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Wei Xia

Fabrication of Metal—Organic Framework Derived Nanomaterials and Their Electrochemical Applications



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Wei Xia

Fabrication of Metal–Organic Framework Derived Nanomaterials and Their Electrochemical Applications

Doctoral Thesis accepted by the Peking University, Beijing, China



Author Dr. Wei Xia Department of Materials Science and Engineering, College of Engineering Peking University Beijing China Supervisor Prof. Ruqiang Zou Department of Materials Science and Engineering, College of Engineering Peking University Beijing China

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Supervisor's Foreword

I would like to recommend Dr. Wei Xia's research work to be published in the series of Springer Theses, which is mainly about the design and synthesis of nanostructured materials from a new strategy—metal–organic framework route and in-depth analysis of the relationship between material texture and electrochemical behavior in energy storage and conversion.

Metal-organic frameworks (MOFs) represent one of the best examples of materials from molecular engineering. Great efforts have been devoted to the structural design and applications of MOFs. More recently, fabricating MOF-derived nanostructures for electrochemical applications emerges as a new research area in MOF field and grows rapidly, which has also demonstrated huge impact on Li-ion batteries, supercapacitors, and fuel cells researches. The new strategy stands out because of the unique properties of MOF-derived materials such as high surface areas, high degree of porosity, homogeneous distribution of nanopores, and in-situ heteroatom doping, which could contribute to the superior electrochemical performance than materials prepared from conventional methods.

In this thesis, Dr. Wei Xia first presents systematical summary on MOFs, including their composition, structure, property, synthesis, and applications. He also introduces the design and preparation of MOF-derived nanomaterials and the related electrochemical applications. It is beneficial for a clear understanding for readers coming from wider scientific community. In the following sections, Dr. Wei Xia provides a series of original research work in fabricating well-designed nanostructures from MOFs, which includes metal–nitrogen co-doped carbon nanoparticles, core–shell metal oxide nanoparticles, hollow metal oxide nanoparticles, and 3D porous carbons. The formation mechanisms for these well-designed nanostructures are given for the first time, and the structure–property relationships are thoroughly analyzed. The case of the carbon nanoparticles from nanosized MOFs is a good demonstration of the benefit in downsizing MOF precursors to fulfill best electrochemical properties in the derived materials. It opens up new ways for designing MOFs for target electrochemical energy storage and conversion applications.

The book that Dr. Wei Xia is presenting here brings together the most representative studies of MOF-derived nanostructures, which is very helpful for us to understand the electrochemical reactions at nanoscale and optimize the materials from rational design to obtain better electrochemical performance. The strategies he proposed in the thesis will have deep influence on the fundamental research for advanced electrochemical energy storage materials and generate broad interests in nanostructured materials synthesis.

Beijing, China November 2017 Prof. Ruqiang Zou

Abstract

Electrochemical energy storage and conversion systems, such as lithium-ion batteries and fuel cells, are developing rapidly. In these systems, energy is generated via mild electrochemical processes without combustion. The overall conversion efficiency is not limited by the Carnot cycle laws and can reach a high value. Moreover, bearing the high energy/power density, the electrochemical systems can be integrated into a small size and be used in portable devices. However, it should be noted that the performance of the systems depends on the electrode materials and is affected by the microstructure of the electrode considering that the electrochemical reactions occur at multi-phase boundaries. In order to ensure complete reaction, the electrode materials should be designed with high-density active sites together with advanced nanostructures that are beneficial for good mass transport. However, it remains a great challenge to control the properties in those obtained from conventional hydrothermal method.

In this dissertation, a metal–organic framework (MOF)-based strategy has been developed to prepare electrochemical active materials with advanced nanostructures. MOF, assembled from selected metal–ligand coordination, possesses unique properties like high surface area, tunable pore textures, and rich functionalities. Based on the flexibility in MOF construction, a series of new nanostructures were built from MOFs and latterly converted into nanoporous carbon or metal oxides. The nanostructures and composition of the obtained materials were optimized in a controlled manner, making them very suitable for electrochemical applications such as fuel cells and lithium-ion batteries. The research has focused on the following topics:

 A new strategy of developing nanoscale MOF for electrochemical research has been proposed. The influence of reaction temperature and solvent on the size of MOF was studied systematically, which revealed that a room temperature reaction with methanol as the solvent could produce MOF crystals with uniform nanosize. They were further converted into N-doped carbon nanoparticles by simple thermal activation. Their catalytic activities for oxygen reduction reaction (ORR) were investigated by cyclic voltammetry and rotating disk electrode. By changing the structure, composition, or size of the MOF precursor, the ORR activity of corresponding carbon nanoparticles was adjusted, providing information for the development of non-precious catalysts with enhanced activity. Moreover, reversible intercalation of Li^+ in the obtained N-doped carbon nanoparticles was demonstrated, which suggests the possible application as anode materials in lithium-ion batteries.

- 2. The influence of the microstructure of MOF-derived catalysts on their ORR activity was studied. Slit-type pore is the main type of pore in conventional MOF-derived materials, which is not good for the mass transport properties. Moreover, the in-situ generated metal nanoparticles are embedded in carbon, losing their functionality for ORR process. Herein, a Co-MOF was introduced as an ordered porous carbon matrix (CM) to produce Co@Co₃O₄@C cor-e@bishell nanoparticles. The fine nanostructure and the ORR catalytic activity of the Co@Co₃O₄@C-CM composite were systematically studied and related, which provided guideline for optimizing MOF-derived nanostructures for ORR.
- 3. A diffusion behavior of MOF on carbon surface was observed and systematically investigated. It was found that the heat activated metal and carbon atoms from MOF crystals could diffuse on carbon surface and generate new nanostructures. Based on this phenomenon, defect-rich cobalt oxide hollow nanoparticles were successfully introduced on the surface of graphene sheets. The formation mechanism of this fine nanostructure was further investigated. Moreover, the graphene supported cobalt oxide hollow nanoparticles were employed as a highly active ORR catalyst, showing the advantages of the structural merits.
- 4. Metal-organic gel (MOG) was first proposed for the synthesis of new type of carbon nanostructure possessing high surface area, large pore volume, and hierarchical pores. The application of such porous carbon materials as sulfur host for Li–S batteries was suggested and investigated. A remarkable enhancement in Li–S cell output as well as stability was observed. The influence of the carbon nanostructure on the performance of carbon/sulfur cathode was further studied, demonstrating the advantages of hierarchically porous nanostructure in casting advanced carbon/sulfur cathode for Li–S batteries.

Keywords Metal–organic framework · Porous carbon · Metal oxide Nanostructure · Oxygen reduction reaction · Lithium–sulfur batteries

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- [1] W. Xia, C. Qu, Z. Liang, B. Zhao, S. Dai, B. Qiu, Y. Jiao, Q. Zhang, X. Huang, W. Guo, D. Dang, R. Zou, D. Xia, Q. Xu, M. Liu, High-performance energy storage and conversion materials derived from a single metal–organic framework/graphene aerogel composite. Nano Letters, 2017, **17**, 2788–2795.
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- [3] W. Xia, R. Zou, L. An, D. Xia, S. Guo, A metal-organic framework route to in situ encapsulation of Co@Co₃O₄@C core@bishell nanoparticles into a highly ordered porous carbon matrix for oxygen reduction. Energy & Environmental Science, 2015, 8, 568–576.
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Chapter 1 Introduction



1.1 Metal–Organic Framework Nanomaterials

Generally, nanomaterials refer to materials with at least one dimension in the nano-scale range (1–100 nm), or the corresponding aggregates. Nanomaterials have displayed excellent performance in optics, electrics, magnetics and catalysis, and appeared to be a research focus. Designing and constructing functional nanomaterials at molecular level have long been a hot topic, however are facing tremendous challenges. With the advances in engineering and deepened understanding of micro/nano world by some new characterization techniques, it gradually become a reality to construct nanomaterials based on molecular design. Metal–organic frameworks (MOFs), also known as porous coordination polymers (PCPs), microporous coordination polymers (MCPs), or porous coordination networks (PCNs), are a typical example [1]. They are a new type of nanoporous materials which have ultra-low density, high surface area and regular pore structure. Compared with the traditional porous materials like active carbons or zeolites, MOFs demonstrate more flexibility in tuning the structure and surface chemistry, making them excellent candidates 222 for the application in gas sorption/separation, catalysis, and sensor [2].

1.1.1 Brief Introduction of Metal–Organic Frameworks

Metal–organic frameworks are inorganic-organic hybrid materials assembled from inorganic nodes and organic linkers through covalent coordination [3]. The inorganic moieties can be metal ions (such as Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Mg²⁺, Mn²⁺, Al³⁺, Fe³⁺) or metal clusters, while the organic linkers are usually mono-, di-, tri-, or tetravalent ligands containing oxygen or nitrogen (Fig. 1.1). Due to the diverse choices of metal and linker, it is possible to construct a large variety of MOF materials. In 1999, MOF-5 [Zn₄O(BDC)₃] was synthesized from the combination of Zn²⁺ ions

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Fig. 1.1 Schematic illustration of the composition of MOFs. Reproduced from Ref. [6] with permission of the Nature Publishing Group

and 1,4-dicarboxybenzene (H₂BDC), and its structure was analyzed by single crystal X-ray diffraction and gas sorption. It was the first report on MOF which possesses stable framework and rich porosity [4]. In MOF-5, the Zn₄O secondary building units (SBUs) are linked through the benzene ring of H₂BDC, forming a three-dimensional network with micropores (diameter less than 2 nm). MOF-5 demonstrated a high specific surface area of 2900 m²/g (Langmuir model), regular pore texture and high thermal stability (up to 300 °C), as well as excellent H₂ and CO₂ storage properties. Shortly afterwards, another representative MOF, HKUST-1 [Cu₃(BTC)₂, BTC=1,3,5-Benzenetricarboxylic acid] was reported [5]. The key SBU in HKUST-1 is a pair of Cu nodes chelated by four carboxylate bridges, which is known as paddle wheel unit. It creates a three-dimensional architecture of square channels with a side length of 0.90 nm. Another network with 0.50 nm one-dimensional pore channels appears after removing the water molecules that are bound to the metal sites together with the formation of unsaturated Cu (II) sites, which adds more sorption sites for small molecules and contributes to an excellent overall gas sorption property. The pioneering work on MOF-5 and HKUST-1 are the milestones in the fast development of MOF research.

A more stable MOF, MIL-101 [Cr₃OF(BDC)₃], was reported in 2005 [7]. It has hierarchical tunnels and mesoporous cavities with a BET (Brunauer-Emmet-Teller) and Langmuir surface area as high as 4100 m²/g and 5900 m²/g, respectively. ZIF-



Fig. 1.2 Structure models of some representative MOFs

74 [Zn₂(dhbdc), dhbdc=2,5-dihydroxy-1,4-benzenedicarboxylate] was developed in the same year [8]. It possesses one-dimensional hexagonal channels with a pore aperture in the range of 1.1-1.2 nm, as well as unsaturated metal sites that have excellent adsorption ability toward H₂ and CO₂. Shortly afterwards, a series of ZIF-74(Zn) analogues were synthesized using the dhbdc linker with different metals (Co, Ni, Mg, Mn, Fe, etc.) [9–13]. In 2006, a new class of MOFs, Zeolitic Imidazolate Frameworks (ZIFs), emerged with the successful development of ZIF-8 [Zn(mIM)₂, mIM=2-methylimidazole] [14]. The metal-imidazole-metal angle in ZIFs is around 145° , which is similar to the Si–O–Si angle in zeolites. ZIFs have high thermal stability, chemical resistance and rich porosity. ZIF-8, for example, is stable up to 550 °C and possesses a high Langmuir surface area of 1810 m²/g and excellent gas sorption/separation properties. Recently, MOFs with much complex structure (Fig. 1.2) and enhanced gas sorption/separation properties have been developed. In addition to the gas sorption, more applications such as in catalysis, fluorescence and magnetism have been explored. In general, the research on MOFs is still in its infancy. With the developments in computer simulation and synthesis technology, more structures and applications could be anticipated.

1.1.2 The Characters of Metal–Organic Frameworks

MOFs are hybrid inorganic-organic materials, which means that they have the characters of both inorganic (defined structure and good stability) and organic materials (low density and high flexibility). In addition, MOFs possess unique architectures and properties that are not fund in the single component, such as intelligent responses to external stimuli. The features of MOFs can be concluded as the following three aspects: high surface area and rich porosity, regular and tunable pore texture, and flexibility in surface chemistry.

(1) High surface area

The specific surface area is one of the key parameters in evaluating porous materials. A high surface area is beneficial for the exposure of active sites, thus promoting good physical or chemical properties. MOFs usually possess a BET surface area in the range of 1000–8000 m²/g, which is higher than that of traditional porous materials like zeolites (\sim 500 m²/g) and active carbons (\sim 1500 m²/g). Since the development of first stable MOF with high surface area in 1999, that is MOF-5 (the BET surface area is 2320 m²/g), the record of the highest surface area of MOF have been broken constantly. Table 1.1 summarizes several kinds of representative MOFs with high surface area.

In 2004, researchers reported MOF-177 (Zn₄O(BTB)₂, BTB=4,4',4"-benzene-1,3,5-triyl-tris(benzoic acid)) with a BET surface area of 3780 m^2/g which was the highest at that time [20]. In 2007, this record was elevated to 4730 m^2/g by UMCM-1 (Zn₄O(BDC)(BTB)_{4/3}) [24]. This material consists of two kinds of ligands, BDC and BTB, with different topologies, bridging with Zn²⁺ cations into a new structure with cage-like micropores and 1D mesoporous channels, distinct from MOF-5 (Zn + BDC) and MOF-177 (Zn + BTB). In 2010, MOF-210 $(Zn_4O)_3(BTE)_4(BPDC)_3$ (BTE=4,4',4''-[benzene-1,3,5-triy]-tris(ethyne-2,1-diyl)] tribenzoate, BPDC=biphenyl-4,4'-dicarboxylate) was successfully synthesized with an unprecedented BET surface area of 6240 m²/g and Langmuir surface area as high as 10,400 m²/g [26]. Its volumetric specific surface area reached 2060 m²/cm³, comparable to 3 nm cubic nanoparticles, approaching the adsorption upper limit of solid materials. Currently, the reported solid material with highest surface area was NU-100E, a MOF material synthesized in 2012, with BET surface area of 7140 m^2/g [31]. Computational fitting results indicate that the surface area of MOFs could probably reach up to 14,600 m²/g at most, leaving a lot of room for further improvement.

(2) Tunable porous structures

The properties of porous materials, especially performances in gas adsorption and separation as well as in catalysis, are tightly related to their porous structures. Strong host-guest interactions within the interior of pores that are the origin of specific functions of materials can only take place when the size and shape of pores meet certain requirements. For traditional porous materials, the intrinsic structural disadvantages limit their applications. Active carbons have considerable surface area and porosity, but their porous structures are inhomogeneous. Compared with active carbons, inorganic molecular sieves have relatively lower surface area, but more uniform apertures. These materials have been utilized in fields like industrial catalysis, but their poor tunability of porous structures limits their application. As mentioned above, inorganic nodes and organic ligands are two basic building blocks of MOFs, and based on their intrinsic geometrical coordination modes, it is possible to get

Compound	BET surface area (m ² /g)	Pore volume (cm ³ /g)	References
MOF-5	2320	1.04	[4]
MFU-4l	2750	1.26	[15]
NOTT-102	2942	1.14	[16]
PCN-61	3000	1.36	[17]
Cu ₂₄ (TPBTM) ₈ (H ₂ O) ₂₄	3160	1.27	[18]
SNU-77	3670	1.52	[19]
MOF-177	3780	1.59	[20]
NOTT-112	3800	1.62	[21]
UMCM-1-NH ₂	3917	-	[22]
PCN-66	4000	1.63	[17]
Be ₁₂ (OH) ₁₂ (BTB) ₄	4030	-	[23]
UMCM-1	4160	-	[24]
MIL-101c	4230	2.15	[7]
Bio-MOF-100	4300	4.30	[25]
MOF-205	4460	2.16	[26]
MOF-200	4530	3.59	[26]
NOTT-116	4664	2.17	[27]
DUT-6	4810	2.26	[28]
DUT-23(Co)	4850	2.03	[28]
PCN-68	5109	2.13	[17]
UMCM-2	5200	2.32	[29]
NU-100	6143	2.82	[30]
MOF-210	6240	3.60	[26]
NU-109E	7010	3.75	[31]
NU-110E	7140	4.40	[31]

Table 1.1 Pore textures of some representative MOFs

framework structures with specific topologies by choosing appropriate metal/ligand self-assembly at molecular level, so as to achieve regulation over the dimension and shape of apertures to meet the requirement of target applications.

According to the definition by International Union of Pure and Applied Chemistry (IUPAC), porous materials can be classified into three categories according to their pore size (d), which are macroporous materials (d > 50 nm), mesoporous materials (2 nm < d < 50 nm) and microporous materials (d > 2 nm). Microporous materials can be further divided into ultra-microporous (0.7 nm < d < 2 nm) and super-microporous (d < 0.7 nm) materials. According to this definition, most of the MOF materials belong to microporous materials, while a few of them are mesoporous. MOFs with microporosity have shown good performance in gas adsorption and separation, while mesoporous frameworks are appropriate for the adsorption of



Fig. 1.3 Pore structure model of the IRMOF-74 series. Reproduced from Ref. [35] with permission of the American Association for the Advancement of Science

large molecules and facilitate the mass transportation within pores, benefiting the kinetics of catalytic reactions. It is thus highly important to control the pore size in MOFs. Studies revealed that the pore size is closely connected with the length of organic ligands in MOFs. The more benzene rings on the ligand, the longer the ligand is, and the pores in the final MOFs are possibly larger. For example, in the IRMOF-n (n = 1–16, IR for isoreticular) series with IRMOF-1 (MOF-5) as prototype, the framework topology can be well retained by modification of functional groups and elongation of ligands, while pore sizes can be tuned from micropores to mesopores in the range of 3.8–28.8 Å [32–34]. As more materials were synthesized, the pore sizes of these materials were further expanded. Figure 1.3 shows another representative series of isoreticular MOFs, the IRMOF-74-I to XI, with MOF-74 as the prototype. As the ligand was expanded from one benzene ring to 2, 3, 4, 5, 6, 7, 9, 11 benzene rings, the pores of frameworks was gradually expanded from 14 to 98 Å, with the latter one being the largest reported in MOF materials [35].

