) The dependence of j^{-1} on $\omega^{-1/2}$ of NHPC-0.5 derived from d); e) the initial and half-wave potential of NHPCs derived from b).

Table 1

ORR performance of carbon-based materials.

Samples	Measurement condition	Onset potential (V)	Half-wave potential (V)	Current density (mA cm^{-2})	Ref.
Nitrogen-doped porous carbon	0.1 M KOH, 1600 rpm, 10 mV s^{-1}	0.95 (RHE)	0.86 (RHE)	4.8 (at 0.2 V vs. RHE)	[35]
rGO/CB/Co-Bi	0.1 M KOH, 1600 rpm, 10 mV s^{-1}	0.88 (RHE)	0.7 (RHE)	5.4 (at 0.1 V vs. RHE)	[43]
Fe-N/C	0.1 M KOH, 1600 rpm, 10 mV s^{-1}	0.99 (RHE)	—	4.8 (at 0.45 V vs. RHE)	[44]
Nitrogen-doped holey graphene nanocapsules	0.1 M KOH, 1600 rpm, 5 mV s^{-1}	1.03 (RHE)	0.85 (RHE)	5.2 (at 0.5 V vs. RHE)	[45]
N-doped porous carbon spheres	0.1 M KOH, 1600 rpm, 10 mV s^{-1}	—	0.25 (SCE)	4.6 (at 0.7 V vs. SCE)	[46]
Ammonia modification of activated carbon	0.1 M KOH, 1600 rpm, 5 mV s^{-1}	0.05 (Ag/AgCl)	—	4.55 (at -1 V vs. Ag/AgCl)	[47]
N-doped hierarchically porous carbons	0.1 M KOH, 1600 rpm, 5 mV s^{-1}	0.84 (RHE)	0.85 (RHE)	4.32 (at 0.8 V vs. RHE)	[48]
NHPC-0.5	0.1 M KOH, 1600 rpm, 5 mV s^{-1}	1.004 (RHE)	0.883 (RHE)	3.47 (at 0.3 V vs. RHE)	This work

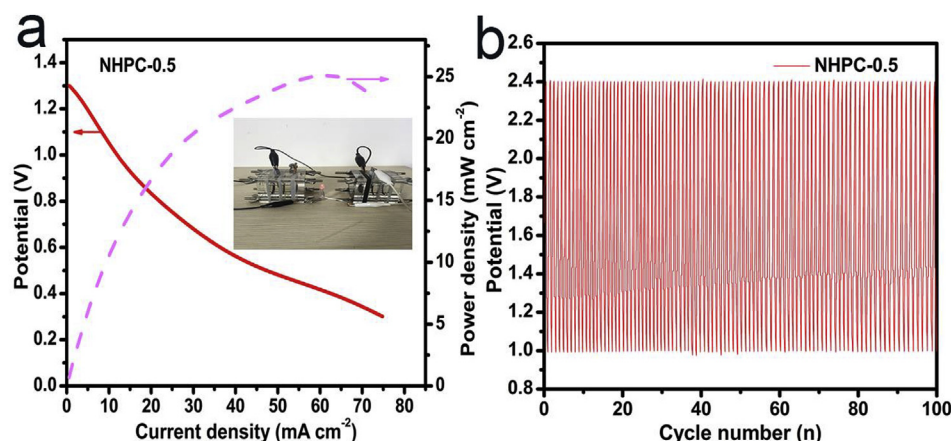


Fig. 5. Zinc-air battery test of NHPC-0.5: a) the polarization curve and output power density curve, sweep rate of 100 mV s^{-1} (6 M KOH); b) cycle stability after 100 cycles, current density of 10 mA cm^{-2} (6 M KOH).

curves cycling test at a sweep speed of 100 mV s^{-1} , negative shift in half-wave potential of NHPC-0.5 is 11 mV, which is less than half of Pt/C (27 mV). In addition, the negative shift in half-wave potential of NHPC-0.5 and Pt/C is 10 and 12 mV after the injection of 5 mL of 2 M methanol into the testing electrolyte (0.1 M KOH, 40 mL), respectively. It indicated the NHPC-0.5 exhibited superior stability and better resistance to methanol than those of the benchmark Pt/C catalyst, making it a promising cathodic catalyst for electrodes in metal-air batteries application.

Inspired by the outstanding ORR activity and durability of NHPCs in alkaline media, the performance of NHPC-0.5 catalyst was further investigated in a self-made zinc-air battery to investigate its possibility for commercial zinc-air batteries. The battery possesses an open circuit potential of 1.3 V in Fig. 5a. Fig. 5a also showed that the output power density was 25.1 mW cm^{-2} when the current density was about 5 mA cm^{-2} . This was ascribed to that NHPC-0.5 has a hierarchical porous structure, which can broaden the ion transport space and accelerate the mass transfer rate of ions. Moreover, it is also helpful to improve performance since a certain amount of nitrogen doping can endow abundant active sites for NHPC-0.5. Charging and discharging performance was also an indicator to measure the performance of the battery. Generally, the lower charging voltage and the higher discharging voltage indicated the advantage of NHPC-0.5 with relatively low energy consumption and higher power supply voltage in practical applications. A cycling durability test was carried out at the current density of 20 mA cm^{-2} (Fig. 5b). Notably, NHPC-0.5 exhibits a stable charge–discharge profile, suggesting its favorable charge–discharge ability. After 100 cycles, a negligible potential loss can be observed on both the charge and discharge curves, proving superior durability of the self-made Zn–air battery. As illustrated in the inset of Fig. 5a, two self-contained Zn–air batteries connected in series can illuminate a light, further confirmed the practical applications of NHPC-0.5 in energy storage devices.

3.3. Supercapacitor performance of NHPCs

Given the above desirable characterization and excellent ORR performance, the as-prepared NHPCs were further studied as electrode for supercapacitor, and the supercapacitor performance of the NHPCs were put into effect in a three-electrode system in 1 M H_2SO_4 electrolyte. Fig. 6a showed the CV curves of the NHPCs at a sweep speed of 10 mV s^{-1} in the potential range from -0.02 to 0.98 V (vs. RHE). The CV curves of the NHPCs electrodes exhibit a quasi-rectangular with distinct reversible hump, suggesting that

the capacitive performance of the samples derived from the combination of electric double-layer capacitance (EDLC) and pseudocapacitance owing to the presence of redox active nitrogen functional group. The NHPC-0.5 presents the larger integral area than other samples, indicating the highest capacitance can be expected. Fig. 6b and S7 presented the CV curves of NHPC-0.5 and other samples at different sweep speeds. It can be observed from Fig. 6b that the CV curves still retain the original shape even at high sweep speed of 200 mV s^{-1} , confirming the excellent rate capability. Fig. 6c and S7 displayed the GCD curves of NHPC-0.5 and other samples at different current densities from 1 to 50 A g^{-1} . The GCD curves obviously derived from linearity, illustrating the coexistence of EDLC and pseudocapacitance behavior of the NHPC-0.5, which is consistent with the CV measurement. The specific capacitances of NHPCs were calculated based on the formula (4) and presented in Fig. 6d. The specific capacitances of the as-prepared NHPCs are higher than other carbon materials ever reported and traditional commercial activated carbon material ($80\text{--}120 \text{ F g}^{-1}$) [49]. As expected, among the NHPCs, the NHPC-0.5 delivers the highest specific capacitance of 283.7 F g^{-1} at a current density of 1 A g^{-1} with capacitance retention of 84% at a high current density of 20 A g^{-1} , which is superior than those previously reported carbon-based electrodes, as shown in Table 2 [4,5,24,37,39,50–54]. The superior capacitive behavior of NHPC-0.5 mainly because of its highest amount of N functional groups offer extra pseudocapacitance and moderate surface area with proper micro/mesopore ratios render effective electrode/electrolyte interface for EDLC. Electrochemical impedance spectroscopy (EIS) is significant to clarify kinetics information of electrode, including capacitive property, electrical resistance property and electrolyte ion transport behavior. EIS of NHPCs were measured over a frequency range of $10^{-2}\text{--}10^5 \text{ Hz}$ at open circuit potential and corresponding Nyquist plots are illustrated in Fig. 6e and Fig. S8a. At high frequency, the intercept of curves at real axis (Z') represents the value of equivalent series resistance (R_s), which is the total internal resistance of electrode system. The diameter of semicircle signifies interfacial charge transfer resistance (R_{ct}) between electrolyte and electrode/electrolyte interface. As showed in Fig. 6e and S8a, NHPC-0.5 exhibit smaller R_s and lower R_{ct} value, demonstrating the low internal resistance, favorable electrical conductivity, and faint charge transfer resistance. At low frequency, almost vertical lines of NHPC-0.5 clearly showing better capacitive behaviors. Furthermore, the cycle stability was performed by repeated GCD to further examine the electrochemical stability of electrodes. Fig. 6f illustrated the capacitance retention and the

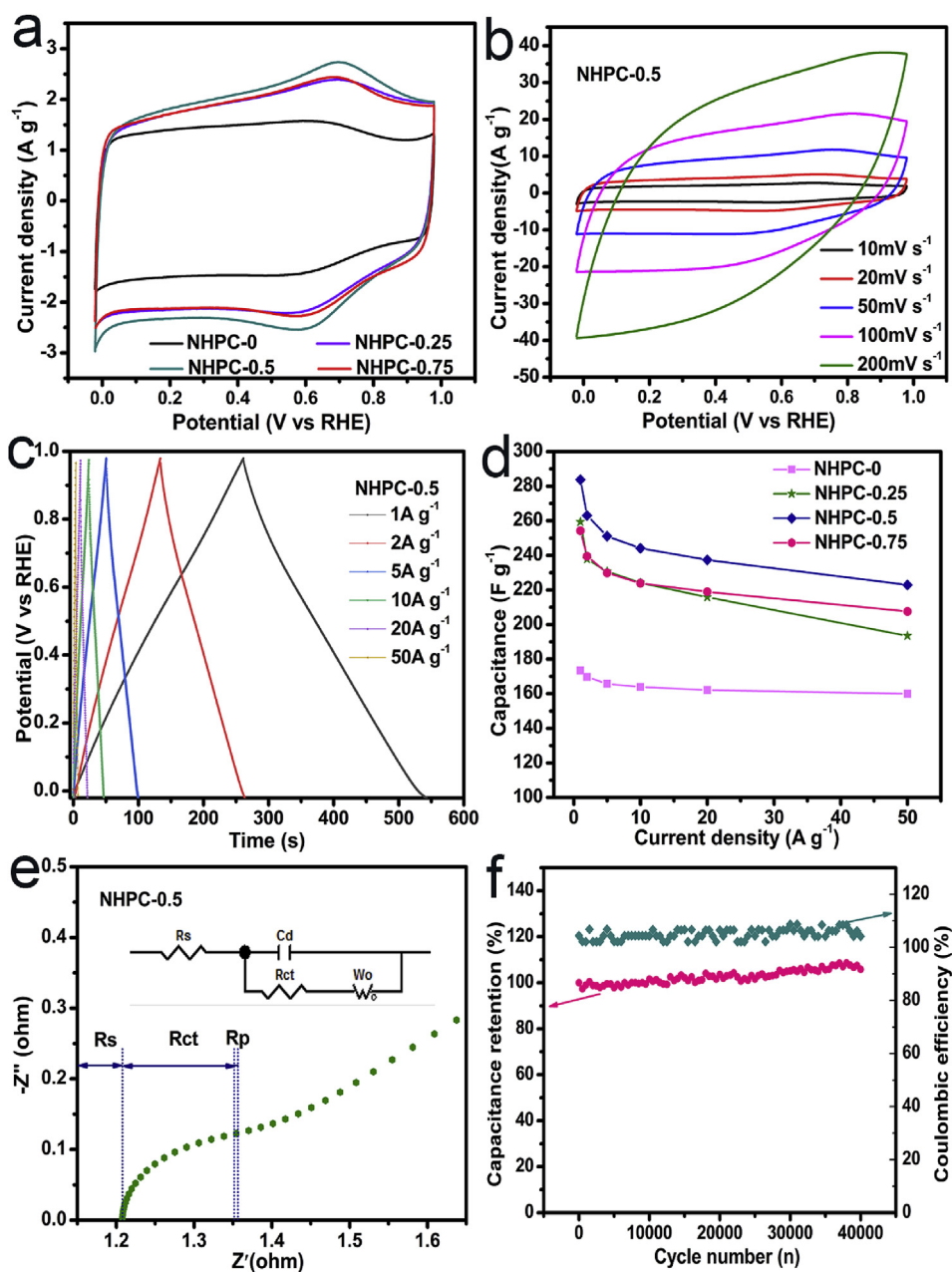


Fig. 6. Capacitance test of three-electrode system: a) CV of NHPCs with a sweep speed of 10 mV s⁻¹ (1 M H₂SO₄); b) CV of NHPC-0.5 with different scan speeds from 10 mV s⁻¹ to 200 mV s⁻¹ (1 M H₂SO₄); c) GCD curves of NHPC-0.5 with different current density from 1 A g⁻¹ to 50 A g⁻¹ (1 M H₂SO₄); d) specific capacitance change of NHPCs with different current densities; e) EIS of NHPC-0.5 (1 M H₂SO₄); f) capacitance retention and coulomb efficiency curves of NHPC-0.5 after circulating for 40,000 cycles at a current density of 4 A g⁻¹ (1 M H₂SO₄).

coulomb efficiency curve for NHPC-0.5 after circulating for 40,000 cycles at a current density of 4 A g⁻¹. The NHPC-0.5 presents a high capacitance retention of 105.8% and coulomb efficiency of 104.2% after 40,000 cycles, demonstrating the superb cycling performance of NHPC-0.5.

The NHPC-0.5 was assembled into a symmetric supercapacitor (NHPC-0.5//NHPC-0.5) device to investigate the practical device behavior of NHPCs. Fig. 7a showed the CV curve of NHPC-0.5//NHPC-0.5 at different sweep speeds. It can be observed that all the curves exhibited a regular rectangle even at a high sweep speed of 200 mV s⁻¹, indicating ideal capacitive behavior and high rate performance. The GCD curves of the NHPC-0.5//NHPC-0.5 measured at different current density of (Fig. 7b) display nearly

isosceles triangle shape, demonstrating seductive capacitive behavior. The calculated specific capacitance values of NHPC-0.5//NHPC-0.5 presented in Fig. 7c are 81.6 F g⁻¹, 80.5 F g⁻¹, 78.8 F g⁻¹, 76.8 F g⁻¹ and 73.6 F g⁻¹ at current density from 1 A g⁻¹ to 20 A g⁻¹, respectively. Even at a high current density of 20 A g⁻¹, it still maintains a high specific capacitance of 73.6 F g⁻¹ (capacitance retention of 90.2%), suggesting remarkable rate capability. The small internal resistance of NHPC-0.5//NHPC-0.5 supercapacitor, as shown in Fig. S8b, suggests that the device possess an ideal capacitance characteristic. The inset of Fig. 7c displayed the ragone plot of the energy density versus power density to further assess the energy storage performance of the NHPC-0.5//NHPC-0.5 supercapacitor. The NHPC-0.5//NHPC-0.5 supercapacitor exhibits

Table 2
Supercapacitance performance of carbon-based supercapacitors.

Samples	Measurement condition	Current density (A g^{-1})	Capacitance (F g^{-1})	Rate capability (%)	Cycle numbers	Capacity retention (%)	Ref.
Yolk-shelled carbon spheres	2-electrode, 6 M KOH	0.5	120	75 (20 A g^{-1})	—	—	[4]
Monodisperse starburst carbon spheres	2-electrode, 1 M Na_2SO_4	0.24	60	95 (1 A g^{-1})	4000	95%	[5]
N-doped ordered mesoporous carbon	3-electrode, 1 M H_2SO_4	0.25	212	79 (20 A g^{-1})	—	—	[24]
Hierarchically porous carbon	3-electrode, 1 M H_2SO_4	0.1	274	59 (20 A g^{-1})	5000	100	[50]
N, B co-doped hierarchically porous carbons	3-electrode, 6 M KOH	0.5	247	68 (20 A g^{-1})	4000	96.2	[51]
N-doped porous monolithic carbons	3-electrode, 1 M H_2SO_4	0.2	270	72 (100 A g^{-1})	5000	100	[52]
N-doped porous carbon spheres	3-electrode, 6 M KOH	1	247	64 (30 A g^{-1})	5000	97	[53]
N-doped carbon aerogels	3-electrode, 6 M KOH	1	253.7	48 (20 A g^{-1})	10000	94.5	[54]
N-doped porous carbon nanofibers	3-electrode, 1 M H_2SO_4	0.5	335	52 (32 A g^{-1})	10000	86	[37]
Mesoporous carbon sheet-like framework	3-electrode, 6 M KOH	1	276.5	82 (20 A g^{-1})	5000	91	[39]
NHPC-0.5	3-electrode, 1 M H_2SO_4	1	283.7	84 (20 A g^{-1})	40000	105.8	This work
NHPC-0.5	2-electrode, 1 M H_2SO_4	1	81.6	90.2 (20 A g^{-1})	12000	99.3	This work

