S, N-Containing Co-MOFs Derived Co_9S_8 @S,N-Doped Carbon Materials as Efficient Oxygen Electrocatalysts and Supercapacitor Electrode Materials

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Controllable synthesis of metal-organic frameworks (MOFs) materials with tunable morphologies, sizes, compositions and pore structures is critically important for MOFs materials and their pyrolysis derivatives' applications in environmental and energy fields. Here we report the synthesis of Co-MOFs crystals with controllable morphologies, sizes and S/N ratios in water/NaOH and ethylene glycol/NaOH systems using thiophene-2,5-dicarboxylate (Tdc) and 4,4'-bipyridine (Bpy) as S, N dual organic ligands by a "pillar-layer" assembly method. Water and ethylene glycol with different viscosities result in various crystallization processes of $[\text{Co}(\text{Tdc})(\text{Bpy})]_n$ crystals in corresponding reaction system, thus respectively obtaining three-dimensional (3D) Co-MOFs ($[\text{Co}(\text{Tdc})(\text{Bpy})]_n$) bulk and cuboid structures in water/NaOH and ethylene glycol/NaOH reaction systems. The as-prepared Co-MOFs crystals in two different reaction systems were further pyrolytically treated at 800 °C in N_2 atmosphere to obtain Co_9S_8 @S,N-doped carbon materials with different surface areas, pore distributions and S/N doping ratios. As electrocatalysts, the Co_9S_8 @S,N-doped carbon cuboid (Co_9S_8 @SNCC) obtained in ethylene glycol/NaOH system demonstrates superior bifunctional electrocatalytic activities toward both oxygen reduction and evolution reactions resulted from Co_9S_8 and S, N doping in carbon structure providing catalytic active sites, better than that of Co_9S_8 @S,N-doped carbon bulk (Co_9S_8 @SNCB) obtained in water/NaOH system and comparable to commercial Pt/C and RuO_2 catalysts. Owing to its high surface area and porous structure, Co_9S_8 @SNCC also exhibits great potential as electrode material for supercapacitor application with high performance and recycling stability.

Introduction

Metal-organic frameworks (MOFs) are a class of crystalline porous materials formed by the assembly of metal ions/clusters and organic ligands.^{1,2} Recently, it was found that the MOFs-derived materials have been attracting great attentions for energy conversion and storage applications due to their tunable sizes, morphologies, surface areas, pore structures, and easy to obtain heteroatom (e.g., N) doping. These advantages of MOFs derived materials contribute their high application performance.^{3,4} To date, many studies have reported that MOFs can be transformed into several products including high-surface-area micro-porous carbon,^{5,6} metals^{7,8} and metal oxides^{9,10} decorated carbon materials by direct pyrolysis under an inert atmosphere. Attractively, compared

with bulk carbon-based materials obtained by direct pyrolysis of bulky MOFs materials, the derivatives from controllably grown MOFs with decreased sizes, desirable morphologies, structures and heteroatom-contained ligands exhibit higher performance for applications in supercapacitor and electrocatalysis,¹¹⁻¹³ due to the pyrolytically converted carbon materials inheriting the merits of controllably grown MOFs precursors, such as higher surface area, porous structure, larger pore volume and easy to obtain heteroatom doping/co-doping in carbon structure, favourable for the exposure of catalytic active sites, mass transport and electron transfer. Therefore, development of new strategies for controlling the dimensions, sizes, morphologies and structures of heteroatom-containing MOFs crystals is of great importance for their pyrolysis derivatives' applications.¹⁴⁻¹⁸

Recently, many studies have demonstrated that the viscosity of ionic liquid significantly affects the crystallization process of MOFs, resulting in different morphologies and structures.^{19,20} In this respect, Shieh *et al.* reported that smaller ZIF-90 particles can be fabricated in H_2O /alcohol/PVP solution with larger viscosity, revealing that the solvent viscosity is a key factor for controlling the sizes of the synthesized ZIF-90.²¹ Inspired by the phenomena that the reaction solvents with different viscosities contribute significant effects on the MOFs crystal formation, here we

