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Crystalline-water/Coordination Induced Formation of 3D Highly Porous Heteroatom-doped Ultrathin Carbon Nanosheet Networks for Oxygen Reduction Reaction

Tingting Liu,^{a,†} Shi Feng,^{a,†} Jia Huo,^{a,b,*} Qiling Li,^a Chao Xie,^a and Shuangyin Wang^{a,*}

Abstract: Development of highly efficient electrocatalysts with low cost for oxygen reduction reaction (ORR) is crucial for their application in fuel cells and metal-air batteries. In this work, we report a synthesis of 3D heteroatom-doped ultrathin carbon nanosheet networks directly starting from solid raw materials. This method represents an operationally simple, general, and sustainable strategy to various ultrathin carbon nanosheet networks. Evaporation of crystalline water and coordination interaction are proposed to be responsible for the formation of the 3D carbon nanosheet networks. The carbon nanosheet networks possess high surface area with micro- and macropores, large pore volume, ultrathin nanosheet structure, and effective N/S-co-doping. The as-prepared materials show outstanding electrocatalytic ORR performance with more positive onset potential and half-wave potential, good methanol tolerance, and excellent stability, compared with those of the porous carbons derived from the ZIF counterpart and commercial Pt/C. This work not only provides highly active ORR electrocatalysts via an operationally simple and green process and also demonstrates a general method to prepare 3D ultrathin carbon nanosheet networks without any additional template and solvent.

Introduction

Development of highly efficient oxygen reduction reaction (ORR) electrocatalysts has received intensive attention, ^{1,2} since ORR is a critical and also kinetically sluggish process for fuel cells and metal-air batteries.³⁻⁶ Although Pt-based materials are the currently well-known ORR catalysts, the exorbitant cost, CO deactivation, and poor operational stability seriously hamper their practical application.^{7,8} Henceforth, various strategies have been developed to circumvent the above issues, such as decreasing loading of Pt and employing non-precious metal catalysts and even metal-free catalysts.⁹

Heteroatom-doping (such as N, S, or P) porous carbonbased electrocatalysts, exhibiting high stability and resistance toward CO poisoning, satisfactory cost, and more exposed active sites, are regarded as one of the most promising Pt alternatives.¹⁰⁻¹⁴ Various heteroatom-containing materials have been used as precursors or templates to prepare heteroatomdoping porous carbons, such as graphene, carbon nanotubes, biopolymers, supramolecular polymers, and metal organic frameworks (MOFs).¹⁰⁻¹⁹ Among these materials, MOFs, especially, zeolitic imidazolate frameworks (ZIFs), contain abundant heteroatoms, transition metals, and pores. These materials have demonstrated tremendous potential for facile preparation of highly porous heteroatom-doped carbon-based electrocatalysts with ample catalytically active sites.¹⁵⁻¹⁹ To further expose more active sites, it is desirable to construct twodimensional (2D) porous carbon nanosheets. Few examples have been reported on synthesis of porous nanosheets starting from MOFs and the synthetic processes required use of template (such as graphene, NaCl) or preformation of 2D MOFs. ²⁰⁻²⁶ However, these methods often require complicated fabrication processes but also led to production of polluted wastes, such as solvents and byproducts.²⁰⁻²⁶ Moreover, it is a big challenge to prepare 3D porous carbons constructed with 2D carbon nanosheets from MOFs, which are expected to avoid the aggregation of carbon nanosheets and increase the substrate diffusion during the electrocatalysis.

In this work, we have developed an operationally simple and general approach to prepare 3D highly porous heteroatomdoped ultrathin carbon nanosheet networks. The synthesis is directly starting from mechanically ground mixture of solid raw materials without any additional template. The formation mechanism of carbon nanosheet networks is proposed as the induction of evaporation of the intrinsic crystalline water from metal salts. Water actually acts as a pore-forming agent but also an additive for formation of coordination bond between zinc ions and imidazole-based ligands to stabilize the overall frameworks. Additionally, the release of volatile components, especially Zn, at high temperature resulted in the formation of micropores within ultrathin walls to produce hierarchically porous carbon nanosheet networks, which would create numerous defects at the edges over micropores. The heteroatom-doping was easily achieved through changing the ligand, for example, 2methylimidazole for N-doping and mixture of 2-methylimidazole and 2-mercaptoimidazole for N/S-co-doping. Compared with porous carbon derived from ZIF-8, the ultrathin carbon nanosheet networks possess not only high surface area but also abundant active sites and low diffusion resistance owing to the 3D ultrathin hierarchically porous structure. These features result in unexpectedly high ORR activity, especially for the N/Sco-doped carbon nanosheet network, which exhibits comparable activity with Pt/C. To our knowledge, this is also the first example that the crystalline water is used as a soft template to produce highly porous ultrathin carbon nanosheet networks.