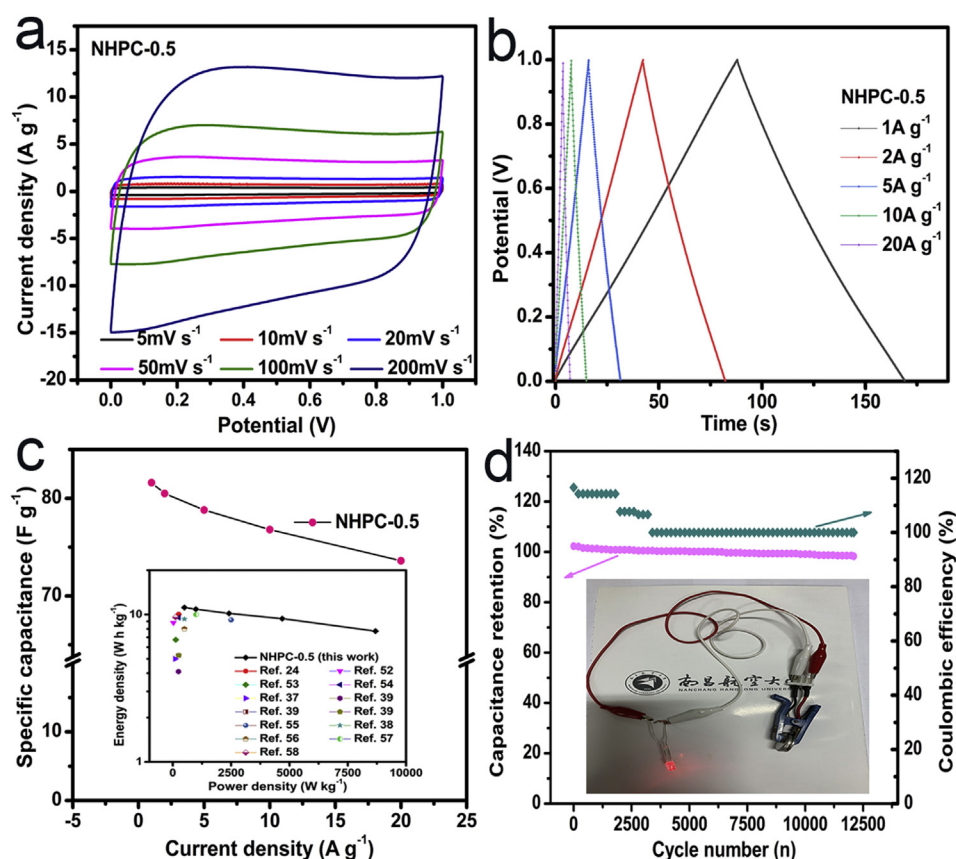


Fig. 7. a) CV of NHPC-0.5//NHPC-0.5 with different sweep speed from 5 mV s^{-1} to 200 mV s^{-1} ($1 \text{ M H}_2\text{SO}_4$); b) GCD curves of NHPC-0.5//NHPC-0.5 with different current density from 1 A g^{-1} to 20 A g^{-1} ($1 \text{ M H}_2\text{SO}_4$); c) specific capacitance change of NHPC-0.5//NHPC-0.5 at different current densities (the inset is Ragone plot of porous carbon materials that can be found in the previous reports and NHPCs-based supercapacitor); d) capacitance retention and coulomb efficiency curves of NHPC-0.5//NHPC-0.5 after circulating for 12,000 cycles at a current density of 6.7 A g^{-1} (the inset is two button batteries connected in series can illuminate a light: the voltage of the light is 1.5 V) ($1 \text{ M H}_2\text{SO}_4$).

an energy density of 11.3 W h kg^{-1} at the power density of 502 W kg^{-1} . Even at a high power density of 8691 W kg^{-1} , the energy density can still retain 7.7 W h kg^{-1} , which is much higher than previously reported N-doped hierarchical porous carbon (the inset of Fig. 7c) [28,37–39,52–58]. Fig. 7d displayed the cycling stability of the NHPC-0.5//NHPC-0.5 supercapacitor tested for 12,000 cycles by GCD at a current density of 6.7 A g^{-1} . The NHPC-0.5//NHPC-0.5 supercapacitor exhibits good stability with almost no loss of the initial capacitance after 12,000 cycles (capacitance retention of 99.3% after 12,000 cycles). In addition, two NHPC-0.5//NHPC-0.5 supercapacitor connected in series can illuminate a light (the inset of Fig. 7d), which further demonstrates the potential of

the sample NHPC-0.5 for supercapacitor applications.

4. Conclusion

To conclude, a series of N-doped hierarchical porous carbon (NHPCs) were successfully synthesized by a simple, benign and convenient synthesis method. In this method, the utilization of ZnCl_2 enhancing the solubility of porogen, and enables the solubilization of PAN template as well as dispersion of porogenic particle in water, consequently enhances the surface area. The resultant NHPCs were provided with large pore volume, interconnected hierarchical porous structure, high specific surface area

and high content of nitrogen doping. Benefiting from the synergistic effect of above advantages, the as-prepared NHPCs presented excellent performance as both ORR (half-wave potential 0.883 V vs RHE, initial potential 1.004 V vs RHE, and favorable tolerance against methanol) and supercapacitor (the gravimetric specific capacitance can reach up to 283.7 F g⁻¹ at current density of 1 A g⁻¹ in 1 M H₂SO₄ electrolyte, outstanding cyclic stability of 105.8% capacitance retention after 40,000 cycles, and an energy density of 11.3 W h kg⁻¹ at the power density of 502 W kg⁻¹, even at a high power density of 8691 W kg⁻¹, the energy density can still retains 7.7 W h kg⁻¹) electrodes. The facile material synthesis and impressive performance make the NHPCs competitive for practical applications in high performance energy storage devices.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Hang Sun: Visualization, Writing - original draft, Data curation, Writing - review & editing. **Hongying Quan:** Conceptualization, Writing - review & editing. **Menghua Pan:** Investigation. **Zhiming Zhang:** Data curation. **Yong Zeng:** Data curation. **Dezhi Chen:** Conceptualization, Funding acquisition, Writing - review & editing.

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Appendix A. Supplementary data

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References

- [1] W. He, C. Jiang, J. Wang, L. Lu, High-rate oxygen electroreduction over graphitic-N species exposed on 3D hierarchically porous nitrogen-doped carbons, *Angew. Chem.* 53 (2014) 9503–9507.
- [2] G. Tao, L. Zhang, L. Chen, X. Cui, Z. Hua, M. Wang, J. Wang, Y. Chen, J. Shi, N-doped hierarchically macro/mesoporous carbon with excellent electrocatalytic activity and durability for oxygen reduction reaction, *Carbon* 86 (2015) 108–117.
- [3] Y.-L. Liu, C.-X. Shi, X.-Y. Xu, P.-C. Sun, T.-H. Chen, Nitrogen-doped hierarchically porous carbon spheres as efficient metal-free electrocatalysts for an oxygen reduction reaction, *J. Power Sources* 283 (2015) 389–396.
- [4] J. Wang, S. Feng, Y. Song, W. Li, W. Gao, A.A. Elzathary, D. Aldhayan, Y. Xia, D. Zhao, Synthesis of hierarchically porous carbon spheres with yolk-shell structure for high performance supercapacitors, *Catal. Today* 243 (2015) 199–208.
- [5] S.K. Kim, E. Jung, M.D. Goodman, K.S. Schweizer, N. Tatsuda, K. Yano, P.V. Braun, Self-assembly of monodisperse starburst carbon spheres into hierarchically organized nanostructured supercapacitor electrodes, *ACS Appl. Mater. Interfaces* 7 (2015) 9128–9133.
- [6] A.J. Amali, J.K. Sun, Q. Xu, From assembled metal-organic framework nanoparticles to hierarchically porous carbon for electrochemical energy storage, *Chem. Commun.* 50 (2014) 1519–1522.
- [7] Z. Li, X. Liu, L. Wang, F. Bu, J. Wei, D. Pan, M. Wu, Hierarchical 3D all-carbon composite structure modified with N-doped graphene quantum dots for high-performance flexible supercapacitors, *Small* 14 (2018), e1801498.
- [8] S. Yue, H. Tong, L. Lu, W. Tang, W. Bai, F. Jin, Q. Han, J. He, J. Liu, X. Zhang, Hierarchical NiCo₂O₄ nanosheets/nitrogen doped graphene/carbon nanotube film with ultrahigh capacitance and long cycle stability as a flexible binder-free electrode for supercapacitors, *J. Mater. Chem.* 5 (2017) 689–698.
- [9] J.X. Feng, H. Xu, S.H. Ye, G. Ouyang, Y.X. Tong, G.R. Li, Silica-polypyrrole hybrids as high-performance metal-free electrocatalysts for the hydrogen evolution reaction in neutral media, *Angew. Chem.* 56 (2017) 8120–8124.
- [10] Z.Y. Sui, Y.N. Meng, P.W. Xiao, Z.Q. Zhao, Z.X. Wei, B.H. Han, Nitrogen-doped graphene aerogels as efficient supercapacitor electrodes and gas adsorbents, *ACS Appl. Mater. Interfaces* 7 (2015) 1431–1438.
- [11] J. Jeong, M. Choun, J. Lee, Tree-bark-shaped N-doped porous carbon anode for hydrazine fuel cells, *Angew. Chem. Int. Ed.* 56 (2017) 13513–13516.
- [12] Y.Q. Zhao, M. Lu, P.Y. Tao, Y.J. Zhang, X.T. Gong, Z. Yang, G.Q. Zhang, H.L. Li, Hierarchically porous and heteroatom doped carbon derived from tobacco rods for supercapacitors, *J. Power Sources* 307 (2016) 391–400.
- [13] M.R. Benzigar, A.N. Talapaneni, S. Joseph, K. Ramadass, G. Singh, J. Scaranto, U. Ravon, K. Al-Bahily, A. Vinu, Recent advances in functionalized micro and mesoporous carbon materials: synthesis and applications, *Chem. Soc. Rev.* 47 (2018) 2680–2721.
- [14] W. Yang, W. Yang, L.N. Kong, A.L. Song, X.J. Qin, G.J. Shao, Phosphorus-doped 3D hierarchical porous carbon for high-performance supercapacitors: a balanced strategy for pore structure and chemical composition, *Carbon* 127 (2018) 557–567.
- [15] N. Mao, H.L. Wang, Y. Sui, Y.P. Cui, J. Pokrzywinski, J. Shi, W. Liu, S.G. Chen, X. Wang, D. Mitlin, Extremely high-rate aqueous supercapacitor fabricated using doped carbon nanoflakes with large surface area and mesopores at near-commercial mass loading, *Nano Res.* 10 (2017) 1767–1783.
- [16] K. Shen, X. Chen, J. Chen, Y. Li, Development of MOF-derived carbon-based nanomaterials for efficient catalysis, *ACS Catal.* 6 (2016) 5887–5903.
- [17] K. Yuan, C.B. Lu, S. Sfaelou, X.X. Liao, X.D. Zhuang, Y.W. Chen, U. Scherf, X.L. Feng, In situ nanoarchitecturing and active-site engineering toward highly efficient carbonaceous electrocatalysts, *Nano Energy* 59 (2019) 207–215.
- [18] Z.D. Lei, X. Long, M. Yang, D.G. Yang, H.B. Chen, H.M. Li, Nitrogen-doped porous carbon with brain-like structure derived from quaternary bipyridinium-type framework for efficient oxygen reduction electrocatalysis and supercapacitors, *Chemelectrochem* 6 (2019) 848–855.
- [19] Q.Y. Liang, H. Su, J. Yan, C. Leung, S.L. Cao, D.S. Yuan, N-doped mesoporous carbon as a bifunctional material for oxygen reduction reaction and supercapacitors, *Chin. J. Catal.* 35 (2014) 1078–1083.
- [20] C. Zhu, M. Takata, Y. Aoki, H. Habazaki, Nitrogen-doped porous carbon as mediated by a facile solution combustion synthesis for supercapacitor and oxygen reduction electrocatalyst, *Chem. Eng. J.* 350 (2018) 278–289.
- [21] M. Yang, Z. Zhou, Recent breakthroughs in supercapacitors boosted by nitrogen-rich porous carbon materials, *Adv. Sci.* 4 (2017) 1600408.
- [22] X.Y. Yang, A. Leonard, A. Lemaire, G. Tian, B.L. Su, Self-formation phenomenon to hierarchically structured porous materials: design, synthesis, formation mechanism and applications, *Chem. Commun.* 47 (2011) 2763–2786.
- [23] Z.-Y. Yuan, B.-L. Su, Insights into hierarchically meso-macroporous structured materials, *J. Mater. Chem.* 16 (2006) 663–677.
- [24] D. Liu, G. Cheng, H. Zhao, C. Zeng, D. Qu, L. Xiao, H. Tang, Z. Deng, Y. Li, B.-L. Su, Self-assembly of polyhedral oligosilsesquioxane (POSS) into hierarchically ordered mesoporous carbons with uniform microporosity and nitrogen-doping for high performance supercapacitors, *Nano Energy* 22 (2016) 255–268.
- [25] X. Meng, F. Nawaz, F.-S. Xiao, Templating route for synthesizing mesoporous zeolites with improved catalytic properties, *Nano Today* 4 (2009) 292–301.
- [26] N.D. Petkovich, A. Stein, Controlling macro- and mesostructures with hierarchical porosity through combined hard and soft templating, *Chem. Soc. Rev.* 42 (2013) 3721–3739.
- [27] J. Du, L. Liu, Y. Yu, Z. Hu, B. Liu, A. Chen, N-doped hollow carbon spheres/sheets composite for electrochemical capacitor, *ACS Appl. Mater. Interfaces* 10 (2018) 40062–40069.
- [28] W. Wang, H. Quan, W. Gao, R. Zou, D. Chen, Y. Dong, L. Guo, N-Doped hierarchical porous carbon from waste boat-fruited sterulia seed for high performance supercapacitors, *RSC Adv.* 7 (2017) 16678–16687.
- [29] A. Raza, J. Wang, S. Yang, Y. Si, B. Ding, Hierarchical porous carbon nanofibers via electrospinning, *Carbon Lett.* 15 (2014) 1–14.
- [30] C. Triantafyllidis, M.S. Elsaesser, N. Husing, Chemical phase separation strategies towards silica monoliths with hierarchical porosity, *Chem. Soc. Rev.* 42 (2013) 3833–3846.
- [31] K. Kanamori, K. Nakanishi, Controlled pore formation in organotrialkoxysilane-derived hybrids: from aerogels to hierarchically porous monoliths, *Chem. Soc. Rev.* 40 (2011) 754–770.
- [32] L. Chen, T. Ji, L. Brisbin, J. Zhu, Hierarchical porous and high surface area tubular carbon as dye adsorbent and capacitor electrode, *ACS Appl. Mater. Interfaces* 7 (2015) 12230–12237.
- [33] P. Huang, H. Li, X. Huang, D. Chen, Multiheteroatom-doped porous carbon catalyst for oxygen reduction reaction prepared using 3D network of ZIF-8/polymeric nanofiber as a facile-doping template, *ACS Appl. Mater. Interfaces* 9 (2017) 21083–21088.
- [34] Z.M. Sheng, X.J. Chang, Y.H. Chen, C.Y. Hong, N.N. Li, C.K. Chang, R.P. Jia, S. Han, Doping-template approach of porous-walled graphitic nanocages for superior performance anodes of lithium ion batteries, *RSC Adv.* 7 (2017) 42083–42087.
- [35] H.W. Liang, W. Wei, Z.S. Wu, X. Feng, K. Mullen, Mesoporous metal-nitrogen-doped carbon electrocatalysts for highly efficient oxygen reduction reaction, *J. Am. Chem. Soc.* 135 (2013) 16002–16005.
- [36] D. Nan, J.-G. Wang, Z.-H. Huang, L. Wang, W. Shen, F. Kang, Highly porous carbon nanofibers from electrospun polyimide/SiO₂ hybrids as an improved

- anode for lithium-ion batteries, *Electrochim. Commun.* 34 (2013) 52–55.
- [37] F. Miao, C. Shao, X. Li, K. Wang, Y. Liu, Flexible solid-state supercapacitors based on freestanding nitrogen-doped porous carbon nanofibers derived from electrospun polyacrylonitrile@polyaniline nanofibers, *J. Mater. Chem.* 4 (2016) 4180–4187.
- [38] Y. Cheng, Q. Zhang, C. Fang, Z. Huang, J. Chen, L. Wu, H. Wang, Synthesis of N-doped porous carbon materials derived from waste cellulose acetate fiber via urea activation and its potential application in supercapacitors, *J. Electrochem. Soc.* 166 (2019) A1231–A1238.
- [39] Q. Wang, J. Yan, T. Wei, J. Feng, Y. Ren, Z. Fan, M. Zhang, X. Jing, Two-dimensional mesoporous carbon sheet-like framework material for high-rate supercapacitors, *Carbon* 60 (2013) 481–487.
- [40] J. Yang, H. Wu, M. Zhu, W. Ren, Y. Lin, H. Chen, F. Pan, Optimized mesopores enabling enhanced rate performance in novel ultrahigh surface area meso-/microporous carbon for supercapacitors, *Nano Energy* 33 (2017) 453–461.
- [41] W. Wang, H. Quan, W. Gao, R. Zou, D. Chen, Y. Dong, L. Guo, N-Doped hierarchical porous carbon from waste boat-fruited sterulia seed for high performance supercapacitors, *RSC Adv.* 7 (2017) 16678–16687.
- [42] M. Yang, Z. Zhou, Recent breakthroughs in supercapacitors boosted by nitrogen-rich porous carbon materials, *Adv. Sci.* 4 (2017) 1600408.
- [43] J. Sun, D. Yang, S. Lowe, L. Zhang, Y. Wang, S. Zhao, P. Liu, Y. Wang, Z. Tang, H. Zhao, X. Yao, Sandwich-Like reduced graphene oxide/carbon black/amorphous cobalt borate nanocomposites as bifunctional cathode electrocatalyst in rechargeable zinc-air batteries, *Adv. Energy Mater.* 8 (2018) 1801495.
- [44] W. Niu, L. Li, X. Liu, N. Wang, J. Liu, W. Zhou, Z. Tang, S. Chen, Mesoporous N-doped carbons prepared with thermally removable nanoparticle templates: an efficient electrocatalyst for oxygen reduction reaction, *J. Am. Chem. Soc.* 137 (2015) 5555–5562.
- [45] Z. Zhang, T. Cao, S. Liu, X. Duan, L.-M. Liu, S. Wang, Y. Liu, Substrate-Induced synthesis of nitrogen-doped holey graphene nanocapsules for advanced metal-free bifunctional electrocatalysts, *Part. Part. Syst. Char.* 34 (2017).
- [46] D. Gu, R. Ma, Y. Zhou, F. Wang, K. Yan, Q. Liu, J. Wang, Synthesis of nitrogen-doped porous carbon spheres with improved porosity toward the electrocatalytic oxygen reduction, *ACS Sustain. Chem. Eng.* 5 (2017) 11105–11116.
- [47] Y. Wang, S. Zuo, Y. Liu, Ammonia modification of high-surface-area activated carbons as metal-free electrocatalysts for oxygen reduction reaction, *Electrochim. Acta* 263 (2018) 465–473.
- [48] H.W. Liang, X. Zhuang, S. Brüller, X. Feng, K. Mullen, Hierarchically porous carbons with optimized nitrogen doping as highly active electrocatalysts for oxygen reduction, *Nat. Commun.* 5 (2014) 4973.
- [49] Z. Chen, J. Wen, C. Yan, L. Rice, H. Sohn, M. Shen, M. Cai, B. Dunn, Y. Lu, High-performance supercapacitors based on hierarchically porous graphite particles, *Adv. Energy Mater.* 1 (2011) 551–556.
- [50] J. Jiang, M. Zhou, H. Chen, Z. Wang, L. Bao, S. Zhao, S. Guan, J. Chen, Hierarchically porous carbon derived from an aqueous curable composition for supercapacitors, *Electrochim. Acta* 168 (2015) 300–307.
- [51] D.-C. Guo, J. Mi, G.-P. Hao, W. Dong, G. Xiong, W.-C. Li, A.-H. Lu, Ionic liquid C16mimBF₄ assisted synthesis of poly(benzoxazine-co-resol)-based hierarchically porous carbons with superior performance in supercapacitors, *Energy Environ. Sci.* 6 (2013) 652–659.
- [52] Y. Shu, J. Maruyama, S. Iwasaki, S. Maruyama, Y. Shen, H. Uyama, Fabrication of N-doped and shape-controlled porous monolithic carbons from polyacrylonitrile for supercapacitors, *RSC Adv.* 7 (2017) 43172–43180.
- [53] X. Li, Y. Song, L. You, L. Gao, Y. Liu, W. Chen, L. Mao, Synthesis of highly uniform N-doped porous carbon spheres derived from their phenolic-resin-based analogues for high performance supercapacitors, *Ind. Eng. Chem. Res.* 58 (2019) 2933–2944.
- [54] Z. Zhang, L. Li, Y. Qing, X. Lu, Y. Wu, N. Yan, W. Yang, Hierarchically interconnected N-doped carbon aerogels derived from cellulose nanofibrils as high performance and stable electrodes for supercapacitors, *J. Phys. Chem. C* 122 (2018) 23852–23860.
- [55] Y. Zhao, Y. Zhao, X. Ma, Y. Liu, Z. Li, T. Wang, H. Chen, J. Zhou, J. Li, X. Pan, E. Xie, Ammonia-assisted thermal activation of graphene-embellished biological fiber for flexible supercapacitors, *J. Alloys Compd.* 785 (2019) 944–950.
- [56] X. Zhang, Y. Jiao, L. Sun, L. Wang, A. Wu, H. Yan, M. Meng, C. Tian, B. Jiang, H. Fu, GO-induced assembly of gelatin toward stacked layer-like porous carbon for advanced supercapacitors, *Nanoscale* 8 (2016) 2418–2427.
- [57] H. Zhu, X. Wang, F. Yang, X. Yang, Promising carbons for supercapacitors derived from fungi, *Adv. Mater.* 23 (2011) 2745–2748.
- [58] E. Raymundo-Piñero, F. Leroux, F. Béguin, A high-performance carbon for supercapacitors obtained by carbonization of a seaweed biopolymer, *Advanced materials* 18 (2006) 1877–1882.