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reported a simple method for synthesis of S, N-containing Co-MOFs nanocrystals with controllable morphologies and sizes by using water and ethylene glycol as solvents with different viscosities. It was found that water and ethylene glycol as solvents can effectively regulate Co-MOFs ($[\text{Co}(\text{Tdc})(\text{Bpy})]_n$) crystal growth using thiophene-2,5-dicarboxylate (Tdc) and 4,4'-bipyridine (Bpy) as S, N dual organic ligands by a "pillar-layer" assembly method,²² obtaining S, N-containing Co-MOFs crystals with different sizes and morphologies. The as-prepared Co-MOFs crystals using water and ethylene glycol as solvents were further pyrolytically treated at 800 °C in N_2 atmosphere to obtain $\text{Co}_9\text{S}_8@\text{S,N-doped carbon bulk}$ ($\text{Co}_9\text{S}_8@\text{SNCB}$, water as solvent) and $\text{Co}_9\text{S}_8@\text{S,N-doped carbon cuboid}$ ($\text{Co}_9\text{S}_8@\text{SNCC}$, ethylene glycol as solvent) with different sizes, morphologies, pore structures and S/N doping ratios. Compared to the $\text{Co}_9\text{S}_8@\text{SNCB}$, the $\text{Co}_9\text{S}_8@\text{SNCC}$ shows porous structure (micropore and mesopore) with a surface area of $212.1 \text{ cm}^2 \text{ g}^{-1}$, exhibiting better bifunctional electrocatalytic activities of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), ascribed to its high surface area favourable for the exposure of catalytic active sites resulted from Co_9S_8 and S, N doping in carbon structure, porous structure beneficial for electrocatalysis-related mass transport, and graphitic carbon structure to improve electron transfer. These advantages combined with Co_9S_8 active species enable $\text{Co}_9\text{S}_8@\text{SNCC}$ promising electrode material for supercapacitor application with higher performance and recycling stability in comparison with $\text{Co}_9\text{S}_8@\text{SNCB}$. Compared with the reported methods utilizing MOFs precursors for fabricating cobalt sulfides based composites,^{11, 23} our strategy facilitates access to composites with Co_9S_8 nanoparticles embedded porous graphitic carbon structures without additional S, N doping sources using S, N-containing Co-MOFs precursors, demonstrating great potential in energy applications.

Experimental

Preparation of $[\text{Co}(\text{Tdc})(\text{Bpy})]_n$ crystals and their pyrolysis derivatives

For a typical synthesis of $[\text{Co}(\text{Tdc})(\text{Bpy})]_n$ -bulk, 228 mg $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was first dissolved in 10 mL of deionized water, and then 10 mL of Co^{2+} solution was added into a mixture (20 mL) including 280 mg Tdc, 296 mg 4,4'-Bpy and 132 mg NaOH at room temperature under stirring for 5 min. The above mixture was transferred to a Teflon-lined steel autoclave (80 mL) and kept at 120 °C for 12 h, the obtained product was filtered to collect and dried at 60 °C for overnight to obtain three-dimensional (3D) $[\text{Co}(\text{Tdc})(\text{Bpy})]_n$ -bulk material. The same process was also applied to synthesize $[\text{Co}(\text{Tdc})(\text{Bpy})]_n$ -cuboid crystals except for ethylene glycol substitute for water as reaction solvent.

The as-prepared $[\text{Co}(\text{Tdc})(\text{Bpy})]_n$ -bulk and $[\text{Co}(\text{Tdc})(\text{Bpy})]_n$ -cuboid materials were used as precursors for pyrolytic treatment at 800 °C at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ for 2 h in N_2 atmosphere to obtain $\text{Co}_9\text{S}_8@\text{SNCB}$ and $\text{Co}_9\text{S}_8@\text{SNCC}$. After

removing the Co_9S_8 by HCl etching, S, N-doped carbon cuboid (SNCC) was prepared for comparison.

Characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Philips X-Pert Pro X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($1.5418 \text{ \AA}$). Field emission scanning electron microscopy (FESEM) images of the samples were taken on a FESEM (Quanta 200 FEG) operated at an accelerating voltage of 10.0 kV. Transmission electron microscopy (TEM) images of the samples were recorded by a high resolution TEM (JEOL2010), operated at an acceleration voltage of 200 kV. The surface area and porosity of samples were measured by a Surface Area and Porosity Analyzer (Tristar 3020M). X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with $\text{Al K}\alpha_{1,2}$ monochromatized radiation at 1486.6 eV X-ray source. Raman spectra of the samples were recorded on a LabRAM HR800 confocal microscope Raman system (Horiba Jobin Yvon) using an Ar ion laser operating at 632 nm.

Electrochemical measurements

All the electrochemical measurements were performed on an electrochemical workstation (CHI 760D, CH Instruments, Inc., Shanghai, China) and a PINE rotating disk electrode (RDE) system (Pine Instruments Co. Ltd. USA). A conventional three-electrode cell, composed of a catalyst coated glassy carbon (GC) working electrode, an Ag/AgCl reference electrode and a platinum wire counter electrode, was applied to perform electrochemical measurements. The potentials vs. Ag/AgCl were converted to the reversible hydrogen electrode (RHE) using the following relationship.