Conclusively, the control of the pore sizes of MOFs could be achieved by changing the length of rigid organic ligands without changing their connection mode, which is one of the important features that differ MOF from traditional porous materials.



Fig. 1.4 Schematic illustration of the formation of unsaturated metal sites as active centers



Fig. 1.5 Schematic illustration of the formation of functionalized surface through ligand modification

(3) Functionalized surface

Traditional porous materials like active carbon and zeolite molecular sieves have relatively simple and homogeneous surface chemical environment. Most of their applications are based on the characteristics from their porous structures, thus the application fields of these materials are relatively narrow. Comparatively, MOF materials have rich components, and the chemical environment of pore surfaces can be purposely designed by choice of metal nodes and organic ligands to achieve surface functionalization. Typically, the metal nodes in MOFs (such as Al, Fe, Cu, Ni, etc.) could serve as Lewis acid catalysts. By removing the weakly bonded solvent molecules through proper methods, such coordination unsaturated metal sites could be exposed as highly active catalytic centers which have strong interaction with guest molecules, greatly improving the efficiency of catalysis and gas adsorption (Fig. 1.4). Moreover, ligands with specific functional groups could be used for synthesis of MOFs to grand the pore surface with acidity/basicity or charges to boost the progress of specific reactions or small molecule adsorption (Fig. 1.5).

Besides pre-design of pore surface before synthesis, the chemistry of framework could also be modified after the formation of MOFs, i.e. the post-synthetic modification strategy (PSM). Such strategy is to introduce new functional sites by partial or complete exchange of metal and/or ligands based on the given MOF materials. One example is the prototypical MOF-5 ($Zn_4O(BDC)_3$), where the Zn nodes could be replaced by Fe cations of the same valence [36]. The metal-exchanged framework remained its original porous structure, while the pore surface was granted with redox reactivity to activate small molecules like NO. By means of post-synthetic modification, Ti (IV) species could be exchanged into the stable Zr (IV) MOFs to give the materials activity towards photocatalytic reduction of CO_2 [37]. By partial substitution of surface ligands in the ZIF-8 framework, the surface hydrophobicity was improved to enhance the hydrothermal stability of the material [38]. Majorly four characteristics of post-synthetic modification methods could be concluded: (i) for given MOF material, metal/ligand exchange could yield derivatives with similar topologies but different functionalities; (ii) By changing the ligand/metal, one or more functional sites could be introduced into the frameworks; (iii) PSM is performed based on as-formed MOFs under mild reaction conditions, and could acquire structures which are generally impossible or hard to synthesis by conventional methods; (iv) The degree of modification could be controlled by reaction condition to tune the properties of the derivative materials.

1.1.3 The Synthesis of Metal–Organic Frameworks

(1) Solvothermal synthesis

By solvothermal method, organic ligands and metal salt precursors are dissolved or dispersed with certain ratio in solvents, then loaded into glass tubes or stainless steellined Teflon autoclaves and sealed before being heated in temperature-programmed ovens. The reaction temperature is generally set between 100 and 200 °C, above the boiling point of solvent. Under such condition, a relatively high pressure is generated inside the reaction vessel to increase the solubility of reactants and accelerate reaction rates, promoting the nucleation and growth of MOF crystals, and target crystalline products could be acquired in 2–4 days. The mostly used organic solvents include N, N'-dimethylformamide, N, N'-diethylformamide, glycol, acetonitrile, acetone, ethanol, methanol, etc. Water, as a clean solvent, is also frequently used, with corresponding reactions specifically called hydrothermal reactions. In many cases people use mixed solvents considering the different solubility of precursors, but also to tune the polarity or pH of the solution. The advantage of solvothermal method include simple operation and equipment, short reaction time, high-quality crystalline products for structural resolving and property study, making it the most used method in MOF synthesis. However, solvothermal reactions are conducted in sealed containers with high temperature and pressure, making the reaction environment rather complicated, and the reaction progress is hard to monitor.

(2) Microwave/ultrasonic-assisted synthesis

Microwave-assisted heating is widely used in solvothermal synthesis of nanomaterials, providing a facile and rapid synthetic route. In microwave reactions, the oscillating electric fields can accelerate the movement of dipole molecules within the system, thus the liquid phase can be heated rapidly, improving the nucleation rate of MOFs. Microwave heating is also more homogeneous compared to traditional heating, and large amount of homogenous micro/nanocrystals with controlled size and morphology can be acquired within a short period of time. In 2006, researchers applied microwave-assisted method to synthesize IRMOF-1, 2 and 3 in an extremely short time of 25 s [39]. The acquired IRMOF-1 products were perfect cubic microcrystals with an average size of around 4 μ m. IRMOF-2 and 3 presented similar morphology to that of IRMOF-1 but with slightly smaller sizes. It was revealed that by changing the concentration of reactants, the size of product could be effectively tuned, around $0.2-4 \,\mu$ m in the case of IRMOF-1. Microwave-assisted synthesis has the advantage of high efficiency and good quality of products, but potential dangers like microwave leakage and explosion should be paid with additional attention during operation.

Ultrasonic-assisted synthesis is also a method for rapid and homogeneous nucleation, which can shorten the preparation time of MOFs, acquiring micro/nanocrystals of relatively homogeneous size. In such method, strong ultrasonic radiation (20 kHz–10 MHz) causes cavitation phenomenon in solution, forming tiny bubbles [40]. These bubbles grow to a certain extend and fracture, forming transient hotspots with ultrahigh local temperature (~5000 K) and pressure (~1000 bar), leading to extremely rapid heating or cooling (>10¹⁰ K/s) [41]. Under such extreme condition, the formation of MOF is greatly accelerated, forming large amounts of homogeneous crystal nucleus. For example, large amount of high-quality MOF-74 (Mg) products were synthesized by ultrasonic-assisted method within 1 h, with an average size of 0.6 μ m and a BET surface area of 1640 m²/g that was even higher than that of those synthesized from traditional solvothermal methods (1525 m²/g) [42].

(3) Solid-state synthesis

Solid-state synthesis is a green synthesis method where reactants in solid state are mixed by due ratio, followed by heating or grounding to trigger the reaction. By mixing ZnO with 2-methylimidazole and heating at 100 °C for 24 h, formation of the highly porous and stable MAF-4 (ZIF-8) was observed in the products [43]. When the reaction temperature was elevated to 200 °C, XRD diffraction peaks from MAF-4 became sharper while the characteristic peaks from ZnO gradually decreased, indicating the transformation of ZnO to MAF-4 under such condition. At 180 °C, the transformation completed within 12 h. The BET surface area of the product was 1450 m²/g, comparable to those from traditional solvothermal synthesis. The above reaction utilizes the transformation of thermal energy into chemical energy, while mechanical energy could also be applied in the breakdown and formation of chemical bonds to synthesize new compounds. When the same ZnO and 2-methylimidazole precursors were mixed and applied with hand grinding or ball milling, an nonporous



Fig. 1.6 a Schematic illustration of the electrochemical synthesis of HKUST-1 and b corresponding device. Reproduced from Ref. [46] with permission of the Royal Society of Chemistry

framework $Zn(Im)_2$ was acquired as product [44]. Addition of small amount of solvent and NH_4NO_3 followed by ball milling could promote the formation of porous ZIF-8 product. Addition of solvents increases the mobility of molecules and benefits the progress of reaction, while solvents also play the role of structural directing agents. Currently, solid-state synthesis is only used for the production of certain MOF materials, however with relatively low yields.

(4) Electrochemical synthesis

BASF first reported the electrochemical synthesis of MOF materials [45]. As shown in Fig. 1.6, a 5 mm thick copper plate was used as the sacrificial anode and placed in an electrolytic cell, and a bias voltage of 12–19 V was applied to the electrode. Under the interaction of electric field, metallic Cu lost electrons to form Cu²⁺ cations, then coordinated with the BTC ligands in the solvent to form greenish blue MOF, HKUST-1 as solid precipitates [46]. After reacting for 150 min, product was filtered out and dried under reduced pressure to obtain MOF materials with good porosity, with BET surface area as high as 1820 m²/g.

In other reported methods, metal ions came from metal nitrates, sulfates, oxides, hydroxides etc., and reaction tended to stop when the precursors were depleted in the reaction system. In the electrochemical synthesis, metal ions are fed from anodic dissolution of elemental metal plates, and react with organic ligands in the electrolytes to form the target MOF. Thus by replenishing ligand-rich electrolytes and replacing metal plates regularly, reaction precursors can be provided without interruption to achieve continuous production. On the other hand, the reaction condition of electrochemical synthesis is relatively mild without involving high temperature or pressure, thus consuming less energy, which is the obvious advantage over other synthetic methods, making electrochemical synthesis the most promising method for industrial production of MOF materials. Actually, several important MOF material

als like HKUST-1 and ZIF-8 have already been commercialized and utilized in the field of gas adsorption and storage, and electrochemical synthesis is the key for the successful mass production of these materials.

(5) Crystal transformation

Crystal transformation is a new strategy to synthesize MOF structures, which refers to the formation of a new material by means of structural transformation or component substitution based on given MOF materials. Change of substance induced by structural transformation is also called single-crystal to single-crystal transformation, specifically referring to that the crystal structure of the original MOF is changed under external induction into another crystal structure, followed by changes in physical properties. Another way of crystal transformation is through metal substitution or ligand exchange. In this method, the original MOF plays the role of structural directing agent, and under specific condition new metal nodes or ligands replace the corresponding units in the old framework to form a new matter. It is noteworthy that for MOFs which are hard to acquire directly by traditional methods, such crystal transformation mechanism could lower the reaction potential barriers, so as to promote the formation.

1.1.4 Applications of Metal–Organic Frameworks

(1) Gas adsorption and separation

Application of porous materials for adsorption and separation of small gaseous molecules is highly important. Typically, hydrogen and methane are two kinds of clean fuels with high calorific values (120 and 50 MJ/kg, respectively, succeeding 45 MJ/kg of petroleum), thus are considered ideal substitutes of fossil fuels. However, in practical applications the gas storage and transportation issues have to be considered due to the low density of these gases. A high pressure is needed to achieve enough storage density, which also brings about more operating pressure and additional cost of equipment and considerable risk. Comparatively, it is more effective to store hydrogen or methane in nanoporous materials. Due to condensed squeezing effect, the gas molecules in the pores are in a high-density condensed state, making it possible to achieve high gas storage capacity under relatively low pressure. MOFs have high specific surface area, rich porosity and low density, with extensive inner space for gas storage. Also, MOFs contain functionalized pore surfaces, open metal sites or modified functional groups, which can exert weak intermolecular interactions with the guest molecules to enhance gas adsorption. Currently, researches using MOFs for gas storage are mainly focused on the storage of hydrogen, methane and carbon dioxide, while studies on other gases like CO, NO, O₂ are less reported [40]. Figure 1.7 gives the examples of some representative MOFs for specific gas storage.

In 2003, O. M. Yaghi et al. reported the hydrogen storage property of MOF-5, which reached a hydrogen adsorption capacity of 4.5 wt% at 78 K and 1 bar,



Fig. 1.7 Examples of representative MOFs for gas adsorption and separation. Reproduced from Ref. [40] with permission of the International Union of Crystallography

and 1.0 wt% at room temperature and 20 bar [33]. In 2007, they improved the adsorption property of the same material by modified post-treatment to reach a value of 10 wt% at 77 K and a relatively safe pressure of 100 bar, corresponding to a volumetric hydrogen density of 66 g/L, comparable to liquid hydrogen (71 g/L at 20.4 K and 1 bar) [47]. Among the currently reported MOFs, NU-100 presents the highest hydrogen adsorption capacity of 99.5 mg/g at 77 K and 56 bar [30], indicating its great potential application. Among all the dry solid materials, the MOF PCN-14 presents the most appealing methane adsorption property, with a capacity of 212 mg/g at 290 K and 35 bar [48]. As for CO₂ adsorption, MOF-200 and MOF-210 present the highest adsorption capacities among all the porous materials, reaching 2400 mg/g at 298 K and 55 bar [26].

Considering the tunable pore size and surface functionalization, MOFs could work as molecular sieves for gases with different sizes or polarities, so as to achieve separation of mixed gases, which has great significance in industry. Jeffrey R. Long's group studied the separation of C1 to C3 hydrocarbons by Fe-MOF-74 [49]. They firstly discovered the different adsorption capacities of Fe-MOF-74 towards methane, ethane, ethylene, propane and propene by static adsorption isothermals, then revealed the excellent separation property of Fe-MOF-74 towards ethylene/ethane and propane/propene mixed gases by dynamic breakthrough exper-

iments. Molecular simulation indicated that such separation ability originated from the unsaturated metal sites exposed in the 1D channels, which had obviously distinct interactions with different gas molecules, thus displaying different adsorption properties.

(2) Catalysis

MOFs have high surface areas, open channels and functionalized surfaces, which is ideal for the study of small molecule catalysis. The catalytic application of MOFs can be divided into two categories: one is to utilize the intrinsic catalytic activity of the framework, like catalysis by specific metal sites and modified ligands; the other is to use MOFs as substrates to load some active species, where the framework could stabilize the catalyst and present synergetic size sieving effect. Based on different loaded catalysts, the composite material could present variable catalytic properties. Here we focus on the intrinsic catalytic properties of MOFs.

MOFs themselves have exhibited catalytic activities towards various reactions, including hydrogenation/dehydrogenation reactions, oxidation reactions, coupling reactions, photocatalytic reactions, electrocatalytic reactions, etc. In 2015, Peidong Yang and Omar M. Yaghi et al. synthesized a stable cobalt-porphyrin-based MOF material, $Al_2(OH)_2TCPP$ -Co [50]. In this material, porphyrin units were linked by Al oxide chains, forming 3D networks with 6 × 11 Å² channels. This framework material exhibited electrochemical catalytic activity to reduce CO₂ into CO with a high selectivity of over 76% and good stability. In situ spectroelectrochemical analysis revealed that the catalytic activity came from the Co(II) centers on the porphyrin rings, which were reduced to Co(I) that had higher catalytic activity to reduce CO₂ molecules into CO.

(3) Optical, electrical and magnetic properties

The optical properties of MOFs could be introduced by metal ions. For example, in lanthanide cations, electron transportation from d shell to f shell is followed by photon excitation. Based on this phenomenon, MOFs with fluorescent properties for sensing and displaying could be constructed from lanthanide ions. Figure 1.8 shows a strategy to mark fingerprints with Eu₂(bdc)₃ and Tb₂(bdc)₃ micro/nanocrystals [51]: when surface with fingerprints are covered by MOF precursor solution, the proteins in the fingerprints will adsorb metal ions and ligands, accelerating the growth of Eu₂(bdc)₃ and Tb₂(bdc)₃ have specific fluorescent properties, which could reflect the characteristics of fingerprints clearly under UV radiation with high resolution. On the other hand, the organic ligands of MOFs usually have conjugated π bonds, which could also induce light emission property.

MOFs possessing variable-valence metal ions and certain conductivity show electric applications in some cases. Researchers proposed that MOFs could be utilized for electron storage considering their large surfaces which could adsorb large amount of electrons, and the valence transformation of metal ions. A nickel-based MOF was



Fig. 1.8 a $Eu_2(bdc)_3$ (left) and $Tb_2(bdc)_3$ (right) marked fingerprints; **b** the image of marked fingerprints under UV light; **c** schematic illustration of the preparation process. Reproduced from Ref. [51] with permission of the John Wiley and Sons

synthesized and showed good electron storage property with a specific capacitance of 634 F/g. It also demonstrated good stability that 84% of the original capacitance was retained after 2000 cycles in 6 M KOH electrolyte [52]. MOFs with proton conductivity have also been studied as solid electrolytes for fuel cells. A copper-based MOF with 2D structure was constructed with proton conductivity originated from the H₃O⁺ ions within the pores. Despite the relatively low conductivity (1.5×10^{-5} s/cm), this work started a new research direction [53]. In following works the proton conductivity of MOFs has been continuously improved by modification of framework structures and surfaces, which currently reaches the value of 4.2×10^{-2} s/cm (25 °C), with good performance at higher temperature (1.0×10^{-4} s/cm at 150 °C) [54].

MOFs with magnetic properties are mainly constructed from proper organic ligands with paramagnetic transition metal nods. The metal nodes are majorly transition metals with variable oxidation states, such as Fe, Co, Ni, Cu, Mn, V, Cr etc., where transition between different valences results in the transformation of magnetic anisotropy. Hiroshi Kitagawa et al. synthesized a bimetallic M–Cr magnetic MOFs (M=Mn, Fe or Co), the corresponding magnetic transition point of MnCr, FeCr and CoCr composites being 5.5, 9.0 and 10.0 K [55]. Utilizing the magnetic properties of MOFs, Wenbin Lin et al. developed the application as magnetic resonance imaging contrast agents, showing good results with potential biomedical application [56].

1.2 Metal–Organic Framework Derived Nanomaterials

In recent years, another branch of important nanomaterials is developed based on MOF materials, which is MOF derivatives. MOF derivatives refer to nanomaterials prepared by transformation reactions using MOFs as templates. According to

their composition, MOF derivatives can be mainly concluded into carbon, metal oxides, metal sulfides, metal nitrides, metal phosphides and their composites. The transformation process is closely related to the nature of MOFs. On the one hand, MOFs are constructed from organic ligands and metal nodes, and the organic ligands could be transformed into carbon under high temperature, while metal nodes can be transformed into elemental metals or metal compounds under certain conditions. On the other hand, the high surface area and rich porosity of MOF are beneficial for external molecules to substitute the original elements, and also good for the formation of porous structures or highly dispersed nanoparticles in MOF derivatives.