8-羟基喹啉及其衍生物的锌配合物合成研究进展

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摘要: 简述了有机发光材料 8-羟基喹啉金属螯合物的发展, 综述了固相法和液相法合成 8-羟基喹啉锌, 例举了在喹啉环上的 2、5 和 7 号位引入供电子基团或大共轭基团的 8-羟基喹啉衍生物的锌配合物性质, 介绍了通过改变聚合度制备 8-羟基喹啉衍生物的锌配合物方法, 杂环和 8-羟基喹啉共同做锌的配体合成新的发光材料的方法; 最后对 8-羟基喹啉和 8-羟基喹啉衍生物的锌配合物的合成进行总结和展望。

关键词: 8-羟基喹啉锌; 8-羟基喹啉衍生物; 8-羟基喹啉衍生物的锌配合物; 进展

中图分类号: O62

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电致发光 (electro luminescence, EL) 是将电能通过转换变为光能的一种发光方式。按材料的化学组成可分为无机 EL、有机 EL、无机有机复合 EL^[1-2]。其中有机 EL 又称为 OLED (organic light emitting diode), 由于具备一系列的优点而备受科技及产业界的青睐, 通常的发光器件都是以单层或多层结构出现^[3-4]。目前的一个研究热点是新型平面显示器发光技术的研发, 其目标是用新型的、效率高的、质量轻的显示器来代替传统笨重的、高耗能的阴极射线管^[5-6]。目前, 液晶显示器在某些领域里已经替代了阴极射线管, 在平面显示器的市场上占有一定的份额^[7]。而近几年来, 一种新型的有机电致发光平面显示器 (OLEDs) 受到了人们的广泛关注^[8]。有机电致发光平面显示器与目前的液晶平面显示器相比, 具有发光主动、质轻、薄, 且对比度好、无角度依赖性、低能耗等显著特点, 在平面显示器应用上有明显优势, 有很好的市场前景^[9-10]。

近年来, 金属配合物在催化、材料、生物活性等方面得到了广泛应用, 因此关于该类化合物的研究引起了人们极大的兴趣^[11-12]。8-羟基喹啉和 8-羟基喹啉衍生物因为吸光系数大、配位能力强而被广泛用于制备金属有机配合物发光材料^[13]。自从 1987 年 Tang 等^[14]报道了以 8-羟基喹啉铝为发光层制备的高亮度电致发光器件以来, 有机电致发光材料的研究受到广大科研工作者的极大关注。本文综述了 8-羟基喹啉及 8-羟基喹啉衍生物锌配合物的合成过程, 分析了未来发展方向, 为以后从事这方面的科研人员提供一点帮助。

1 8-羟基喹啉锌的合成研究

8-羟基喹啉锌分子结构图如图 1 所示。8-羟基喹啉锌在低压 26 V 下发黄光, 发光强度达到 16 200 cd/m², 是较好的发光材料^[15]。目前合成 8-羟基喹啉锌的方法有固相法和液相法, 液相法又叫溶剂热法。

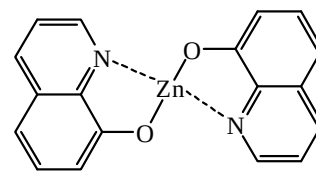


图 1 8-羟基喹啉锌分子结构

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1.1 固相法合成 8-羟基喹啉锌的研究

贾殿赠等^[16]以水合醋酸锌和 8-羟基喹啉为原料，室温下研磨充分后放置 6 h，最终得到产率为 77% 的 8-羟基喹啉锌。这种方法合成的产物不仅产率太低，而且产物的质量不稳定，放置一段时间后，产物的颜色变浅。钟学明等^[17]用湿固相—真空热熔法合成 8-羟基喹啉锌，将无水醋酸锌和 8-羟基喹啉按摩尔比 1:2 投料，并在研磨的过程中滴加无水乙醇，将研磨后的原料放入真空干燥器内，90~110℃ 加热 2~3 h，最终得到纯度达 97% 以上的 8-羟基喹啉锌。这种方法合成的 8-羟基喹啉锌，操作简单，通过加热强化了反应，使得产品纯度直接达到发光材料的要求^[18]。Li^[19]将七水合硫酸锌和 8-羟基喹啉按摩尔比 1:2 放入研钵中，在红外灯照射下保证研磨时的温度控制在 35~40℃，研磨完成后，在超声波振荡条件下先用蒸馏水洗涤再用酒精洗，最后得到纳米材料二水合 8-羟基喹啉锌。再通过改变锌盐，分别以氯化锌、氢氧化锌、二水合醋酸锌为原料，按上述步骤均合成出二水合 8-羟基喹啉锌。产物 TEM 测试表明用 $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ 作原料得到的产物颗粒最小， ZnSO_4 的颗粒最大。通过实验得出通过改变反应物、反应物的配比、加入惰性物质或加入溶剂会影响最终产物的形貌、粒径和尺寸。

1.2 液相法合成 8-羟基喹啉锌的研究

卫芳芳等^[20]在乙醇体系下，以 8-羟基喹啉和二氯化锌为反应物，考察了 8-羟基喹啉的浓度、反应的时间、反应的温度以及溶液的 pH 等影响因素，得出在 8-羟基喹啉为饱和浓度、反应 1 h、反应温度为 70℃、溶液 pH 为 8 的条件下，得到的产物的纯度和产率最高。但得到的产物需要用特制的装置真空升华提纯，操作过于繁琐且增加了合成的成本。Wang 等^[21]介绍了将 ZnCl_2 和 8-羟基喹啉作原料在甲醇中溶解完后加入反应釜中，然后在 150℃ 条件下反应 8 h，后在真空条件下 60℃ 加热 12 h 得到产物 8-羟基喹啉锌。这种方法能够合成高纯 8-羟基喹啉锌，但实验过程繁琐、耗时较长，溶剂甲醇对身体危害较大，不适用于大规模生产。Chen 等^[22]以 8-羟基喹啉和二水合醋酸锌为原料，按照 1:1 的摩尔比溶解在乙二醇中，溶解完成后转移到有聚四氟乙烯内衬的不锈钢反应釜中，密封后在 180℃ 下反应 24 h，反应完成冷却到室温，离心分离后用蒸馏水和无水乙醇洗涤，室温下干燥得到淡黄色粉末。通过这种方法得到了正八面体的 8-羟基喹啉锌，经测试有较好的发光性能。Tsuboi 等^[23]将 8-羟基喹啉和氧化锌按摩尔比 2:1 加入到蒸馏水中，在 90℃ 下反应 0.5 h，产物颜色由橙红色逐渐变为黄色，将最终得到的产物在 110℃ 下干燥，得到的产物的光致发光量子效率达到 0.45，是很好的发光材料。Marisa 等^[24]首先将 8-羟基喹啉溶解在乙酸中，后再和硫酸锌反应，用氨水调节 pH 至 5~9，反应完全后过滤，将得到的产物用水洗去多余的配体和硫酸根离子，在 60℃ 下干燥后保存在干燥器中。

2 8-羟基喹啉衍生物的锌配合物的合成研究

8-羟基喹啉金属螯合物电致发光材料具有较好的电子传输性能、荧光效率高、稳定性好等优点，但由于其颜色单一、难溶于有机溶剂等缺点限制了其发展前景，因此以 8-羟基喹啉衍生物为配体的金属螯合物便得到研究者的重视^[25-26]。研究者以 8-羟基喹啉为配体，改变配合物的聚合度^[27-28]、在 8-羟基喹啉环中引入新的基团或改变配体^[29-30]，可调节材料的电致发光颜色、得到成膜性更好、热稳定性更高的发光材料^[31]。8-羟基喹啉衍生物引入基团的位置如图 2 所示^[32-33]，研究较多的衍生物的种类及其发光颜色如表 1 所示。

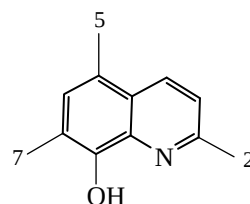


图 2 8-羟基喹啉衍生物引入基团的位置

表1 8-羟基喹啉衍生物种类及其发光颜色

衍生物名称	取代基位置			发光颜色
	2	5	7	
5-磺胺基-8-羟基喹啉锌	H	磺胺基	H	绿光
5,7-二甲基-8-羟基喹啉锌	H	甲基	甲基	橙色
5-取代-2-甲基-8-羟基喹啉锌	甲基	取代基	H	橙红色
5-聚乙烯醇-8-羟基喹啉锌	H	聚乙烯醇	H	蓝绿色
2-甲基-2,5'-乙烯基-二-8-羟基喹啉锌	甲基	乙烯基	H	橙色
2-(2-羟基苯乙烯基)-8-羟基喹啉锌	2-羟基苯乙烯基	H	H	黄绿色
2-呋喃乙烯基-8-羟基喹啉锌	呋喃乙烯基	H	H	黄色
2-[2-(2-氟代苯基)乙烯基]-8-羟基喹啉锌	取代基	H	H	青绿色
2-[2-(3-氟代苯基)乙烯基]-8-羟基喹啉锌	取代基	H	H	钠黄色

2.1 小分子 8-羟基喹啉衍生物的锌配合物的合成研究

刘鸿等^[34]研究了 2-呋喃乙烯基-8-羟基喹啉锌的合成, 首先将 2-甲基-8-羟基喹啉和糠醛溶解在乙酸酐中再转移到三口烧瓶中, 在 130℃ 下回流 40 h, 自然冷却到室温后过滤得到棕黑色沉淀, 将此沉淀溶于富马酸二甲酯溶液中后升温至 150℃ 并搅拌, 再向其中加入三乙胺反应 2 h 后冷却过滤得到黑色沉淀 2-呋喃乙烯基-8-羟基喹啉, 将得到的产物溶解到乙醇中并向其中加入醋酸锌反应 2 h 后过滤得到黄绿色沉淀, 即 2-呋喃乙烯基-8-羟基喹啉锌。产物经性能测试表明, 在最大激发波长下发黄色荧光, 且热稳定性良好。Singh 等^[35]用 5,7-二甲基-8-羟基喹啉和硫酸锌反应生成 5,7-二甲基-8-羟基喹啉锌。分别测试配体和锌配合物的紫外吸收光谱显示, 配体的最大吸收峰为 320 nm, 锌配合物的最大吸收峰为 412 nm, 发生红移。再将锌配合物和有机材料光发射装置配合使用, 证明有优良的真空升华成膜性, 是较好的橙光材料。Kunkely 等^[36]研究了 5,7-二碘-8-羟基喹啉锌的合成, 将 5,7-二碘-8-羟基喹啉和水合醋酸锌按摩尔比 2:1 加入到乙醇中, 加热至沸腾再将叔丁醇钾分次加入, 最终得到橙黄色沉淀, 过滤后先用热的酒精水溶液洗涤再用纯酒精洗涤, 最后得到产物。

2.2 多聚合 8-羟基喹啉锌配合物的合成研究

Huo 等^[37]利用 2-甲基-8-羟基喹啉和 4-3 氟甲基甲醛反应生成 2-(2-(4-3 氟甲基)乙烯基)8-羟基喹啉 (产物 1), 反应原料 2-甲基-8-羟基喹啉先和乙酸酐发生反应, 将羟基保护起来。再将得到的产物 1 和高氯酸锌反应最终得到六[2-(2-(4-3 氟甲基)乙烯基)8-羟基喹啉]三锌 (产物 2)。配体与锌配合物荧光发射光谱对比显示, 产物 1 的最大波长为 470 nm, 产物 2 的最大波长为 590 nm, 配合物相对于配体发生了红移。Yuan 等^[38]先用乙酸酐和 2-甲基-8-羟基喹啉反应, 保护喹啉环上的羟基, 后和 2-甲醛萘反应合成 2-(2-萘基-乙烯基)-羟基喹啉。再和 $\text{ZnBr}_2 \cdot 2\text{H}_2\text{O}$ 反应生成四[2-(2-萘基-乙烯基)-羟基喹啉]二锌。为了确定配体和 Zn^{2+} 的作用过程, 采用紫外滴定法最终确定配体和 Zn^{2+} 按照 2:1 的比例反应, 荧光测试表明其发黄光。王华等^[39]将 $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ 水溶液和 8-羟基喹啉乙醇溶液按体积比 1:1 混合搅拌加热, 在 70~80℃ 下反应 2 h, 得到的产物用乙醇重结晶后得到四-8-羟基喹啉锌, 其在 361℃ 下加热分解成 8-羟基喹啉锌。光致发光光谱测试表明, 在 365 nm 的波长激发下, 四-8-羟基喹啉锌和 8-羟基喹啉锌的最大激发波长分别为 550 nm 和 540 nm, 且前者比后者的强度大。两种材料镀膜后制成的发光器件经电致发光测试显示二者的光谱基本一致, 证明在蒸发镀膜的过程中四-8-羟基喹啉锌分解为 8-羟基喹啉锌。这种方法制得的四-8-羟基喹啉锌无法满足发光器件的制备。

2.3 高分子 8-羟基喹啉锌配合物的合成研究

周建萍^[40]研究了聚乙烯醇/8-羟基喹啉锌的合成, 首先将 8-羟基喹啉、甲醛和浓盐酸在 HCl 气体的保护下反应, 合成中间产物 5-氯甲基-8-羟基喹啉。再将 5-氯甲基-8-羟基喹啉加入到乙醇中回流加热后用水洗涤后得到白色沉淀 5-氯甲基-8-乙酰喹啉。后将聚乙烯醇溶解在富马酸二甲酯 (DMF) 中, 再向其中加入金属钠, 待其反应完全后再加入 5-氯甲基-8-乙酰喹啉, 最终制得聚乙烯醇/8-羟基喹啉, 最后将聚乙烯醇/8-羟基喹啉和氯化锌加入到 DMF 中, 反应完成后得到黄绿色粉末即聚乙烯醇/8-羟基喹啉锌。这种方法合成高分子化的 8-羟基喹啉锌操作繁琐, 且副产物过多。例如, 在第一步合成 5-氯甲基-8-羟基喹啉时, 当反应温度较低时得到 5-氯甲基-8-羟基喹啉, 当温度过高时得到二聚体 5,5'-亚甲基双(8-羟基喹啉)。产物聚乙烯醇/8-羟基喹啉锌经荧光测试表明其发光颜色介于蓝绿之间, 有较强的荧光发射峰。

2.4 含杂环的 8-羟基喹啉锌配合物的合成研究

Rai 等^[41]合成了 2,2'-二吡啶 8-羟基喹啉锌, 反应原料 8-羟基喹啉、2,2'-二吡啶和二水合醋酸锌按摩尔比 1:1:1 进行反应, 首先将二吡啶溶解在乙醇中后, 加入到三口烧瓶中在通氮气的条件下搅拌 30 min, 后将溶解了等量摩尔的 8-羟基喹啉乙醇加入三口烧瓶中, 在 70℃ 下搅拌 2 h, 搅拌完成后自然冷却到 50℃, 再向其中加入溶解了等摩尔质量的醋酸锌的去离子水, 搅拌 2 h 后, 将混合液过滤, 得到的沉淀洗涤后在 70℃ 下加热 24 h, 最终得到淡黄色的产物。产物的热重分析和电致发光测试表明其有很好的热稳定性和发光性能, 是很有应用前景的黄色发光材料。

3 结论

现有文献表明合成 8-羟基喹啉锌的方法有固相法和液相法, 二者各有优缺点, 固相法操作简单, 原子利用率高, 便于大规模合成, 但是得到的产品质量不稳定, 放置一段时间后产品颜色会变浅。液相法能制得高纯的产品, 但实验过程繁琐, 耗时较长, 得到的产物需进一步纯化。8-羟基喹啉锌衍生物的合成主要是在喹啉环上的 2、5 和 7 号位接入新的基团, 通常是一些供电子基团、大共轭取代基, 或通过引入杂环配体、改变聚合度或是将 8-羟基喹啉锌变成高分子聚合物以此和锌配合物合成新的材料。这些方法得到的新材料不仅使得 8-羟基喹啉锌体系获得了更多的发光颜色, 而且增强了材料的热稳定性, 有较好的应用前景。

8-羟基喹啉及其衍生物的金属螯合物虽然研发时间较短, 可已经取得可喜的成果, 但要满足亮度高、成膜性好、高效率、寿命长仍需要科研工作者的不懈努力。随着人们对 8-羟基喹啉锌衍生物的不断探索, 性能更加优良的材料将会进一步被发现, 而后运用到实际生产中, 并最终改变人们的生活。

参考文献:

- [1] 葛葆珪. 电致发光原理及应用[M]. 北京: 北京测绘出版社, 1985: 1-3.
- [2] Hu B, Li D P, Prakash M, *et al.* Modeling study of mesh conductors and their electroluminescent devices[J]. *Applied Physics Letters*, 2015, 106(7): 1-5.
- [3] 刘念, 谢明贵, 蒋青, 等. 有机 EL 发光材料的现状[J]. *液晶与显示*, 1996, 11(2): 136-141.
- [4] Slawinski M, Weingarten M. Investigation of large-area OLED devices with various grid geometries[J]. *Organic Electronics*, 2013, 14(10): 2387-2391.
- [5] 滕鹤松. 迅速发展的有机电致发光 (OEL) 显示器件[J]. *固体电子学研究和进展*, 2002, 22(8): 266-267.
- [6] 唐超, 刘烽, 徐慧, 等. 聚芴类电致发光材料[J]. *化学进展*, 2007, 19(10): 1553-1561.