Results and Discussion

Nitrogen-doped ultrathin carbon nanosheet networks (denoted as N-UCNN-n, where n is the ratio of $Zn(NO_3)_2$ ·H₂O and 2-methylimidazole), was prepared by direct pyrolysis of mechanically ground mixture of zinc nitrate hexahydrate and 2-methylimidazole under Ar atmosphere at 150 °C for 2 h and then 1000 °C for 6 h. The synthesis is quite straightaway and does not require preformation of MOFs, and any additional

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template or precursors. The molar ratio of reactants, the hydrated metal salts, and the pyrolysis temperature play very important roles in the formation of carbon nanosheet networks (the preparation procedure is shown in Scheme 1). As a comparison, N-doped porous carbon nanoparticles (NPCN) derived from ZIF-8 were prepared with the same starting materials.



Scheme 1. Schematic illustration for preparation of heteroatom-doped ultrathin carbon nanosheet networks (UCNNs) and N-doped porous carbon nanoparticles (NPCN).

The surface morphology and microstructure of N-UCNN-2 were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images (Figure 1a, 1b, S1a, and S1b) reveal that the N-UCNN-2 is indeed a 3D carbon network consisting of macropores interconnected with ultrathin carbon nanosheets. TEM images (Figure 1c and S1c) indicate the formation of transparent vesicle structures implying the carbon sheets are extremely thin. High resolution TEM (HRTEM) image reveals that the ultrathin walls are constructed with disordered graphene-like layers with a plenty of defects and the corresponding FFT image (Figure 1d) confirms the formation of disordered structure with abundant active sites. Atomic force microscopy (AFM) was employed to detect the thickness of nanosheets of the as-prepared carbon nanosheet networks. N-UCNN-2 was strongly sonicated in ethanol to produce the dispersion of carbon nanosheets suitable for AFM characterization, as shown in Figure 1e. The average thickness of tested nanosheets is about 3.7 nm (Figure 1f), validating the ultrathin structure of N-UCNN-2. In addition, control samples were synthesized at the same condition for synthesis of N-UCNN-2, including materials prepared with different ratio of Zn(NO3)2.6H2O and 2-methylimidazole (1:2.5 and 1:1.5) (N-UCNN-2.5 and N-UCNN-1.5) and N-doped porous carbon nanoparticles derived from ZIF-8 (NPCN). Pyrolyzing ZIF-8 produced porous carbon nano-polyhedrons without any macroporous interconnected networks (Figure S2). Interestingly, only large bulk materials were formed when the ratio became 1:2.5 (although the resultant material is a bulk material, we still named it as N-UCNN-2.5 for convenience). But N-UCNN-1.5 was a porous 3D carbon network similar with N-UCNN-2 (Figure S3 and S4), suggesting that the content of crystalline water was an important parameter to form the macroporous carbon networks.



Figure 1. SEM images of N-UCNN-2: low magnification (a) and high magnification (b); c) TEM image of N-UCNN-2; d) HRTEM image of N-UCNN-2 (inset in (d) shows the corresponding FFT pattern); e) AFM image of N-UCNN-2; and f) Height profile a, b, and c derived from the white line a, b and c in (e), respectively.