1.2.1 Metal–Organic Framework Derived Porous Carbons

Porous carbon materials have wide applications including adsorption, catalysis and electrochemistry due to their high surface area, good electric/thermal conductivity and thermal/chemical stability. Porous materials can be prepared from template method, electrochemical deposition, phase separation reaction, physical or chemical activation, etc. Among these methods, template method is the most frequently used one, which could be used to purposely tune the pore textures of the obtained materials. Typically, traditional inorganic molecular sieves (like SBA-15) are often used as template to synthesize carbon materials with particular porous structures, but such strategy is relatively complicated, involving multiple steps including template synthesis, introduction of carbon source, thermal treatment and template removing (Fig. 1.9a). Moreover, toxic reagents are used during template removing process, limiting their large-scale application.

On the other hand, MOF materials have ordered porous structures and stable frameworks, thus can also be used as templates for porous carbon materials. For example, MOF-5 with 3D interconnected channels (with a diameter of 18 Å) could accommodate furfuryl alcohol molecules (with the size of $8.43 \times 6.44 \times 4.28$ Å³) as secondary carbon source [57]. When treated at 1000 °C in Ar atmosphere, both the furfuryl alcohol molecules and the organic ligands in MOF were carbonized, while the metal nodes were reduced into Zn nanoparticles that then evaporated from the carbon matrix due to the low boiling point of Zn (908 °C), leading to the formation of highly porous carbon. N₂ sorption analysis results suggested that the BET surface area of the product was as high as $2872 \text{ m}^2/\text{g}$, far beyond the carbon materials prepared by conventional methods, demonstrating the great potential of MOFs as template for synthesis of porous carbon.

Considering that the organic ligands in MOF structures can also be easily carbonized under high temperature treatment, MOF itself can serve as both template and carbon source, thus the addition of secondary carbon source can be avoided, which greatly simplifies experimental operations. Calcinating MOF-5 directly at 900 °C under Ar flow for 3 h, carbon material with rich porosity was prepared with a BET surface area of 3174 m²/g [58], even higher than the above mentioned one prepared with external carbon source. By characterizations like powder X-ray diffraction and



Fig. 1.9 a Schematic illustration of the conventional method for preparing porous carbon; b structure models of zeolite and MOF templates



Fig. 1.10 Structure evolution of MOF-5 during calcination. Reproduced from Ref. [58] with permission of the American Chemical Society

temperature-programmed desorption-mass spectrum, the structure evolution from MOF to carbon material was revealed. As shown in Fig. 1.10, the crystal structure remained integrated until 300 °C. The organic frameworks gradually decomposed upon further increasing the temperature and released CO₂, CO and benzene, forming amorphous carbon, while the metal nodes transformed into ZnO embedded in the carbon matrix. During this process, the original micropores in parent MOF disappeared, forming large amount of mesopores and macropores in the thermal treated sample. When the temperature was further increased to 750 °C, ZnO was gradually reduced into Zn by the surrounding carbon that was oxidized into CO and CO₂. After 900 °C, most of the Zn evaporated, and completely disappeared from carbon matrix after 50 min, forming the final stable porous carbon.



Fig. 1.11 TEM images of a Al–PCP carbonized at 800 °C and b Al–PCP after carbonization and acid wash. Reproduced from Ref. [59] with permission of the American Chemical Society

The temperature for the carbonization of MOFs is usually between 700 and 1000 °C, and the boiling points of common metal nodes of MOF (e.g. Fe, Co, Al) are higher than this temperature. In these cases, metals cannot be removed from the system by evaporation under heating, and residue metals can be removed by acid or base corrosion, further expanding the apertures of carbon materials during the process. For example, an Al-based MOF, Al–PCP [Al(OH)(1,4-NDC)·2H₂O] was carbonized at 800 °C to form a composite with a BET surface area of 760 m²/g and pore volume of 0.68 cm³/g [59]. After acid washing to remove residue metal species, the BET surface area and pore volume of the material were increased to 5500 m²/g and 4.4 cm³/g, respectively. As seen in Fig. 1.11, the material displayed a rod-like morphology with rich internal porosity, and the pore size mainly distributed in the range of 1–5 nm according to NLDFT (Non-Localized Density Functional Theory) fitting.

With the development of various MOF-templated carbons, researchers started to investigate the effect of structure and composition of MOF precursors on the derived carbon materials. During the carbonization process, the original framework collapses and turns into new structures, resulting in contradictory results, i.e. derived materials with higher surface area (like ZIF-9) or lower surface area (like MOF-5) than the parent MOF. Since the thermal triggered structure transformation is hard to control, the relationship between the structures of precursors and carbonized materials is hard to define. Some reports revealed that MOFs consisted of aromatic ligands had better rigidity and tended to remain the original porous structures after carbonization. Therefor choosing MOFs with high surface area and high aromaticity is beneficial for the synthesis of porous carbon materials with high surface area [60]. Aside from precursor material, the structure of carbonized product is affected by some other factors like carbonizing temperature, heating time, ramping rates, etc. In-depth investigation of these internal and external factors is essential for purposive design and construction of porous carbon materials with specific structures.

Moreover, carbon nanomaterials with 0D, 1D and 2D structures have been developed on the basis of MOFs. 0D carbon nanoparticles with an average size of 2.2 nm were successfully prepared by heat treatment of ZIF-8 at a relatively low temperature of 500 °C (Fig. 1.12a) [61]. By proper heat treatment, MOFs containing Fe, Co, Ni nodes could be converted into a classical 1D porous carbon material, carbon nanotube. Fe, Co, Ni nanoparticles from the reduction of metal nodes at high temperature possess high catalytic activity and catalyze the growth of carbon nanotubes on the surface of nanoparticles. As shown in Fig. 1.12b, a nickel-based MOF [Ni₃(btc)₂·12H₂O] was carbonized under high temperature into multi-walled carbon nanotubes with an outer diameter of 10–30 nm and length of 0.3–0.5 μ m [62]. MOFs can also be converted into 2D carbon materials. The mixture of ZIF-7 and glucose was carbonized under 950 °C for 5 h, resulting in graphene-like carbon nanosheets (Fig. 1.12c) [63]. Glucose was found to be crucial for the formation of such 2D structure because that the pre-molten glucose molecules polymerized and served as 2D templates before complete carbonization of ZIF-7.

1.2.2 Metal–Organic Framework Derived Metal Oxides

Metal oxides have important electrochemical applications in electrocatalysis, lithium ion batteries, supercapacitors, etc. These systems involve various heterogeneous interfacial reactions, thus a high density of active sites and fast mass and charge transportation are critical to guarantee good performance of the system. Porous materials with high surface area are good candidates which possess rich surface for exposure of active sites and interconnected channels for promoted mass transport. Design and synthesis of metal oxides with nanoporous structures are thus essential to enhance their electrochemical performance.

It is hard to control the pore structure and size by ordinary physical or chemical methods, where metal oxides tend to agglomerate under high temperature, resulting in products with low surface area. Metal oxides prepared based on MOF templates have fine nanostructures which can be tuned on purpose by changing reaction conditions. The metal nodes in MOFs are periodically distributed in the framework with high densities. Upon high temperature treatment these metal nodes are striped from the framework and agglomerate with nearby atoms, forming metal clusters. In oxy-



Fig. 1.12 MOF-derived carbons with different dimensions: **a** 0D [61], **b** 1D [62], and **c** 2D [63]. Reproduced with permissions of the John Wiley and Sons and Royal Society of Chemistry

gen or ambient atmosphere, these metal clusters can be converted into metal oxide nanoparticles, which further accumulate into 3D structures with rich porosity.

As shown in Fig. 1.13, a Fe-based MOF was used as precursor to prepare porous prisms consisted of Fe₂O₃ nanoparticles [64]. The MOF precursor, MIL-88-Fe, was firstly synthesized by solvothermal method as microcrystals with a regular prism-like morphology and average size of 1.3 μ m in length and 0.6 μ m in width. The acquired MOF was then carbonized at 500 °C under inert atmosphere to get FeO_x–C composite. The composite was further treated at 380 °C under air to convert the FeO_x into porous Fe₂O₃ nanoparticles, leaving lots of voids inside the material by oxidation and evaporation of carbon. The final product inherited the prism-like morphology of parent MOFs and consisted of porous Fe₂O₃ nanoparticles with the size smaller than 20 nm. N₂ sorption analysis revealed that the product had a BET surface area of 75 m²/g and pores mainly below 10 nm.

The composition and structure of oxidized products are affected by MOF precursors, the variety of which brings about rich metal oxide nanostructures. As shown in Fig. 1.14, the same metal nodes (Zn for example) coordinate with different organic ligands to form MOF precursors with different morphologies. After thermal treatments, they could be converted into a same compound (ZnO) but with distinct



Fig. 1.13 a SEM image of MIL-88-Fe; b TEM image of Fe_2O_3 ; c schematic illustration of the synthesis process. Reproduced from Ref. [64] with permissions of the American Chemical Society

structures [65–69]. On the other hand, by changing the metal nodes constructing MOFs, a variety of metal oxide nanomaterials could be synthesized, for example ZnO [65–69], Co_3O_4 [68], Mn_3O_4 [68], CuO [70], In_2O_3 [71], Fe_2O_3 [72], CeO_2 [73], NiO [74], Al₂O₃ [75], CdO [76], Eu₂O₃ nanostructures [77]. The structure and phase of the oxide products are also affected by the heating process. Generally, the higher heating temperature used, the better crystallinity of the products is. However, the particles tend to agglomerate at high temperatures, leading to severely decreased surface area and increased particle size. Herein, both factors need to be considered when constructing MOF-derived nanomaterials towards particular electrochemical applications.

Another advantage of using MOFs as templates to prepare metal oxides is that mixed metal oxide nanostructures can be easily prepared. Mixed metal oxides or multi-metallic oxides have more complicated chemical components with possible synergetic effects between multi-components and exhibit enhanced electric, chemical and magnetic properties, drawing wide interests. However, controlled synthesis of this kind of materials remains challenging. The aforementioned metal nodes in



Fig. 1.14 MOF-derived nanostructures: **a** ZnO nanopillar [65]; **b** ZnO concave nanopolyhedron [66]; **c** ZnO nanostick [67]; **d** ZnO nanoflake [68]; **e** ZnO nanoring [69]; **f** Co₃O₄ nanoplate [68]; **g** Mn₃O₄ nanoflake [68]; **h** CuO hollow nanooctahedron [70]; **i** In₂O₃ nanoshuttle [71]; **j** Fe₂O₃ nanocube [72]; **k** CeO₂ nanostick [73]; **l** NiO nanospheres [74]; **m** Al₂O₃ cluster [75]; **n** CdO nanofiber [76]; **o** Eu₂O₃ nanostick [77]. Reproduced with permissions of the Royal Society of Chemistry, John Wiley and Sons, American Chemical Society and Elsevier

MOFs could be modified by using mixed metal precursors during synthesis or postsynthetic metal exchange, thus granting multiple kinds of metal nodes within a single framework. On this basis, mixed metal oxides can be easily acquired by simple heat treatment of these multi-metallic MOFs.

By replacing the potassium with zinc in potassium cobalticyanide ($K_3[Co(CN)_6]$), researchers successfully developed bimetallic MOF, $Zn_3[Co(CN)_6]$. This material was thermal treated at 500 °C in air for 1 h and converted into ZnO/Co_3O_4 nanoporous spheres [78]. Due to the short thermal treatment time, the ZnO and Co_3O_4 did not form a single phase (like the spinel-type $ZnCo_2O_4$), but homogeneously dispersed in the nanospheres as separated phases. Similarly, $Mn_3[Co(CN)_6]_2$ nanocubes were synthesized and heated at 450 °C in air for 2 h with a slow ramping rate (1 °C/min) to get spinel-type $Mn_xCo_{3-x}O_4$ nanocages [79]. The BET surface area of the product was 77.1 m²/g, more than two times than that of $Mn_xCo_{3-x}O_4$ nanoparticles synthesized from conventional methods (33.1 m²/g), and the strong interaction between MnO_x and CoO_x in $Mn_xCo_{3-x}O_4$ improved the catalytic property of the material.

1.2.3 Metal–Organic Framework Derived Metal Oxide/Carbon Composites

Though metal oxides themselves have certain electrochemical activity, their electric conductivity and stability are relatively poor. They displayed large volume change as active materials in lithium batteries, resulting in powdering and detachment from the electrode after several charge-discharge cycles. A secondary phase is thus introduced to stabilize the nanostructures of metal oxides while keeping their original electrochemical activity. Carbon substrates are considered a good candidate, firstly considering that the addition of carbon can improve the overall conductivity of the composite, and the stabilization effect of carbon can improve the stability of interior active metal oxides; secondly, the porous structure of carbon could ensure the effective mass transport and good contact between active metal oxides and electrolytes to fully present the intrinsic performance of materials. Also, the possible interaction between metal oxides and carbon could induce synergetic effect, leading to the variation of the surface work function of composite materials, so as to improve the overall performance.

Currently the most frequently used methods to construct metal oxide-carbon composite materials can be concluded into two main categories, which are carbon coating on pre-formed oxides, and growth of metal oxides on pre-synthesized carbon matrix. In practical operation, both methods involve complicated processes, and the former is hard to form integrate and homogeneous carbon shell, while the latter is hard to control the size of metal oxides. In comparison, using MOF precursors for the synthesis of metal oxide-carbon composites is much easier and more effective. In MOF structures, metal nodes and organic ligands periodically distribute in alternation, forming metal oxide-carbon composites after simple heat treatment in which metal oxides homogeneously dispersed in the carbon substrate. Limited by the surrounding carbon substrate, the in situ formed metal oxides generally have smaller size with better activity.

Recently, researchers reported a representative one-step synthesis of carboncoated ZnO quantum dot material from the prototypical MOF-5 (Fig. 1.15) [80]. During the synthesis, dried MOF was rapidly heated to 550 °C at a heating rate of 10 °C/min, then immediately cooled to room temperature after reaching the target temperature to get the target ZnO–C composite. The ZnO quantum dots in the material had high crystallinity with an average size of 3 ± 1 nm, and were highly dispersed in the amorphous carbon matrix. The size of metal oxides in the composite was also affected by temperature, and the ZnO nanoparticles grew into 22 nm at a higher temperature of 600 °C. On the other hand, elongating the heating time and decreasing the heating rate also led to obvious increase of the size of ZnO in products. Metal-oxides/carbon composites prepared from ordinary methods usually have relatively low BET surface area, but in this work the carbon-coated ZnO quantum dot material had rich porosity with a BET surface area as high as 513 m²/g and pore volume of 1.27 cm³/g. Based on its advanced structure, the composite showed good performance as cathode materials in lithium ion batteries. This report provides a highly


Fig. 1.15 Models of IRMOF-1 (left) and it's derived carbon coated ZnO quantum dots (right). Reproduced from Ref. [80] with permission of the American Chemical Society

efficient and universal synthetic strategy to prepare metal oxide/carbon composite nanomaterials for the development of advanced electrode materials.

Thermal treatment of MOFs in inert atmosphere will generate reductive elemental carbon or gases like CO, thus elemental metals rather than metal oxide materials are often obtained in some cases. Researchers studied the relationship between the precursors and the products, and discovered that the reduction potential of metal played an essential role [81]. They carbonized several kinds of MOF materials consisted of different metal nodes (Zn, Mn, Cd, Co, Cu, Mg) at the same temperature (900 °C), and discovered the boundary between the formation of elemental metals and the generation of metal oxides by examination of the products. As shown in Fig. 1.16, when the reduction potential of metal is higher than -0.27 V, carbonized products are generally elemental metals; on the contrary when the reduction potential is lower than -0.27 V, metal oxides are generated.

When the metal elements existe as metal oxides in the product, the targeted metal oxide-carbon composite materials can be acquired from one-step heat treatment. When elemental metals are generated, proper oxidation procedures can be applied to transform the metals into target metal oxides. For example, in inert atmosphere, a Co-based MOF, ZIF-9 was transformed into carbon-metallic cobalt composites in the temperature range of 700–900 °C [82]. The acquired cobalt nanoparticles had high activity, and were oxidized into cobalt oxides upon heating at 250–300 °C in air, while the carbon remained the pre-formed porous structures.



Fig. 1.16 The effect of reduction potential of metal atoms present in the MOFs on the formation of the metal/metal oxide nanoparticles. Reproduced from Ref. [81] with permission of the Royal Society of Chemistry

1.2.4 Other Metal–Organic Framework Derived Inorganic Compounds

Besides metal oxides, the metal nodes can also be converted into other inorganic nanoparticles including metal carbides, nitrides, sulfides and phosphides that have wide applications in fields like catalysis and lithium ion batteries.

Similar to metal oxides, metal carbides and nitrides can also be synthesized by thermal treatment. At elevated temperatures, metal ions are reduced into elemental metals while organic ligands decompose into porous carbon and tightly cover the surface of metal particles. The carbon-coated structure benefits the diffusion of carbon atoms into the interior metal, promoting the formation of metal carbides. For example, Fe-BTC was carbonized at 500 °C in nitrogen for 8 h and formed carbon-coated FeC_x (26%) and FeO (76%) nanoparticles with a size between 2 and 4 nm [83]. Under 400 °C and hydrogen atmosphere, the 76% FeO in the material was reduced into Fe⁰. By putting the pre-treated sample under Fischer-Tropsch reaction condition for 5 h (mixed gas with H₂/CO=1, at 340 °C), 86% of the Fe atoms were converted into Fe₅C₂ with high catalytic activity toward Fischer-Tropsch synthesis. Reports of MOF-derived metal nitrides are relatively rare. Iron nitride and nickel nitride were prepared by one-step carbonization of MOFs with high nitrogen content, and by ammonification under ammonia atmosphere, respectively [84, 85].

Preparing metal sulfides from MOFs can be concluded into two main categories, vapor vulcanization and liquid-phase vulcanization. Vapor vulcanization refers to the direct vulcanization of MOF or carbonized MOF products (like metal or metal oxides) using gaseous sulfur phase to produce metal sulfides. For example, a cobalt-based MOF, ZIF-67 was mixed with sulfur powder and heated at 500 °C, where sulfur



Fig. 1.17 a Schematic illustration of the formation of NiS nanoframes from MOFs; SEM images of the product after different reaction time: $\mathbf{b} \ 0 \ h; \mathbf{c} \ 0.5 \ h; \mathbf{d} \ 2 \ h; \mathbf{e} \ 6 \ h.$ Reproduced from Ref. [90] with permission of the John Wiley and Sons

sublimed into vapor and reacted with ZIF-67 to form CoS_x products that inherited the original polyhedron morphology of the parent MOF [86]. Vapor vulcanization method is able to yield products with high crystallinity, but the reaction temperature is relatively high and product structures is hard to control. By liquid-phase vulcanization, metal sulfides can be synthesized at lower temperature with fine nanostructures.