- [7] Huang B J, Chen W, Ong C D, *et al.* Development of constant-power driving control for light-emitting-diode (LED) luminaire[J]. Applied Thermal Engineering, 2013, 50(1): 645-651.
- [8] 欧阳新华, 曾和平, 谢彦. 8-羟基喹啉衍生物及其金属配合物的合成与光致发光特性[J]. 有机化学, 2007, 27(3): 402-408.
- [9] Sapochak L S, Benincasa F E, Schofield R S, *et al.* Electroluminescent zinc(II) bis(8-hydroxyquinoline): structural effects on electronic states and device performance[J]. American Chemical Society, 2002, 124(21): 6119-6125.
- [10] 丁洪流. 喹啉锌类有机电致发光材料、器件的制备及光电性能研究[D]. 上海: 华东师范大学, 2008, 5.
- [11] 文芳岱, 王海桥, 李效玉. 一种新型双8-羟基喹啉锌高分子配合物的合成及光致发光性能[J]. 北京化工大学学报, 2006, 33(5): 46-49.
- [12] Royzen M, Canary J W. Structural parameters of Zn(II) complexes of 8-hydroxyquinoline-based tripodal ligands affect fluorescence quantum yield[J]. Polyhedron, 2013, 58(10): 85-91.
- [13] Nosova E V, Stupina T V, Lipunova G N, *et al.* Synthesis and fluorescent properties of 2-styryl-6,7-difluoro-8-hydroxyquinoline and its Zn(II) complex[J]. Journal of Fluorine Chemistry, 2013, 150(1): 36-38.
- [14] Tang C W, Van Slyke S A. Organic electroluminescent diodes[J]. Applied Physics Letters, 1987, 51(12): 913-915.
- [15] 吕青竹. 8-羟基喹啉金属配合物的有机发光材料研究进展[J]. 辽宁师专学报, 2008, 10(3): 13-14.
- [16] 贾殿赠, 李昌雄, 傅岩, 等. 一步法室温(准室温)固相化学反应合成 8-羟基喹啉的 Co(II)、Ni(II)、Cu(II)、Zn(II) 配合物[J]. 化学通报, 1993, 51: 363-367.
- [17] 钟学明, 康建壮. 一种直接合成有机发光材料 8-羟基喹啉锌的方法: 中国, CN104649970A[P]. 2015-02-09.
- [18] 朱见杰. 有机小分子半导体材料升华提纯工艺的改进[D]. 陕西: 西北大学, 2011, 6.
- [19] Li D H, Li X Q. Ultrasonication solid state chemical reaction synthesis and characterization of nanocrystalline Zn(Oxin)₂·2H₂O (zinc 8-quinolinolate)[J]. Transactions of Nonferrous Metals Society of China, 2006, 16(1): 388-392.
- [20] 卫芳芳, 王华, 徐阳, 等. 8-羟基喹啉金属配合物的制备与提纯[J]. 人工晶体学报, 2009, 38(3): 757-760.
- [21] Wang X H, Shao M W, Liu L. High photoluminescence and photoswitch of bis(8-hydroxyquinoline)zinc nanoribbons[J]. Synthetic Metals, 2010, 160(7-8): 718-721.
- [22] Chen X B, Yang X D, Hu X W, *et al.* Fabrication and electrogenerated chemiluminescence properties of uniform octahedral 8-hydroxyquinoline zinc (Znq₂)[J]. Materials Research Bulletin, 2013, 48(4): 1675-1680.
- [23] Tsuboi T, Nakai Y, Torii Y. Photoluminescence of bis(8-hydroxyquinoline) zinc(Znq₂) and magnesium (Mgq₂)[J]. Central European Journal of Physics, 2012, 10(2): 524-528.
- [24] Marisa S C, Clóvis A R, Valentina C M, *et al.* Preparation and thermaldecomposition of copper(II), zinc(II) and cadmium(II) chelates with 8-hydroxyquinoline[J]. Quimica Nova, 1999, 22(1): 41-46.
- [25] 张蕾. 8-羟基喹啉衍生物锌配合物的合成及性能研究[D]. 山西: 中北大学, 2012, 6.
- [26] Yuan G Z, Shan W L, Chen J B, *et al.* Synthesis, structure and photophysical properties of a binuclear Zn(II) complex based on 8-hydroxyquinoline ligand with naphthyl unit[J]. Journal of Luminescence, 2015, 160(1): 16-21.
- [27] 李会丽, 潘宁, 李奇, 等. 新型 8-羟基喹啉衍生物及其金属锌配合物的制备与荧光性能[J]. 陕西师范大学学报, 2011, 39(1): 55-59.
- [28] 王崇侠, 余忠清, 李邗, 等. 二(2-苯基-8-羟基喹啉)锌和喹啉锌的合成和荧光性质[J]. 发光学报, 2004, 25(4): 415-418.
- [29] 苏斌, 赵静, 刘春波, 等. 基于 8-羟基喹啉及其衍生物的有机小分子电致发光材料[J]. 化学进展, 2013, 25(7): 1091-1100.
- [30] 雷钢铁, 张志勇, 曹胡军, 等. 8-羟基喹啉-[2-(2-羟基苯基-5-苯基-1,3,4-噁二唑)合锌 (Zn(ODZ)q) 的合成及性能研究[J]. 湘潭大学自然科学学报, 2012, 34(3): 56-59.
- [31] Li S J, Li Y, Zhang J A. Synthesis and performances of a tridentate 8-hydroxyquinoline derivative ligand and its zinc

- complex[J]. *Inorganic Chemistry Communications*, 2012, 20(1): 334-339.
- [32] Nosova E V, Stupina T V, Lipunova G N, *et al.* Synthesis and fluorescent properties of 2-styryl-6,7-difluoro-8-hydroxyquinoline and its Zn(II) complex[J]. *Journal of Fluorine Chemistry*, 2013, 150(1): 36-38.
- [33] Li C N, Wong C Y, Lai P T, *et al.* Improved performance of OLEDs with ITO surface treatments[J]. *Thin Solid Films*, 2005, 477(1-2): 57-62.
- [34] 刘鸿, 蔡建伟, 陈耀来, 等. 8-羟基喹啉衍生物及其锌配合物的合成[J]. *化学研究与应用*, 2010, 22(10): 1321-1325.
- [35] Huo Y P, Wang C P, Lu J G, *et al.* A novel trimeric Zn(II) complex based on 8-hydroxyquinoline with trifluoromethylbenzene group: Synthesis, crystal structure, photophysical properties and DNA binding[J]. *Journal of Molecular Structure*, 2015, 1098(1): 311-317.
- [36] Kunkely H, Vogler A. Optical properties of Zinc(II) 5,7-diiodo-8-quinolinolate in solution. Phosphorescence under ambient conditions[J]. *Chemical Physics Letters*, 2003, 376(1): 226-229.
- [37] Singh K, Kumar A, Srivastava R, *et al.* Synthesis and characterization of 5,7-dimethyl-8-hydroxyquinoline and 2-(2-pyridyl)benzimidazole complexes of Zinc(II) for optoelectronic application[J]. *Optical Materials*, 2011, 34(1): 221-227.
- [38] Yuan G Z, Shan W L, Chen J B, *et al.* Synthesis, structure and photophysical properties of a binuclear Zn(II) complex based on 8-hydroxyquinoline ligand with naphthyl unit[J]. *Journal of Luminescence*, 2015, 160(1): 16-21.
- [39] 王华, 郝玉英, 李洁, 等. 两种以 Znq_2 为基体的新型电致发光材料的合成与性能[J]. *发光学报*, 2006, 27(2): 249-253.
- [40] 周建萍. 高分子化 8-羟基喹啉金属配合物的制备及其发光性能的研究[D]. 湖南: 湘潭大学, 2002, 4.
- [41] Rai V K, Srivastava R, Chauhan G, *et al.* Synthesis and electroluminescence properties of zinc(2,2'-bipyridine)-8-hydroxyquinoline[J]. *Materials Letters*, 2008, 62(17-18): 2561-2563.

Progress in Synthesis of Zinc Complexes of 8-Hydroxyquinoline and 8-Hydroxyquinoline Derivatives of Luminescent Materials

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Abstract: The paper had summerized the development of organic light emitting material 8-hydroxyquinoline metal chelates, detailed introduction the solid and liquid phase synthesis of 8-hydroxyquinoline zinc, as well as the number 2,5,7-quinoline ring bit introduction of electron donating groups or large conjugate groups, or in order to prepare a zinc complex method of 8-hydroxyquinoline derivative of zinc alter the degree of polymerization, and describe heterocyclic and 8-hydroxyquinoline derivative together did zinc ligand synthesis of new luminescent materials methods, and the development of zinc and 8-hydroxyquinoline derivatives was summarized and discussed.

Key words: 8-hydroxyquinoline zinc; zinc complex of 8-hydroxyquinoline derivative; synthesis; progress

LED 封装硅胶增黏剂的合成及黏接性能研究

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[摘 要] 以羟基乙烯基硅油、 γ -(2,3-环氧丙氧)丙基三甲氧基硅烷(KH-560)、 γ -甲基丙烯酰氧丙基三甲氧基硅烷(KH-570)为原料, 通过缩合反应制备得到含环氧基、丙烯酰氧基和乙烯基的聚硅氧烷增黏剂。以乙烯基硅油与含氢硅油为基础材料制备得到加成型 LED 封装胶空白胶, 添加不同增黏剂后对其黏接性能进行研究。结果表明: $n(\text{KH560}):n(\text{KH570})$ 的摩尔比为 9:1 时制得的有机硅增黏剂, 在 LED 封装胶中添加量为 2% 时黏接性能达到最佳状态, 且对 LED 铁支架的黏接性能优于 LED 铜支架。

[关键词] 封装硅胶; 增黏剂; 黏接性能

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Synthesis and Properties of Adhesion Promoter Used in LED Packaging Silicone Rubber

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Abstract: Taking hydroxyvinyl silicone oil, γ -(2,3-epoxypropoxy) propyltrimethoxysilane (KH-560), γ -methacryloxypropyl trimethoxysilane (KH-570) as raw materials, silicone adhesion promoters containing epoxy, acryloyloxy and vinyl groups were synthesized by condensation reaction. The blank LED packaging silicone rubber were prepared by vinyl silicone oil and hydrogen silicone oil, the properties were studied by adding different kinds of adhesion promoters. The experiments demonstrated that the silicone adhesion promoter synthesized by KH560 and KH570 with the molar ratio of 9:1 has the best adhesion performance when its containing ratio in the LED packaging silicone rubber is 2%. And the adhesion performance of the LED iron bracket is superior to that of the LED copper bracket.

Key words: LED silicone rubber; adhesion promoter; adhesion property

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引言

传统的小功率LED一般使用环氧树脂作为封装材料,因其与聚邻苯二甲酰胺(PPA)、铝和银等LED支架材料黏接力好,且其热膨胀系数与PPA相近,封装后LED具有很高的可靠性^[1]。但是,随着LED功率越来越大,对封装材料的要求也越来越高,环氧树脂在高温下易黄变,不耐紫外老化,已经很难满足大功率LED封装的要求^[2-3]。

有机硅材料具有非常好的化学稳定性,耐温耐老化性能优异,目前已经成为大功率LED封装的首选材料^[4]。然而,由于有机硅材料表面能低,缺少有效的活性基团,其与各类LED基材的黏接力较差^[5],在大多数情况下不能直接用于LED封装。如何通过使用增黏剂使硅胶与基材之间的黏接效果得到改善,适当地提升有机硅材料的表面能,成为有机硅材料研究领域的一个热点^[6-7]。在LED封装硅胶材料中,使用合适的增黏剂,对发光二极管的亮度、效率和寿命等有至关重要的影响^[8-10]。

目前LED封装硅胶上使用的增黏剂基本是以偶联剂为基础进行改性得到的,常用的改性方法包括缩合反应和硅氢加成反应两种。硅氢加成反应是以含氢硅油或者含氢硅烷单体等为原料,与含乙烯基的硅烷偶联剂在铂金催化下进行硅氢加成反应制备而成^[11-12],该类增黏剂由于使用了铂金催化剂,存在催化剂残留的问题,会影响LED封装硅胶的储存稳定性。通过缩合反应制备增黏剂,合成过程简单,产品产率高,得到的产品与硅胶相容性好,

缩合反应常用的催化剂包括无机酸、无机碱、离子交换树脂和金属络合物等^[9,13]。

本文采用不同结构的硅烷偶联剂,通过与羟基乙烯基硅油进行缩合反应,制备得到不同结构的硅胶增黏剂,对增黏剂的结构进行表征,并对制备的LED封装硅胶的黏接性能进行深入的研究。

1 实验

1.1 主要原料及仪器设备

乙烯基硅油、乙烯基MQ树脂和含氢硅油:工业级,浙江润禾有机硅新材料有限公司;羟基乙烯基硅油:工业级,建德市聚合新材料有限公司;KH-560, KH570:工业级,曲阜晨光化工有限公司;铂金催化剂:工业品,东莞市科贝硅胶材料有限公司;乙炔基环己醇:分析纯,北京百灵威科技有限公司;钛络合物:工业级,山东和瑞东精细化学有限公司。

红外光谱仪: Shimadzu IR Prestige-2, 岛津公司;阿贝折射仪: WYA-2WAJ型, 武汉格莱莫检测设备有限公司;万用电子拉力机: CTM2500型, 上海协强仪器有限公司;电动搅拌器: JJ-1型, 江苏晨阳电子仪器厂;电子分析天平: FA2004型, 上海上平仪器有限公司;数显控温电热套: SXKW型, 北京市永光明医疗仪器有限公司;循环水真空泵: SHB-3型, 郑州杜甫仪器厂;LED支架: 5050、3528、5730, 江西亚中电子科技股份有限公司。

1.2 硅胶增黏剂的合成

增黏剂的合成反应机理如图1所示,具体的合成过程如下:在带有机机械搅拌、温度计和回流冷凝

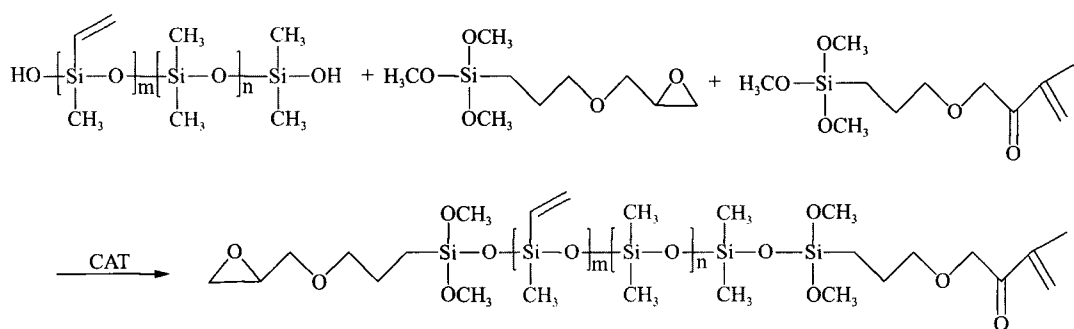


图1 增黏剂合成反应机理

管的三口瓶中,按照配方加入一定量的羟基乙烷基硅油、KH-560 和 KH-570,先搅拌 5 min 使其混合均匀,再加入质量分数为 0.5% 的钛络合物催化剂,继续搅拌并升温至 80 ℃,反应 5 h。反应结束后,升温至 100 ℃ 并通过减压蒸馏除去低沸物,待收集的烧瓶内无液滴凝聚而流下时停止加热,冷却至室温然后关掉真空泵并出料,得到目标产物。

1.3 加成型 LED 封装胶的制备

根据乙烷基硅油、乙烷基 MQ 硅树脂的乙烷基含量和含氢硅油的含氢量,按照 Si-H/Si-Vi 的摩尔比为 1.5,计算得到空白硅胶配方。准确称取乙烷基 MQ 硅树脂、乙烷基硅油和催化剂,电动搅拌混合均匀得到 A 组分,准确称取乙烷基硅油、含氢硅油和抑制剂,电动混合均匀得到 B 组分。

1.4 硅胶黏接强度测试

将制备的空白 A、B 组分按照质量比 1:1 混合,添加增黏剂后搅拌混合均匀,真空脱除气泡。使用铝板作为测试基材,按照图 2 所示制备所需的黏接强度测试试样,根据 GB/T 7124—2008 标准对硅胶与铝板的剪切黏接强度进行测试。

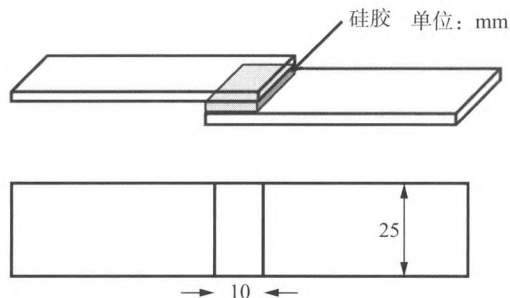


图 2 剪切黏接强度测试试样示意图

1.5 硅胶的 LED 封装性能测试

将制备的空白 A、B 组分按照质量比 1:1 混合,添加增黏剂后搅拌混合均匀,真空脱除气泡,在经过 150 ℃ 高温烘烤的 LED 支架上进行点胶。将点胶后的支架放入烘箱中,按照 80 ℃ 1 h,随后 150 ℃ 3 h 的条件进行固化。