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E_{\text{Ag/AgCl}}^{\circ}$$

where E_{RHE} is the converted potential vs. RHE, $E_{\text{Ag/AgCl}}^{\circ} = 0.197 \text{ V}$ at 25 °C, and $E_{\text{Ag/AgCl}}$ is the experimentally measured potential against Ag/AgCl reference. A rotating disk electrode (RDE) with a diameter of 5.0 mm was served as the substrate for the working electrode. The electrolyte was 0.1 M KOH solution prepared from deionized water.

Prior to use, RDE was first polished with 5.0, 0.3 and 0.05 μm alumina slurry, sequentially, and then washed ultrasonically in ethanol and deionized water for 30 s, respectively. 4.0 mg catalyst was dispersed ultrasonically in 1000 μL of solvent mixture of Nafion (5%), absolute ethanol, deionized water (V: V: V=1: 1: 8), to obtain a well-dispersed catalyst ink. Subsequently, 20 μL of catalyst ink was cast onto the GC electrode surface and dried at room temperature for further use.

ORR measurements: The cyclic voltammogram (CV) tests were performed between 0.2 V and 1.0 V (vs. RHE) at room temperature in N_2 - and O_2 -saturated 0.1 M KOH solution with a scan rate of 50 mV s^{-1} . RDE experiments were carried out in an O_2 -saturated 0.1 M KOH solution at room temperature, a sweep rate of 10 mV s^{-1} under different rotating rates (400, 625, 900, 1225 and 1600 rpm). All the potentials in this study were reported with respect to the RHE reference electrode. Commercial 20 wt. % platinum on carbon black (Alfa Aesar)

was used for comparison, with all the testing parameters kept the same as those used for the as-prepared electrocatalyst electrodes.

The electron transfer number (n) per oxygen molecule at different potentials during the oxygen reduction reaction (ORR) was calculated based on the Koutecky-Levich (K-L) equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

$$B = 0.2nFC_0(D_0)^{2/3}\nu^{-1/6}$$

$$J_K = nFkC_0$$

where J is the measured current density, J_L and J_K are the diffusion- and kinetic-limiting current densities, ω is the rotation speed, n represents the number of electrons transferred per oxygen molecule, F is the Faraday constant (96485 C mol⁻¹), C_0 is the O₂ concentration in the electrolyte (1.26 × 10⁻⁶ mol cm⁻³), D_0 is the diffusion coefficient of O₂ in the electrolyte (1.9 × 10⁻⁵ cm² s⁻¹), and ν is the kinetic viscosity (0.01 cm² s⁻¹)

OER measurements: Oxygen evolution experiments were measured in 0.1 M KOH solution by purging with O₂ for at least 30 min before the measurement. Polarization curves were obtained by sweeping the potential from 1.0 to 1.7 V (vs. RHE) with a sweep rate of 10 mV s⁻¹ at 1600 rpm. The OER potential was obtained by iR compensation approach using the $E-iR \times 0.95$ relation, where i is the current and R is the uncompensated electrolyte ohmic resistance, and the resistance of the electrolyte was measured using the catalyst-loaded RDE in 0.1 M KOH solution, and determined to be 48 Ω by iR compensation method.

Capacitance measurements: For electrochemical measurements, the working electrode was fabricated by mixing active materials, conductive carbon black, and PTFE at a weight ratio of 8:1:1, and then the mixture was coated onto a piece of nickel foam with a geometrical area of 1.0 cm², and pressed into a thin foil at a pressure of 10.0 MPa. The fabricated electrode was then dried at 60 °C for overnight under vacuum condition. Cycle voltammetry (CV) and capacitive performance measurements were conducted using a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument, Inc.) in an aqueous KOH electrolyte (6.0 M) with a three-electrode cell. In this setup, the platinum wire served as the counter electrode and an Hg/HgO electrode served as the reference electrode. The mass loading of 3D Co₉S₈@SNCC and Co₉S₈@SNCC on the nickel foam was approximately 2.4 mg cm⁻². Specific capacitance was calculated based on the total mass of active material using the following formula:²⁴

$$C = I\Delta t / (m\Delta V)$$

where I is the discharge current, Δt is the discharge time, m is the mass of active material, and ΔV is the voltage window. All the electrochemical measurements were performed at room temperature. Electrochemical impedance spectrometry (EIS) was measured using a CHI 660D electrochemical workstation at a frequency ranging from 100 kHz to 10 mHz.