Raman spectroscopy was applied to analyze the surface electronic properties of the N-UCNN-n and NPCN as shown in **Figure 2**a and S5. The peaks at 1320 and 1590 cm⁻¹ are observed for both N-UCNN-n and NPCN in Figure 2a, which are assigned to the D and G band, respectively, indicative of the presence of both graphitic and disordered carbon atoms.²⁷ The

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values of I_D/I_G of N-UCNN-2 and NPCN are 1.26 and 1.10, respectively, declaring that more defects exist in N-UCNN-2 than NPCN, consistent with the HRTEM results, which might result from the ultrathin layered carbon structures within N-UCNN-2 ^{28,29}. To further confirm the presence of disordered carbon layers, the carbon samples were characterized by powder X-ray diffraction (PXRD) (Figure S6). Only a broad (002) basal plane diffraction is observed for N-UCNN-2, implying as-prepared materials are made up of partly disordered structures.^{30,31} The specific surface area and pore size distribution of N-UCNN-2 and NPCN were analyzed by the nitrogen adsorption-desorption isotherms at 77 K. Both samples display typical type-I isotherms (Figure 2b), indicating that they are predominantly microporous materials and the average pore size is around 0.9 nm.32Importantly, compared with the surface area of NPCN, the surface area of N-UCNN-2 does not decrease because of using the solid raw materials as precursors. N-UCNN-2 exhibited a ultrahigh surface area of 1921.4 m² g⁻¹, as estimated by the Brunauer-Emmett-Teller (BET) method, exceeding those of NPCN (1912.6 m² g⁻¹) and most of the MOF-derived carbon materials.33,34 The above data confirm the formation of hierarchically porous carbons with macro- and micropores. The highly microporosity within the ultrathin carbon layers should result from the evaporation of Zn atoms, which would also expose more edge defects as the active sites for electrocatalysis. The macropores would facilitate the mass diffusion so that to increase the electron transfer efficiency during electrocatalysis.33,34



Figure 2. a) Raman spectra of N-UCNN-2 and NPCN; b) Nitrogen adsorption/desorption isotherms of N-UCNN-2 and NPCN at 77 K (Inset is the corresponding micropore size distribution); and High-resolution C 1S (c) and N 1S (d) XPS spectra of N-UCNN-2 and NPCN.

The elemental compositions and chemical states of N-UCNN-2 were examined by X-ray photoelectron spectroscopy (XPS). The survey spectrum (Figure S8) of N-UCNN-2 explicitly exhibits a mainly narrow graphtic C 1s peak at around 285 eV accompanied by a N 1s peak at 400 eV. Furthermore, an O 1s peak also appears at around 540 eV, possibly owing to the

adsorbed water or oxygen from physically external environment.^{35,36} No signal of Zn was detected (Figure S8), implying the obtained materials are the metal-free N-doped porous carbons.^{37,38} From the high resolution C 1s spectrum (Figure 2c), there are two main peaks assigned to the crystalline graphitic sp2 carbon (C-C sp2) and the defect sp3 carbon (C-C sp3). The ratio of sp2/sp3 of N-UCNN-2 and NPCN are 4.83 and 5.53, respectively, indicating that the N-UCNN-2 has more edge defects than NPCN.²⁸ The high-resolution N 1s spectrum (Figure 2d) suggests the presence of four configurations of nitrogen, including pyridinic N (298.3 ± 0.2 eV), pyrrolic N (399.7 ± 0.2 eV), graphitic N (401.1 \pm 0.2 eV), and oxidized N (403.0 \pm 0.3 eV). The contents of N for N-UCNN-2 and NPCN are 1.0 and 1.8 at%, respectively, consistent with those of ZIF-derived carbons obtained at the high temperature in the literatures.^{33,34} Moreover, N-UCNN-2 possesses higher content of pyridinic-N and graphitic-N (65.3 %) than NPCN (59.8 %), which were allegedly beneficial for ORR.39

The effective N-doping together with abundant active sites and hierarchically porous structures encourage us to investigate the potential of N-UCNN-2 as ORR electrocatalyst. The electrocatalytic ORR activity of N-UCNN-2 was characterized firstly by the cyclic voltammogram (CV) measurements in 0.1 M KOH solution saturated with oxygen at room temperature with a sweep rate of 50 mV s⁻¹, with that of NPCN as a comparison. As shown in Figure 3a, no obvious redox peak was detected in the CV curves of N-UCNN-2 and NPCN measured in the N2saturated 0.1 M KOH solution. This phenomenon further proves that zinc was entirely removed during the formation process of N-UCNN-2 and NPCN. When tested in O₂-saturated 0.1 M KOH, the CV curves demonstrate sharp reduction peaks for both carbon nanomaterial-modified electrodes, indicating their evident ORR activities. Apparently, N-UCNN-2 presents a significant electrocatalytic ORR activity with a more positive cathodic peak potential (0.70 V) than NPCN (0.68 V), close to that of the commercial 20 wt% Pt/C (Figure S9). In addition, with changing the molar ratio of raw materials, the peak potential shifted negatively from 0.70 V (N-UCNN-2) to 0.60 V (N-UCNN-1.5) and 0.56 V (N-UCNN-2.5) (Figure S11 and Figure S12), suggesting that N-UCNN-2 has the highest ORR activity among the as prepared N-doped carbon nanosheet networks.

