1. Introduction

As a relatively new class of porous materials, metal–organic frameworks (MOFs) have captured widespread interests due to their diversified and tailorable structures as well as potential applications in various fields.\[1–9\] In recent years, MOFs have been demonstrated to be excellent templates/precursors to provide diverse porous derivatives with multifunctional properties.\[10–16\] The MOF-derived nanoporous carbon materials (MOFCs) not only inherit the merits of MOF materials with high surface area and porosity to some extent, but also exhibit other important properties (e.g., good electrical conductivity, excellent chemical and thermal stability). Therefore, the MOFCs have been demonstrated to be electrode materials and electrocatalysts in energy conversion and storage such as supercapacitors,\[17–20\] batteries,\[21–25\] and fuel cells\[26–33\] due to their high surface area and uniform doping of heteroatoms. Furthermore, nanosized MOFCs show significantly improved electrochemical properties in reference to their bulk counterparts owing to their more exposed active sites and convenient mass transport.\[34–36\] In the process of the formation of MOFCs, it is inevitable to aggregate among the close-contact MOF particles in nanoscales at high temperatures, resulting in the formation of porous carbon agglomerates.\[37\] The aggregation phenomenon should cause negative effects for electrochemical performance because of the reduced effective surface area, the block of active sites, etc. Therefore, the essential solution to this predicament lies in the avoidance of the contact and aggregation of MOF precursors.

Aerogels are a type of unique monolithic materials that integrate the characters of ultralow density, super large inner surface space, and high porosity.\[38,39\] Therefore, aerogels are very promising to prepare well-dispersed products by annealing. To date, there have been very few research reports on MOF-based aerogels.\[40–43\] Although some MOF nanoparticle-based metal–organic gels have been used as templates for the preparation of hierarchically porous carbon, the aggregation behavior...
is still an inevitable concern in the synthesis process owing to the disordered structure of metal–organic gels obtained from nanoparticle stacking.[44–46] Very recently, A ZIF-8 and agarose composite aerogel with layered microstructure has been reported for the preparation of a mesoporous carbon aerogel without aggregation behavior after carbonization.[47]

According to the previous study on the nanowire-directed templating approach to the synthesis of MOF nanofibers (MOFN-x, x represents the diameter of Te nanowires, which were simply as TeNWs),[48] we are aware of that such 1D structure is a potential building block for the fabrication of gels and aerogels. Therefore, we here fabricate a kind of novel MOF nanofiber aerogels by the self-assembly of uniform MOFN and subsequent freeze-drying. Such nanofiber-based aerogels are ideal carbon sources/templates for the preparation of derived materials with intact morphologies and microstructures even suffering from long-time carbonization at high temperatures. Expectedly, the final hollow porous carbon nanofibers (HPCN-x, x is corresponding to the diameter of TeNWs for the synthesis of MOFN-x) derived from the MOF aerogels show good dispersion in contrast to the aggregated HPCNs derived from the MOF powder. The preparation process from 1D templates to nanofiber aerogels and resulting HPCNs is illustrated in Scheme 1. Furthermore, we demonstrate well-dispersed HPCN-40 and aggregated HPCN-20 as sulfur host materials for Li–S batteries and electrocatalysts for oxygen reduction reaction (ORR).

The results clearly indicate that the dispersion situation of nanomaterials can significantly influence their electrochemical performance. In addition, single atom electrocatalysts originated from bimetal MOF nanofiber aerogels exhibit a superior electrocatalytic ORR activity, which is better than state-of-the-art Pt/C electrocatalyst in the alkaline system.

2. Results and Discussion

2.1. MOF Nanofiber Aerogels

Typically, we chose two types of TeNWs with the diameters of around 20 and 40 nm, to synthesize zeolitic imidazolate framework-8 (ZIF-8) nanofibers and compare their dispersion situation and the final electrochemical performance of as-derived carbon materials. In a typical synthesis, the methanol solutions of zinc nitrate hexahydrate and 2-methylimidazole as well as the purified TeNWs were mixed thoroughly and quickly at room temperature, and then the mixture remained undisturbed for 3 h.