Liquid-phase method to convert MOFs into metal sulfides can be regarded as an ion-exchange process, where S^{2-} anions diffuse towards the interior of material, while the MOF ligands diffuse outwards driven by concentration gradient. The different diffusion rates of both sides result in the formation of hollow nanostructures. For example, Co₉S₈, CuS and ZnS were synthesized based on MOF templates by liquid-phase vulcanization. The products inherited the homogeneous size and regular morphology of the MOF precursors but with new hollow structures [87–89]. Utilizing the different reaction activities of edges or faces in MOF crystals, a structure-directed anisotropic chemical etching-ion exchanging method was developed to successfully convert the Ni₃[Co(CN)₆]₂ nanocubes into novel NiS nanoframework structures with high surface area, open porous structures and good electrochemical properties (Fig. 1.17) [90]. Metal sulfides prepared from liquid-phase methods have relatively low crystallinity, which could be improved by further thermal treatment for enhanced stability and activity.

Currently, the most frequently used sulfur sources in vapor vulcanization are elemental S and H_2S , while in liquid-phase methods thioacetamide and sodium sulfide are the mostly used [91, 92]. Synthesis of metal phosphides is similar to that of metal sulfides, typically by mixing MOFs with sodium dihydrogen phosphate followed by high temperature treatment to get target products like CoP, Co_2P , Ni_2P , $Ni_{12}P_5$, etc. [93, 94].

1.3 The Application of MOF-Derived Materials in Electrochemical Energy Storage and Conversion

Electrochemical energy, which possesses a high conversion efficiency and moderate operating condition, has been viewed as the most prosing energy type and used in many fields. With the large-scale application of Li-ion batteries in the markets and increasing demand from customers, the development of next-generation electrochemical energy storage and conversion systems has become a new focus in scientific research and already cost tremendous efforts. Although remarkable progress has been made, there still exists some problems, such as low utilization, limited activity and poor stability of the active materials. On the other hand, MOF-derived materials usually possess high surface area, which is beneficial for the exposure of active sites in electrolyte. Moreover, the open porous structure in MOF-derived materials can contribute to fast mass transport, thus accelerating the electrochemical reaction. In recent years, MOF-derived materials demonstrate excellent performance in electrochemical energy storage and conversion, mainly in supercapacitors, lithium-ion batteries and electrocatalysis.

1.3.1 MOF-Derived Materials for Supercapacitor

Supercapacitor is a high-power energy storage device with excellent stability. Based on the different energy storage mechanisms, it can be divided into two main types, electric double layer capacitor (EDLC) and pseudocapacitor. Energy storage in EDLC is achieved by the formation of Helmholtz double layer of separated charges at the interface between electrode and electrolyte, which is able to provide a high capacitance value. Moreover, EDLC possesses a high charge/discharge rate due to the fast ion diffusion inside the system. Generally speaking, the charge/discharge in EDLC is more likely a physical process and not involved in chemical reaction, thus contributing a very high stability. It can be concluded from the working mechanism that the performance of EDLC is related to the specific surface area, pore size distribution and pore volume of the electrode materials. Microporous carbon materials with high stability, large surface area and pore volume are a promising electrode material for EDLC. Pseudocapacitor stores electrical energy on the basis of reversible faradaic reaction occurred on redox species. The energy density in pseudocapacitor is an order of magnitude higher than that in EDLC. Transition metal oxides and hydroxides are typical active materials for pseudocapacitor. The corresponding capacitance value is associated to the redox active center, the specific surface area and pore texture.

Precursor	Temperature (°C)	Surface area (m^2/g)	Pore volume (cm ³ /g)	Capacitance (F/g)	References
MOF-5	1000	2872	2.06	204 @ 5 mV/s	[57]
ZIF-8	900	1215	0.57	214 @ 5 mV/s	[95]
MOF-2	1000	1378	-	165 @ 10 mV/s	[60]
ZIF-69	1000	2264	2.16	168 @ 5 mV/s	[96]
ZIF-8	800	2972	2.56	211 @ 10 mV/s	[97]
IRMOF-3	950	553	0.34	239 @ 5 mV/s	[98]
ZIF-7	950	783	0.56	185 @ 25 mV/s	[99]
ZIF-67	800	943	0.84	238 @ 20 mV/s	[100]
Al-PCP	800	1103	1.04	174 @ 1 A/g	[101]
HKUST-1	800	50	1.46	83 @ 1 A/g	[101]

 Table 1.2
 The capacitance values and basic physical parameters of several MOF-derived carbons

MOF-derived carbon materials usually possess high specific surface area and tunable pore texture, making them a promising candidate for EDLC. Liu et al. first reported the MOF-5 derived carbon as EDLC electrode material [57]. The BET surface area and pore volume of the sample is up to $2872 \text{ m}^2/\text{g}$ and $2.06 \text{ cm}^3/\text{g}$, respectively. A hierarchically porous structure (coexistence of micro-, meso- and macropores) was found in this material, which is beneficial for the sorption of charge (mainly by micropores) and fast mass diffusion (by the meso- and macropores). It demonstrated a capacitance value of 204 F/g at the scan rate of 5 mV/s, which was much higher than that of SBA-15 (a typical mesoporous zeolite) derived carbon material (102-163 F/g). Afterwards researchers tested the capacitance value of several carbon materials derived from MOFs, as shown in Table 1.2. Normally, the capacitance increases as the surface area increases for pure carbons. However, IRMOF-3 derived carbon demonstrated a high capacitance value (239 F/g at the scan rate of 5 mV/s) even though it has a relatively low surface area (553 m^2/g). It can be attributed to the existence of -NH₂ functional group in the ligand of IRMOF-3 that are converted into nitrogen dopants in the carbon layer. Nitrogen doping can increase the electron sorption sites in the carbon material, which enhances the overall electrochemical performance. Thus, it's feasible to tune the composition or microstructure of MOF precursors in order to fabricate advanced carbon derivatives for capacitor application, for example the usage of N-, P- or S-rich ligands or the enhancement in microporosity and surface area.

MOF-derived transition oxides are redox active, which can be used as electrode materials for pseudocapacitor. For example, Co_3O_4 nano/micro superstructures were prepared by pyrolyzing a Co-based MOFs in air [102]. They were assembled from 2D nanosheets composing of 30 nm Co_3O_4 nanoparticles as the primary building

unit. Their Faradaic pseudocapacitive activity are generated through the following two redox reactions (Eqs. 1.1 and 1.2).

$$Co_3O_4 + OH^- + H_2O \leftrightarrow 3CoOOH + e^-$$
(1.1)

$$CoOOH + OH^{-} \leftrightarrow CoO_{2} + H_{2}O + e^{-}$$
(1.2)

Cyclic voltammetry test showed that the capacitance of the material reached 210 F/g at a scan rate of 5 mV/s. It is known that the diffusion of ions in electrochemical reactions is affected by the microstructure of the electrode material. The porosity in conventional electrode is very limited, resulting in incomplete diffusion of the ions into the electrode at a high scan rate and eventually a low utilization of active material and obvious decrease in capacitance. However, the Co_3O_4 nano/micro superstructures could accommodate enough electrolyte and reduce the diffusion length of ions, contributing to a high capacity retention even at a very high rate. It showed that the capacitance value kept 179 F/g even though the rate was increased to 6 times of the original value (30 mV/s).

1.3.2 MOF-Derived Materials for Lithium-Ion Batteries

Lithium-ion batteries (LIBs) possess higher energy density than supercapacitors and have been used in more areas. The working mechanism of LIBs is quite simple, which is based on the movement of Li ions between cathode and anode. Thus the charge and discharge processes in LIB have been named as rocking chair reaction. During the charge process, Lithium ions move from the cathode to the anode and get back when discharging. Theoretically materials with the capability of Li intercalation can be used for the electrode materials of LIB. However, the cathode materials are usually Li-rich transition metal oxides which have high potential and considerable stability in air (e.g. LiCoO₂), while the anode materials are graphite or metal oxides/sulfides that have relatively low potential.

Carbon based anodes have relatively low capacity of 372 mAh/g even based on the fully lithiated state (LiC₆), which accounts for the main limit of present commercial LIB. Recently, researchers found that nitrogen doping could effectively improve lithium storage in carbon materials [103]. They pyrolyzed a nitrogen-rich MOF, ZIF-8, in a N₂ flow for 8 h and obtained carbon polyhedrons that were assembled by graphene-like nanoparticles after the removal of Zn impurities via acid wash. The nitrogen content in this material reached a remarkable value of 17.72 wt%, surpassing most of the nitrogen doped carbons (normally at around 10 wt%). It showed a high capacity and stability for lithium storage. As shown in Fig. 1.18a, the capacity maintained a high value of 2132 mAh/g after 50 cycles at a rate of 785 mA/g. At a higher rate of 5 A/g, it still demonstrated a capacity of 785 mAh/g after 1000 cycles. Computational simulation revealed that the extraordinarily high



Fig. 1.18 ZIF-8 derived carbon material for Li storage: **a** cycle performance at 100 mA/g and 5 A/g; **b** schematic illustration of the formation process and Li storage sites. Reproduced from Ref. [103] with permission of the Nature Publishing Group

capacity might originate from two lithium storage sites: the nanopores between the graphene analogous aggregate and the nitrogen atoms at the edge (Fig. 1.18b).

In addition to the direct application as active materials for anode, MOF-derived carbons can act as porous host for sulfur in lithium-sulfur batteries. Sulfur is a new cathode material for high-energy batteries. The theoretical capacity of sulfur is up to 1675 mAh/g, much higher than that of the commercial LiCoO₂ and LiFePO₄ cathode materials. Moreover, as an abundant elements on earth, sulfur is inexpensive and environmentally friendly, making it a promising candidate for the next generation batteries. However, sulfur cathode is subject to low electrical conductivity (5 \times 10⁻³⁰ s/cm at 25 °C) and dissolution problems at discharge form, which eventually reduces the utilization of active material and decreases the stability after cycling. A lot of efforts have been devoted to addressing these issues. A feasible method is to confine sulfur in the pores of carbon frameworks. On the one hand, the addition of carbon can provide 3D electron conducting network, which improve the overall conductivity. On the other hand, nanosize sulfur particles can be produced in the confined space of the carbon host, increasing the utilization and reactivity of the sulfur cathode. In addition, the confinement from the pores can alleviate the diffusion of polysulfides, thus improving the cycle performance.

Bearing the high surface area and rich porosity, MOF-derived carbon materials are an ideal candidate for sulfur host. As shown in Fig. 1.19a, a rod-like carbon material was synthesized from an Al-MOF precursor (named as FLHPC) [104]. It possesses rich micro- and mesopores with a BET surface area of $1124 \text{ m}^2/\text{g}$ and a pore volume of $1 \text{ cm}^3/\text{g}$. Sulfur was introduced to the pores by a melt-diffusion method, which realized a sulfur loading of 58 wt%. The obtained S/FLHPC composite delivered a capacity up to 1206 mAh/g at the first cycle (Fig. 1.19b), which is much higher



Fig. 1.19 a Al-MOF derived porous carbon for sulfur confinement; b cycle performance of the C/S composites. Reproduced from Ref. [104] with permission of the Royal Society of Chemistry

than that in normal S/Super P composite (900 mAh/g). Moreover, the S/FLHPC composite demonstrated considerable cycle stability. Its capacity maintained a high value of 856 mAh/g after 100 cycles.

Metal oxide based electrode materials can be divided into two main categories according to the different lithium storage mechanisms. The first type is similar to carbon anode, where lithium intercalation and extraction are highly reversible (Fig. 1.20). The charge and discharge processes in these materials are accompanied by small change in lattice structure and not involved in phase change, thus the volume variation is small. However, the choice of these materials are limited to a few candidates, such as TiO₂, Li₄Ti₅O₁₂ and MoO₂. All of them have relatively low capacity for lithium storage. MOF-derived metal oxides with such properties are rare and TiO_2 is the only reported example [105]. It was prepared from the Ti-based MOF, MIL-125, by heat treatment in air. The anatase-type TiO_2 inherited the porous structure of the MOF precursor and the surface area reached 220 m²/g, which cannot be obtained through conventional method. Electrochemical measurements showed that the TiO₂ possessed a reversible capacity of 166 mAh/g at 1°C after 500 cycles. The tested result is identical to the theoretical value (168 mAh/g based on the final discharge product of Li_{0.5}TiO₂). At higher discharge and charge rates, 5 and 10 °C for example, the MOF-derived TiO₂ still gave high capacities of 106 and 71 mAh/g after 500 cycles, respectively. The extraordinary capacity in the TiO_2 comes from the lithium stored in the TiO₂ lattice as well as the porous interfaces. Moreover, the porous structure contributes to fast Li⁺ diffusion, and eventually the excellent rate performance.

Another lithium storage style is based on conversion reaction which involves the formation/decomposition of Li_2O and the reduction/oxidation of metal nanoparticles. As shown in Fig. 1.20b, the original crystal structure of metal oxide will be destroyed when reacting with lithium during the first discharge process, forming ultrafine metal nanoparticles embedded in Li_2O matrix. During the charge process, Li_2O decomposes and promotes the formation of metal oxide. The overall reaction is displayed as Eq. (1.3).

$$MO + 2Li^+ + 2e^- \leftrightarrow Li_2O + M$$
 (M=Fe, Co, Ni, Cu, Mn) (1.3)



Fig. 1.20 Lithium storage mechanisms in metal oxides: a intercalation; b conversion reaction

Sample	Capacity (mAh/g)	Sample	Capacity (mAh/g)
FeO	746	NiO	718
Fe ₂ O ₃	1007	CuO	375
Fe ₃ O ₄	926	Cu ₂ O	674
CoO	715	MnO	756
Co ₃ O ₄	890	MnO ₂	1233

Table 1.3 Theoretical capacities of several metal oxides

FeO, Fe_2O_3 , Fe_3O_4 , CoO, Co_3O_4 , NiO, CuO, Cu_2O , MnO, and MnO₂ are common candidates for the conversion reaction active anode materials. The theoretical capacities of these materials are calculated according to Eq. (1.3) and listed in Table 1.3.

As shown in Table 1.3, the capacities of the reaction based anode materials are between 400 and 1000 mAh/g and much higher than that of the carbon-based anode. However, the electrochemical performance of the medal oxides are affected by the particle size and microstructure. Due to the large volume change in active material during the electrochemical reactions, the electrode structure tends to collapse and pulverize after several cycles, resulting in the detachment of active materials to the current collector and eventually rapid decrease in capacity. Thus, it is critical to develop advanced metal oxide nanostructure so as to alleviate the side effect caused by volume change.

From the above introduction, MOFs can be used as precursors to prepare a variety of metal oxides which covers almost all the electroactive metal oxides for LIB. The structure of the MOF-derived metal oxides can be tuned accordingly. For example, MOF $Fe_4[Fe(CN)_6]_3$ microcubes can be converted into Fe_2O_3 microboxes with hollow interior and hierarchically porous shells [72]. The unique structure is particularly useful for fast and stable lithium storage. On the one hand, the hollow interior and

porous shells facilitate the penetration of electrolyte and the diffusion of lithium ions. On the other hand, the hierarchically porous structure and hollow interior can effectively relieve the stress caused by the volume change during lithium intercalation and extraction. The Fe₂O₃ microboxes displayed a high reversible capacity of 950 mAh/g at a current density of 200 mA/g, closing to the theoretical value (1007 mAh/g). At a high current density (1000 mA/g), the material kept a high capacity of 500–1000 mAh/g. The formation of this special structure is related to the different diffusion rate of various atoms (Kirkendall Effect in short). The synthesis of hollow metal oxide by MOF has a certain universality. Using a similar method, researchers also obtained hollow CuO and Co₃O₄ nanostructures that displayed excellent lithium storage properties [70, 106].

In addition to the above advantages in structure variation, the composition of the metal oxide product can be regulated by adjusting the MOF precursor to obtain mixed metal oxide anode material. The mixed metal oxides possess complex chemical composition, which probably introduce synergistic effects among the various components and produce high electrochemical activity. Due to the advantages, they has received extensive attention [107]. Traditional hydrothermal synthesis is not that effective in the preparation of mixed metal oxides. It is quite difficult to achieve uniform chemical composition in the product with controlled nanostructure. In contrast, it's easier to adjust the structure and composition of the derived mixed metal oxide through rational design of MOF precursor. For example, researchers synthesized a bimetallic MOF, $Mn_3[Co(CN)_6]_2$ by ion exchange and converted it into spinel $Mn_xCo_{3-x}O_4$ after a simple thermal treatment process [108]. Due to the periodic distribution of Mn and Co atoms in the MOF precursor, the two metals are also uniformly distributed in the product, forming a single-phase bimetallic oxide with good lithium storage properties. The composition and structure of mixed metal oxides can be tuned by adjusting the metal distribution in the MOF precursor. Fe sites in a Fe-based MOF, Fe-MIL-88, was partially replaced by Ni, forming a Fe₂Ni-MIL-88 precursor [109]. Then the Fe₂Ni-MIL-88 nanorods were coated by a layer of Fe-MIL-88, resulting in a Fe₂Ni-MIL-88/Fe-MIL-88 core-shell nanostructure. The material was oxidized at 450 °C to form NiFe₂O₄/Fe₂O₃ composite in which the two phases are homogenously mixed. Electrochemical tests showed that the material has a high lithium storage capacity and good stability. It delivered a capacity value up to 936.9 mAh/g at a current density of 100 mA/g after 100 cycle, and maintained a reversible capacity of 423.6 mAh/g at a high current density of 2000 mA/g.