To further investigate the electrocatalytic activity of N-UCNN-2, linear sweep voltammograms (LSVs) were measured in O2saturated 0.1 M KOH solution with a scanning rate of 10 mV s⁻¹ on a rotating disk electrode (RDE). For comparison, we also prepared electrodes with NPCN or commercial 20wt% Pt/C using the same procedure. As shown in Figure 3b, the polarization curves tested with a rotation rate of 1600 rpm show that the N-UCNN-2 electrode presents a more positive ORR onset potential, E_{onset} (0.89 V) and half-wave potential, $E_{1/2}$ (0.78 V) than those of NPCN ($E_{\text{onset}} = 0.84$ V, $E_{1/2} = 0.72$ V). Meanwhile, the limiting diffusion current of N-UCNN-2 (5.15 mA cm⁻²) is close to that of Pt/C (5.30 mA cm⁻²). A rotating ring-disk electrode (RRDE) technique was applied to identify whether the ORR process underwent a two-electron or four-electron pathway and measure the quantity of H₂O₂ produced during the ORR process. Figure S10a presents the disk and ring currents for N-UCNN-2 and NPCN. The electron transfer number (n) was calculated as 3.81-3.90 for N-UCNN-2 (Figure S10d) in the

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potential range of 0.0-0.75 V, indicating that the ORR on N-UCNN-2 proceeds with a dominant four-electron reaction pathway.



Figure 3. a) CV curves of N-UCNN-2 and NPCN in N₂-saturated and O₂-saturated 0.1 M KOH; b) ORR polarization curves for N-UCNN-2, NPCN and Pt/C at 1600 rpm; c) Current-time (I-t) chronoamperometric responses of N-N-UCNN-2, NPCN, and Pt/C in O₂-saturated 0.1 M KOH at -0.15 V; and d) Current-time (i-t) chronoamperometric responses of N-UCNN-2, NPCN, and Pt/C (1600 rpm) in O₂-saturated 0.1 M KOH at -0.15 V followed by the introduction of methanol (3 mL) at 100 s.

Based on the values of the disk and ring currents, the H₂O₂ vield of the N-UCNN-2 is less than 10 % (Figure S10e), while the NPCN has a relatively higher H₂O₂ yield (14 %). Those results demonstrate that the ORR activity of N-UCNN-2 is superior to that of NPCN. By consideration of the difference of the morphology between N-UCNN-2 and NPCN, the excellent ORR performance of N-UCNN-2 could be attributed to the ultrathin carbon layers with abundant micropores and unique hierarchical porous structures, which would increase active surface area and enhance the mass transfer. Furthermore, as displayed in Figure 3c, N-UCNN-2 exhibits only a slight current reduction with 90 % retention after a 20000 s of chronoamperometry test while Pt/C shows a more current loss with only 75 % retention, emphasizing the higher long-term stability for N-UCNN-2. Meanwhile, the N-UCNN-2 also shows better methanol tolerance than commercial Pt/C (Figure 3d). Since both N-UCNN-2 and NPCN are N-doped carbon materials, NPCN exhibits similar ORR stability and methanol tolerance with N-UCNN-2.