The transmission electron microscopy (TEM) images show MOFN-20 and MOFN-40 are nanofibrous morphologies with average diameters of 70 and 190 nm, respectively (Figure 1a,b; Figure S1, Supporting Information). TeNWs are covered uniformly by ZIF-8 crystals and no isolated ZIF-8 particles are nucleated in solution. Very interestingly, gel-like behavior of MOFN-40 was observed (inset in Figure 1b). Control experiments were carried out and the discussion was presented to further understand the gelation behavior (Figure S2, Supporting Information, and caption). The as-prepared MOFN-40 gel is relatively fragile and easily dispersed, thus forming a colloidal-like nanofibers dispersion solution after stirring. As can be seen in Figure 1c, the dispersibility of MOFN-40 is better than that of MOFN-20. The lower dispersibility of MOFN-20 might be attributed to the interpenetration of ZIF-8 nanofibers with each other because of TeNWs showing a high aspect ratio with the thinner diameter.[49] Thanks to the uniform morphology and well-dispersion, MOFN-40 could be reassembled into an ordered aerogel by freeze-drying (Figure 1e). In contrast, MOFN-20 became a heap of powder after freeze-drying (Figure 1f), similar to the previously reported 10 nm TeNW-induced ZIF-8 nanofibers.[48] Figure 1g shows that 40 nm TeNWs can be synthesized in a large scale for preparation of ZIF-8 nanofibers and subsequent aerogels.

The different characteristics between the powder and the aerogel can be clearly distinguished by N_2 sorption isotherms. MOF-40 aerogel displays a type-I sorption curve (Figure 1d), which is the same as that of ZIF-8 crystals, indicating that the MOF-40 aerogel has typically microporous texture, large inner surface space, and few contacts of nanofibers to each other. This result is different from other MOF-based aerogels,[40,41,44] which were formed by the aggregation of MOF nanoparticles. The N_2 sorption isotherm of MOFN-20 shows a certain degree of rise at high relative pressure, implying the presence of pores formed by close-packed nanofibers, in consistent with the above hypothesis regarding intertwined nanofibers. The pore size distribution further confirms the micropore characteristic of MOFN-40 without piled pore (Figure S3, Supporting Information). The Barrett–Emmett–Teller (BET) surface area of MOFN-40 reaches 1015 m^2 g^{-1} but MOFN-20 shows a lower BET surface area (779 m^2 g^{-3}). The higher BET surface area of MOFN-40 is attributed to its thicker shell and high content of ZIF-8 on nonporous TeNW templates. The average diameter of MOFN-40 is around 210 nm (the thickness of MOF shell is 85 nm, Figure 1b), which is much larger than that of MOFN-20 around 77 nm (the thinness of MOF shell is 29 nm, Figure 1a). The higher content of ZIF-8 in MOFN-40 also is confirmed by inductively coupled plasma mass spectrometry (ICP-MS) data showing that the Zn/Te atom ratio of MOFN-40 and MOFN-20
are ≈3.5 and 1.5, respectively. Based on powder X-ray diffraction (XRD) patterns confirm the presence of well-retained structure of ZIF-8 and metal Te (Figure S4, Supporting Information).

2.2. Derived Hollow Porous Carbon Nanofibers

The MOFN-20 powder and the MOFN-40 aerogel were employed as precursors to fabricate MOFCs for the investigation of their aggregation behavior after calcination. The scanning electron microscopy (SEM) and TEM images of HPCN-20 and HPCN-40 show the resulting products are well-retained 1D morphologies (Figure 2a,b; Figure S5, Supporting Information). The low-magnification SEM images in Figure 2a,b exhibit that both HPCN-20 and HPCN-40 are micrometer-scale agglomerates. However, scattered nanofibers in HPCN-40 are significantly different from close-packed nanofibers in HPCN-20, which can be clearly observed by high-magnification SEM images (insets in Figure 2a,b). Meanwhile, a control sample of naturally dried MOFN-40 was carbonized for comparison. The obtained product shows serious aggregation phenomenon composed by largely fractured nanofibers (Figure S6, Supporting Information). The investigation of the dispersibility of different samples (bulk carbon derived from naturally dried MOFN-40, HPCN-20, and HPCN-40) and detailed discussion are demonstrated in Figure S7, Supporting Information, and caption. The result confirms that HPCN-40 has excellent dispersibility to form a highly homogeneous solution easily by ultrasonication within several minutes.