Results and discussion

In this work, water (H₂O, viscosity of 1.00 mPa·s, 25°C) and ethylene glycol (EG, viscosity of 16.1 mPa·s, 25°C)²⁵ were used as reaction solvents to controllably grow Co-MOFs crystals with different structures under hydrothermal and solvothermal conditions (120 °C, 12h) (Fig. 1a). The aim of addition of NaOH in reaction systems is to deprotonate Tdc to promote the linkage of Co²⁺ and Tdc, forming Co-MOFs growth units.²⁶ Fig. 1b shows the XRD patterns of Co-MOFs samples obtained at water and ethylene glycol reaction systems, demonstrating the [Co(Tdc)(Bpy)]_n MOFs crystals were successfully fabricated.²² The morphologies and sizes of the products were also characterized, as shown in Fig. 1c and d. Irregular bulky-like structures with the sizes of tens to hundreds micrometers were observed the Co-MOFs crystals obtained in H₂O reaction system (Fig. 1c), while relatively uniform cuboid-shape structures with a length of 1~2 μ m, a width of 0.5~1 μ m and a thickness of 0.1~0.2 μ m were obtained in ethylene glycol reaction system (Fig. 1d). The difference in morphology and size of Co-MOFs crystals can be due to water and ethylene glycol reaction systems with different viscosities,^{20, 21} moreover, ethylene glycol with higher viscosity also acts as a stabilizer to prevent the aggregation of seed crystals, favourable for growth of small-sized Co-MOFs crystals.²⁰ Owing to relatively low viscosity of water reaction system, reactant species is more easy movement, thus resulting in large-sized Co-MOFs crystals,^{21, 27-29} on the contrary, small-sized Co-MOFs crystals are more easy to form in ethylene glycol reaction system with relatively high viscosity during solvothermal process. The above results indicated that the reaction solvents have critically important influence on the resulting morphology, structure and size of Co-MOFs, possibly resulting in Co-MOFs derived carbon-based products with different surface areas, pore structures.

Further, the as-prepared Co-MOFs crystals derived carbon products were obtained by a simple pyrolysis process in N₂ atmosphere. Fig. 2a shows the XRD patterns of the carbon products derived from Co-MOFs crystals obtained in water and ethylene glycol reaction systems. As shown, the diffraction peaks around 29.84°, 31.19°, 44.70°, 47.58°, 52.09° for these two samples can be indexed to the (311), (222), (422), (511) and (440) planes of Co₉S₈ (JCPDS: No. 86-2273), respectively,³⁰

Fig. 1 (a) Schematic illustration of the preparation process of Co-MOFs crystals in water and ethylene glycol reaction systems. (b) XRD patterns of Co-MOFs-bulk and Co-MOFs-

cuboid. (c) and (d) SEM images of Co-MOFs-bulk and Co-MOFs-cuboid.

Fig. 2 (a) XRD patterns of Co_9S_8 @SNCC (black line) and Co_9S_8 @SNCB (red line). (b) SEM image of Co_9S_8 @SNCC. (c) and (d) Low and high magnification TEM images of Co_9S_8 @SNCC, the insets are corresponding SAED patterns and HRTEM image. (e)-(h) Elemental mapping images of Co, S, C and N in Co_9S_8 @SNCC obtained from c.

indicating the formation of Co_9S_8 during the pyrolysis of Co-MOFs. Fig. 2b shows the SEM image of Co_9S_8 @SNCC derived from Co-MOFs crystals obtained in water reaction system. As shown, the cuboid-shape structures with coarse surface can be still observed for Co_9S_8 @SNCC, while the bulk-shape structures with coarse surface are found for Co_9S_8 @SNCB derived from Co-MOFs crystals obtained in ethylene glycol reaction system (Fig. S1, ESI[†]), indicating the essential morphology inheriting from Co-MOFs precursors after pyrolysis. TEM analysis was further performed to confirm the detailed structure information of Co_9S_8 @SNCC. As shown in Fig. 2c and 2d, abundant Co_9S_8 nanoparticles with the sizes of ~ 50 nm are uniformly distributed over porous carbon network, indicating the formation of Co_9S_8 @SNCC composite. The corresponding SAED patterns (inset of Fig. 2c) can be assigned to the diffraction planes of crystalline Co_9S_8 . The lattice spacing of 0.248 nm in the HRTEM image of Co_9S_8 @SNCC can be ascribed to the (400) plane of Co_9S_8 . The above results confirm the formation of Co_9S_8 nanoparticles in porous carbon network after pyrolysis of cuboid Co-MOFs crystals obtained in ethylene glycol reaction system. Similar results can be also obtained for Co_9S_8 @SNCB derived from bulky Co-MOFs crystals obtained in water reaction system. The elemental mapping analysis (Fig. 2e-h) obtained from Fig. 2c demonstrates that C, N, S and Co elements are relatively homogeneously distributed over the entire hybrid structure, and S element distribution is more obvious at the locations of Co_9S_8 nanoparticles. The above