To understand the formation mechanism of N-UCNN-2, a series of control experiments were carried out. The influence of molar ratio of raw materials on the formation of carbon nanosheet networks has suggested the importance of crystalline water. Therefore, we first investigate the effect of crystalline water during the preparation of macropoorus carbon networks. $Zn(NO_3)_2 \cdot GH_2O$ was dehydrated by heating in a flask, quickly transferred into a glove box filled with N₂, and then grinded with 2-equimolar 2-methylimidazole, which was calcined under the same condition for preparation of N-UCNN-2. It was found only small amount of bulk powders were obtained finally (Figure S14

and S15). Instead, the mixture of hydrated zinc salt and 2methylimidazole would form a paste after grinding and the subsequent calcination at 150 °C led to expansion and upwrap, where water was evaporated (Figure S13). SEM image of the as-obtained material shows that the macroporous carbon networks formed at this stage, which indicates that the evaporation of the crystalline water is the primary reason for the formation of macroporous networks (Figure S23). Interestingly, when the dehydrated mixture of $Zn(NO_3)_2$ and 2-methylimidazole was rehydrated with the same amount of water for N-UCNN-2, ultrathin carbon nanosheet networks were regenerated, further confirming the role of water (Figure S16 and S17).

The coordination interaction is also important for the formation of final carbon nanosheet networks. PXRD patterns, FT-IR spectra, and N₂ sorption isotherms prove that grinding mixture of hydrated zinc salt and 2-methylimidazole actually produces nonporous zinc-imidazolate coordination polymer (Figure S18-S21), but no any coordination polymer was formed after grinding dehydrated Zn(NO₃)₂ and 2-methylimidazole (Figure S18), which is reasonable considering that minute amount of solvent is required during mechanochemical synthesis of metal organic frameworks.¹⁹ Calcination of this mixture only produces very small amounts of powders (NC) without macroporous carbon networks, which clarifies the importance of coordination interaction on the stabilization of frameworks during the pyrolysis. We further overall demonstrated the role of coordination interaction by annealing the grinded products of Zn(NO₃)₂·6H₂O and 1-ethyl-3methylimidazolium chloride, where the N-position of organic ligand was capped with an ethyl group to prohibit the formation of infinite coordination polymer. Similar with the case of dehydrated zinc salt, almost no product left finally after calcination at 1000 °C (Figure S22).

The above results inform us that the evaporation of crystalline water from zinc nitrate hexahydrate induces the formation of macroporous carbon networks and the coordination interaction stabilizes the overall framework during the pyrolysis. However, after heat treatment of the ground product at 150 °C, the walls of networks are still quite thick (around 200 nm) (Figure S23). To investigate the reason for the formation of ultrathin wall, the pyrolysis process was monitored by preparing samples at the different stages, including samples with different calcination temperature (400, 500, 600, 700, 800, 900, and 1000 °C) without holding time (named as N-UCNN-2-400-0, -500-0, -600-0, -700-0, -800-0, -900-0, and -1000-0) and samples calcined at 1000 °C with different holding time (3 and 6 h) (Shorten as N-UCNN-2-1000-3, and -1000-6). SEM images of these samples in Figure S23-S31 indicate that the wall thickness becomes thinner gradually from 200 nm to 100 nm with increasing the temperature from 150 to 700 °C possibly because of slow gasification of organic ligands. Continual increasing the temperature results in the pronounced reduction of wall thickness mainly owing to vaporization of zinc atoms and remaining organic components (the wall thickness decreases to ~12 nm at 900 °C). The wall thickness was then slowly reduced to 3.7 nm after pyrolyzing the sample at 1000 °C for 6 h because of the loss of residual ingredients, such as zinc and carbon. The relationship between wall thickness and temperature is shown in Figure S32, which matches well with the TGA curve of grinded

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mixture of $Zn(NO_3)_2$ ·6H₂O and 2-methylimidazole (Figure S33), confirming the formation process mentioned above.

Based on the above results, the formation of ultrathin carbon nanosheet networks originates from the evaporation of crystalline water, formation of coordination polymers, and vaporization of ingredients including zinc, carbon, and hydrogen. The formation mechanism is depicted in **Scheme 2**. Firstly, a paste of zinc- imidazolate coordination polymer was formed after grinding the mixture of $Zn(NO_3)_2 \cdot 6H_2O$ and 2-methylimidazole,

where the crystalline water accelerated the coordination interaction between zinc ions and 2-methylimidazole (step a). The water would evaporate after heating the paste at 150 °C to form the macroporous carbon networks, where the water served as a pore-filling agent (step b). Carbonization and evaporation of zinc and other organic components (step c-d) would rapidly reduce the wall thickness to form the ultrathin carbon nanosheet networks finally.