More interestingly, carbon-metal oxide composite structure can be obtained directly from MOF given that the ligands in MOF can be converted into carbon while the metal nods can in situ introduce metal oxide to the carbon host. The carbon-metal oxide composite structure is more advanced than single metal oxide. The addition of carbon could enhance the electrical conductivity and improve the stability of metal oxides by physical confinement or protection. Fe₃O₄–C [110], Co₃O₄–C [111], ZnO–C [80] and ZnO/ZnFe₂O₄–C [112] composite materials were synthesized from Fe-MOF, Co-MOF, Zn-MOF and bimetallic FeZn-MOF, respectively. Battery test showed that the addition of carbon host could effectively enhance the overall performance of metal oxides.

Moreover, MOF-derived metal sulfides (e.g. CoS, ZnS and NiS) were also explored as anode materials for LIB [113–115], which is similar to the metal oxides.

1.3.3 MOF-Derived Materials for Fuel Cells

Fuel cells have higher energy density, higher conversion efficiency and less impact to environment in comparison with other energy conversion devices and become more important nowadays when energy and environment crises are getting more serious. In fuel cells, the chemical energy in fuels (such as hydrogen, methanol, ethanol, etc.) is released through mild electrochemical processes instead of direct combustion. The overall energy conversion efficiency is not limited by the Carnot cycle laws. The ideal thermodynamic efficiency of hydrogen fuel cell can reach 83% at 25 °C. In contrast, direct combustion of hydrogen in an internal combustion engine only give an efficiency of 10–20% [116, 117]. However, the efficiency in practical low temperature fuel cells is not that high mostly because of the sluggish reaction kinetics at the cathode.

The cathode and anode in a fuel cell are separated by a membrane/electrolyte. Fuels are oxidized at the anode and give off electrons that travel from external circuit to the cathode. Oxygen molecules at the cathode capture the electrons and are reduced to water in acidic solution or hydroxyl ions in alkaline solution. Thus the chemical energy in fuels is converted into electrical energy directly through the reactions at the electrode. In a typical hydrogen fuel cell, the hydrogen oxidation reaction (HOR) at the anode and the oxygen reduction reaction (ORR) at the cathode can be described as two half-cell reactions (Eqs. 1.4 and 1.5):

HOR:
$$2H_2 \rightarrow 4H^+ + 4e^-$$
, $E^0 = 0V$ (vs.RHE) (1.4)

ORR:
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O, E^0 = 1.23 V (vs.RHE)$$
 (1.5)

The kinetics of the reactions are critical to the output of fuel cells, however are limited by the large activation energy barriers. It is critical to introduce a lower energy intermediate with the help of catalysts in both electrode. Moreover, the kinetics of ORR is five-orders-of magnitude slower than that of HOR, which leads to more catalyst usage in cathode [118]. Platinum is the commercialized catalyst for ORR, but its reserves are limited and the price is quite high. The price of platinum catalyst in commercial fuel cells accounts for about 50% of the fuel cell module. In addition, platinum catalyst is subject to unsatisfying stability, which is reflected by the phenomena of dissolution, sintering and agglomeration during cell operation. Moreover, platinum is susceptible to poor tolerance to methanol. Thus, the development of non-platinum catalyst with high efficiency and excellent stability is of great importance in fuel cell research.

The finding of M–N–C (M, N and C stand for metal, nitrogen and carbon, respectively) catalysts is a major breakthrough in searching for the non-platinum catalysts



Fig. 1.21 MOF-derived ORR catalysts. The TEM images are adapted from [126–128] with permissions of the Royal Society of Chemistry and Wilegy-VCH

[119]. These materials include macrocycle molecules with transition-metal centers coordinated to four neighboring nitrogen atoms (e.g. cobalt phthalocyanine and iron phthalocyanine) [120], and M–N–C composites formed by the reaction of cheaper N-rich organic molecules with transition metal salts [121]. The M-N-C catalysts can be thermal activated under suitable conditions, resulting in higher activity and stability for ORR catalysis [122]. However, the active site density in the M-N-C catalysts obtained by these two approaches is generally low, and the dense structure is another disadvantage due to the slow mass diffusion. There still exists a big gap between the performances of the M-N-C catalysts and that of the platinum catalyst. Considering that MOFs can be prepared with periodic M-N-C moiety and rich porosity, they can be used as a precursor to introduce high specific surface area and abundant active sites to the derived materials, which will improve the ORR catalytic activity. Ma et al. reported the first example of MOF-derived ORR catalyst [123]. They prepared a cobalt imidazolate (CoIM) MOF in which a cobalt metal center is coordinated to four neighboring nitrogen atoms. The density of Co–N₄ site is up to 3.6×10^{21} /cm³, leading to sufficient active sites in the derived catalyst prepared through a following heat treatment process. The obtained sample displayed excellent catalytic activity toward ORR in acidic solution. Afterward, researchers developed a number of ORR catalysts from MOFs based on three main routes as depicted in Fig. 1.21.

The first strategy is based on the metal nodes of MOFs. In addition to the above mentioned M–N–C structure, the metal nodes can be converted into ORR active metal oxides, metal sulfides and metal carbides. Bai et al. synthesized carbon coated $CoS_{1.097}$ material from ZIF-9 that demonstrated four-electron catalysis behavior in alkaline solution [124]. The activity was much higher than that of the reported cobalt sulfide materials. Kong et al. found that CPM-16-Co-In MOF derived carbon coated $Co_3InC_{0.75}$ nanoparticles possessed good ORR catalytic activity in alkaline solution with an onset potential of 0.84 V (versus reversible hydrogen electrode, RHE) [125]. This material was further functionalized by introducing nitrogen sources to the MOF precursor, which lead to nitrogen doping in the carbon layer and enhanced activity toward ORR catalysis. The onset potential shifted to 0.91 V, closing to the value of commercial platinum based catalyst.

The second route is based on the nitrogen-rich organic ligands in MOFs. The ligands can be converted into nitrogen doped porous carbons which is an important ORR catalyst with rather stability and activity. Aijaz et al. prepared a nitrogen doped carbon from ZIF-8 which contains abundant nitrogen in the ligand [129]. The metal impurities in the pyrolyzed sample was removed by acid etching, leaving behind a highly porous structure. The obtained metal-free carbon material demonstrated excellent catalytic activity as well as good stability. Moreover, it also display the potential of being used in acidic medium. In addition, other heteroatoms such as sulfur and phosphorus can also be doped into carbon materials though the MOF strategy, introducing different behaviors upon ORR catalysis [130, 131].

Thirdly, MOFs are used to introduce micropores in the corresponding catalyst. It has been suggested that the M–N–C active centers are produced in the micropores [132]. More active catalytic sites can be produced by loading M–N precursor in the micropores of MOFs. Researchers synthesized ferrous acetate and phenan-throline loaded ZIF-8, and converted into ORR catalyst with enhanced activity and mass transport properties. The catalyst displayed a high volumetric ORR activity of 230 A/cm³ at the voltage of 0.8 V, which is the best performance for non-platinum catalysts [133].

1.3.4 Applications in Other Electrochemical Processes

The oxygen evolution reaction (OER) is a key process in lithium-air batteries as well as in electrolysis of water. Currently precious metal based catalysts (e.g. IrO_2) are the best performed catalysts for this process. More recently, MOF-derived metal oxides, sulfides and phosphides have demonstrated considerable activity toward OER catalysis. Ma et al. prepared Co_3O_4 –C nanoarrays on copper foil through pyrolyzing a cobalt-based MOF [134]. The composite delivered a low onset potential (1.47 V) and steady current density (10.0 mA/cm² at 1.52 V) in alkaline solution, which was similar to that in the best performed precious metal catalysts. Chen et al. synthesized carbon loaded metal sulfide nanoparticles from ZIF-67 [92]. They also displayed excellent catalytic activity and stability for OER catalysis.

Hydrogen evolution reaction (HER) is an important process for hydrogen production from water electrolysis. Pt and Pd are the best catalysts for HER. Recently, MOF-derived metal phosphides and sulfides have shown the potential to replace the precious metal catalysts. Yu et al. converted a nickel-based MOF to a NiS nanoframe (Fig. 1.17) and used it as HER catalyst [90]. The material demonstrated a current density of 10 mA/cm² with an over-potential of only 0.094 V and a low current decay of 8% after 16 h' operation.

1.4 The Significance of This Study and Research Content

Electrochemical reactions are a clean and efficient process for energy storage and conversion, with wide applications and promising prospects. They often involve multi phases including gas, liquid and solid. The microstructure of the interfaces is critical to the reaction kinetics. Thus, it is necessary to design the nanostructure of electrochemical active materials in order to satisfying the demands from different applications. The traditional method for the synthesis of electrochemical active materials are not uniform, resulting in a large deviation in their performance. Second, it's difficult to tune the microstructure of the product, which is reflected as large particle size and low porosity. As a result, the utilization of active atoms is usually low and the mass transportation inside the materials is slow. Therefore, there is an urgent need to develop a convenient and effective method for synthesizing electrochemical active materials with optimized structure.

Theoretical and experimental results have demonstrated the feasibility of using MOFs as precursors for synthesizing nanomaterials. MOFs are a kind of material which can be designed at molecular level and possesses high specific surface area and rich porosity. MOF can be converted into electrochemical active nanomaterials, such as porous carbon, metal oxides, sulfides, phosphides, carbides and nitrides. By designing the composition and structure of the MOF precursors, it has the potential to modulate the composition and structure of their derived materials, favoring the formation of advanced nanomaterials with excellent electrochemical properties.

This dissertation focuses on the design, synthesis and properties of MOF-derived nanomaterials. Through the successful construction of a variety of fine nanostructures, the advantages and universality of the MOF-template route are demonstrated and the structure evolution process from MOF precursor to the derived materials is revealed, which will provide new ideas and experimental references for the development of nanomaterials in the future. At the same time, the activities of the derived materials in ORR catalysis and lithium-ion batteries are studied. The following aspects are included in this dissertation.

 The size effect on the electrochemical performance of MOF-derived materials is systematically investigated. The idea of using MOF nanoparticles for electrochemical research is proposed.

- 1.4 The Significance of This Study and Research Content
- 2. A new method to prepare core-shell metal oxide nanoparticles from MOFs is developed. The material was tested for ORR catalysis. The effects of the core-shell structure on the catalytic performance is systematically studied.
- 3. A diffusion behavior of thermal activated MOF on carbon surface is revealed. Graphene and carbon nanotube supported metal oxides hollow nanoparticles a constructed based on the diffusion mechanism and their catalytic activities toward ORR are studied.
- 4. An extended MOF structure, 3D metal–organic gel is developed and applied as a new precursor to construct hierarchically porous carbon monolith that demonstrates the potential to be used as sulfur host in lithium-sulfur batteries.

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Chapter 2 Synthesis and Characterization of MOF-Derived Nanomaterials



2.1 Instruments and Chemicals

2.1.1 Instruments

The instruments list is shown in Table 2.1.

2.1.2 Chemicals Used in Synthesis of N-Doped Nanoparticles

Chemicals used in synthesis of N-doped nanoparticles are listed in Table 2.2.

2.1.3 Chemicals Used in Synthesis of Core-Shell Metal Oxide Nanoparticles

Chemicals used in synthesis of core-shell metal oxide nanoparticles are listed in Table 2.3.

2.1.4 Chemicals Used in Synthesis of Hollow Metal Oxide Nanoparticles

Chemicals used in synthesis of hollow metal oxide nanoparticles are listed in Table 2.4.

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Instrument	Model	Manufacturer
Analytical balance	XP105DU	METTLER TOLEDO
Magnetic stirrer	RCT Basic	IKA
Ultrasonic cleaner	KQ-250DE	Kunshan Ultrasonic Instrument Co., Ltd.
Oven	DHG-9030A	Luxikeji Co., Ltd.
Vacuum oven	DZF-150	Zhengzhou Changcheng Kegongmao Co., Ltd.
Furnance	SK-G10123 K	Tianjinshi Zhonghuanshiyandianlu Co., Ltd.
Centrifuge	TG16-II	Changsha Pingfan Yiqi Yibiao Co., Ltd.
Supercritical CO ₂ drying machine	HQG-1	Jiangsu Huaan Keyanyiqi Co., Ltd.
Simultaneous thermal analyzer	SDT Q600	TA Instruments
Automatic physical/chemical adsorption analyzer	Autosorb-iQ	Quantachrome
X-ray powder diffractometer	D8 Advance	Bruker
MSR rotator	AFMSRCE	PINE
Battery sealing machine	MSK-110	Hefei Kejing Cailiao Jishu Co., Ltd.
Glove box	Glove box system	OMNI-LAB
Electrochemical workstation	CHI 760C/D	Shanghai CHI
Battery testing system	CT-3008 W	NEWARE
X-ray photoelectron spectrometer	Axis Ultra	Kartos
Raman spectrometer	inVia	Renishaw
ICP-AES	Profile Spec	Leeman
SEM	S-4800	Hitachi
TEM	Tecnai T20	FEI
HRTEM	Tecnai F20	FEI
Field emission HRTEM	Tecnai F30	FEI

 Table 2.1
 Instruments list

2.1.5 Chemicals Used in Synthesis of 3D Porous Carbon

Chemicals used in synthesis of 3D porous carbon are listed in Table 2.5.

Chemical	Purity (%)	Manufacturer
Co(Ac) ₂ ·4H ₂ O	≥99.0	Xilong Scientific Co., Ltd.
Co(NO ₃) ₂ ·6H ₂ O	≥99.0	Xilong Scientific Co., Ltd.
$Zn(NO_3)_2 \cdot 6H_2O$	≥99.0	Xilong Scientific Co., Ltd.
2-Methylimidazole	98	Beijingouhekeji Co., Ltd.
CH ₃ OH	≥99.7	Beijing Tongguang Fine Chemicals Company
C ₂ H ₅ OH	≥99.7	Beijing Chemical Works

 Table 2.2
 Chemicals used in synthesis of N-doped nanoparticles

 Table 2.3
 Chemicals used in synthesis of core-shell metal oxide nanoparticles

Chemical	Purity	Manufacturer
$Co(NO_3)_2 \cdot 6H_2O$	≥99.0%	Xilong Scientific Co., Ltd.
Benzimidazole	98%	Beijingouhekeji Co., Ltd.
Sucrose $C_{12}H_{22}O_{11}$	AR	Sinopharm Chemical Reagent Beijing Co., Ltd.
SBA-15	6–11 nm	Shanghai Zhuorui Huagongkeji Co., Ltd.
H ₂ SO ₄	95.0–98.0%	Xilong Scientific Co., Ltd.
HNO ₃	65.0–68.0%	Xilong Scientific Co., Ltd.
HF	40%	Beijing Institute of Chemical Reagents
DMF	≥99.5%	Xilong Scientific Co., Ltd.
C ₂ H ₅ OH	≥99.7%	Beijing Chemical Works

2.2 Synthesis of N-Doped Carbon Nanoparticles

2.2.1 Synthesis of Co-MOF with Different Sizes

(1) Co-MOF of 300 nm

1.436 g of $Co(NO_3)_2$ and 3.244 g of 2-methylimidazole are dissolved in 100 mL methanol, respectively. The $Co(NO_3)_2$ solution is poured into the 2-methylimidazole solution under vigorous stirring. After 12 min the stirring is stopped followed by standing for 20 h. The purple product is centrifuged and washed with methanol for at least 3 times. After vacuum drying at 150 °C for 8 h, the final product is obtained.

(2) Co-MOF of 800 nm

The synthetic method of Co-MOF of 800 nm is the same as 300 nm except the reaction is carried out at 60 $^\circ\text{C}.$

		· · · · · · · · · · · · · · · · · · ·
Chemicals	Purity	Manufacturer
Co(NO ₃) ₂ ·6H ₂ O	≥99.0%	Xilong Scientific Co., Ltd.
2-Methylimidazole	98%	Beijing Ouhekeji Co., Ltd.
Graphite powder	200–325	Sinopharm Chemical Reagent Beijing Co., Ltd.
$K_2S_2O_8$	AR	Sinopharm Chemical Reagent Beijing Co., Ltd.
P ₂ O ₅	≥98.0%	Beijing Yili Fine Chemicals Co., Ltd.
KMnO ₄	≥99.5%	Beijing Chemical Works
H ₂ SO ₄	95.0–98.0%	Xilong Scientific Co., Ltd.
HCl	36.0–38.0%	Xilong Scientific Co., Ltd.
H ₂ O ₂	30%	Beijing Shemical Works
CH ₃ OH	≥99.7%	Beijing Tongguang Fine Chemicals Company
NH ₃ ·H ₂ O	25.0–28.0%	Beijing Tongguang Fine Chemicals Company

Table 2.4 Chemicals used in synthesis of hollow metal oxide nanoparticles

Table 2.5 Chemicals used in synthesis of 3D porous carbon

Chemical	Purity (%)	Manufacturer
$Al(NO_3)_3 \cdot 9H_2O$	≥99.0	Xilong Scientific Co., Ltd.
1,3,5-Benzenetricarboxylic acid	98	Beijing Ouhekeji Co., Ltd.
КОН	≥85.0	Xilong Scientific Co., Ltd.
HCl	36.0–38.0	Xilong Scientific Co., Ltd.
C ₂ H ₅ OH	≥99.7	Beijing Chemical Works

(3) Co-MOF of 1.7 μm

0.450 g of Co(NO₃)₂ and 5.500 g of 2-methylimidazole are dissolved in 12 ml of 60 °C water, respectively, which are mixed and kept stirring for 12 min. Afterwards, stirring is stopped followed by standing for 20 h. The final product is obtained following the method described in (1).

(4) Bulk Co-MOF

3.321 g of $Co(Ac)_2$ and 3.284 g of 2-methylimidazole are dissolved in 100 mL of ethanol, which is transferred to Teflon-lined autoclave and heated at 120 °C for 3 days. The product is centrifuged and washed with ethanol for 3 times. The final product is obtained after vacuum drying at 150 °C for 8 h.

2.2.2 Synthesis of Multi-component ZnCo-MOF

(1) Solid solution type ZnCo-MOF

0.744 g of Zn(NO₃)₂ and 0.728 g of Co(NO₃)₂ are dissolved in 100 mL methanol (solution A). 3.284 g of 2-methylimidazole is dissolved in another 100 mL of methanol (solution B). Solution A is poured into solution B under vigorous stirring, which is kept stirring for 15 min followed by standing for 24 h. The purple product is centrifuged and washed with methanol for 3 times. The final product is obtained after vacuum drying at 150 °C for 8 h.