results further indicate the formation of Co_9S_8 @SNCC composite with Co_9S_8 nanoparticles incorporated into S, N doped porous carbon networks.

The surface chemical composition of Co_9S_8 @SNCC was examined by XPS technique. The XPS survey spectrum (Fig. 3a) indicates the existence of C, N, S, O and Co elements in Co_9S_8 @SNCC. The high resolution C 1s spectrum (Fig. 3b) verifies a successful doping of S, N elements in carbon structure owing to the formation of C-N and C-S bonds.¹³ The high resolution N 1s spectrum (Fig. 3c) shows that the doped N in carbon structure contains pyridinic-N (0.80 at.%), pyrrolic-N (0.54 at.%), graphitic-N (0.84 at.%) and oxidized-N (0.93 at.%).³¹ A total N doping content of 3.11 at.% can be obtained based on XPS analysis, further indicating the successful doping of nitrogen atoms in carbon structure. The Co_9S_8 @SNCC with predominant pyridinic-N may be very efficient as an electrocatalyst for oxygen reduction reaction (ORR).³² The high resolution S 2p spectrum (Fig. 3d) indicates the existence of Co-S and C-S-C bonds, confirming the formation of cobalt sulfides and S doping in carbon structure.³³ In the Co 2p spectrum of Co_9S_8 @SNCC (Fig. 3e), the peaks at 781.61 eV and 784.88 eV are assigned to the $2p_{3/2}$ of Co^{2+} and Co^{3+} , and the peaks at 779.36 eV and 784.88 eV are attributed to the $2p_{1/2}$ of Co^{2+} and Co^{3+} , as well as the corresponding two shakeup satellites (abbreviated as "Sat."), respectively, suggesting the formation of cobalt sulfides in carbon structure.³⁴ Further, Co_9S_8 @SNCC and Co_9S_8 @SNCB were also characterized by the Raman spectrum technique (Fig. 3f). The Raman spectra of Co_9S_8 @SNCC (black line) and Co_9S_8 @SNCB (red line) display typical Raman peaks of carbon materials at

Fig. 3 (a) XPS survey spectra of the Co_9S_8 @SNCC (red line) and Co_9S_8 @SNCB (black line). (b-e) High resolution C1s, N1s, S2p, Co2p spectra. (f) Raman spectra of Co_9S_8 @SNCC (black line) and Co_9S_8 @SNCB (red line).

and Co 2p XPS spectra of Co₉S₈@SNCC. (f) Raman spectra of the Co₉S₈@SNCB and Co₉S₈@SNCC.

1350 cm⁻¹ of D-band and 1595 cm⁻¹ of G-band, corresponding to the vibrations of the carbon atoms with dangling bonds in plane terminations of disordered graphite and E_{2g} mode of graphite layer.³⁵ Generally, the intensity ratio of G band to D band can be used to evaluate the degree of graphitization. The I_G/I_D values are 1.03 and 1.00 for Co₉S₈@SNCC and Co₉S₈@SNCB, respectively, indicating an intact graphitic carbon structure of the Co₉S₈@SNCC, favourable for electron transfer in electrocatalysis and supercapacitor applications. In addition, the peak in the region of wavenumber <750 cm⁻¹, which is indexed to Co₉S₈ for these two samples.³⁶