固化完成后,将支架放入 100 ℃ 装有红墨水的恒温水浴锅中进行水煮实验,在红墨水中每煮 1 h 就取出用室温水冷却,观察 LED 支架灯珠中渗入

红墨水的比例,并做好记录,待支架上的大部分灯珠都有红墨水渗入时停止水煮。

2 结果与讨论

2.1 增黏剂的结构表征

图 3 为增黏剂的红外光谱图,其中 a、b 分别为 KH570 和 KH560 的谱图,c 为 $n(\text{KH570}):n(\text{KH560})$ 摩尔比为 1:1 时合成的增黏剂谱图,d 为全部用 KH560 合成的增黏剂谱图。从图中可清晰地观察到 800 cm^{-1} 和 $1000\sim 1100\text{ cm}^{-1}$ 具有很强的特征吸收峰,分别归属于 Si—O 键的对称伸缩振动峰和非对称伸缩振动峰,c、d 在 $1000\sim 1100\text{ cm}^{-1}$ 处峰较宽,说明硅氧键的聚合度较高。此外,在 3030 cm^{-1} 处的特征吸收峰为乙烷基中的碳氢伸缩振动峰, 1730 cm^{-1} 处为 C=O 键的伸缩振动吸收峰,c 谱图在该处吸收峰较明显,说明 KH570 已经成功接枝到反应产物中。通过红外测试说明 KH560 与 KH570 可以成功接枝到了聚硅氧烷的主链上,通过该反应可以得到含有多种活性成分的高分子量硅胶增黏剂。

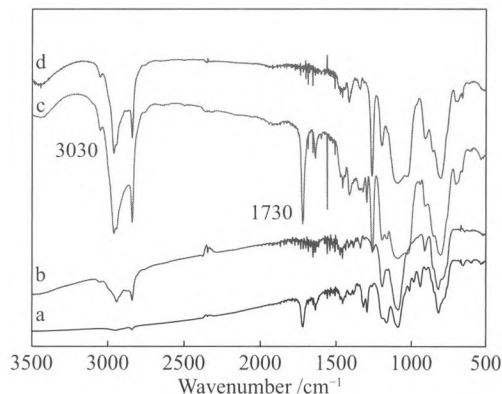


图 3 增黏剂红外光谱图

2.2 原材料对比对增黏剂折射率的影响

表 1 为不同原材料对比对合成增黏剂的折射率的影响,从表中可以看出,由不同摩尔比的两种偶联剂制备得到的有机硅增黏剂折射率都在 1.423 ~ 1.425 之间,且折射率随着 KH560 与 KH570 摩尔比的增大而逐渐减小。将制备的 5 种增黏剂分别按照硅胶总质量的 1.5% 加入到硅橡胶中,混

合均匀, 产品均为无色透明状, 说明其与硅胶相容性较好。

表 1 原材料对比对增黏剂折射率的影响

样品编号	$n(\text{KH560}):n(\text{KH570})$ (摩尔比)	增黏剂折射率
1	1:9	1.425 0
2	3:7	1.425 4
3	5:5	1.423 8
4	7:3	1.423 7
5	9:1	1.423 2

2.3 原材料对比对硅胶黏接强度及 LED 封装性能的影响

以铝板为测试基材, 根据 GB/T 7124—2008 对制备的 5 种增黏剂的黏接强度进行测试, 测试结果如图 4 所示。从图中可以看到, 随着 $n(\text{KH560}):n(\text{KH570})$ 比例的增加, 硅胶与铝板的黏接强度逐渐增加, 当两者摩尔比为 9:1 时, 黏接强度可达 1.76 MPa, 相比不加增黏剂时的 0.4 MPa, 黏接力提升到了原来的 4 倍多。

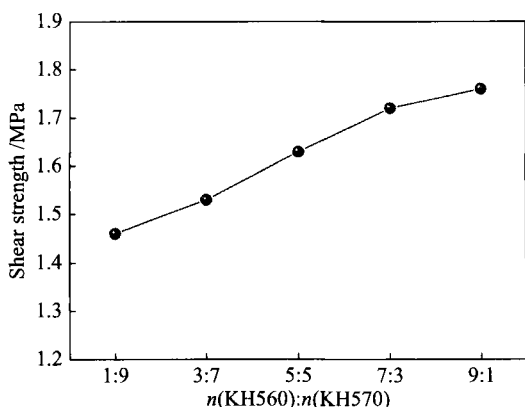


图 4 原材料对比对硅胶与铝板黏接强度的影响 (增黏剂用量 1.5%)

将制备的增黏剂按照硅胶总质量的 1.5% 加入到空白硅胶中混合均匀, 经过真空脱泡后, 分别点胶到 LED 铁支架和铜支架上进行黏接测试, 通过红墨水水煮的方法对其性能进行评价。不同配比的红墨水渗透率随着水煮时间的变化曲线如图 5 所示。

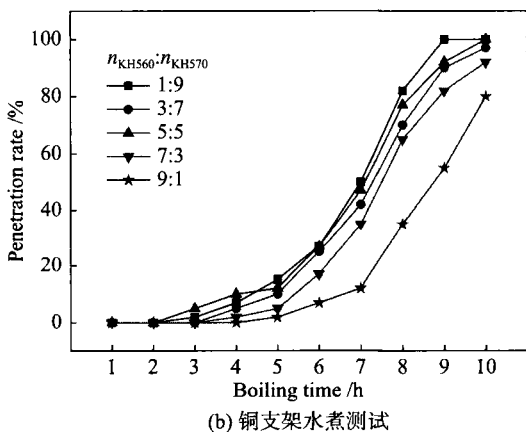
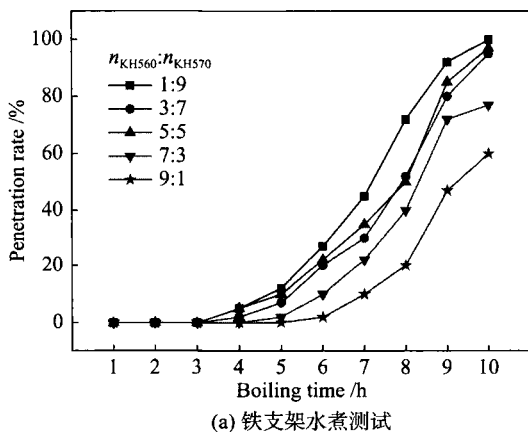


图 5 原材料对比对不同 LED 支架水煮渗透率的影响

从图 5 中可以看出, 5 种硅增黏剂对 LED 铁支架和 LED 铜支架灯珠渗入红墨水的比例都随着水煮时间的增加而增大, 随着 KH560 比例的增加, 红墨水渗入率在下降, 当 $n(\text{KH560}):n(\text{KH570})$ 为 9:1 时制得的有机硅增黏剂黏接性能最佳。对比图 5a 和图 5b, 在相同水煮时间时, LED 铁支架浸入红墨水的比例比 LED 铜支架更小, 说明该反应制备的硅胶增黏剂对 LED 铁支架的黏接性能要优于

LED 铜支架。

2.4 增黏剂用量对硅胶黏接强度及 LED 封装性能的影响

根据 2.3 的测试结果, 选择 $n(\text{KH560}):n(\text{KH570})$ 摩尔比为 9:1 时制备的增黏剂, 添加不同比例到空白胶中, 同样使用铝基板为测试基材, 对增黏剂用量对硅胶的黏接强度的影响进行测试, 结果如图 6 所示。

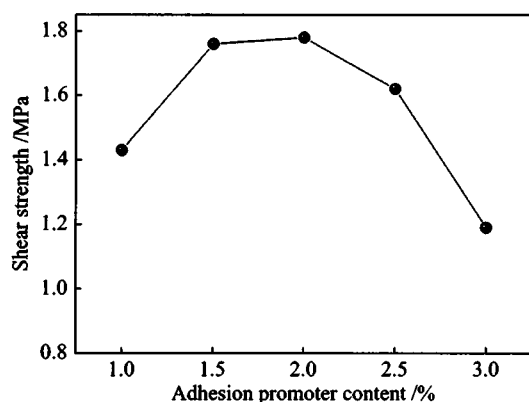


图 6 增黏剂用量对硅胶与铝板黏接强度的影响

从图中可以看到,随着增黏剂用量的提高,硅胶与铝板的剪切黏接强度先升高后降低,当增黏剂用量为 2% 时,黏接强度最高,达到 1.78 MPa。当增黏剂用量再提高后,由于过量的增黏剂对硅胶的结构产生了破坏,硅胶的力学强度出现下降,从而

导致硅胶与铝板的黏接强度也出现迅速下降。

同样,使用制备的 $n(\text{KH560}):n(\text{KH570}) = 9:1$ 的增黏剂,添加不同用量到空白硅胶中,分别点胶到 LED 铁支架和铜支架上进行黏接测试,通过红墨水水煮的方法对其性能进行评价,不同增黏剂用量的红墨水渗透率随着水煮时间的变化曲线如图 7 所示。

从图 7 中可以看出,LED 铁支架和 LED 铜支架灯珠浸入红墨水的比例都随着水煮时间的增加而增大,随着增黏剂用量的增加,红墨水的渗入比例先减小后又增加,当添加量为 2% 时,红墨水的渗入比例最小,性能最佳,与黏接强度测试结果一致。同样水煮时间,LED 铁支架浸入红墨水的比例总体比 LED 铜支架更小,说明该有机硅增黏剂对 LED 铁支架的黏接性能优于 LED 铜支架。

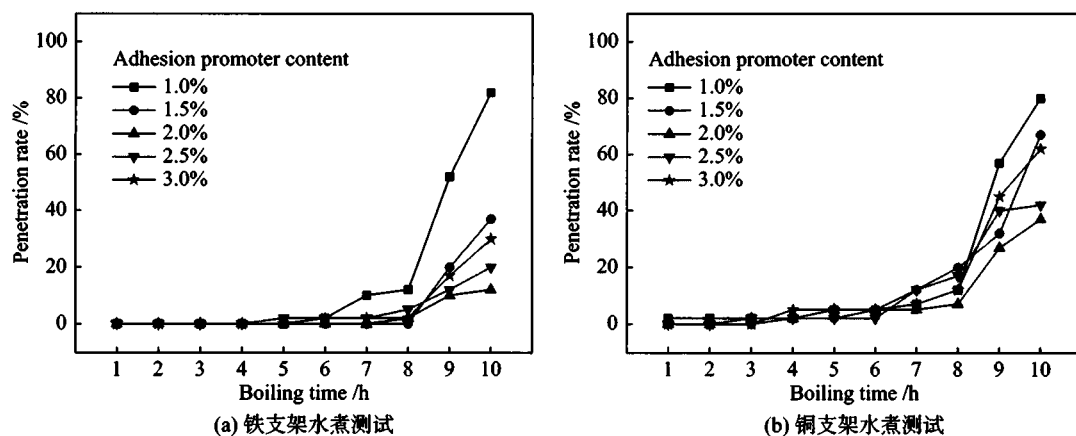


图 7 增黏剂用量对不同 LED 支架水煮渗透率的影响

3 结 论

1) 由羟基乙烯基硅油、KH560 与 KH570 为原材料制备的有机硅增黏剂折射率都在 1.423 ~ 1.425 之间,与甲基硅胶的折射率相近。加入到空白 LED 封装胶中,都为无色透明状,表明增黏剂与硅

胶相容性好。

2) 当 $n(\text{KH560}):n(\text{KH570})$ 摩尔比为 9:1 制得的有机硅增黏剂,在 LED 封装胶中的配比为 2% 时黏接性能达到最佳状态,且对 LED 铁支架的黏接性能优于 LED 铜支架。

【参考文献】

- [1] 杨媛媛,张成祥,赵国静,等. 环氧树脂电子封装胶研究进展 [J]. 化学推进剂与高分子材料,2017,15(3):54-57.

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- pattern analysis and machine intelligence,2015,37(9):1904-1916.
- [7] GIRSHICK R. Fast R-CNN[C]//Proceedings of the IEEE International Conference on Computer Vision,2015:1440-1448.
- [8] REN S,HE K,GIRSHICK R,et al. Faster R-CNN:towards real-time object detection with region proposal networks[C]//Advances in Neural Information Processing Systems,2015:91-99.
- [9] 张银松,赵银娣,袁慕策. 基于改进 Faster-RCNN 模型的粘虫板图像昆虫识别与计数 [J]. 中国农业大学学报,2019,24(5):115-122.
- [10] 莫宏伟,汪海波. 基于 Faster R-CNN 的人体行为检测研究 [J]. 智能系统学报,2018,13(6):967-973.
- [11] 林刚,王波,彭辉,等. 基于改进 Faster-RCNN 的输电线巡检图像多目标检测及定位 [J]. 电力自动化设备,2019,39(5):213-218.
- [12] DAI J,LI Y,HE K,et al. R-FCN:Object detection via region-based fully convolutional networks[C]//Advances in Neural Information Processing Systems,2016:379-387.
- [13] FELZENSZWALB P F,HUTTENLOCHER D P. Efficient graph-based image segmentation [J]. International journal of computer vision,2004,59(2):167-181.
- [14] IOFFE S,SZEGEDY C. Batch normalization:accelerating deep network training by reducing internal covariate shift [J]. Computer science,2015,1502:03167.
- [15] BODLA N,SINGH B,CHELLAPPA R,et al. Soft-NMS-improving object detection with one line of code[C]//Proceedings of the IEEE International Conference on Computer Vision,2017:5561-5569.
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(上接第 72 页)

- [2] CHEN W,FAN J,QIAN C,et al. Reliability assessment of light-emitting diode packages with both luminous flux response surface model and spectral power distribution method [J]. IEEE access,2019,7:68495-68502.
- [3] LOWES T,WILCOX K W,KELLER B,et al. LED packages with chips having insulated surfaces:U.S. Patent 10,622,522[P]. 2020-4-14.
- [4] 冯亚凯,佟琳,孙绪筠,等. 金刚烷改性有机硅 LED 封装材料的制备与性能 [J]. 天津大学学报,2019,52(2):129-135.
- [5] 张利利,程宪涛,李清高,等. 高性能有机硅增粘剂的合成及应用 [J]. 有机硅材料,2015,29(6):444-448.
- [6] 林敏婕,张成洋,葛佳音,等. 含双活性基团有机硅增粘剂制备及性能研究 [J]. 粘接,2018,39(1):23-27.
- [7] PAN Z,SUN R,ZHU S,et al. The synthesis,characterization and properties of silicone adhesion promoters for addition-cure silicone rubber [J]. Journal of adhesion science and technology,2018,32(10):1-14.
- [8] PAN K,ZENG X,LI H,et al. Synthesis of phenyl silicone resin with epoxy and acrylate group and its adhesion enhancement for addition-cure silicone encapsulant with high refractive index [J]. Journal of adhesion science and technology,2016,30(24):1-11.
- [9] LIU Y,LUAN X,FENG Y,et al. Self-adhesive epoxy modified silicone materials for light emitting diode encapsulation [J]. Polymers advanced technologies,2017,28(11):1473-1479.
- [10] 张利利,邱浩孟,程宪涛,等. 有机硅 LED 封装材料的粘接性能研究 [J]. 合成材料老化与应用,2015,44(5):34-36,67.
- [11] KATO N. Addition curable self-adhesive silicone rubber composition:U.S. Patent 8,937,123B2[P]. 2015-1-20.
- [12] 罗洋,霍延平,梁亮,等. 多功能有机硅增粘剂的合成及应用 [J]. 有机硅材料,2019,33(5):365-370.
- [13] KIM Y,LIM Y,LEE D,et al. A highly adhesive siloxane LED encapsulant optimized for high thermal stability and optical efficiency [J]. Journal of materials chemistry c,2016,46(4):10791-10796.

MQ硅树脂的合成及应用研究进展

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摘要: MQ 硅树脂作为一类重要的有机硅材料, 可用于有机硅压敏胶的合成以及硅橡胶的补强等, 其合成和应用已经得到了广泛的研究。随着高性能有机硅材料对产品透光率等要求的提高, MQ 硅树脂的应用得到了越来越多的关注, 尤其在液体硅橡胶领域, 其产量和用量都在不断增加。

关键词: MQ 硅树脂; 硅橡胶; 研究进展

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Research Progress on Synthesis and Application of MQ Silicone Resins

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Abstract: MQ silicone resin, as an important class of silicone materials, which can be used in organic silicone pressure sensitive adhesive and reinforcement of silicone rubber, has been widely studied in synthesis methods and applications. As the requirements of better light transmittance of high-performance silicone materials, MQ silicone resin has attracted increasing attention, especially in liquid silicone rubber. The output and consumption of MQ silicone resin are increasing year by year.