N₂ sorption isotherm indicates the presence of macropores in HPCN-20 according to steep rising curve at high relative pressure (Figure 2d), which is attributed to the aggregation of nanofibers after calcination. HPCN-40 exhibits a type-IV curve with high sorption capacity in low relative pressure, a pronounced hysteresis loop in middle section and stationary in high relative pressure, revealing its micro-/mesoporous hierarchical structure, which is verified by the pore size distribution (Figure S8, Supporting Information). The BET surface areas of HPCN-20 and HPCN-40 reach 2419 and 2450 m² g⁻¹, respectively. After calcination at a high temperature, the non-porous TeNW templates are fully removed, which means that the micropore of HPCNs is originated from the shell of their

![Figure 1. TEM images of a) MOFN-20 and b) MOFN-40. Insets show their gelation phenomenon. c) Comparison of dispersibility between MOFN-20 and MOFN-40 in methanol solvent. d) N₂ sorption isotherms of MOFN-20 and MOFN-40 at 77 K. Digital photographs of e) MONF-40 aerogel, f) MOFN-20 powder, and g) a 500 mL solution of TeNWs with diameter of ≈40 nm.](image-url)
precursors. Both the original shells for HPCN-20 and HPCN-40 are ZIF-8 so they present similar micro-porosity, which offers the main contribution of the BET surface area. Although TeNW templates are nonporous, they can introduce additional mesopore after removal. In this way, the final pore size distribution would be influenced by the diameter of TeNW templates. In addition, the presence of piled pore formed by close-packed carbon nanofibers in HPCN-20 also influences the pore size (Figure S5a, Supporting Information). On the contrary, the TEM images of HPCN-40 in Figure S5b,d, Supporting Information, show the well-dispersed carbon nanofibers. Therefore, the above two samples exhibit close BET surface area but different pore size distributions (Figure S8, Supporting Information). These resulting HPCNs are N-doped amorphous carbons with very low-contents of metals through the detailed characterization (Figure S9 and Table S2, Supporting Information).

2.3. Li–S Batteries Electrochemical Test

Porous carbon materials have been considered as one of the most promising sulfur hosts to enhance conductivity and restrain solubility of the polysulfides in electrolytes for Li–S batteries.[50–54] Given hollow, hierarchically porous structure, high surface area, and pore volume, HPCNs have been employed as potential hosts to fabricate sulfur cathode with high sulfur mass loadings. Figure 3a shows the TEM image of HPCN-40 after the sulfur infusion, demonstrating that sulfur was successfully loaded into the pores and channels of the hollow porous carbon framework. The BET surface area and pore volume of HPCN-40 decrease from 2450 m² g⁻¹ and 3.03 cm³ g⁻¹ to 13 m² g⁻¹ and 0.067 cm³ g⁻¹ before and after sulfur loading, respectively, manifesting the filling of sulfur into the pores of HPCN-40. Thermogravimetric analysis (TGA) shows that the content of sulfur in HPCN-40/sulfur composite is as high as 70.48 wt% (Figure S10c, Supporting Information). Note that the theoretical value of sulfur content is 77.77 wt% based on the pore volume of HPCN-40 (3.03 cm³ g⁻¹) and volume expansion usually occurs after the formation of Li₂S. As a control, HPCN-20 was loaded the same percentage of sulfur by the same method.

Figure 3b shows the typical discharge/charge voltage profiles of the HPCN-40/sulfur composite electrode at the 0.2 C (335 mA h g⁻¹) rate between 1.8 and 2.6 V. The discharge curves exhibit two apparent plateaus at around 2.3 and 2.1 V, which can be assigned to two conversion processes, from sulfur (S₈) to lithium polysulfides (Li₂Sₙ, 4 ≤ n ≤ 8) and further to Li₂S₂/Li₂S, respectively. The HPCN-40/sulfur composite cathode shows a high initial specific discharge capacity of 1337 mA h g⁻¹ and maintains a reversible capacity of 1150 and 982 mA h g⁻¹ after 10th and 100th cycles, respectively, due to the high-quality and well-dispersion of HPCN-40. The cycling performance and coulombic efficiency of the same electrode at 0.2 C are shown in Figure 3c. The results show about 89% capacity retention from the 2nd to 100th and average coulombic efficiency of close to 99%, implying that HPCN-40 successfully encapsulates sulfur inside and inhibits the shuttling effect of polysulfides, as well as endures the volume expansion of sulfur species during the discharge/charge process. The rate performance of the HPCN-40/sulfur composite is shown in Figure S10d, Supporting Information.

The cycling stability comparison between HPCN-20/sulfur composite and HPCN-40/sulfur composite at 0.2 C is shown in Figure 3d and Figure S11, Supporting Information. HPCN-40/sulfur composite cathode exhibits good cycle stability, while the
HPCN-20/sulfur displays the rapid capacity fading that only 68.5% of specific capacity retained after 20 cycles. It is speculated that a part of sulfur without the carbon encapsulation is loaded among close-packed nanofibers and nanoparticles in HPCN-20/sulfur composite, leading to the irreversible dissolution of polysulfides in the electrolytes.