The surface area and pore distribution of Co₉S₈@SNCC and Co₉S₈@SNCB were analyzed by N₂ adsorption and desorption measurements (Fig. 4). The isotherms of Co₉S₈@SNCC and Co₉S₈@SNCB exhibit a typical type-IV curve and an H₃-type hysteresis loop (Fig. 4a), indicating the presence of micropore and mesopore structures in these two composites. The surface area of 212.1 m² g⁻¹ can be obtained for Co₉S₈@SNCC, much higher than that (88.1 m² g⁻¹) of Co₉S₈@SNCB. The high surface area of Co₉S₈@SNCC is favourable for the exposure of active sites, thus improving the application performance of electrocatalysis and supercapacitors. The corresponding pore size distribution (Fig. 4b) shows that there exists two pore-size distributions in Co₉S₈@SNCC, namely, concentrated at ~1.8 nm and ~19 nm, indicating the presence of micropore and mesopore structures. This dominant mesopore structure in Co₉S₈@SNCC may be beneficial for mass transport in applications. Comparatively, Co₉S₈@SNCB exhibits a pore size distribution mainly concentrated at ~1.9 nm (dominant micropore) with very low percentage of mesopore (centered at ~12 nm). Moreover, the pore volume of Co₉S₈@SNCB (0.394 cm³ g⁻¹) is much lower than that of Co₉S₈@SNCC (0.828 cm³ g⁻¹). The higher surface area, larger pore volume and dominant mesopore structure of Co₉S₈@SNCC are very favourable for the exposure of more active sites and mass transfer when applied to electrocatalysis and supercapacitors, thus contributing higher application performance.^{13, 37}

In this work, we first evaluated the electrocatalytic performance of ORR and OER using Co₉S₈@SNCC and Co₉S₈@SNCB catalysts. Commercial Pt/C and RuO₂ catalysts were also measured under the identical experimental conditions. In ORR measurements, the linear sweep voltammogram (LSV) curves (Fig. 5a) obtained in O₂-saturated 0.1 M KOH solution at 1600 rpm show that Co₉S₈@SNCC exhibits an onset potential of 0.84 V and a half-wave potentials of 0.75 V, which are slightly negative to those of Pt/C (onset potential of 0.92 V and half-wave potential of 0.80 V) and much better than those of Co₉S₈@SNCB (onset potential of 0.81 V and half-wave potential of 0.66 V). The above results demonstrate that Co₉S₈@SNCC possesses good ORR activity owing to Co₉S₈ and S, N doping in porous graphitic carbon structure providing catalytic active sites combined with its higher surface area and desirable porous structure.¹³ Remarkably, the limiting current density of Co₉S₈@SNCC is obviously higher than that of Co₉S₈@SNCB, and almost

identical with Pt/C catalyst, further indicating its good ORR performance. Fig. 5b shows the LSV curves of Co₉S₈@SNCC in

Fig. 4 (a) N₂ adsorption-desorption isotherms of Co₉S₈@SNCC and Co₉S₈@SNCB. (b) Their corresponding pore size distribution curves.

O₂-saturated 0.1 M KOH solution under different rotating rates. The Koutecky-Levich (*K-L*) plots (Fig. S2a, ESI[†]) show good linear relationships within the potential range of 0.2~0.6 V and the calculated average electron transfer number ($\bar{n}$) is 3.94, close to commercial Pt/C ($\bar{n}$ is 3.99) (Fig. S3, ESI[†]), indicating a 4e transfer process of ORR. Under the identical conditions, the $\bar{n}$ value was calculated to be 2.84 for Co₉S₈@SNCB (Fig. S4, ESI[†]), further indicating higher ORR activity of Co₉S₈@SNCC. Further, the OER activities of Co₉S₈@SNCC and Co₉S₈@SNCB were also measured. Fig. 5c shows the stability test of Co₉S₈@SNCC and Pt/C catalysts in an O₂-saturated 0.1 M KOH solution. Co₉S₈@SNCC exhibits 16% decrease over 15,000 s of continuous operation at a rotation rate of 1600 rpm, while Pt/C displays a faster current loss with 30% decrease under identical experimental conditions. As shown in Fig. 5d, the potentials at current density of 10 mA cm⁻² are 1.56, 1.65, 1.59 and 1.53 V for Co₉S₈@SNCC, Co₉S₈@SNCB, IrO₂ and RuO₂, respectively, and their corresponding overpotentials are 0.33, 0.42, 0.36 and 0.31 V. Obviously, the obtained overpotential value at 10 mA cm⁻² of Co₉S₈@SNCC is very close to that of RuO₂ and much lower than that of Co₉S₈@SNCB and IrO₂, indicating its high OER activity. By comparison, the obtained Co₉S₈@SNCC in this work displays much better OER performance than most of recently reported other Co₉S₈-based electrocatalysts (Table. S1, ESI[†]). The high OER performance of Co₉S₈@SNCC can be further verified by the Tafel polarization curves (Fig. 5e), the obtained Tafel slope for Co₉S₈@SNCC is ca. 80 mV dec⁻¹, which is significantly smaller than that of Co₉S₈@SNCB (129 mV dec⁻¹), and closed to commercial RuO₂ catalyst (65 mV dec⁻¹) and IrO₂ (82 mV dec⁻¹). The superior bifunctional ORR/OER performance of Co₉S₈@SNCC can be due to the rich catalytic active sites provided by Co₉S₈ and S, N doping in carbon structure, higher surface area, larger pore volume, dominant mesoporous structure and graphitic carbon structure, favourable for the exposure of catalytic active sites, mass transport and electron transfer.^{38, 39} It can be seen from Fig. 5f that, after 1000 cycles, the polarization curve for the Co₉S₈@SNCC electrocatalyst shows a similar onset potential to the initial one with a slightly positive shift to a higher potential. The above result reveals good stability of Co₉S₈@SNCC in alkaline conditions. The crystal phase of Co₉S₈@SNCC after OER measurement was also