(2) Core-shell Co-ZIF@ZnCo-MOF

0.728 g of $Co(NO_3)_2$ is dissolved in 50 mL of methanol (solution A), 3.284 g of 2-methylimidazole is dissolved in another 100 mL of methanol (solution B), and 0.744 g of $Zn(NO_3)_2$ is dissolved in another 50 mL of methanol (solution C). Solution A is poured into solution B under vigorous stirring. After 5 min, solution C is poured, followed by stirring for 10 min and standing for 24 h. The purple product is centrifuged and washed with methanol for 3 times. The final product is obtained after vacuum drying at 150 °C for 8 h.

2.2.3 Synthesis of N-Doped Carbon Nanomaterials

MOF precursors obtained in 2.21 and 2.22 are heated to 750 °C at a rate of 5 °C/min and maintained for 2 h, which is naturally cooled to room temperature.

2.3 Synthesis of Core-Shell Metal Oxide Nanoparticles

2.3.1 Synthesis of Ordered Porous Carbon Matrix

Ordered porous carbon matrix (CM) is synthesized according to a reported method [1]. 0.14 g of H_2SO_4 is added into 5 g of water, followed by addition of 1.25 g sucrose and slow addition of 1 g SBA-15. The mixture is stirred and heated in the oven at 100 and 160 °C for 6 h, respectively. Afterwards, the product is carbonized at 900 °C under vacuum and washed with 5 wt% HF and ethanol, followed by drying at 120 °C.

2.3.2 Zif-9@CM

CM is first modified by HNO₃: 100 mg of CM is added into 20 mL of HNO₃, which is heated to 80 °C for 5 h. Afterwards, the product is washed with water and ethanol, and then dried at 100 °C for 5 h.

0.210 g of Co(NO₃)₂ is dissolved into 20 mL of DMF, followed by addition of 0.050 g of modified CM, which is subjected to sonication for 5 min. Then 52 mL of DMF solution of benzimidazole (0.170 g) is poured, followed by stirring for 10 min. The mixture is transfer to Teflon-lined autoclave, and maintained at 130 °C for 48 h. After natural cooling to room temperature, the product is centrifuged at 2000 rpm to remove the ZIF-9 that is not loaded on CM. The above solution is centrifuged and washed with ethanol, followed by drying at 100 °C for 8 h to obtain the final product ZIF-9@CM.

2.3.3 Synthesis of Core-Shell Metal Oxide Nanoparticles

ZIF-9@CM is heated to 700 °C and maintained for 2 h under Argon atmosphere, which is naturally cooled to room temperature. The product is transferred to oven, and heated at 90 °C for 48 h to obtain the final product $Co@Co_3O_4@C$.

2.4 Synthesis of Hollow Metal Oxide Nanoparticles

2.4.1 Synthesis of Nitrogen-Doped Graphene Aerogel

(1) Synthesis of graphene oxide

Graphene oxide is synthesized through modified Hummers method [2, 3]: $K_2S_2O_8$ and 2.5 g of P_2O_5 were dissolved in 12 mL of concentrated H_2SO_4 . This solution was heated to 80 °C, followed by addition of 3 g of graphite powder. The mixture was kept at 80 °C for 4.5 h and then cooled down to room temperature. Next, 500 mL of DI water was added into the mixture. The diluted solution was kept overnight and then filtered and washed with DI water. The resulting product was dried in air overnight to make the pre-oxidized graphite powder. The powder was added into 120 mL of cold (0 °C) concentrated H_2SO_4 . Afterward, 15 g of KMnO₄ was added slowly under stirring during which the solution temperature was kept below 20 °C. Then, the mixture was stirred at 35 °C for 2 h, followed by slow addition of 250 mL of DI water in an ice bath to keep the temperature below 50 °C. The resulting mixture was stirred for another 2 h, and then 700 mL of DI water was added; thereafter 20 mL of 30% H_2O_2 was immediately injected into the mixture. The solution was kept for 12 h, and the supernatant was removed. The left solution was washed with 10% diluted HCl and 1 L of DI water. In the final step, GO dispersion was purified by dialysis for 7 days. The final concentration of the GO dispersion was around 15 mg/mL.

(2) Synthesis of nitrogen-doped graphene aerogel

The nitrogen-doped graphene hydrogel was synthesized through a hydrothermal process using NH_4OH as the chemical dopant. Typically, 2.5 mL of GO dispersion was diluted with 8 mL of DI water, followed by sonication for 2 h. Next, 10 mL of NH_4OH was added into this diluted GO dispersion. The mixture was stirred for 1 h and then sealed in a Teflon-lined autoclave. The reaction was carried out at 160 °C for 24 h to form hydrogel with a shape of cylinder. The resulting hydrogel was immersed in DI water, which was exchanged with fresh DI water several times to completely remove the residual NH_4OH . Finally, the DI water was exchanged with methanol.

2.4.2 Nitrogen-Doped Graphene Aerogel Supported Co-MOF

0.144 g of Co(NO₃)₂·6H₂O and 0.324 g of 2-methylimidazole was each dissolved in 10 mL of methanol. And then the former salt solution was poured into the latter ligand solution under vigorous stirring. After 60 s, stirring was stopped, and nitrogen-doped graphene hydrogel was added into the mixture, kept at room temperature for 24 h. Latter, the cylinder-like hydrogel, whose color became slightly purple, was took out and immersed into ethanol. The ethanol was exchanged with fresh ethanol several times in order to remove the residual reagent. Afterward, the resulting cylinder-like gel was dried using supercritical carbon dioxide, leading to the nitrogen-doped graphene aerogel supported Co-MOF.

2.4.3 Synthesis of Hollow Metal Oxide Nanoparticles

The nitrogen-doped graphene aerogel supported Co-MOF is heated and maintained at 750 °C for 2 h and naturally cooled to 100 °C, when the product is taken out.

2.5 Synthesis of 3D Porous Carbon

2.5.1 Synthesis of Metal–Organic Aerogel/Xerogel

1.42 g of Al(NO₃)₃ and 0.52 g of 1,3,5-benzenetricarboxylic acid are dissolved in 18 mL of ethanol, which is transferred to Teflon-lined autoclave and heated at 120 °C for 1 h. The resultant gel is dried through supercritical CO₂ drying to obtain metal–organic aerogel (MOA). For metal–organic xerogel (MOX), the gel is dried in oven at 80 °C for 12 h to get MOX.

2.5.2 Synthesis of 3D Porous Carbon from MOA

MOA is heated at 800 °C under Argon atmosphere for 5 h and naturally cooled to room temperature. Then the resultant product is washed with 3 M HCl for 3 times to remove the metal species, and then H_2O to remove the residual acid. The final product is obtained after drying at 120 °C under vacuum for 5 h.

2.5.3 Synthesis of Porous Carbon from MOX

MOX is heated at 800 °C under Argon atmosphere for 5 h and naturally cooled to room temperature. The resultant product is washed with 3 M HCl for 3 times to remove the metal species and then water to remove the residual acid. After drying at 120 °C under vacuum for 5 h, the product is mixed with KOH with weight ratio of 1:4, and then heated at 700 °C under Argon atmosphere for 1 h. The resultant product is washed with 3 M HCl for 3 times to remove the inorganic impurity and then water to remove the residual acid, followed by drying at 120 °C under vacuum for 5 h to obtain the final product.

2.6 Characterization of Materials

2.6.1 X-Ray Diffraction (XRD)

XRD analysis can reveal the phase components and their relative contents. Bruker D8 Advance diffractometer at 40 kV and 40 mA is used in this thesis.

2.6.2 Thermogravimetric Analysis (TGA)

TGA can reveal the weight change as a function of temperature, which can characterize the decomposition temperature or component content of materials. TA Instruments SDT Q600 analyzer under nitrogen or air is used in this thesis.

2.6.3 Energy Dispersive Spectroscopy (EDS)

EDS analysis can reveal the interaction between the excitation source and the sample, which can characterize the element content of the sample. Energy dispersive X-ray spectrometer attached to the SEM (Hitachi S4800) and TEM (FEI F30) is used in this thesis.

2.6.4 X-Ray Photoelectron Spectroscopy (XPS)

XPS can reveal the binding energy of the electron of the sample, which can characterize the element content and valence state of the atoms on the surface of sample. Kratos Axis Ultra Imaging Photoelectron Spectrometer using the monochromatic Al K α line (1486.7 eV) is used in this thesis.

2.6.5 Inductively Coupled Plasma (ICP)

ICP analysis can characterize the element content of sample. Profile Spec inductively coupled plasma emission spectrometer of Leeman is used in this thesis.

2.6.6 Raman Spectroscopy

Raman spectroscopy is based on Raman scattering that leads to the energy shift of the laser photons, which can used to identify molecules and study chemical bonding. Renishaw inVia Raman spectrometer is used in this thesis.

2.6.7 Nitrogen Sorption Measurement

Nitrogen sorption measurement characterizes the nitrogen uptake at different pressure at 77 K, which can reveal the specific surface area and pore structure of sample. Quantachrome Autosorb-iQ gas adsorption analyzer is used in this thesis.

2.6.8 Scanning Electron Microscope (SEM)

SEM measurement can form images of the sample by scanning the surface with an electron beam. The electron beam can interact with atoms of the sample, generating signals that contain information about the topography and composition. Hitachi S-4800 SEM is used in this thesis.

2.6.9 Transmission Electron Microscope (TEM)

TEM measurement forms images by using an electron beam to transmit through the sample. FEI Tecnai T20, F20, and F30 are used in this thesis.

2.7 Electrochemical Measurements

2.7.1 ORR Measurements

(1) Working electrode

Typically, 2 mg of catalyst is dispersed in 2 mL of ethanol by sonication, then 20 μ L of the dispersion is drop-wise added on the surface of a clean glassy carbon electrode (diameter 5 mm), followed by addition of 5 μ L of 0.1 wt% Nafion solution. The catalyst loading is about 0.1 mg/cm².

(2) Electrochemical testing

Electrochemical testing is carried out in a three-electrode system with catalystmodified glassy carbon electrode as working electrode, Pt foil as counter electrode, and KCl-saturated Ag/AgCl electrode as reference electrode. The electrolyte is 0.1 M KOH or HClO₄, which is bubbled with oxygen gas for at least 30 min before testing. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) are obtained at scanning rate of 50 and 10 mV/s, respectively.

The potentials are transferred to reversible hydrogen electrode (RHE): for example, CV curve is tested using Pt wire as working electrode and KCl-saturated Ag/AgCl electrode as reference electrode in 0.1 M HClO₄ (Fig. 2.1). It can be obtained that $V_{RHE} = V_{Ag/AgCl} + 0.265$ V.

(3) ORR performance evaluation

A typical LSV curve is shown in Fig. 2.2. The LSV curve can be divided into three region: (a) in kinetic controlled region, the current density almost remain unchanged; (b) in mixed kinetic-diffusion controlled region, the current density increases dramatically as the overpotential increases; (c) in diffusion controlled region, the reaction



rate is limited by the mass diffusion rate, resulting in a relatively stable current density.

Onset potential (E_{onset}) and half-wave potential ($E_{1/2}$) are usually used to evaluate ORR performance of a catalyst: the more positive they are, the more active the catalyst is. Kinetic-limiting current density $J_{\rm K}$ is also an important parameter for ORR catalyst, which can be obtained using Koutechy–Levich equation (Eq. 2.1).

$$1/J = 1/J_{\rm K} + 1/J_{\rm L} = 1/J_{\rm K} + 1/(B\omega^{1/2})$$
(2.1)

where J is the measured current density, J_K and J_L are the kinetic- and diffusionlimiting current densities, ω is the angular velocity (rad s⁻¹). At the same potential, the higher the J_K is, the higher the intrinsic activity of the catalyst is. J_K of Pt-based catalysts are always compared at 0.9 V [6]. Before calculating J_K , the capacitive current should be eliminated to obtain the true J_K .



Fig. 2.3 Pathways of ORR on the surface of catalysts. Figure adapted from [5] with permission of the John Wiley and Sons

Electron transfer number (*n*) is also an important criterion, which should ideally be 4 for efficient ORR electrocatalysis. Several steps are involved during ORR (Fig. 2.3) [7–9]: The oxygen molecule first diffuses to the electrode surface, forming an adsorbed oxygen molecule (O_2^* , where * denotes a site on the surface). After that, there are three pathways for the reduction of O_2^* , which are distinguished by the sequence during the O–O bond cleavage step. The first pathway, named the dissociation pathway, involves the O–O bond breaks directly to form an O* intermediate, which is reduced to OH* and then to H_2O^* . The second pathway is the associative pathway where OOH* is first formed from O_2^* and then the O–O bond is cleaved, forming O* and OH* intermediates. The third pathway is the peroxo pathway, where O_2^* is reduced to OOH* and to HOOH* before the O–O bond cleavage [5].

n can be calculated through Eq. 2.2 using RDE data or Eq. 2.3 using RRDE data.

$$J_{\rm L} = B\omega^{1/2} = 0.62nFC_0 (D_0)^{2/3} (\upsilon)^{-1/6} \omega^{1/2}$$
(2.2)

$$4I_{\rm d} = n \left(I_{\rm d} + I_{\rm r} / N \right) \tag{2.3}$$

where ω is the angular velocity, n is transferred electron number, F is the Faraday constant, C₀ is the bulk concentration of O₂, υ is the kinematic viscosity of the electrolyte, I_d is disk current, I_r is ring current, and N is current collection efficiency of the Pt ring.

2.7.2 Battery Test

(1) Assembly of coin-cell

The working electrode is prepared using active material (80 wt%), Super P (10 wt%) and poly(vinylidene diffuoride) (PVDF, 10 wt%), which are dissolved in N-methyl pyrrolidone. The resultant slurry is then spread onto stainless steel, pressed, and dried under vacuum at 80 °C for 8 h. Coin batteries are assembled in an argon-filled glovebox with the as-prepared material as cathode, metallic lithium as anode, 1 M LiPF₆ in EC:DMC (1:1 in volume) as electrolyte, and Whatman GF/D borosilicate glass-fiber sheets as the separator.

In the case of 3D porous carbon materials for Li–S batteries, the carbon materials are mixed with S powder at weight ratio of 1:1 and sealed in a glass tube, which is heated at 155 and 300 °C for 12 h, respectively. 80 wt% of the resultant active material, 10 wt% of Super P, and 10 wt% of PTFE is added into isopropanol, which is sonicated for 3 h. The slurry is added onto stainless steel and dried under vacuum at 60 °C for 12 h. Coin batteries are assembled in an argon-filled glovebox with the as-prepared material as cathode, metallic lithium as anode, 1 M LiTFSI solution in 1,3-dioxolane (DOL) and 1,2-dimethoxyetahne (DME) (1:1 volume ratio) as the electrolyte, and Whatman GF/D borosilicate glass-fiber sheets as the separator.

Coin cells were tested at a current density of 400 mAg^{-1} within a voltage range of 1.0–3.0 V versus Li/Li⁺ using Neware battery test system.

(2) Coin cell test

For N-doped carbon materials, coin cells were tested at a current density of 50, 100, 200, 300, and 500 mA/g within a voltage range of 0.005–3.0 V versus Li/Li⁺ using Neware battery test system.

For 3D porous carbon materials, coin cells were tested at a current density of 400 mA/g within a voltage range of 1.0-3.0 V versus Li/Li⁺ using Neware battery test system.

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Chapter 3 Formation of N-Doped Carbon Nanomaterials for ORR Catalysis and Li Storage



3.1 Introduction

Caron materials have been widely used as sorption, electrode, and catalyst support materials due to the low density, high surface area, high stability and excellent conductivity. Nitrogen can be doped in carbon materials to modify the electron structure of carbon atoms to boost their electrochemical performances (e.g. ORR catalysis) [1]. Using MOFs as precursors, N-doped carbon materials with high surface area and uniformly distributed N can be facilely fabricated [2]. Before this work, there is one report on MOF-derived carbon material for ORR catalysis. However, the precursor MOFs in this report were of large particle sizes, resulting in limited mass diffusion [3]. In this chapter, nano-sized MOFs are synthesized, which are then carbonized to form N-doped carbon materials with very small size for efficient electrochemical energy storage and conversion.

3.2 Synthesis of N-Doped Carbon Nanoparticles

3.2.1 Formation of Co-MOFs of Different Particle Sizes

Co-MOF (or ZIF-67) is composed of Co^{2+} ions and 2-methylimidazole (Fig. 3.1) [4]. Each Co^{2+} ion is coordinated with four nitrogen atoms from the 2-methylimidazle ligands to form tetrahedron. These tetrahedral units are connected with the ligands to form a SOD topology. It has cage-like pores with a pore diameter of 1.16 nm and window diameter of 0.34 nm.

XRD patterns show that the Co-MOFs are successfully synthesized in different conditions, all of which have high crystallinity and purity (Fig. 3.2). SEM and TEM images of Co-MOF synthesized with methanol as solvent at room temperature has an uniform particle size of ~300 nm (Fig. 3.3).

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Fig. 3.1 Structural model of Co-MOF. Figure adapted from [5] with permission of the Royal Society of Chemistry





The particle size can be tuned by changing the reaction condition: Co-MOF of ~800 nm can be synthesized at 60 °C (Fig. 3.4a), Co-MOF of ~1.7 μ m can be synthesized using water as solvent at 60 °C (Fig. 3.4b), Co-MOF of bulk size can be synthesized through solvothermal method (Fig. 3.4c1–2).

3.2.2 Formation of Multi-component ZnCo-MOF

When Co^{2+} is replaced completely by Zn^{2+} , another MOF, Zn-MOF (ZIF-8), can be synthesized. Zn-MOF has the same SOD topology with ZIF-67. It is possible to partially replace the Co^{2+} of ZIF-67 with Zn^{2+} to prepare multi-component ZnCo-MOF with tunable compositions and properties.

Different types of multi-component ZnCo-MOF are shown in Fig. 3.5. Uniform distribution of both Co^{2+} and Zn^{2+} can lead to solid solution type ZnCo-MOF, while non-uniform distribution can lead to core-shell type ZnCo-MOF.