2.4. ORR Performance of Single Atom Electro catalysts Derived from Bimetallic MOF Nanofiber Aerogels

Previously, we demonstrated that 1D nanostructured MOFC possesses a high surface area and enhancement of electrocatalytic performance in reference to the corresponding bulk MOFC.[48] Nevertheless, there still exist a quantity of the aggregation phenomenon in the conversion process from MOF nanofibers to MOFC nanofibers. For the preparation of electrocatalysts or electrode materials in energy-related applications, well-dispersed nanomaterials are beneficial to the formation of homogeneous solution or slurry. Usually, it requires more than several hours even a few days of ultrasonication for the high-temperature treated electrocatalysts to give a uniform ink prior to the investigation of their electrocatalytic properties. Highly dispersed electrocatalysts are highly desired not only because of increased contact area and active sites but also owing to reduced time length for ultrasonic dispersion for reducing energy consumption and cost.

Here, we would further examine the ORR performance of aggregated HPCN-20 and well-dispersed HPCN-40 after ultrasonication at 10 min and 2 h for comparison. Dramatically, HPCN-40 shows much better ORR activity than HPCN-20 after ultrasonic dispersion for 10 min (Figure 4). After ultrasonication at 2 h, HPCN-40 reveals the highest electrocatalytic performance owing to its great dispersion with more accessible active sites and improved mass transport.

To further explore the efficient ORR electrocatalysts, single atom Co-doped porous nanofibers derived from a bimetallic MOF nanofiber aerogels were further investigated. Bimetallic ZIFs with controllable Zn/Co ratios were recently reported.

Figure 3. a) TEM image of HPCN-40/sulfur. b) Typical charge/discharge voltage profiles of HPCN-40/sulfur electrode in the voltage range of 2.6–1.8 V and at 0.2 C rate. c) Cycle life and coulombic efficiency of HPCN-40/sulfur electrode. d) Comparison of cycling stability of HPCN-20/sulfur and HPCN-40/sulfur electrodes at 0.2 C.

Figure 4. Linear sweep voltammetry (LSV) curves of HPCN-20 and HPCN-40 by ultrasonication for different time length in O2-saturated 0.1 M KOH with a sweep rate of 10 mV s−1 and rotation speed of 1600 rpm.
as precursors for efficient ORR electrocatalysis. Here, based on above-mentioned MOFN-40, we obtained a series of bimetallic MOF nanofiber aerogels and their derived single atom cobalt on nitrogen-doped porous nanofibers for electrocatalytic ORR. Figure 5a shows a typical TEM result of the MOFN-40, which is converted from a bimetallic MOF nanofiber aerogel (inset in Figure 5a), indicating unchanged nanofibrous morphology in the presence of Co element. No Co particles can be observed in the TEM image. We further conducted aberration-corrected high-angle annular dark-field scanning TEM (HADDF-STEM) investigation. Single atom Co is undoubtedly discerned from nitrogen doped carbon matrix and highlighted with red circles in Figure 5b. The BET surface areas are 688 and 1914 m² g⁻¹ for MOFN-40-3% Co aerogel and derived HPCN-40-3% Co, respectively.

As shown in Figure 5c,d, among all investigated samples, the HPCN-40-3% Co shows the best catalytic activity with half-wave potential of ≈−0.133 V (vs Ag/AgCl), which is superior to the previous reported N,P-doped porous carbon nanofibers (P-Z8-Te-1000) and also the commercial Pt/C electrocatalyst. For the stability test of HPCN-40-3% Co, polarization curves were conducted before and after continuous cyclic voltammetry (CV) scans from −0.4 to 0 V at 100 mV s⁻¹ in O₂-saturated 0.1 M KOH solution for 20 000 times. The difference of half-wave potential (ΔE½) of HPCN-40-3% Co showed a slightly negative shift of ≈12 mV (Figure S15, Supporting Information), indicating the good stability of such MOF-derived nanocatalysts.