Scheme 2. Proposed formation mechanism of the ultrathin carbon nanosheet networks induced by evaporation of crystalline water, coordination interaction and vaporization of ingredients (step a: grinding for formation of coordination polymers, step b: water evaporation for formation of macroporous carbon networks, step c: carbonization, step d: continual evaporation of organic components and zinc for formation of ultrathin carbon nanosheet networks; and SEM images under the proposed formation mechanism represent the grinded mixture, samples pyrolyzed at 150 °C and 700 °C without holding time, and 1000 °C for 6 h, respectively). (2-methylimidazole is denoted as Hmim in the Scheme)

The simplicity of the method and the superior electrocatalytic activity of dual-doping push us to extend this method to prepare dual-heteroatom-doped carbon networks, such as N/S-co-doping.^{40,41} The N/S-co-doped ultrathin carbon nanosheet network (NS-UCNN) was prepared using the same procedure for preparation of N-UCNN-2 except the mixture of 2-methylimidazole and 2-mercaptoimidazole (molar ration is 5:1) were used instead of pure 2-methylimidazole. NS-UCNN has a hierarchically porous 3D carbon network interconnected with ultrathin walls similar with N-UCNN-2 and a high specific surface area of 1028.7 m² g⁻¹(Figure 4 and S34). Too much 2-mercaptoimidazole would produce bulk ZnS and less S-containing imidazole would decrease the ORR activity (Figure S35).



Figure 4. High magnification (a) and low magnification (b) SEM images of NS-UCNN.

The high-resolution N 1s and S 2p spectra, as shown in Figure 5a and 5b, verify the successful doping of N and S atoms into the NS-UCNN.^{42,43} The S 2p spectrum confirms the presence of C-S_x-C and -C=S- bonds at 163.9 eV and 165.1 eV, respectively. Besides, the sulfur peaks at 168.2 eV were attributed to C-SOx-C.44 No signal of Zn is discovered, indicating that the NS-UCNN was a metal-free carbon material (Figure S36). The amounts of N and S are 1.5 and 1.4 at%, respectively. NS-UCNN exhibits remarkable ORR catalytic performance with a high cathodic peak potential (0.75 V) and positive ORR onset potential (0.93 V) and half-wave potential (0.83V), which makes it among the best metal-free ORR electrocatalysts in the literatures, comparable with Pt/C (Figure S37a and Figure 5c), and better than other ZIF-derived metalcontaining porous carbons in terms of the onset potential and half-wave potential (Table S1).^{10,11,15-19} The electron transfer number was 3.73-3.97 for NS-UCNN with extremely low H₂O₂ yield (Figure 5d). NS-UCNN presents an excellent durability with 90 % retention of the current density after a 20000 s of chronoamperometry test (Figure S37b). The unexpected ORR activity of NS-UCNN can be attributed to the effective doping of N and S plus the hierarchically porous structures with ultrathin walls.



Figure 5. a) High-resolution N 1S XPS spectrum of NS-UCNN; b) High-resolution S 2p XPS spectrum of NS-UCNN; c) ORR polarization curves for NS-UCNN and Pt/C at 1600 rpm; and d) Current-time (I-t) chronoamperometric response of NS-UCNN in O₂-saturated 0.1 M KOH at - 0.15V (black) and H₂O₂ yields of NS-UCNN (red).

Conclusions

We have successfully developed an operationally simple, general, and sustainable strategy to prepare 3D heteroatomdoped ultrathin carbon nanosheet networks as ORR electrocatalysts via direct pyrolysis of the ground mixture of raw materials. We propose that the evaporation of crystalline water and coordination interaction are responsible for the formation of 3D carbon networks. The method can be generalized to prepare different heteroatom-doped carbon networks, such as N and/or S-doping. The heteroatom-doped ultrathin carbon nanosheet networks, especially the N/S-co-doped one, show outstanding ORR catalytic performance with more positive onset potential (0.93 V) and a half-wave potential (0.83V) comparable with that of commercial Pt/C, and better methanol tolerance and longterm stability. The excellent activity can be ascribed to the effective doping with N and S, ultrathin carbon layers with highly microporosity, and unique hierarchical porous structures, which would increase electrocatalytic active sites and enhance the mass transfer. The strategy is very simple and green, which could extremely simplify the process and thus reduce the total cost, and alleviate the damage to the nature. Considering the convenience, generalizability, and special structure, this method has the potential to replace the current MOF-route to prepare a series of heteroatom-doping carbons, single atom catalysts, noble metal/transition metal-based carbon, and so on. This work not only provides highly active electrocatalysts and also demonstrates a facile and sustainable strategy to prepare 3D carbon nanosheet networks for various applications using solely crystalline water as the pore-forming agent.