Fig. 3.3 Morphology of Co-MOF of 300 nm: **a–b** SEM, **c** TEM images and **d** structural models. Figure adapted from [5] with permission of the Royal Society of Chemistry

The formation pattern of multi-component ZnCo-MOF should be figured out in order to realize the controllable synthesis of multi-component ZnCo-MOF with different structures. The formation process of Co-MOF and Zn-MOF is first revealed using digital photograph (Fig. 3.6). In the case of ZIF-67, the color of the reactant mixture immediately becomes dark blue after mixing two precursors, and then becomes purple and cloudy after 1 min. For ZIF-8, the mixture is transparent until 2 min, when the mixture gradually becomes milky. The different phenomena may be due to different growth kinetics of these two MOFs.

In situ UV–Vis–NIR experiments are carried out to reveal the growth kinetics of Co-MOF and Zn-MOF [7–9]. The solvent window is found out to be 250–1100 nm, within which no signal from the solvent methanol may interfere with the observation. A wavelength of 360 nm is selected because significant and similar signal can be obtained for colloidal suspensions of Co-MOF and Zn-MOF, while no absorbance from the precursors is presented (Fig. 3.7).



Fig. 3.4 SEM images of Co-MOF of different sizes: a 800 nm, b 1.7 μ m, and c bulk. Figure adapted from [5] with permission of the Royal Society of Chemistry



Fig. 3.5 Structural model of single- and multi-component MOFs. Figure adapted from [6] with permission of the John Wiley and Sons



Fig. 3.6 Digital photographs of, **a** Co-MOF and **b** Zn-MOF illustrating the color change in 20 min. Figure adapted from [6] with permission of the John Wiley and Sons

Fig. 3.7 Absorption spectra of 2-mIM, Zn(NO₃)₂, Co(NO₃)₂, Co-MOF and Zn-MOF. Figure adapted from [6] with permission of the John Wiley and Sons





Fig. 3.8 a Kinetic curves of Co-MOF and Zn-MOF formation as a function of time by in situ optical monitoring; **b** Kinetic curves of multi-component MOF formation as a function of time by in situ optical monitoring. Figure adapted from [6] with permission of the John Wiley and Sons

The kinetic curves of Co-MOF and Zn-MOF are shown in Fig. 3.8a, indicating different growth kinetics of these two MOFs. Formation of Zn-MOF follows a typical two-step pattern. After a short inducing period of 1 min the first step appears with weak scattering. From 4 min on the second step appears where the kinetic curve increases steadily in a nearly linear way, until reaction reaches equilibrium at 7.5 min. Unlike Zn-MOF, Co-MOF exhibits a much quicker one-step growth kinetic: the scattering signal dramatically increases from 1 min, and the reaction completes within 2 min.

(1) Solid solution type multi-component MOFs

Formation of multi-component MOFs can also be investigated through the same method. Individual nucleation of different MOFs may happens due to the different growth rate of these two MOFs, based on which the kinetic curve can be calculated to be the dashed line shown in Fig. 3.8b. However, the real measured kinetic curve is quite different from the calculated curve, because the nucleation of these two MOFs influence each other during the formation of solid solution type Zn-Co-MOF.

Solid solution type $Zn_{0.5}Co_{0.5}$ -MOF is characterized (Fig. 3.9). XRD patterns of the solid solution type ZnCo-MOFs show same characteristic peaks of Zn-MOF and Co-MOF, indicating the same crystalline structure. SEM and TEM images of Zn_{0.5}-Co_{0.5}-MOF show regular morphology of rhombic dodecahedron with a particle size of ~100 nm. HAADF-STEM image and the related elemental mapping prove the uniformly distribution of Co and Zn throughout the nanocrystal.

The Zn:Co ratio of the solid solution ZnCo-MOF can be tuned by adjusting the Zn:Co cation ratio of the reactant. SEM and TEM images of these MOFs show uniform nanoparticles of rhombic dodecahedron shape (Fig. 3.10a, b). It is worth noting that the particle size decreases from 275 nm to 65 nm as the Zn:Co ratio increases from 1:9 to 9:1. XRD patterns indicate the high purity and crystallinity of the as-prepared ZnCo-MOFs (Fig. 3.10c). Kinetic curves of the ZnCo-MOFs changes gradually from the shape of Zn-MOF to Co-MOF as the Zn:Co ratio deceased (Fig. 3.10d).



Fig. 3.9 Characterization of solid solution type $Zn_{0.5}Co_{0.5}$ -MOF: **a** SEM, **b** TEM, and **c** HAADF-STEM images; **d**–**e** EDS elemental mapping. Figure adapted from [6] with permission of the John Wiley and Sons

(2) Core-shell multi-component MOFs

The aforementioned solid solution multi-component MOFs are fabricated by addition of both Co^{2+} and Zn^{2+} cation at the beginning of the reaction. It is found that if the Zn^{2+} is introduced in the middle stage of the reaction of Co-MOF (the fifth minute), multi-component MOFs with core-shell structure can be obtained (Co-MOF@ZnCo-MOF). HAADF-STEM images of Co-MOF@ZnCo-MOF show distinct core-shell structure of the nanocrystals with a core diameter of ~160 nm and shell thickness of ~95 nm (Fig. 3.11). The EDS elemental mapping confirms the core-shell structure, indicating that the core is Co-MOF while the shell is composed of ZnCo-MOF.

The core diameter can be tuned by adjusting the time when Zn^{2+} is added (Fig. 3.11d). The core diameters are 100, 145, and 210 nm for Co-MOF@ZnCo-MOF synthesized by adding Zn^{2+} into the solution after 2, 3, and 10 min, respectively.

Nitrogen sorption measurements show that all of the solid solution type MOFs exhibit typical type I isotherms, similar to those of Co-MOF and Zn-MOF (Fig. 3.12). The high nitrogen uptake at low relative pressure indicates the existence of micropores, while the increasing uptake at high relative pressure reveals the existence of macropores. The BET surface areas, total pore volumes, and micropore volumes of the aforementioned MOFs are shown in Table 3.1.



Fig. 3.10 Characterization of solid solution MOFs with different Zn:Co ratio: a SEM, b TEM images, c XRD patterns and d Kinetic curves. Figure adapted from [6] with permission of the John Wiley and Sons

It shows that all the multi-component MOFs are of high surface areas and porosities, which may benefit the synthesis of MOF-derived materials with high surface areas and porosities.

3.2.3 Formation of N-Doped Carbon Nanoparticles

N-doped carbon nanoparticles (DCN) can be synthesized through pyrolysis of the aforementioned MOFs at high temperature under Ar atmosphere. Figure 3.13a–c show SEN images of DCN obtained by pyrolysis of Co-MOF, indicating uniform nanoparticles of ~300 nm. XRD pattern of DCN confirms the existence of both metallic Co and carbon (Fig. 3.13d). TEM images of DCN show that unltrafine Co nanoparticles are embedded in the carbon matrix (Fig. 3.13e–h). These Co nanoparticles are derived from the Co node of Co-MOF during high temperature pyrolysis. It is worth noting that the Co nanoparticles are wrapped by few layers of graphitic carbon, which form due to the catalytic effect of the Co nanoparticles at high temperature.



Fig. 3.11 Characterization of core-shell Co-MOF@ZnCo-MOF: **a**–**b** HAADF-STEM images; **c**–**d** EDS elemental mapping of Co-MOF@ZnCo-MOF with different core diameters. Figure adapted from [6] with permission of the John Wiley and Sons

The content of metallic Co in DCN is measured by TGA (Fig. 3.14a). 51.5% of the relative weight (Co_3O_4) is remained in air atmosphere, revealing a Co weight percentage of 37.8%, which is higher than that of the precursor Co-MOF. XPS analysis shows atomic content of Co and N of 2.56 and 6.4%, respectively (Fig. 3.14b). The N atoms originate from the N of the ligands of Co-MOF, which are doped into the carbon matrix during high temperature pyrolysis. These doped N atoms are supposed to be active for electrochemical catalysis of ORR [1].

After pyrolysis, DCN to some extent inherits the porosity of Co-MOF, with BET surface area of $386 \text{ m}^2/\text{g}$ (Fig. 3.15a). The high nitrogen uptake at low relative



Fig. 3.12 Nitrogen sorption isotherms of a solid solution type and b core-shell type MOFs

Sample	BET surface area	Total pore volume	Micropore volume
Zn-MOF	1620	0.64	0.59
Zn _{0.9} Co _{0.1} -MOF	1702	0.83	0.61
Zn _{0.7} Co _{0.3} -MOF	1595	0.99	0.57
Zn _{0.5} Co _{0.5} -MOF	1671	0.99	0.60
Zn _{0.3} Co _{0.7} -MOF	1586	0.79	0.56
Zn _{0.1} Co _{0.9} -MOF	2086	0.89	0.73
Co-MOF	1885	0.70	0.62
Co-MOF@ZnCo-MOF_2 min	1882	0.81	0.64
Co-MOF@ZnCo-MOF_3 min	1770	0.69	0.62
Co-MOF@ZnCo-MOF_6 min	1824	0.71	0.64
Co-MOF@ZnCo-MOF_10 min	1970	0.76	0.69

 Table 3.1
 Summary of the BET surface areas, total pore volumes, and micropore volumes of the aforementioned MOFs

pressure indicates the existence of micropores, while the hysteresis loop reveals the presence of mesopores. The pore size distribution of DCN is shown in Fig. 3.15b, exhibiting micropores centered at 0.9–1.1 nm, mesopores of 2.0–5.0 nm, and micropores larger than 26 nm.

3.3 ORR Activity of N-Doped Carbon Nanoparticles

3.3.1 Electrochemical Measurement

(1) CV and LSV curves in acidic solution

Figure 3.16 shows the CV curves of DCN measured in Ar-/O₂-saturated 0.1 M $HCIO_4$. A pronounced cathodic peak at 0.67 V is observed for O₂-saturated condition,



Fig. 3.13 Characterization of DCN: a-c SEM images; d XRD pattern; e-f TEM images; g HRTEM image; h SAED pattern. Figure adapted from [5] with permission of the Royal Society of Chemistry



Fig. 3.14 a TGA curves of Co-MOF after pyrolysis and Co-MOF in air; **b** XPS spectrum of Co-MOF after pyrolysis. Figure adapted from [5] with permission of the Royal Society of Chemistry

which can be assigned to the reduction of O₂, indicating the electrochemical activity for ORR of DCN.

Figure 3.17 shows the LSV curves of DCN and commercial Pt/C. The onset potential and half-wave potential of DCN are 0.86 and 0.71 V, respectively, which are near the top of the reported earth-abundant electrocatalysts (Table 3.2). The limiting current density of DCN is comparable to that of Pt/C, indicating excellent ORR activity. Because of the facile synthesis of DCN, it shows a promising prospect in the field of ORR electrocatalysis.



Fig. 3.15 a Nitrogen sorption isotherms of Co-MOF before and after pyrolysis; **b** Pore size distribution of Co-MOF after pyrolysis (Inset: pore size distribution of Co-MOF). Figure adapted from [5] with permission of the Royal Society of Chemistry



(2) Electron transfer number

The ideal electron transfer number for efficient ORR is 4. LSV curves measured at different rotation rate are used to calculate the electron transfer number of DCN (Fig. 3.18a). The Koutechy-Levich plots and the corresponding electron transfer number of DCN are shown in Fig. 3.18b, indicating efficient 4-electron pathway under the catalysis of DCN.

3.3.2 Influence of the Particle Size on ORR Performance

DCN of different particle sizes can be synthesized by adjusting the reaction condition (Fig. 3.19).



Fig. 3.17 LSV curves of DCN and commercial Pt/C at 1600 rpm. Figure adapted from [5] with permission of the Royal Society of Chemistry

Sample	Electrolyte	Onset potential (V)	Half-wave potential (V)	Reference
DCN	0.1 M·HClO ₄	0.86	0.71	This work
N–CX	0.5 M·H ₂ SO ₄	0.81	0.65	[10]
Co _{0.5} Mo _{0.5} O _y N _z /C	0.1 M·HClO ₄	0.645	0.413	[11]
CoP-CMP800	0.5 M·H ₂ SO ₄	0.74	0.64	[12]
C–N–Co	0.5 M·H ₂ SO ₄	0.87	0.79	[13]
C–N–Fe	0.5 M·H ₂ SO ₄	0.84	0.73	[13]
1–750	0.1 M·HClO ₄	0.83	0.68	[3]
Co _{1-x} S/RGO	0.5 M·H ₂ SO ₄	0.80	-	[14]

Table 3.2 Comparison of ORR performances of electrocatalysts in acidic solution

Figure adapted from [5] with permission of the Royal Society of Chemistry

LSV curves of DCN of different particle sizes are shown in Fig. 3.20. As the particle size decreases, the ORR performance is improved. The DCN of the smallest particle size (300 nm) has the highest limiting current density and most positive half-wave potential.

The electron transfer numbers of DCN of different particle sizes are shown in Fig. 3.21a. As the particle size decreases, the electron transfer number increases and approaches to 4, indicating more efficient pathway for DCN of smaller particle size. Also, the J_k increases as the particle size decreases, revealing higher intrinsic activity for DCN of smaller particle size (Fig. 3.21b).

It shows that DCN of smaller size exhibits higher ORR activity. The chemical compositions of DCN of different sizes are almost the same. The higher performance may be attributed to the higher surface area and porosity of smaller DCN. Figure 3.22 shows the nitrogen sorption isotherms and the corresponding pore size distributions



Fig. 3.18 a LSV curves at different rotation rate and **b** the corresponding electron transfer number of DCN. Figure adapted from [5] with permission of the Royal Society of Chemistry



Fig. 3.19 Schematic illustration of synthesis of DCN of different particle sizes. Figure adapted from [5] with permission of the Royal Society of Chemistry

of DCN of different particle sizes. The BET surface area decreases from 386 to 165 m²/g as the particle size increases from 300 nm to bulk size. The pore size distributions of DCN of different particle sizes are similar, but higher porosity is presented by DCN of smaller size.



Fig. 3.20 LSV curves of DCN of different particle sizes. Figure adapted from [5] with permission of the Royal Society of Chemistry



Fig. 3.21 a Electron transfer numbers and b J_k of DCN of different particle sizes. Figure adapted from [5] with permission of the Royal Society of Chemistry

It can be concluded that DCN derived from MOF with smaller particle size has more exposed active sites and more facile mass transport, leading to higher ORR activity.

3.3.3 Influence of Heating Temperature

The heating temperature plays an important role on the ORR performance of DCN. Figure 3.23 shows LSV curves of DCN obtained at different temperature. The optimum temperature is found to be 750 °C, with the most positive half-wave potential and highest limiting current density.



Fig. 3.22 a Nitrogen sorption isotherms and b the corresponding pore size distributions of DCN of different particle sizes. Figure adapted from [5] with permission of the Royal Society of Chemistry



Nitrogen sorption isotherms of DCN obtained at different temperature are shown in Fig. 3.24. The BET surface areas are 327, 353, 386, 348, and 461 m^2/g for DCN pyrolyzed at 600, 700, 750, 800, and 900 °C. It can be seen that the specific surface area is not a key factor that influences the ORR performance.

XPS analysis of DCN pyrolyzed at different temperature is carried out to Fig. out the chemical composition differences. The results are shown in Table 3.3. As the temperature increases, the N content decreases while the C content increases, which may be due to the loss of the N atoms at elevated temperature.

There are many type of N atoms that doped into carbon layers, including pyridinic N, pyrrolic N, graphitic N, and oxidized N (Fig. 3.25a) [15]. XPS N 1s spectra of DCN reveal 4 types of N, including pyridinic N (398.9 eV), pyrrolic N (400.4 eV), graphitic N (401.3 eV), and oxidized N (403.8 eV). It shows that the graphitic N content increases as the pyrolytic temperature increases [16]. It has been reported that the pyridinic and graphitic N are active towards ORR [17]. The total atomic percentage of pyridinic and graphitic N of DCN pyrolyzed at 900 °C is the highest,



Fig. 3.24 Nitrogen sorption isotherms of DCN obtained at different temperature. Figure adapted from [5] with permission of the Royal Society of Chemistry

Temperature (°C)	C (at%)	N (at%)	Co (at%)
600	74.77	13.87	3.96
700	86.31	6.40	2.56
900	90.69	2.91	1.19

 Table 3.3 Chemical composition of DCN obtained at different temperature

Figure adapted from [5] with permission of the Royal Society of Chemistry

however, the N content in the whole sample is low, therefore an optimum pyrolytic temperature is found to be 750 $^{\circ}$ C.

3.3.4 Influence of the Composition of MOF Precursors

The role of the Co species of the catalysts is investigated by tuning the Co content with the introduction of Zn^{2+} . Solid solution type ZnCo-MOF (Zn:Co = 1:1) is synthesized and then carbonized to prepare DCN. The LSV curve of the resultant DCN is shown in Fig. 3.26, indicating a poorer ORR performance after introduction of Zn. The reduced activity may be attributed to the lower content of graphitic N, which is formed under the catalysis of Co at elevated temperature.

The Co plays an important role on the formation of highly active DCN. Co can not only catalyze the formation of graphitic N, but also generate active Co–N–C sites.



Fig. 3.25 a Structural model of N-doped carbon layer; b-d High resolution XPS N 1s spectra of DCN obtained at different temperature. Figure adapted from [5] with permission of the Royal Society of Chemistry



HClO₄



3.4 N-Doped Carbon Nanoparticles for Li Storage

3.4.1 Charge-Discharge Curves of N-Doped Carbon Nanoparticles

The charge-discharge curves of N-doped carbon nanoparticles are shown in Fig. 3.27. A platform can be observed at 1.0 V in the first discharge curve, which can be attributed to the formation of SEI film that leads to the irreversible loss of capacity. From the second cycle, the capacities remain steady, indicating excellent cycling stability.

3.4.2 Cycling and Rate Performances of N-Doped Carbon Nanoparticles

The uniform particle size of nanoscale can promote the stability of the N-doped carbon nanoparticles. Figure 3.28 shows cycling performances of N-doped carbon nanoparticles and bulk particles. For nanoparticles, capacity of 643 mAh/g can remains after 50 cycles, while only 310 mAh/g survives in the case of bulk particles.