Key words: MQ silicone resin; silicone rubber; research progress

MQ 硅树脂通常是指由单官能硅氧链节 (M, $R_3SiO_{1/2}$) 与四官能硅氧链节 (Q, $SiO_{2/4}$) 组成的硅树脂, 可以广泛应用于有机硅压敏胶的合成、透明有机硅凝胶和硅橡胶的补强等领域, 是一类重要的有机硅原料。MQ 硅树脂从形态上可以分为液体和固体两类, 从结构上可以分为甲基 MQ 硅树脂、乙烯基 MQ 硅树脂以及含氢 MQ 硅树脂等。其中, 含乙烯基和含氢的 MQ 硅树脂主要应用于液体硅橡胶的补强中, 与白炭黑等传统的补强填料相比, 使用 MQ 硅树脂补强的产品透明度更高, 且加入到产品中后黏度上升不明显, 非常适用于对透明度要求更高的液体硅橡胶产品的生产中。

本文从合成和应用两方面对 MQ 硅树脂的研究进展进行了综述。

1 MQ硅树脂的合成

根据使用原料的不同, MQ 硅树脂的合成方法主要有两种: 以正硅酸乙酯 (TEOS) 为原料和以水玻璃 (硅酸钠的水溶液) 为原料。两者各有优缺点, 水玻璃的方法成本低, 但分子量分布宽, 反应过程不易控制; 而正硅酸乙酯的方法可以得到更高的产率, 所得产品分子量分布窄, 过程也更容易控制, 但是成本较高。

1.1 以正硅酸乙酯为原料

曾启华等采用六甲基二硅氧烷、四甲基二乙烯基二硅氧烷, 与正硅酸乙酯通过受控水解反应合成了不同乙烯基含量的 MQ 硅树脂。该 MQ 硅树脂为白色粉末, 在多种溶剂中都具有良好的溶解性, 同时具有很好的热稳定性。辛帅等以正硅酸乙酯, 六甲基二硅氧烷和乙烯基二甲基乙氧基硅烷为原料, 通过水解缩聚反应制备了乙烯基 MQ 硅树脂, 对产物的结构进行了分析, 并求得了乙烯基 MQ 硅树脂在最大失重区的热分解动力学方程。

胡生祥等采用六甲基二硅氧烷、四甲基二乙烯基二硅氧烷、二氢四甲基二硅氧烷为封端剂, 与正硅酸乙酯进行水解缩合反应制备甲基、乙烯基以及含氢的 MQ 硅树脂, 对产品的耐温性能进行了研究, 结果表明, 乙烯基的 MQ 硅树脂耐温性最好, 甲基次之, 含氢的耐温性最差。

Ji 等以正硅酸乙酯和乙烯基双封头等经水解缩聚制得含有乙烯基的 MQ 硅树脂, 再将制备的 MQ 硅树脂与含氢苯基硅油通过硅氢化反应制备得到含有苯基的 MQ 硅树脂。所得产品分子量高, 有望用于高耐温性、高透明、高黏结性能的液

体硅橡胶产品的补强, 以及耐高温涂层的制备, 具有很高的应用潜力。

1.2 以水玻璃为原料

孟江燕采用六甲基二硅氧烷和硅酸钠为原料, 乙醇为溶剂, 盐酸为催化剂, 二甲苯为萃取剂, 制备甲基 MQ 硅树脂。将产品用于提高有机硅胶黏剂的黏接强度, 当 MQ 硅树脂的添加量为 15% 时, 黏结强度可以提高 143%。

王亮等通过水玻璃法, 以硅酸钠、六甲基二硅氧烷、乙烯基乙氧基二甲基硅氧烷等为主要原料成功合成出 MQ 树脂, 所合成 MQ 树脂的 M/Q 值为 0.8, 乙烯基含量 2.6%, 热分析结果显示其具有较好的热性能, 应用于压敏胶制备后, 产品性能达到较高水平。

刘小兰等以水玻璃和四甲基二烷基二硅氧烷为原料, 通过在酸性条件下水解, 制备得到 MQ 硅树脂, 考察了原材料加料顺序、配比等对产品性能的影响, 得到了较佳的树脂制备工艺, 同时对其补强有机硅压敏胶的性能进行了研究。

2 MQ硅树脂的应用

2.1 MQ硅树脂在有机硅压敏胶中的应用

有机硅压敏胶是一种用途广泛的优质压敏胶, 能在 -73~260℃ 的温度范围内广泛使用, 又能黏接各种材料甚至像聚四氟乙烯、未处理的聚烯烃等低表面能的难黏材料。有机硅压敏胶具有优良的耐高温性能、耐候性能、耐化学性能和电气性能, 被广泛用于汽车制造、船舶制造、发电机和电动机的电器绝缘、印刷电路板制造过程中的遮蔽保护和航空航天等领域。李坚辉等通过使用甲基乙氧基 MQ 硅树脂和含氢硅油与苯基硅橡胶反应, 以过氧化苯甲酰为引发剂, 二月桂酸二丁基锡和氯铂酸-异丙醇为催化剂制备了双交联型有机硅压敏胶, 并深入探讨了催化剂含量、交联剂含量、以及交联工艺等对双交联型有机硅压敏胶剥离强度和持黏力等性能的影响。

杨华新等通过 MQ 硅树脂和端羟基聚二甲基硅氧烷的硅醇缩合反应制备有机硅压敏胶, 研究了压敏胶的合成配料、工艺以及胶带生产工艺对压敏胶带性能的影响。结果表明, 硅树脂/硅橡胶比例在 1.2~1.4 具有良好的初黏、持黏和剥离力, 硅树脂含量增加胶带耐热性增强。

2.2 MQ硅树脂在硅橡胶补强中的应用

硅橡胶常用的增强填料有白炭黑, 乙烯基 MQ 树脂和含氢 MQ 硅树脂等。虽然白炭黑可以有效提高硅树脂的强度, 但当它和基础胶混合后会使得黏度显著增大, 使成型加工困难, 而且所得产品的透明度会有一定程度降低。使用 MQ 硅树脂做增强剂, 可以增加其与基础胶的相容性, 产品在固化前的

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黏度不至于过大,有利于施工,而且所得产品的透明度不受影响。

梁银杏等使用正硅酸乙酯等原料,通过水解缩合反应制备了乙烯基MQ硅树脂,考察了聚合条件对产物性能的影响。并以MQ硅树脂为补强填料,制备了加成型室温硫化硅橡胶,探讨了制备工艺对硫化硅橡胶力学性能和透明性的影响。通过调整配方,制得的硫化硅橡胶的拉伸强度可达7.2MPa,并具有很好的透明性,说明MQ硅树脂的增强作用明显,且对透光率影响较小。

龚彦等同样使用正硅酸乙酯为原材料制备MQ硅树脂,用于制备加成型电子硅橡胶,所得产品硫化后电阻率 $>1.0 \times 10^{16} \Omega \cdot \text{cm}$,电气强度为20kV/mm,介电常数为3.02,介电损耗因数为 7.17×10^{-4} ,非常适用于电子芯片产品的封装。

用MQ树脂补强液体硅橡胶,可使其获得与用有机硅处理白炭黑补强相近的机械性能,同时具有更好的流动性。王传吉等比较了白炭黑和MQ树脂这两种不同类型的填料对硅橡胶的补强效果,并研究了不同的Si-Vi与Si-H用量对硅橡胶补强的影响,探求加成型液体硅橡胶最佳的补强体系。

邸明伟等以MQ硅树脂增强加成型硅橡胶为基体,采用机械共混方式加入少量纳米 SiO_2 ,研究了纳米 SiO_2 对MQ硅树脂增强硅橡胶的性能影响。结果表明,纳米 SiO_2 在硅橡胶中以聚集体的形式存在,纳米 SiO_2 填充MQ硅树脂增强的硅橡胶的邵尔A硬度、拉伸强度和扯断伸长率与未填充纳米 SiO_2 的硅橡胶基本相当,撕裂强度增大,其高温热稳定性优于未填充纳米 SiO_2 的硅橡胶,但其透明性稍有下降。

宁志强等采用机械共混方式,加入少量纳米二氧化钛对MQ硅树脂增强加成型硅橡胶为基体进行改性,制备了纳米二氧化钛改性硅橡胶。结果表明,MQ硅树脂增强的硅橡胶中,加入少量纳米二氧化钛改性后,能够改善硅橡胶的力学性能,其硬度和断裂伸长变化不大,而拉伸强度和抗撕强度提高,硅橡胶的耐热性提高。溶胀实验表明,添加纳米粒子后,硅橡胶的溶胀比降低,凝胶质量分数和交联密度增加。

2.3 MQ硅树脂在复合材料改性方面的应用

除了在有机硅压敏胶和硅橡胶补强方面的应用外,对MQ硅树脂的其他应用也在不断开发和研究,比如用于合成硅橡胶的增黏剂,用于环氧树脂改性等。

汪昱辰等以含氢MQ硅树脂和1,6-己二醇二丙烯酸酯为原料,通过硅氢加成反应合成了含氢MQ硅树脂型增黏剂,并配制成加成型液体硅橡胶黏剂,用于硅橡胶与PC基材的黏接。结果发现,当反应温度为80℃、反应时间为3h、铂质量分数为 2×10^{-6} 、1,6-己二醇二丙烯酸酯中的乙烯基和含氢MQ硅树脂中的硅氢基的量之比为2.0时,产物对硅橡胶具有良好的增黏作用,产品用于与PC基材之间的黏接,其180°剥离强度为5.45kN/m,比空白样(0.1kN/m)提高了54.5倍。

朱茂电等通过使用乙烯基MQ硅树脂对环氧树脂进行改性,根据对改性后产物的红外光谱分析、相对分子质量及分

布的测定、环氧值测定,结果表明,乙烯基MQ硅树脂能与环氧树脂中的羟基发生反应,产物中大部分为环氧树脂的低聚物。通过对改性物的力学性能和耐热性能分析可知,与物理共混改性方法相比,化学共聚改性方法得到的产物具有相对较好的力学性能和较佳的耐热性能。

3 结束语

MQ硅树脂作为一类重要的有机硅材料,其需求量越来越高,应用范围也越来越广,尤其是随着高性能有机硅材料在电子、光伏和母婴用品等领域的应用,对高透明性与高力学性能有机硅材料的需求逐年递增,MQ硅树脂在这些领域中的应用也将会更加广泛。

参考文献

- [1] 彭笛,张群朝,徐惠,等.水捕获法制备MQ硅树脂[J].有机硅材料,2019,33(3):171-175.
- [2] 曾启华,王柏人.MQ硅树脂的制备及热性能研究[J].有机硅材料,2013,27(4):252-254.
- [3] 辛帅,孙超,马凤国.正硅酸乙酯法乙烯基MQ硅树脂的结构及热性能研究[J].有机硅材料,2016,30(3):181-185.
- [4] 胡生祥,杨潇珂,秦瑞瑞.MQ硅树脂的热稳定性研究[J].有机硅材料,2014,28(1):25-28.
- [5] 孟江燕.MQ硅树脂的制备及改性有机硅胶黏剂的应用[D].南昌:南昌航空大学,2016.
- [6] 王亮,黄志雄,宋九强,等.MQ硅树脂的合成及其对硅压敏胶性能的影响[J].武汉理工大学学报,2017,39(1):6-11.
- [7] 刘小兰,律微波,李金辉,等.高性能有机硅压敏胶的研制[J].有机硅材料,2010,24(5):293-297.
- [8] 杨玉昆,吕凤亭.压敏胶制品技术手册[M].北京:化学工业出版社,2014.
- [9] 杨华新,牛正发,曹刚,等.电气胶带用有机硅压敏胶的研制[J].塑料助剂,2020,(1):34-39.
- [10] 王月祥,张贵恩,王晓明,等.铝镀银微珠/有机硅导电电压敏胶的制备及性能研究[J].化工新型材料,2019,47(9):70-73.
- [11] 李坚辉,刘彩召,张斌,等.硅氢加成和自由基双交联有机硅压敏胶的研究[J].中国胶黏剂,2017,26(6):31-34.
- [12] 杨华新,牛正发,曹刚,等.电气胶带用有机硅压敏胶的研制[J].塑料助剂,2020,24(1):34-39.
- [13] 梁银杏,郭鹏,任碧野,等.MQ硅树脂制备工艺对RTV硅橡胶补强效果的影响[J].华南理工大学学报(自然科学版),2013,41(2):123-128.
- [14] 龚彦,翟金国,凌钦才.电子级乙烯基MQ硅树脂的制备及应用[J].有机硅材料,2016,30(3):186-191.
- [15] 王传吉,陈国栋.加成型液体硅橡胶补强体系优化[J].广东橡胶,2014,24(6):12-15.
- [16] 邸明伟,张丽欣,何世禹,等.纳米 SiO_2 对有机硅树脂增强加成型硅橡胶性能的影响[J].合成橡胶工业,2006,29(3):220-222.

季戊四醇四苯甲酰甲酸酯的合成及光引发性能

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摘 要 大分子光引发剂可以解决小分子光引发剂残留碎片带来的毒性对其在食品和医用材料领域应用的限制,为此,本文以苯甲酰甲酸(BF)和季戊四醇(PET)为原料,通过酰氯法在季戊四醇主链上引入了4个苯甲酰甲酸酯基团,制备了多官能度的季戊四醇四苯甲酰甲酸酯(PTF)大分子光引发剂。PTF在225℃时失重15%,热稳定性优于2-羟基-2-甲基-1-苯基-1-丙酮(1173)光引发剂,与1173光引发剂相比,用PTF作光引发剂所制备的光固化涂料,在起始分解温度以及失去相同比例质量所需温度均提高了100℃以上。PTF引发三羟甲基丙烷三丙烯酸酯(TMPTA)聚合时最大反应速率为 0.037 s^{-1} ,最终双键转化率为39.5%,PTF光引发活性大于1173光引发剂。在同等实验条件下,PTF的相对小分子残留量仅为1173光引发剂的5%。

关键词 季戊四醇四苯甲酰甲酸酯;紫外光固化;光引发性能

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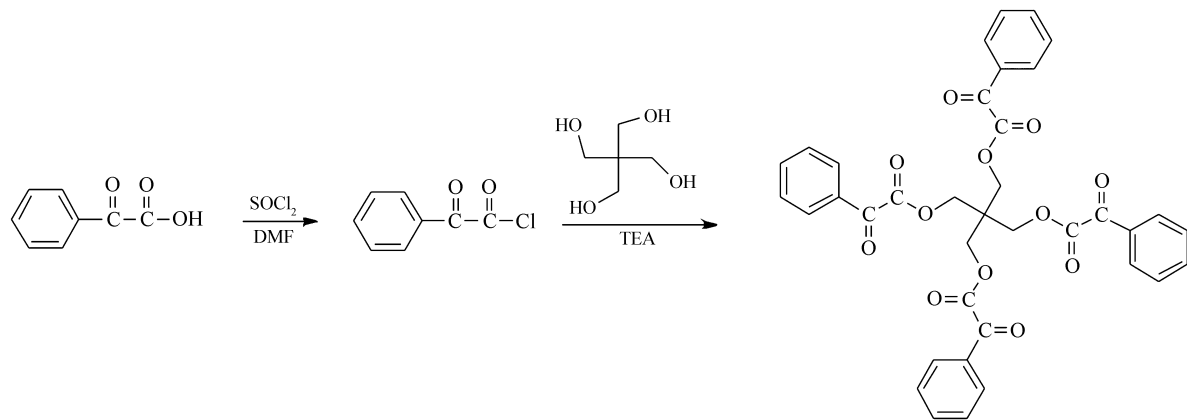
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随着紫外光(UV)固化技术的迅猛发展,根据不同的需求,UV固化技术可赋予不同领域材料不同的功能。例如,赋予角蛋白织物优异的抗菌活性、抗静电性和亲水性;增加化妆品的生物相容性;减少有毒物质在食品包装的迁移性和在临床药物输送领域的细胞毒性等^[1-5]。UV固化涂料是将传统涂料和UV固化技术结合起来的一项新技术,特别适用于一些要求比较特殊的场所,如无挥发性有机化合物(VOC)排放、低温涂装、快速固化、高效率生产等场合^[6-10]。而以苯甲酰甲酸酯裂解型光引发剂为原料,适合制备较厚涂层的固化材料,可以得到具有良好装饰效果和优良耐候性能UV固化涂料^[11-12]。

季戊四醇多酯是一种重要的增塑剂、润滑剂和表面活性剂,具有反应活性高、交联密度高、硬度佳、高光泽等特点,常应用于涂料、油墨、粘合剂、聚合物等领域^[13-15]。在UV固化领域,季戊四醇酯类多官能度单体常用作稀释剂和交联剂,可用于调节涂料体系的黏度,改善施工性能,同时也可参与固化反应,增加涂料体系的交联密度,从而提高材料的力学性能和耐化学品性能等^[16-17]。

之前对于苯甲酰甲酸酯类的光引发剂研究很少^[18-20]。本文拟采用酰氯法^[21]合成支链状的液体季



Scheme 1 Synthesis route of pentaerythritol tetraphenoyl formate

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戊四醇四苯甲酰甲酸酯(PTF),以期使其同时具有苯甲酰甲酸酯和季戊四醇多酯的性能。低相对分子质量的光引发剂往往具有不耐高温、迁移性大、毒性大等缺点^[22-24],而PTF作为一种多苯甲酰甲酸酯类光引发剂克服了小分子光引发剂热稳定性低、挥发性大、迁移性高的缺点。该类化合物在紫外光固化材料领域上将扩展苯甲酰甲酸酯类光引发剂的应用,PTF的合成路线如Scheme 1所示。

1 实验部分

1.1 仪器和试剂

TG-209型热重分析仪(TGA,德国Netzsch公司);Bruker 400 MHz型核磁共振仪(NMR,德国Bruker公司),CDCl₃为溶剂,TMS为内标;T6型紫外可见分光光度计(UV-Vis,北京普析通用仪器有限责任公司),乙腈为溶剂;Magna380型傅里叶变换红外光谱仪(FT-IR,美国Nicolet公司),KBr压片;UVA-T-400W手提式UV紫外线固化灯(东莞市固得佳机械设备有限公司);光-差示扫描量热仪(Photo-DSC,美国Perkin Elmer公司)。

苯甲酰甲酸(分析纯)和季戊四醇(工业级)购自于阿拉丁试剂有限公司;二氯甲烷、甲苯、三乙胺、石油醚和乙酸乙酯购自于西陇化工有限公司,均为分析纯试剂;乙腈和氯化亚砷购自于国药集团化学试剂有限公司,均为分析纯试剂;2-羟基-2-甲基-1-苯基-1-丙酮(1173光引发剂)(工业级)购自于德国良制化学(中国)有限公司;B-265型聚氨酯丙烯酸酯、1,6-己二醇二丙烯酸酯(HDDA单体)和三羟甲基丙烷三丙烯酸酯(TMPTA单体)购自于广东博兴新材料科技有限公司,均为工业级。所有试剂未经纯化直接使用。

1.2 实验方法

将5.0 mL二氯亚砷(45 μmol)和4 g(26 μmol)苯甲酰甲酸加至干燥的三口烧瓶中,然后加入30 mL甲苯做溶剂,滴加2滴*N,N*-二甲基甲酰胺,在N₂气保护下,于40℃水浴锅中恒温搅拌加热回流4 h至冷凝管上方干燥管的导气管处无气体放出,反应结束,70℃下,旋转蒸发,得到粗产物。粗产物用二氯甲烷进行重结晶,得到黄色粉末状固体苯甲酰甲酰氯2.4 g。

称取0.136 g(0.8 μmol)季戊四醇溶于30 mL二氯甲烷,然后加至干燥的三口烧瓶中,加入0.158 g(1.6 μmol)三乙胺,将0.708 g(4 μmol)苯甲酰甲酰氯溶于30 mL二氯甲烷的混合溶液滴加到上述反应体系中,在N₂气保护下,40℃,搅拌,加热回流5 h。反应结束后过滤,滤液用饱和碳酸氢钠溶液和去离子水各洗涤3次,用无水硫酸镁干燥,过滤,有机相经柱层析进一步提纯,其中硅胶柱中的展开剂为*V*(石油醚):*V*(乙酸乙酯)=2:1,最终得到黄色液体0.575 g,收率86.51%(以季戊四醇计)。