Experimental Section

Materials and chemicals. All chemicals were from commercial and used without further purification: Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98.5%, Sinopharm Chemical Reagent Co., Ltd.), 2-methylimidazole (99.0%, Aladdin), 2-mercaptoimidazole (99.0%, Energy).

Preparation of N-UCNNs. Typically, the molar ratios of Zn(NO₃)₂·6H₂O and 2-methylimidazole were 1:1.5, 1:2, and 1:2.5, respectively. The mixture was ground together in an agate mortar for 5 min. Next, the precursors were transfer into a quartz boat and placed inside a tube furnace. The furnace was heated with a heating ramp of 5 °C min⁻¹ and maintained at 150 °C for 2 h under continuous Ar, then heated to 1000 °C for 6 h. The corresponding samples made from various molar ratio of 1:1.5, 1:2, and 1:2.5 were named as N-UCNN-1.5, N-UCNN-2, and N-UCNN-2.5, respectively.

Preparation of NPCN. 0.2 mg ZIF-8 powers, which were prepared according to the literature,¹⁸ were transferred into a quartz boat and placed inside a tube furnace. The furnace was heated with a heating ramp of 5 °C min⁻¹ and maintained at 150 °C for 2 h under continuous Ar, then heated to 1000 °C for 6 h.

Preparation of NS-UCNN. Typically, the molar ratios of $Zn(NO_3)_2.6H_2O$ and the mixture of 2-methylimidazole and 2-mercaptoimidazole were 1:2. The molar ratios of 2-methylimidazole and 2-mercaptoimidazole were 1:1, 3:1, 5:1, 7:1, respectively. The mixture was ground together in an agate mortar for 5 min. Next, the precursors were transfer into a quartz boat and placed in a tube furnace. The furnace was heated with a heating ramp of 5 °C min⁻¹ and maintained at 150 °C for 2 h under continuous Ar, then heated to 1000 °C for 6 h. The corresponding sample made from molar ratio of 5:1 was named as NS-UCNN.

Electrocatalytic Performance Investigations. All the electrochemical measurements were conducted in a typical three electrode setup with an electrolyte solution of 0.1 M KOH, a working electrode, a Pt counter electrode, and a saturated calomel electrode (SCE) reference electrode. In all measurements the SCF reference electrode was calibrated with respect to reversible hydrogen electrode (RHE). LSV measurements were conducted in 0.1 M KOH with scan rate of 5 mV s-1. All the potentials reported in our work were vs. the reversible hydrogen electrode (RHE). E(RHE) = E(SCE) + 0.059lgpH+0.244. The onset potential (Eonset) for ORR is defined as the critical potential where the reduction current density reaches 1% of the limiting current density. The working electrodes were prepared as follow: Catalyst ink was prepared by dispersing 4 mg of the catalyst into 1 mL of ethanol solvent containing 50 µL of 5 wt% Nation through sonication for 90 min. Then 6.4 µL of the catalyst ink was loaded onto a glass-carbon electrode (GCE) of 4 mm in diameter.

Characterization. The morphology of all electrocatalysts was investigated by scanning electron microscope (SEM, Hitachi, S-4800) and transmission electron microscope (TEM, FEI Tecnai G20). The size and thickness of electrocatalysts were determined by atomic force microscope (AFM, Brucker Bioscope system). The crystal structures of the samples were characterized using powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer, Cu Kα1). The X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250Xi X-ray photoelectron spectrometer using Mg as the excitation source. The nitrogen adsorption- desorption isotherms were measured at 77 K with a JW-BK200C (JWGB SCI&TECH) gas adsorption device.

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FULL PAPER

3D highly porous heteroatom-doped ultrathin carbon nanosheet networks have been synthesized directly starting from solid raw materials without any additional template. The ultrathin structure, hierarchical porosity, and heteroatom-doping endow as-prepared ultrathin carbon nanosheet networks with outstanding eletrocatalytic ORR performance.



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