studied, as shown in Fig. S5 (ESI[†]), encouragingly, Co₉S₈@SNCC exhibits high stability during OER.

To better understand the role of Co₉S₈ and S, N-doping in the resulting Co₉S₈@SNCC, the ORR and OER activities of SNCC without Co₉S₈ were investigated, as shown in Fig. S6 (ESI[†]). It was found that SNCC also shows bifunctional catalytic performance for OER and ORR with relatively higher overpotential at current density of 10 mA cm⁻² for OER and slightly lower onset potential and current density than Co₉S₈@SNCC for ORR, indicating SNCC possesses excellent ORR and relatively inferior OER activities. The above results imply that S, N doping in carbon structure is mainly responsible for ORR and Co₉S₈ creates more catalytic active sites for OER. The whole ORR/OER bifunctionality is collectively due to a synergetic effect of all these catalytic active components in carbon material.⁴⁰⁻⁴²

The as-prepared Co₉S₈@SNCC and Co₉S₈@SNCB were also used as electrode materials for supercapacitors and evaluated in 6.0 M KOH solution (vs. Hg/HgO). Fig. S7a and Fig. S8a (ESI[†]) show the typical cyclic voltammetry (CV) curves of Co₉S₈@SNCC and Co₉S₈@SNCB electrodes. With increasing scan rate, the cathodic and anodic current densities increase for these two electrodes. Apparently, the CV curves of Co₉S₈@SNCC exhibit higher current densities than those of

Polarization curves for the Co₉S₈@SNCC electrocatalyst before and after 1000 cycles

Co₉S₈@SNCB at different scan rates (Fig. S7a, Fig. S8a, ESI[†] and Fig. 6a), indicating a higher capacitance. Fig. 6b shows the galvanostatic charge-discharge curves of Co₉S₈@SNCC and Co₉S₈@SNCCB measured at discharge current densities of 2 A g⁻¹ within the potential window of -0.1~0.4 V. Comparatively, the galvanostatic charge-discharge curves at different discharge current densities of Co₉S₈@SNCC and Co₉S₈@SNCB are shown in Fig. S7b and Fig. S8b (ESI[†]). It is well known that the specific capacitance is proportional to the discharge time under the galvanostatic curve.³⁷ The above results demonstrate that the specific capacitance of Co₉S₈@SNCC electrode is much higher than that of Co₉S₈@SNCB electrode under the identical experimental conditions. Further, the specific capacitance as a function of the discharge current density is plotted in Fig. 6c. The Co₉S₈@SNCC electrode exhibits specific capacitance of 429, 415, 396, 368, 356 and 336 F g⁻¹ at the discharge current densities of 1, 2, 5, 10, 20, and 50 A g⁻¹, much higher than 320, 311, 283, 282, 272 and 250 F g⁻¹ of Co₉S₈@SNCB, respectively, indicating that Co₉S₈@SNCC possesses a greatly improved capacitance and enhanced rate capability compared to Co₉S₈@SNCB. In addition, a high specific capacitance of 336 F g⁻¹ can be retained for Co₉S₈@SNCC even when the current density increases to 50 A g⁻¹, confirming its good rate capability. However, by comparison, the obtained Co₉S₈@SNCC exhibits relatively lower capacitance than most of recently reported other Co₉S₈-based composites (Table. S2, ESI[†]), possibly owing to the difference in materials' surface area, pore structure and composition. Cycling performance is another key parameter of an electrode material for practical application of supercapacitor. Therefore, a long time galvanostatic charge-discharge cycling (2000 cycles) of Co₉S₈@SNCC and Co₉S₈@SNCB electrodes were conducted at a constant current density of 5 A g⁻¹. As shown in Fig. 6d, the specific capacitance of Co₉S₈@SNCC electrode exhibits no obvious decrease after 2000 cycles (about 98% of capacitance is retained). However, an obvious decrease of the specific capacitance of