¹H NMR(CDCl₃, 400 MHz), δ: 7.98 ~ 8.00(d, *J* = 82 Hz, 8H, CH, 苯环), 7.64 ~ 7.70(t, *J* = 75 Hz, 4H, CH, 苯环), 7.48 ~ 7.52(t, *J* = 77 Hz, 8H, 苯环), 4.65 ~ 4.36(m, 8H, CH₂); ¹³C NMR(CDCl₃, 101 MHz), δ: 184.91, 135.17, 131.93, 129.98, 128.96, 76.90, 67.30, 42.77; FT-IR(KBr), σ/cm⁻¹: 3066.1, 2649.5, 1976.2, 1779.3, 1721.2, 1662.7, 1594.4, 1456.7, 1001.5, 809.6, 746.1, 682.4; ESI-MS(*m/z*) C₃₇H₂₈O₁₂计算值664.6,实测值665.1。

1.3 涂层的制备

在避光条件下,往烧杯中加入质量分数为60%的B-265型聚氨酯丙烯酸酯、36%的HDDA单体、4%的PTF光引发剂或1173光引发剂,搅拌均匀后静置10 min,然后均匀涂于载玻片上,涂膜厚度约为80 μm,在空气中涂膜用灯距5.5 cm,功率为400 W的手提式固化机(灯源为高压汞灯,主波长为365 nm)上进行固化。

1.4 涂膜性能测试

通过凝胶转化率法^[25-26]来研究PTF光引发聚合TMPTA单体涂层的固化程度。即将光照固化后的涂层放入丙酮溶液中浸泡30 min,使固化的树脂和单体溶于丙酮溶液中,烘干之后涂层的质量和涂层曝光前的质量相比,即可计算出涂层的转化率,表示涂层的固化程度;采用GB/T 1728-1979(1989)中的指触法测试涂层的表干时间;涂层的铅笔硬度参照标准GB-T6739-2006进行测试;涂层的附着力参照标准GB-T1720-1989进行测试;涂层的相容性测试可直接看固化后的涂层是否有橘皮、气泡、分散不均匀等

现象,如果无上述现象说明光引发剂与树脂相容性良好;参照标准 GB/T 1731-1993 对涂层的柔韧性进行测试。

1.5 PTF 的小分子残留测试

分别配制质量分数为1%的PTF和1%的1173光引发剂的TMPTA溶液,将它们分别涂在载玻片上,涂膜厚度约为80 μm ,在空气中涂膜用灯距5.5 cm,功率为400 W的手提式固化机光照3 min。然后将固化膜剪碎,各取0.075 g,用20 mL的乙腈在室温下萃取3 d。最后取相同量的萃取液进行紫外吸收测试。由式(1)及式(2)可得PTF相对于1173光引发剂的相对小分子残留量。

$$c = A/(\varepsilon \times b), \quad (1)$$

$$R = c(\text{PTF})/c(1173) \quad (2)$$

式中, c 为萃取液中光引发剂的浓度(mol/L); A 为吸光度; ε 为摩尔消光系数($\text{L}/(\text{mol} \cdot \text{cm})$); b 为样品池厚度(cm); $c(\text{PTF})$ 为萃取液中PTF的浓度; $c(1173)$ 为萃取液中1173光引发剂的浓度; R 为PTF的相对小分子残留量。

2 结果与讨论

2.1 紫外光谱分析

以乙腈为溶剂并作为参比液,在25 $^{\circ}\text{C}$ 条件下测量PTF(图1曲线a)和1173光引发剂(图1曲线b)在200~400 nm范围内的紫外吸收峰,如图1为这二者的紫外吸收光谱。

由图1可知,1173光引发剂(图1曲线a)的最大吸收峰在243 nm处,PTF(图1曲线b)的最大吸收峰在256 nm处,200~300 nm的紫外吸收归因于 $\pi-\pi^*$ 跃迁转变^[27],1173光引发剂的摩尔消光系数为 $1.70 \times 10^4 \text{ L}/(\text{mol} \cdot \text{cm})$,PTF的摩尔消光系数为 $1.95 \times 10^4 \text{ L}/(\text{mol} \cdot \text{cm})$ 。由此可知,与1173光引发剂相比,PTF的紫外最大吸收波长较大,这可能是由于PTF光引发剂分子结构中含有较多的羰基 $\text{C}=\text{O}$ 等生色基团。

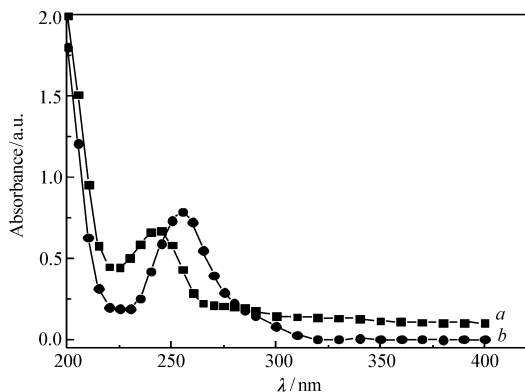


图1 光引发剂1173(a)和PTF(b)的紫外吸收光谱图

Fig. 1 UV-Vis spectra of 1173 and PTF photoinitiators

The concentrations of PTF and 1173 were $4.0 \times 10^{-5} \text{ mol/L}$

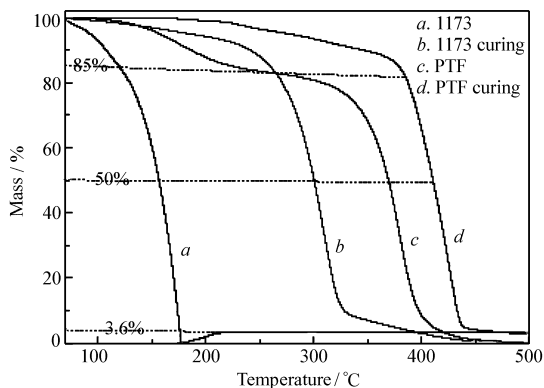


图2 光引发剂1173和PTF固化涂料前后的TGA图

Fig. 2 TGA spectra of 1173 (a, b) and PTF (c, d) photoinitiators before (a, c) and after (b, d) curing coatings

2.2 热重分析

本实验采用热重分析仪研究PTF和1173光引发剂的热稳定性。仪器的升温范围为70~500 $^{\circ}\text{C}$,升温速率为10 $^{\circ}\text{C}/\text{min}$,保持20 min,仪器每隔0.5 s采集1次数据, N_2 气气氛。

按1.3节所述将涂料配方进行固化,由热失重曲线(图2曲线d)可知,PTF光引发剂引发所制备的涂料热降解过程大致可分为3个阶段。第1阶段失重($T < 376.2 \text{ }^{\circ}\text{C}$)主要是PTF固化体系自身吸水而含有的水分和一些游离小分子的挥发;第2阶段($376.2 \text{ }^{\circ}\text{C} < T < 472.8 \text{ }^{\circ}\text{C}$)失重主要是固化体系中PTF光引发剂和B-265型聚氨酯丙烯酸酯的降解所造成,第3阶段($T > 472.8 \text{ }^{\circ}\text{C}$)光固化涂料基本降解完

全,其失重速率趋近于零。此外,通过比较图2 曲线 *a* 和 *c* 可知,与 1173 光引发剂相比,在起始分解温度差以及失去相同比例质量所需的温度,PTF 均提高了 50 ℃ 以上,失重 15% 以上时的温度大于 225 ℃,说明合成的光引发剂 PTF 的热稳定性得到了明显提高,可以降低其挥发性;同时通过比较图2 曲线 *b* 和曲线 *d* 可知,与 1173 光引发剂相比,用 PTF 作光引发剂所制备的光固化涂料,在起始分解温度以及失去相同比例质量所需温度均提高了 100 ℃ 以上。由此可得出结论,与 1173 光引发剂相比,合成的 PTF 光引发剂可以明显地提高光固化涂料的热稳定性能。

2.3 光引发聚合动力学研究

在 25 ℃ 下, N₂ 气氛中,用空铝质坩埚作为参比样,光强为 20 mW/cm²,光照 40 s,分别用 0.006 mol 的 PTF 光引发剂、0.006 mol 的 1173 光引发剂引发 2 g TMPTA 单体聚合,研究了 PTF 和 1173 光引发剂引发 TMPTA 单体聚合的反应速率和光聚合转化率随时间变化的关系,其研究结果分别如图 3 和图 4 所示。

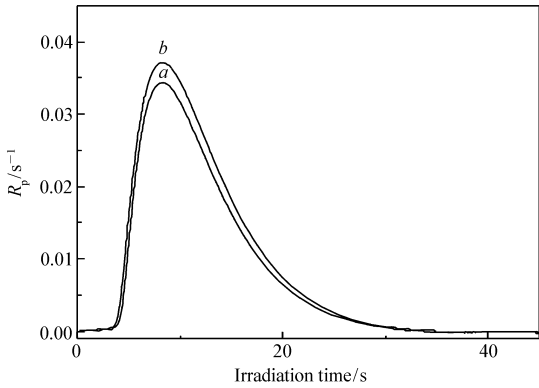


图3 光引发剂 1173(*a*)和 PTF(*b*)引发 TMPTA 光聚合的反应速率曲线
Fig.3 Polymerization rate curves of TMPTA initiated by photoinitiators 1173(*a*) and PTF(*b*)

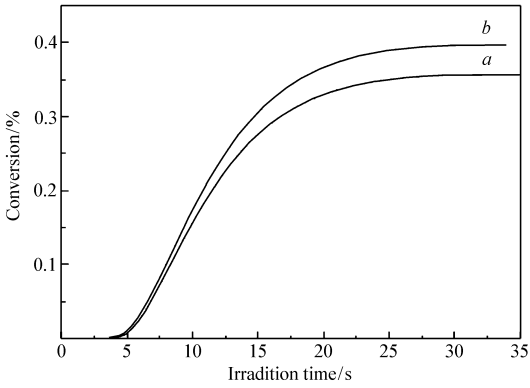


图4 光引发剂 1173(*a*)和 PTF(*b*)引发 TMPTA 光聚合的转化率曲线
Fig.4 Polymerization conversion curves of TMPTA initiated by photoinitiators 1173(*a*) and PTF(*b*)

由图3 和图4 可以看出,1173 光引发剂引发 TMPTA 聚合时最大反应速率(图3 曲线 *a*)为 0.034 s⁻¹,最终双键转化率(图4 曲线 *a*)为 35.4%,PTF 引发 TMPTA 聚合时最大反应速率(图3 曲线 *b*)为 0.037 s⁻¹,最终双键转化率(图4 曲线 *b*)为 39.5%。通过对比可知,当 PTF 和 1173 光引发剂引发 TMPTA 的物质的量相同时,PTF 的光引发活性高于 1173 光引发剂,这主要是由于光引发剂 PTF 分子结构中含有 4 个苯甲酰甲酸酯基团,决定了其具有较高的光引发活性,其光解后产生的活性自由基浓度要高于 1173 光引发剂,从而使得 PTF 引发 TMPTA 聚合的速率较高。已经商品化的苯甲酰甲酸甲酯(MBF)是一种单酯,其光引发活性略低于市售的 1173 光引发剂^[28],由此可知,PTF 光引发活性也大于苯甲酰甲酸甲酯。

2.4 涂膜性能

涂层的制备如 1.3 所述,其性能如表 1 所示。随着光引发剂 PTF 用量的逐渐增加,涂层的光固化速率也逐渐加快。综合考虑光固化效率及经济因素,当 PTF 用量为固化体系质量分数的 4% 时,其光引发效果较佳。由表 2 可知,PTF 的光固化速率要好于市售的 1173 光引发剂,同时其涂膜后硬度高,附着力更好。涂层之间的附着力差异,可能是由于 PTF 光引发剂分子比 1173 光引发剂中含有较多的羰基、酯基等极性基团,从而使得其涂层附着力略好。

表1 不同质量分数 PTF 光引发的涂层固化时间

Table 1 The curing time of the PTF photoinitiated coating with different mass fraction

PTF mass fraction/%	1	2	3	4	5	6	7
Curing time/s	47	42	40	32	35	34	34

表 2 涂膜性能
Table 2 Film properties

Items	PTF	1173 photoinitiator
Curing time/s	32	37
Hardness/H	5	5
Flexibility	Good	Good
Adhesion/grade	1	2
Acid resistance ^a	Intact	Intact
Alkali resistance ^b	Intact	Intact
Membrane traits	Smooth and transparent	Smooth and transparent
Compatibility	Good	Good

a. 1 mol/L HCl soaked for 24 h; *b.* 1 mol/L NaOH soaked for 24 h.

利用凝胶转化率法来测试固化程度的配方如 1.3 节所述,由表 3 可知,聚合物的转化率一直在增加,固化程度一直在加深,当光照 40 s 之后,转化率趋于稳定,继续增加光照时间对提高转化率没有太大的影响,固化程度达到饱和。

表 3 光照时间对聚合物的转化率的影响
Table 3 Effect of irradiation time on the conversion of polymerization

Curing time/s	10	20	30	40	50	60
Conversion/%	66.74	82.36	92.49	93.21	93.42	93.78

2.5 小分子残留结果分析

通过对聚合物中光引发剂萃取液的紫外吸收可以分析光引发剂在聚合物中的小分子残留量。PTF 和 1173 光引发剂萃取液的紫外吸收光谱如图 5 所示。表 4 列出了 PTF 对 1173 光引发剂的相对小分子残留量。

表 4 PTF 的相对迁移率

Table 4 The relative migration of PTF		
Items	PTF	1173 photoinitiator
$A(\lambda_{\max})$	0.068	1.178
$c/(\text{mol}\cdot\text{L}^{-1})$	3.5×10^{-6}	6.9×10^{-5}
$R/\%$	5	100

由图 5 可知,PTF(图 5 曲线 *a*)和 1173(图 5 曲线 *b*)光引发剂在最大波长处的吸收峰还未消失,说明固化膜还残留有光引发剂,同时由表 3 可知,在同等实验条件下,PTF 的相对小分子残留量仅为 1173 光引发剂的 5%,这说明 PTF 大分子光引发剂可有效地固定在固化膜中,从而大大降低固化膜的生物毒性。

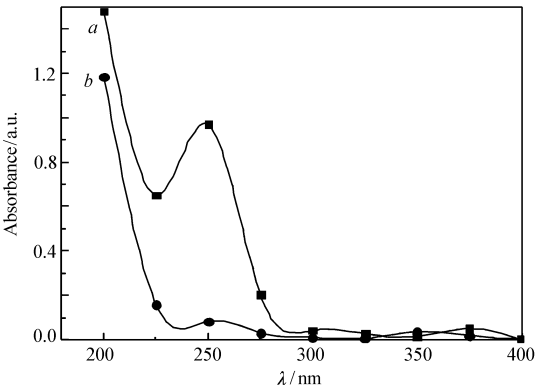


图 5 1173(*a*)和 PTF(*b*)光引发剂萃取液的紫外吸收光谱
Fig. 5 UV-Vis absorption spectra of extraction solutions from 1173(*a*) and PTF(*b*) photoinitiators

3 结 论

采用酰氯法合成了液态的支链状多官能度季戊四醇四苯甲酰甲酸酯大分子光引发剂(PTF),并对其物理性能和光引发性能进行了研究。PTF 引发三羟甲基丙烷三丙烯酸酯(TMPTA)聚合时最大反应速率为 0.037 s^{-1} ,最终双键转化率为 39.5%,PTF 引发 TMPTA 单体的双键转化率和光聚合速率均大于液体 2-羟基-2-甲基-1-苯基-1-丙酮(1173 光引发剂)。与 1173 光引发剂相比,合成的 PTF 光引发剂可以明显地提高光固化涂料的热稳定性能,涂料的附着力得到了提高。并且,PTF 光引发剂具有较高的光引发

活性、优良的热稳定性;此外,光固化成膜后附着力好,小分子残留量低,毒性小。PTF 作为一种苯甲酰甲酸酯类光引发剂,其在紫外光固化涂料中将具有良好的发展前景。

辅助材料(Supporting Information)[目标产物 PTF 的 FT-IR 图、NMR 图和 ESI-MS 图]可以免费从本刊网站(<http://yyhx. ciac. jl. cn/>)下载。