3. Conclusion

In summary, we report that MOF nanofiber aerogels are excellent precursors, which can effectively avoid aggregation among nanofibers for the preparation of MOFC materials under the high-temperature calcination condition. The MOF aerogels derived porous carbon materials can be used as the promising sulfur host and excellent ORR electrocatalysts. Particularly, we demonstrated porous carbon nanofibers with well-dispersion to enhanced electrochemical performances in contrast to the aggregated counterpart, revealing that the dispersion situation of nanomaterials significantly influences their final electrochemical performance. Furthermore, other nanomaterials that can act as building units to construct aerogels including 1D materials (e.g., carbonous nanofibers, carbon nanotubes, bacterial cellulose) and 2D materials (e.g., graphene and MXene) would be used for the templating synthesis of MOF-based composite aerogels and their derivatives. It is believed that the concept of employing aerogels as precursors for MOFCs will be further advanced to achieve monodisperse nanomaterials for expanding their applications in energy storage and conversion.

4. Experimental Section

Materials: All chemical reagents were purchased and used without any further purification.

Preparation of TeNWs: TeNWs with different diameters (20 and 40 nm) were prepared via controlling the ratio of glycol/acetone. PVP (10.0 g, Pka = 30) and sodium tellurite (184.3 mg) were dissolved in glycol...
Preparation of MOFN-20 Powder: Typically, 2 mL of 2-methylimidazole (0.8 M) methanol solution was added into 2 mL of TeNWs methanol solution (15 mL of 20 nm TeNWs raw solution was precipitated by acetone and washed by methanol, and then dispersed in 2 mL methanol), and then 2 mL of Zn(NO$_3$)$_2$·6H$_2$O (0.1 M) methanol solution was thoroughly and quickly mixed into the above solution under stirring for 1 min. The homogenous mixture solution was then allowed to stand at room temperature for 3 h. The product was collected after washing and centrifugation by methanol and deionized water. Finally, the MOFN-20 powder was obtained after freeze-dried in a bulk tray dryer (Labconco Corporation, USA) at a sublimating temperature of −50 °C and a pressure of 0.035 mbar for evaporating the solvent.

Preparation of MOFN-40 Aerogels: Typically, 2 mL of 2-methylimidazole (1.6 M) methanol solution was added into 2 mL of TeNWs methanol solution (7 mL of 40 nm TeNWs raw solution was precipitated by acetone and washed by methanol, and then dispersed in 2 mL methanol), and then 2 mL of Zn(NO$_3$)$_2$·6H$_2$O (0.2 M) methanol solution was thoroughly and quickly mixed into the above solution under stirring for 1 min. The homogenous mixture solution was then allowed to stand at room temperature for gelation. After 3 h, the as-synthesized MOF gels were washed several times by methanol and then were dispersed in deionized water. The gelatinous solution was frozen in liquid nitrogen followed by freeze-drying.

Preparation of Bimetallic MOFN-40 Aerogels: For MOFN-40-3% Co, Zn(NO$_3$)$_2$·6H$_2$O (116 mg), and Co(NO$_3$)$_2$·6H$_2$O (4 mg) were dissolved into 2 mL methanol. The other steps followed a similar process for the preparation of MOFN-40 aerogel.

Preparation of Hollow Porous Carbon Nanofibers: The as-prepared MOF nanofiber-based powder and aerogels were put into a ceramic boat and transferred into a temperature-programmed furnace, then heated to 200 °C for 2 h at a heating rate of 5 °C min$^{-1}$. The further carbonization treatment was performed at 900 °C for 5 h.

Dispersion Evaluation for Different MOFCs: 2 mg of samples were added into 5 mL of methanol, and then dispersed by ultrasonication for 5 min.

Characterization: SEM, TEM and high-resolution TEM images were measured on a Zeiss Supra 40 field-emission scanning microscope operating at 5 kV, Hitachi H7650 transmission electron microscope operating at 120 kV, and JEM-ARM 200F at 200 kV, respectively. HAADF operating at 5 kV, Hitachi H7650 transmission electron microscope measured on a Zeiss Supra 40 field-emission scanning microscope. Powder XRD data were recorded on a Titan Cubed Themis G2 300, FEI Company equipped with an EELS setting at 120 kV, and JEM-ARM 200F at 200 kV, respectively. HAADF-TEM images were obtained using an aberration-corrected STEM instrument operating at 120 kV, and JEM-ARM 200F at 200 kV, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

W.Z. and G.C. contributed equally to this work. S.H.Y. and H.L.J. supervised the project, conceived the idea, and revised the paper. W.Z. and G.C. designed and performed the experiments, analyzed the data, and wrote the paper. R.W. helped with the HADDF-STEM characterization. Z.H. helped with the synthesis of TeNWs. H.B.Y. helped with the test of Li–S batteries. All authors discussed the results and commented on the paper.

Keywords

aerogels, energy storage and conversion, metal–organic frameworks, porous carbon nanofibers, templating synthesis

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