Fig. 5 (a) LSV curves of Co₉S₈@SNCC, Co₉S₈@SNCB and commercial Pt/C catalysts in O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹ and a rotating rate of 1600 rpm. (b) LSV curves of Co₉S₈@SNCC catalyst in O₂-saturated 0.1 M KOH solution at different rotation rates. (c) Chronoamperometric responses of Co₉S₈@SNCC and Pt/C electrocatalysts obtained at 0.6 V in O₂-saturated 0.1M KOH solution with a rotation rate of 1600 rpm. (d) OER currents of Co₉S₈@SNCC, Co₉S₈@SNCB and RuO₂ in 0.1 M KOH solution at a scan rate of 10 mV s⁻¹. (e) Tafel plots derived from (c). (f)

Fig. 6 (a) Cyclic voltammetry curves obtained a scan rate of 50 mV s⁻¹ and (b) galvanostatic charge-discharge curves of Co₉S₈@SNCC and Co₉S₈@SNCB at a current density of 2 A g⁻¹. (c) The variation of specific capacitances with current densities

for Co₉S₈@SNCC and Co₉S₈@SNCB. (d) Cycling performance at a current density of 5 A g⁻¹ of Co₉S₈@SNCC and Co₉S₈@SNCB. Co₉S₈@SNCB electrode is observed after 2000 cycles (83% capacitance retention). The superior performance of Co₉S₈@SNCC could be attributed to its higher surface area and unique porous structure can provide sufficient space for electrolyte transport to contact the reaction active sites during the charge-discharge process, the intimate interaction between the graphitic carbon and Co₉S₈ nanoparticles enables facile electron transport during the redox reaction.⁴³⁻⁴⁶

In order to investigate the detailed electrochemical characteristics of the Co₉S₈@SNCC and Co₉S₈@SNCB electrodes, electrochemical impedance spectroscopy (EIS) were carried out in this work. The Nyquist plots of Co₉S₈@SNCC and Co₉S₈@SNCB and the equivalent circuit proposed to fit the spectra are shown in Fig. S9 (ESI[†]), in which R_s resulting from the resistance of electrode materials, ionic resistance of electrolyte and active materials/current collector interface, R_{ct} corresponds to the charge transfer resistance caused by Faradic reactions.^{47, 48} R_s can be obtained by the high-frequency intercept on the real axis, and the R_s values for Co₉S₈@SNCC and Co₉S₈@SNCB electrodes were measured to be 0.39 Ω and 0.52 Ω , respectively. Apparently, both of the Co₉S₈@SNCC and Co₉S₈@SNCB electrodes exhibit good electrical conductivity is evident from their low R_s values. The R_{ct} value is a well-known critical factor of power density of pseudocapacitors due to the lower R_{ct} value is more effective for fast charge and discharge responses.⁴⁹ Compared to the R_{ct} 1.2 Ω of Co₉S₈@SNCB electrode, the Co₉S₈@SNCC electrode has a lower R_{ct} value 0.9 Ω , the reduced charge-transfer resistance for Co₉S₈@SNCC electrode can remarkably improve the high power density of pseudocapacitors.⁴⁹ In additional, the low frequency straight lines are more vertical for the Co₉S₈@SNCC electrode, also suggesting better capacitive behaviour and lower diffusion resistance of ions within its larger pores.⁵⁰⁻⁵²

Conclusions

In summary, we reported a facile method that uses solvents with different viscosities to regulate growth of Co-MOFs crystals with controllable sizes, structures and morphologies. Compared to the large-sized Co-MOFs crystals obtained in water reaction system, ethylene glycol with high viscosity leads to the formation of relatively small-sized Co-MOFs crystals. Moreover, Co₉S₈ nanoparticles incorporated into S, N doped porous carbon composites were further obtained by using as-prepared Co-MOFs crystals with S, N-containing dual organic linkers as precursors through a simple pyrolysis approach. Owing to its higher surface area, larger pore volume and porous structure, the prepared Co₉S₈@SNCC as electrode material exhibits bifunctional catalytic activities of ORR and OER and superior performance of supercapacitor. The controllable synthesis strategy of MOFs crystals and their derivatives used in this work can be extended to fabricate other metal, metal oxides or metal sulfides incorporated heteroatom-doped/co-doped porous graphitic carbon

composites with controllable sizes, morphologies and pore structures for electrocatalysis and energy storage applications.

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