参 考 文 献

- [1] Liu K, Su Z G, Miao S D, *et al.* UV-curable Enzymatic Antibacterial Waterborne Polyurethane Coating[J]. *Biochem Eng J*, 2016, **113**:107-113.
- [2] Roth M, Hennen D, Oesterreicher A, *et al.* Exploring Functionalized Benzophenones as Low-migration Photoinitiators for Vinyl Carbonate/Thiol Formulations[J]. *Eur Polym J*, 2017, **88**:403-411.
- [3] Zhang Y, Du Z X, Xia X M, *et al.* Evaluation of the Migration of UV-ink Photoinitiators from Polyethylene Food Packaging by Supercritical Fluid Chromatography Combined with Photodiode Array Detector and Tandem Mass Spectrometry[J]. *Polym Test*, 2016, **53**:276-282.
- [4] Wang K M, Yang K, Yu Q. Novel Polymeric Photoinitiators with Side-chain Benzophenone: Facile Synthesis and Photopolymerization Properties Without Cointiator[J]. *Prog Org Coat*, 2014, **77**:1929-1934.
- [5] Jing C, Ding G, Qin X Z, *et al.* New Near UV Photoinitiators Containing Benzophenone Part for Photoinitiating Polymerization of Methyl Methacrylate[J]. *Prog Org Coat*, 2017, **110**:150-161.
- [6] Valdesueiro D, Hetinga H, Drijfhout J P, *et al.* Tuning Roughness and Gloss of Powder Coating Paint by Encapsulating the Coating Particles with Thin Al_2O_3 Films[J]. *Powder Technol*, 2017, **318**:401-410.
- [7] Xu Y J, Wang Q, Cao Y F, *et al.* Preparation of a Reduced Graphene Oxide/ $\text{SiO}_2/\text{Fe}_3\text{O}_4$ UV-curing Material and Its Excellent Microwave Absorption Properties[J]. *RSC Adv*, 2017, **7**:18172-18177.
- [8] Al-Shroofy M, Zhang Q L, Xu J, *et al.* Solvent-free Dry Powder Coating Process for Low-Cost Manufacturing of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ Cathodes in Lithium-Ion Batteries[J]. *J Power Sources*, 2017, **352**:187-193.
- [9] Dai J Y, Ma S Q, Wu Y G, *et al.* High Bio-based Content Waterborne UV-curable Coatings with Excellent Adhesion and Flexibility[J]. *Prog Org Coat*, 2015, **87**:197-203.
- [10] Aznar M, Domo C, Nerín C, *et al.* Set-off of Non Volatile Compounds from Printing Inks in Food Packaging Materials and the Role of Lacquers to Avoid Migration[J]. *Dyes Pigm*, 2015, **114**:85-92.
- [11] ZHANG Jielong, LEI Jinhai. Preparation and Application of Benzoylformic Acid[J]. *J Zhejiang Chem Ind*, 2008, **39**(12): 13-15(in Chinese).
张捷龙, 雷进海. 苯甲酰甲酸的合成与应用[J]. 浙江化工, 2008, **39**(12):13-15.
- [12] CHEN Yinxia, YANG Guozhong, LI Jing, *et al.* Synthesis and Application of Methyl Benzoylformate[J]. *Fine Spec Chem*, 2014, **22**(11):40-43(in Chinese).
陈银霞, 杨国忠, 李静, 等. 苯甲酰甲酸甲酯的合成与应用[J]. 精细与专用化学品, 2014, **22**(11):40-43.
- [13] Sun Y J, Wang X P, Wang D B, *et al.* Measurement and Correlation for Phase Equilibrium of HFO1234yf with Three Pentaerythritol Esters from 293.15 K to 348.15 K[J]. *J Chem Thermodyn*, 2017, **112**:122-128.
- [14] Hwang H D, Park C H, Moon J I, *et al.* UV-curing Behavior and Physical Properties of Waterborne UV-curable Polycarbonatebased Polyurethane Dispersion[J]. *Prog Org Coat*, 2011, **72**:663-675.
- [15] WEI Yuli, WANG Yunpu, CHANG Yue, *et al.* Preparation and Characterization of Pentaerythritol Tetramethacrylate[J]. *J Northwest Nor Univ*(Nat Sci Edit), 2007, **43**(5):63-66(in Chinese).
魏玉丽, 王云普, 常玥, 等. 季戊四醇四甲基丙烯酸酯的制备及表征[J]. 西北师范大学学报(自然科学版), 2007, **43**(5):63-66.
- [16] Llorente O, Fernández-Berridi M J, González A, *et al.* Study of the Crosslinking Process of Waterborne UV Curable Polyurethane Acrylates[J]. *Prog Org Coat*, 2016, **99**:437-442.
- [17] Han X, Hu L H, Zhang Y, *et al.* Sulfur-containing Hyperbranched Polymeric Photoinitiator End-capped with Benzophenone and Tertiary Amine Moieties Prepared via Simultaneous Double Thiol-ene Click Reactions Used for UV Curing Coatings[J]. *Prog Org Coat*, 2011, **72**:572-578.
- [18] Hu S K, Wu X S, Neckers D C, *et al.* Methyl Phenylglyoxylateasa Photoinitiator[J]. *Macromolecule*, 2000, **33**(11):4030-4033.
- [19] Winfield L, Andrsas W, Wiffied D, *et al.* Process for the Preparation of Phenylglyoxylic Acid Esters; US 4596885.
- [20] SUN Jian, ZHENG Kangjian. A Preparation Method of Phenylglyoxylic Acid Ester Photoinitiator; CN, 201510059315.8(in Chinese).
孙建, 郑康健. 一种苯甲酰甲酸酯类光引发剂的制备方法: 中国, 201510059315.8[P], 2015.
- [21] HE Chunhua, FU Shifu, LIU Chuanxiang, *et al.* Synthesis of Dipentaerythritol Hexaacrylate by Acid Chloride Method[J]. *J*

Chem Ind, 2003, **17**(4): 45-46 (in Chinese).

贺楚华,付仕福,刘传湘,等. 酰氯法合成双季戊四醇六丙烯酸酯[J]. 化工时刊, 2003, **17**(4): 45-46.

- [22] Zhang Y, Du Z X, Xia X M, *et al.* Evaluation of the Migration of UV-ink Photoinitiators from Polyethylene Food Packaging by Supercritical Fluid Chromatography Combined with Photodiode Array Detector and Tandem Mass Spectrometry [J]. *Polym Test*, 2016, **53**: 276-282.
- [23] Papilloud S, Baudraz D. Migration Tests for Substrates Printed with UV Ink Systems in Aqueous Simulants [J]. *Prog Org Coat*, 2002, **45**: 231-237.
- [24] Hoeck E V, Schaetzen T D, Pacquet C, *et al.* Analysis of Benzophenone and 4-Methylbenzophenone in Breakfast Cereals Using Ultrasonic Extraction in Combination with Gas Chromatography Tandem Mass Spectrometry (GC MSn) [J]. *Anal Chem Acta*, 2010, **663**: 55-59.
- [25] JIANG Pingkai, WANG Zongguang, WANG Shoutai. Tudy on the Relation Between the Torque of Silanegrafting Polyethylenes and Gel Fraction [J]. *Polym Mater Sci Eng*, 2000, **16**(1): 89-91 (in Chinese).
江平开, 王宗光, 王寿泰. 硅烷交联聚乙烯流变转矩与凝胶率的比较研究 [J]. 高分子材料科学与工程, 2000, **16**(1): 89-91.
- [26] YAN Jinrong. Study on the Methods to Test for Gelling Percent of Silane Crosslinked Polyethylene [J]. *Plast Sci Tech*, 2002, **2**: 62-64 (in Chinese).
严金荣. 硅烷交联聚乙烯凝胶率测定方法的研究 [J]. 塑料科技, 2002, **2**: 62-64.
- [27] Cheng L L, Shi W F. Synthesis and Photoinitiating Behavior of Benzophenone-Based Polymeric Photoinitiators Used for UV Curing Coatings [J]. *Prog Org Coat*, 2011, **71**: 355-361.
- [28] JIN Yangzhi. Properties and Applications Handbook: UV-Curable Materials [M]. Beijing: Chemical Industry Press, 2010 (in Chinese).
金养智. 光固化材料性能及应用手册 [M]. 北京: 化学工业出版社, 2010.

Synthesis and Photoinitiation Properties of Pentaerythritol Tetrabenzoyl Formate

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Abstract The limit of small molecule photoinitiators to applications of food and medical materials due to the toxicity of its residual fragments can be solved by the macromolecular photoinitiators. In this paper, pentaerythritol tetrahydrobenzoylformate (PTF) was synthesized using benzoyl formic acid (BF) and pentaerythritol (PET) as raw materials by acid chloride method. The results of thermal analysis show that there is 15% mass loss at 225 °C for PTF and its thermal stability is better than that of 2-hydroxy-2-methyl-1-phenyl-1-propanone (1173 photoinitiator). The initial decomposition temperature and the temperature with the same mass loss for the photocurable coatings using PTF as the photoinitiator are 100 °C higher than those for coatings using 1173 photoinitiator. The results show that the maximum reaction rate is 0.037 s⁻¹, the final double bond conversion is 39.5%, and PTF has higher photoinduced activity than 1173 in the trimethylolpropane triacrylate (TMPTA) polymerization by light-differential scanning calorimetry. The residue content of PTF is only 5% of that of 1173 photoinitiator under the same experimental conditions.

Keywords pentaerythritol tetraphenoylformate; ultraviolet curing; photoinitiation properties

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加成型液体硅橡胶增粘剂研究概述

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摘要: 加成型液体硅橡胶已经在各个行业得到了广泛应用, 但因其粘结力较差, 需要通过添加偶联剂或者增粘剂来提高其与各类基材的粘结力。本文根据合成增粘剂所用活性基团的种类, 对现有的增粘剂的合成和应用进行了概述。

关键词: 加成型硅橡胶; 液体硅橡胶; 增粘剂

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Review of Research on Additional Type Liquid Silicone Rubber Adhesion Promoter Agent

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Abstract: Additional liquid silicone rubber has been widely used in the industry. Generally, silicone coupling agent or adhesion promoter agent were used to improve the adhesion property between silicone rubber and various substrates. According to the types of active groups used in the synthesis procedure, the synthesis and application of adhesion promoter agent are summarized in this paper.

Key words: additional type silicone rubber; liquid silicone rubber; adhesion promoter agent

加成型液体硅橡胶固化过程中无副产物产生, 固化收缩率低, 能深层固化, 且具有耐候耐老化、生物相容性好等优点, 在电子电气、纺织、医疗等行业都得到了广泛的应用。但是由于加成型硅橡胶固化后分子链呈高度饱和状态, 表面能低, 其与各类基材的粘结力较差, 容易出现与基材脱离的问题。硅烷偶联剂可以在一定程度上提高产品的粘结力^[1], 但是小分子的偶联剂一般与硅橡胶相容性较差, 加入后还会对硅橡胶的耐温性能产生影响, 而且硅烷偶联剂本身的增粘效果一般, 无法满足对粘结力要求更高的应用领域的需要。

为了解决以上问题, 需要对偶联剂分子进行一定的改性, 合成具有特殊结构的高分子量增粘剂, 这个已经成为有机硅领域的一个研究热点^[2]。本文将从合成增粘剂的活性基团入手, 对加成型液体硅橡胶增粘剂合成研究进行概述。

1. 含酯基有机硅增粘剂

在各种极性的基团中, 酯基属于较强的一种, 它可以通过酯基相互之间或者酯基与基材之间形成结合键, 使其相互间作用力得到增强, 从而与基材间能够形成较强结合力。这类增粘剂一般用于硅橡胶与聚碳酸酯等塑料的粘结力改善。

周为等^[3]通过硅氢加成反应将含氢硅油和1, 6-己二醇二丙烯酸酯反应制备得到有机硅增粘剂, 当加成型液体硅橡胶中增粘剂的含量为0. 9%时, 可以与热塑性聚氨酯、聚碳酸酯及聚对苯二甲酸乙二醇酯等基材结合牢固。汪昱辰等^[4]通过使用含氢MQ硅树脂和1, 6-己二醇二丙烯酸酯进行硅氢加成反应制备得到增粘剂, 该增粘剂可以用于加成型液体硅橡胶与聚碳酸酯基材的粘接, 使用后剥离强度可以得到明显的提高。王哲等^[5]同样通过硅氢加成反应制备有机硅增粘剂, 其原料为四甲基环四硅氧烷和1, 6-己二醇二甲基丙烯酸酯, 把这种有机硅增粘剂加入到硅微粉、乙烯基硅油、含氢硅油、

催化剂中并在一定条件下反应, 可以制备导热型灌封胶, 其与PC、PCB和铝等材料的剪切强度得到大幅增加。

Pan Kexue等^[6]将八甲基环四硅氧烷、3-甲基丙烯酰氧基丙基甲基二甲氧基硅烷、四甲基环四硅氧烷和六甲基二硅醚反应制备得到含活性氢的导热硅橡胶用增粘剂, 用其代替普通含氢硅油以后, 产品的粘接性能得到明显的提升, 力学强度也显著提高。

2. 含环氧基的有机硅增粘剂

环氧基团也是反应性较强的基团之一, 它能够与羟基(-OH)、氨基(-NH₂)、巯基(-SH)、羧基(-COOH)等含活泼氢的化合物发生开环反应, 从而通过化学键结合的方式提高与该类基材的粘结力。含环氧基增粘剂通常是通过硅氢加成反应^[7]或者缩合反应来合成^[8]。

张利利等^[9]使用含环氧基团的有机硅低聚物作为增粘剂, 制备得到一种光学透明胶, 当增粘剂添加量达到1%时, 产品与PC、PMMA、PET和玻璃等基材能够形成良好的粘接状态, 粘接强度较高。凌钦才等^[10]使用烯丙基缩水甘油醚和四甲基环四硅氧烷, 通过硅氢加成反应制备得到了一种含环氧基的有机硅增粘剂。当该增粘剂在硅橡胶中的添加量为2%时, 硅橡胶具有最佳的粘接效果。

陈正旺等^[11]采用 γ -(2, 3-环氧丙氧)丙基三甲氧基硅烷、乙烯基三甲氧基硅烷及羟基甲基硅油为原材料, 通过缩合反应合成了含环氧基的适用于LED封装胶的有机硅增粘剂, 当LED器件密封性能达到最佳状态时, 此时增粘剂的添加量为1. 25%。Pan等^[12]将缩合反应的催化剂改为钛络合物, 通过缩合反应制备得含环氧基的有机硅增粘剂, 当增粘剂的用量为2%时, 其与铝片间的剪切强度几乎是未添加增粘剂前的两倍。程宪涛等^[13]通过使用N- β -氨乙基- γ -氨丙基

三甲氧基硅烷引入氨基到环氧增粘剂中, 所得增粘剂加入LED硅橡胶后与支架之间具有良好的粘接力。

3. 含乙烯基硅氧烷增粘剂

加成型硅橡胶是通过硅氢加成反应进行固化的, 在增粘剂中引入乙烯基, 可以在固化过程中将增粘剂分子通过化学反应的方式接入硅橡胶的交联网络中, 从而提高硅橡胶与基材的粘接力。

Kasuya A等^[14]使用烯丙基缩水甘油醚、烯丙基胺制备得到一种含乙烯基的有机硅增粘剂, 当在加成型液体硅橡胶中加入含量为2.5%的该种增粘剂时, 其与Cu、Al、Ni金属片、PB、玻璃、尼龙-6等基材之间具有良好的粘接效果, 但由于该增粘剂分子主要为碳链, 因此该增粘剂与加成型液体硅橡胶间的相容性不够理想。

杨维生等^[15]探究了四烯丙基硅烷、四乙烯基硅烷添加到硅橡胶中时其与基材间粘接效果的变化, 实验表明当这两种含乙烯基的有机硅化合物被加入硅橡胶中时, 硅橡胶与基材之间的粘接效果得到极大的改善。Pan等^[16]通过醚交换反应制备得到三种含乙烯基的聚硅氧烷增粘剂, 使用增粘剂后, 硅橡胶与铝材之间的剪切强度几乎为未添加前的3.5倍。

4. 含硼有机硅增粘剂

硼元素对某些金属材料的基材有良好的粘接效果, 但其与塑料基材之间的粘接效果不佳。通过将硼元素引入到有机硅增粘剂中, 可以达到提高与金属的粘结力的目的, 这类增粘剂统称为含硼有机硅增粘剂。

曾幸荣等^[17]使用硼酸酯、二苯基硅二醇、含环氧基及丙烯酰氧基硅烷偶联剂为原材料, 通过缩合反应制备得到有机硼增粘剂, 使用该增粘剂制备的液体硅橡胶, 对聚对苯二甲酸1,4-环己烷二甲醇、聚邻苯二甲酰胺和聚碳酸酯等具有良好的粘接效果, 其粘接力约为添加前的3.5倍。赵大成等^[18]通过水解缩合反应制备得到含硼有机硅增粘剂, 当该增粘剂被加入到硅橡胶中后, 其与镀银铝板和PPA材料的基材之间具有较好的粘接效果, 粘接力大约为添加前的10倍。熊天宝等^[19]在碱性条件下通过缩合反应制得高折射率的含硼有机硅增粘剂, 应用于LED封装胶中, 可以显著提高灯珠的密封性, 提高LED灯珠的使用寿命。

5. 结束语

加成型硅橡胶的优异性能使其在很多行业内得到了广泛的应用, 而粘结性能是限制其应用范围的一大关键因素。如何通过分子结构设计, 合成含有适当活性基团的增粘剂, 赋予加成型硅橡胶与各类基材的良好粘接力, 是有机硅领域的一大热点, 相信随着研究的进行, 粘接力的问题将会得到进一步的改善, 产品的应用也会得到更大范围的推广。

【参考文献】

- [1]Pape P G. Adhesion promoters: Silane coupling agents [M]. Applied plastics engineering handbook. William Andrew Publishing, 2011: 503-517.
- [2]林敏捷, 张成洋, 葛佳音, 等. 含双活性基团有机硅增粘剂制备及性能研究[J]. 粘接, 2018, 39(1): 23-27.
- [3]周为, 赖学军, 李红强, 等. 加成型硅橡胶用含酯基有机硅增

粘剂的制备及应用性能[J]. 有机硅材料, 2013, 27(6): 409-414.

[4]汪昱辰, 赖学军, 周为, 等. LSR用含氢MQ硅树脂型增粘剂的合成与表征[J]. 有机硅材料, 2014, 28(1): 12-17.

[5]王哲, 夏志伟, 李龙锐, 等. 自粘接导热灌封胶的研制[J]. 有机硅材料, 2016, 30(4): 295-298.

[6]Pan, Kexue, et al. Synthesis of an adhesion-enhancing polyhydrosiloxane containing acrylate groups and its cross-linked addition-cure silicone encapsulant[J]. Journal of Elastomers & Plastics, 2013, 47(5): 416-430.

[7]Wipfelder E, Höhn K. Epoxysiloxane resins by the condensation of 3-glycidyloxypropyltrimethoxysilane with diphenylsilanediol[J]. Angewandte Makromolekulare Chemie: Applied Macromolecular Chemistry and Physics, 1994, 218(1): 111-126.

[8]Huang W, Zhang Y, Yu Y, et al. Studies on UV-stable silicone-epoxy resins[J]. Journal of applied polymer science, 2007, 104(6): 3954-3959.

[9]张利利, 李志才, 侯毅, 等. 有机硅液体光学透明胶水的制备与研究[J]. 有机硅材料, 2017, 31(1): 1-5.

[10]凌钦才, 谢国庆, 郭文欣. 加成型液体硅橡胶用含环氧基的有机硅增粘剂的制备、表征及性能[J]. 有机硅材料, 2012, 26(2): 87-92.

[11]陈正旺, 黎忠林. LED封装胶专用增粘剂的制备[J]. 有机硅材料, 2014, 28(6): 426-428.

[12]Pan K X, Zeng X, Li H, et al. Synthesis of silane oligomers containing vinyl and epoxy group for improving the adhesion of addition-cure silicone encapsulant[J]. Journal of adhesion and technology, 2016, 30(10): 1131-1142.

[13]程宪涛, 张利利, 李清. 高性能有机硅增粘剂的合成及应用[J]. 有机硅材料, 2015, 29(6): 444-448.

[14]Kasuya A. Curable organopolysiloxane composition containing novel adhesion promoter[P]. U.S. Patent 5445891. 1995-8-29.

[15]杨维生, 毛晓丽. 硅橡胶对金属粘合性能的研究[J]. 中国胶粘剂, 2000, 9(6): 15-19.

[16]Pan K, Zeng X, Li H, et al. Synthesis of siloxanes containing vinyl and epoxy group and its enhancement for adhesion of addition-cure silicone encapsulant[J]. Journal of Macromolecular Science, Part A, 2013, 50(11): 1126-1132.

[17]曾幸荣, 潘科学, 赖学军. 高折射率有机硼硅粘接促进剂及其制备方法和应用[P]. CN: 201610079640.5, 2016.

[18]赵大成, 马子洪, 吴艳, 等. 一种LED封装胶用增粘剂及其制备方法[P]. CN: 104910829B, 2015.

[19]熊天宝, 唐强, 叶文波, 等. 一种硅硼增粘剂及其制备方法和用途[P]. CN: 201610541803.7, 2016.

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