Rate performances of N-doped carbon nano/bulk particles are shown in Fig. 3.29. For nanoparticles, reversible low capacity loss is observed at high current densities, while irreversible high capacity loss is observed in the case of bulk particles.

According to the aforementioned results, it can be concluded that N-doped carbon nanoparticles exhibit high capacity and good cycling stability, which is due to the particle size of nanoscale that promote the Li⁺ transport.



3.5 Summary

In this chapter, nanoscale MOFs are synthesized and employed in electrochemical catalysis of ORR. Co-MOF of uniform particle size of 300 nm is successfully synthesized at room temperature. For comparison, Co-MOFs of different particle sizes are also synthesized by adjusting the reaction conditions. Also, the growth kinetics of Co-MOF and Zn-MOF are investigated through an in situ optical method, based on which solid solution and core-shell typed ZnCo-MOFs are successfully designed and synthesized.

N-doped carbon nanoparticle can be fabricated through simple heat treatment of Co-MOF at 750 °C, which inherits the uniform morphology and high porosity of the precursor. It shows excellent electrocatalytic ORR performance in acidic solution, which is near the top of the reported earth-abundant electrocatalysts. The influence of heating temperature, particle size, and composition on the ORR performance of DCN is investigated. It is found that the graphitic and pyridinic N and the Co are of great importance for efficient ORR electrocatalysis.

DCN also exhibits desirable Li storage performance, with high reversible capacity of 643 mAh/g, excellent cycling stability, and good rate performance. It is found that DCN of smaller particle size shows better Li storage performance due to the more facile mass transport.

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Chapter 4 Formation of Core-Shell Metal Oxide Nanoparticles for Oxygen Reduction



4.1 Introduction

Metal oxides are promising alternatives to Pt-based electrocatalysts for ORR due to their facile synthesis and high stability under alkaline and oxidative conditions [1]. However, the large band gap (resulting in low electrical conductivity) and weak adsorption of oxygen on the surface of metal oxides hinder their electrocatalytic performances for ORR [2, 3]. Great efforts have been devoted to constructing nanostructured metal oxides to improve the ORR catalytic performance [4]. In this chapter, a MOF induced strategy leading to formation of unique core-bishell metal oxide nanoparticles embedded in a highly ordered porous carbon matrix was proposed. The rationally designed electrocatalyst exhibited efficient and durable electrocatalytic performance towards ORR due to the facile electron and mass transport.

4.2 Formation of Core-Shell Metal Oxide Nanoparticles

4.2.1 Characterizations of Precursors and the Final Product of Metal Oxide Nanoparticles

(1) ZIF-9/ordered porous carbon matrix composite (ZIF-9@CM)

ZIF-9 is constructed with cobalt ions and benzimidazole (Fig. 4.1) [5]. Cobalt nodes are coordinated with 4 nitrogen atoms of benzimidazoles to form tetrahedron, which are connected by benzimidazoles to form sodalite topological structure. ZIF-9 possesses small cage-like pores with diameters of 0.43 nm. Similar to ZIF-67, ZIF-9 exhibits high stability.

The carbon substrate CM is a typical ordered porous carbonaceous material [7]. As shown in Fig. 4.2, CM possesses open and ordered pore structure with specific surface area and pore diameter of $1340 \text{ m}^2/\text{g}$ and $\sim 7.1 \text{ nm}$, respectively.

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Fig. 4.1 Structure of ZIF-9. Figure adapted from [6] with permission of the Royal Society of Chemistry



Fig. 4.2 Characterizations of CM: a Structural model; b TEM image; c Nitrogen adsorption and desorption isotherms and d corresponding pore size distribution. Figure adapted from [6] with permission of the Royal Society of Chemistry



Fig. 4.3 XRD patterns of ZIF-9, CM, and ZIF-9@CM. Figure adapted from [6] with permission of the Royal Society of Chemistry



Fig. 4.4 Digital photographs of **a** ZIF-9, **b** CM, and **c** ZIF-9@CM. SEM images of **d** ZIF-9, **e** CM, and **f** ZIF-9@CM, **g** SEM image and the corresponding elemental mapping of ZIF-9@CM. Figure adapted from [6] with permission of the Royal Society of Chemistry

ZIF-9@CM was first characterized through powder X-ray diffraction (XRD, Fig. 4.3). The peaks of the XRD pattern of ZIF-9@CM match well with those of asprepared ZIF-9 and simulation result, indicating that ZIF-9 was successfully loaded in CM. The XRD peaks of CM are not obvious for ZIF-9@CM due to the relatively low intensity.

As shown in Fig. 4.4, pristine ZIF-9 are purple crystals (Fig. 4.4a, d) while the carbon substrate CM are black rod-like particles (Fig. 4.4b, e). ZIF-9@CM shows a color of dark purple, a combination of the colors of ZIF-9 and CM (Fig. 4.4c). SEM images show that the morphology of ZIF-9@CM is similar to that of CM (Fig. 4.4f). The EDS analysis shows that carbon and nitrogen are uniformly distributed in ZIF-9@CM, revealing that ZIF-9 was uniformly grown in CM.



Fig. 4.5 a Nitrogen adsorption and desorption isotherms and b corresponding pore size distribution of ZIF-9@CM. Figure adapted from [6] with permission of the Royal Society of Chemistry

Nitrogen sorption measurements show that pristine ZIF-9 adsorbs negligible nitrogen with specific surface area and pore volume of 9 m^2/g and 0.02 cm³/g, respectively. In contrast, ZIF-9@CM exhibits obvious nitrogen uptake with specific surface area and pore volume of 313 m^2/g and 0.35 cm³/g, respectively (Fig. 4.5). The shapes of the nitrogen sorption isotherms of ZIF-9@CM are similar to those of CM, indicating similar pore structure. The micropores and mesopores of ~1.0 and ~4.8 nm respectively may result from gaps and pores between two phases of the composite.

(2) Core-shell metal oxide nanoparticles

After pyrolysis and mild oxidation, ZIF-9@CM was converted into core-bishell metal oxide nanoparticles encapsulated in CM (denoted as $Co@Co_3O_4@C-CM$). XRD pattern of $Co@Co_3O_4@C-CM$ exhibits characteristic peaks of C, Co, and Co_3O_4 (Fig. 4.6a). The sharp peak of 26.1° originated from the carbon shell with high graphitization degree that was derived from the benzimidazole ligands under the catalysis of the metallic cobalt core at high temperature, similar to the formation of CNTs promoted by transition metals [8]. The broad peaks of Co and Co_3O_4 indicate that these two phases are of nano-sizes.

The chemical composition of the surface of $Co@Co_3O_4@C-CM$ was characterized by XPS analysis. The full XPS spectrum confirms the existence of C, Co, N, and O (Fig. 4.6b). The N comes from the decomposition of the benzimidazole linkers, which is mainly located in the carbon shell of the core-bishell nanoparticles with a content of 1.72 at%. The high-resolution XPS spectrum of N shows the existence of pyridinic (398.9 eV), pyrrolic (400.4 eV), and oxidized (403.8 eV) nitrogen in the C shell (Fig. 4.6c) [9, 10], among which the pyridinic nitrogen has been proved the most active for electrocatalysis of ORR [11]. The high-resolution of Co shows two sharp peaks, a high energy peak at ~795.7 eV (Co $2p_{1/2}$) and a low energy peak at ~780.3 eV (Co $2p_{3/2}$) with energy difference of ~15 eV, and two weak satellite peaks (marked by S), indicating the coexistence of Co²⁺ and Co³⁺ species in Co@Co₃O₄@C-CM (Fig. 4.6d) [12].



Fig. 4.6 Characterizations of $Co@Co_3O_4@C-CM$: a XRD pattern, b full XPS spectrum, c highresolution XPS spectrum of N1s, and d high-resolution XPS spectrum of Co2p of $Co@Co_3O_4@C-CM$. Figure adapted from [6] with permission of the Royal Society of Chemistry

The pore structure of $Co@Co_3O_4@C-CM$ was characterized by nitrogen sorption measurements. $Co@Co_3O_4@C-CM$ shows typical IV isotherms according to IUPAC definition with a specific surface area of 616 m²/g (Fig. 4.7). The high nitrogen adsorbed volume at low relative pressure reveals the micropores in $Co@Co_3O_4@C-CM$, while the H1 hysteresis loop indicates the existence of cylindrical mesopores [13]. The corresponding pore size distribution shows highly ordered mesopores with diameter of ~7.1 nm (Fig. 4.7 inset), which is the key for enhancing mass transport during ORR. The micropores with diameter of ~1.0 nm may originate from the carbon shell or the gap between the nanoparticles and CM.

The morphology of $Co@Co_3O_4@C-CM$ was characterized by SEM technology. At low magnification, $Co@Co_3O_4@C-CM$ exhibits rod-like shape similar to CM, without irregular particles that derive from pristine ZIF-9, indicating the absence of unattached ZIF-9 (Fig. 4.8a). At high magnification, it is shown that the $Co@Co_3O_4@C$ nanoparticles with high brightness are uniformly distributed on the surface of CM (Fig. 4.8b,c). Note that the brightness of different $Co@Co_3O_4@C$ nanoparticles is different. Those with high brightness and clear outline are located



on the surface of CM, while those with low brightness and fuzzy outline may be embedded inside the CM (Fig. 4.8d).

The morphology of $Co@Co_3O_4@C$ -CM was further characterized by TEM technology. TEM images of $Co@Co_3O_4@C$ -CM show that $Co@Co_3O_4@C$ nanoparticles with particle size of ~15–30 nm are uniformly embedded into the CM substrate with highly ordered mesoporous structure (Fig. 4.9a, b). Note that the particle size of $Co@Co_3O_4@C$ nanoparticle is larger than the diameter of the mesopore of CM. It has been reported that the sizes of the nanoparticles embedded in ordered porous materials (e.g. SBA-15) are always smaller than the pore widths of the substrates due to the rigid interconnected walls of the channels [14]. In contrast, CM is composed of ordered carbon rods, which form an open structure to enable the enwrapping of several carbon rods by the $Co@Co_3O_4@C$ nanoparticles with size larger than the pore width (Fig. 4.9c).

TEM tilting experiments were carried out to prove that the $Co@Co_3O_4@C$ nanoparticles are located inside the CM rather than only on the surface of CM (Fig. 4.10). The sample was rotated for angles from -30° to $+30^{\circ}$. It was found that as the angle changed, some nanoparticles moved from interior to the edge of CM, indicating that they are located on the surface of CM. In contrast, some nanoparticles almost stayed still, revealing that they are located inside the CM substrate.

In Co@Co₃O₄@C-CM, the nanoparticles are wrapped by carbon shells (marked by arrows in Fig. 4.11). After acid treatment to remove the Co@Co₃O₄ core, the existence of obvious hollow carbon shells and the appearance of new pores with pore width of ~13 nm measured by nitrogen sorption isotherms further prove the presence of carbon shells that wrap the Co@Co₃O₄ core. HRTEM images of Co@Co₃O₄@C-CM show obvious core-shell structure of the nanoparticles: the core is metallic cobalt with lattice spacing of 0.205 nm corresponding to (111) plane of cobalt, while the thin sell is Co₃O₄ with lattice spacing of 0.233 nm corresponding to (111) plane of Co₃O₄. It has been reported that Co₃O₄ is an active earth-abundant electrocatalyst for ORR in alkaline solution, but its relatively low conductivity need to be compensated



Fig. 4.8 SEM images of $Co@Co_3O_4@C$ -CM. Figure adapted from [6] with permission of the Royal Society of Chemistry

by introduction of conductive substrates [2]. In this chapter, in situ formation of $Co@Co_3O_4@C$ fine structure that facilitates the electron transfer and improves the structural stability was achieved by simple thermal treatment, which can promote the electrocatalysis of ORR.

4.2.2 The Role of CM on the Formation of Metal Oxide Nanoparticles

CM plays a key role on the formation of the core-bishell metal oxide nanoparticles. Pristine ZIF-9 is bulk crystal without CM. After pyrolysis, the product $Co@Co_3O_4$ -C exhibits irregular morphology with non-uniform particle size of



Fig. 4.9 a, b TEM images and c structural model of $Co@Co_3O_4@C-CM$. Figure adapted from [6] with permission of the Royal Society of Chemistry

0.5–20 μ m (Fig. 4.12a). TEM images of Co@Co₃O₄–C show that Co@Co₃O₄ nanoparticles are embedded in compact carbon matrix (Fig. 4.12b).

Nitrogen sorption isotherms of $Co@Co_3O_4$ –C and pristine ZIF-9 are shown in Fig. 4.13a. Pristine ZIF-9 shows tiny nitrogen adsorption with BET surface area of 9 m²/g. In contrast, $Co@Co_3O_4$ –C shows obvious nitrogen adsorption with BET surface area of 313 m²/g. Similar to $Co@Co_3O_4@C$ -CM, $Co@Co_3O_4$ –C exhibits hysteresis loop that indicates the existence of mesopores. However, the shape of the hysteresis loops are different: $Co@Co_3O_4@C$ -CM shows H1 type hysteresis loop that reveals the presence of cylindrical mesopores, while $Co@Co_3O_4$ –C shows H4 type that represent the slit pores generated from plate-like particle aggregation [15]. The pore distribution of $Co@Co_3O_4$ –C is shown in Fig. 4.13b, exhibiting narrow distribution of micropores and broad distribution of mesopores.

Without CM, Co@Co₃O₄–C derived from pristine ZIF-9 shows many disadvantages for ORR including large particle size, irregular plate-like pores, low specific surface area and pore volume, and insufficient exposure of the active metal oxide nanoparticles. After the introduction of CM substrate, active sites of the metal oxide



Fig. 4.10 Schematic illustrations of TEM tilting experiments for $Co@Co_3O_4@C-CM$. Figure adapted from [6] with permission of the Royal Society of Chemistry



Fig. 4.11 HRTEM images of $Co@Co_3O_4@C$ -CM. Figure adapted from [6] with permission of the Royal Society of Chemistry

nanoparticles that uniformly embedded into the highly ordered porous CM with open structure can be sufficiently exposed. Moreover, the CM substrate can facilitate the electron transfer and anchor the nanoparticles to afford high stability.



Fig. 4.12 a SEM and b TEM images of Co@Co₃O₄–C. Figure adapted from [6] with permission of the Royal Society of Chemistry



Fig. 4.13 a Nitrogen sorption isotherms and the corresponding pore size distributions, **b** ZIF-9 before and after pyrolysis. Figure adapted from [6] with permission of the Royal Society of Chemistry

4.2.3 Formation Process of the Core-Bishell Metal Oxide Nanoparticles

The proposed formation process of Co@Co₃O₄@C-CM is shown in Fig. 4.14.

The CM is first modified with carboxyl groups [16], which can adsorb the Co^{2+} cations to induce the in situ growth of ZIF-9 in the CM during solvothermal reaction (Fig. 4.14a, b) [17, 18]. During the initial stage of the heat treatment, the framework structure of ZIF-9 collapses to form ultra-small Co clusters in the void of the CM (Fig. 4.14c). These Co clusters aggregate to form larger Co nanoparticles to reduce the surface energy (Ostwald Ripening), which catalyze the carbon to form graphitic carbon shell wrapping themselves (Fig. 4.14d). These Co nanoparticles can be partially oxidized to form core-bishell Co@Co₃O₄@C under controlled heat treatment



Fig. 4.14 Schematic illustrations of the formation process of $Co@Co_3O_4@C-CM$. Figure adapted from [6] with permission of the Royal Society of Chemistry

in air (Fig. 4.14e). The Co_3O_4 shell can prevent the Co core from further oxidation under room temperature [19], thus stable $Co@Co_3O_4@C-CM$ is obtained.

4.3 ORR Performance of Core-Bishell Metal Oxide Nanoparticles

4.3.1 Electrochemical Measurements of Core-Bishell Metal Oxide Nanoparticles

The ORR electrocatalytic performance of $Co@Co_3O_4@C-CM$ was first measured by CVs in N₂- and O₂-saturated 0.1 M KOH solution (Fig. 4.15). The catalyst delivered featureless CV curves in N₂-saturated KOH, while in O₂-saturated 0.1 M KOH an obvious cathodic peak of ORR is observed, indicating electrocatalytic activity of Co@Co₃O₄@C-CM for ORR.

LSV curves of $Co@Co_3O_4@C-CM$ and commercial Pt/C are measured to further evaluate the electrochemical performance (Fig. 4.16). The onset and half-wave potentials are 0.93 and 0.81 V, respectively, which are very close to the commercial Pt/C. The limiting current density of $Co@Co_3O_4@C-CM$ is also comparable to Pt/C, with faster growth rate of and higher value of current density at 0.65–0.8 V.



These results indicate that $Co@Co_3O_4@C-CM$ is highly active for electrocatalysis of ORR, better than most of the reported earth-abundant electrocatalysts [20].

The reaction process of $Co@Co_3O_4@C-CM$ is explored based on LSV curves collected at different rotation rates. As shown in Fig. 4.17a, as the rotation rate increases, the limiting current density increases because of the faster mass transport. Koutechy-Levich plots and the fitting lines at various potentials can be obtained from the LSV curves (Fig. 4.17b). The Koutechy-Levich plots exhibit good linearity and close coincidence, revealing the first-order reaction kinetics and similar electron transfer number at different potentials. The electron transfer number is 3.8-3.9 in the potential range of 0.35-0.75 V, indicating 4-electron ORR process under the electrocatalysis of $Co@Co_3O_4@C-CM$.



Fig. 4.17 a LSV curves and **b** the corresponding Koutechy-Levich plots of $Co@Co_3O_4@C-CM$. Figure adapted from [6] with permission of the Royal Society of Chemistry



Fig. 4.18 a RRDE curves and **b** the corresponding electron transfer number of $Co@Co_3O_4@C-CM$. Figure adapted from [6] with permission of the Royal Society of Chemistry

Electron transfer number can also be measured by RRDE tests (Fig. 4.18), which is similar to that calculated from Koutechy-Levich plots, further proving the 4-electron ORR process catalyzed by $Co@Co_3O_4@C-CM$.

In addition to electrocatalytic activity, the stability of the catalysts is also an important indicator for practical fuel cells. Commercial Pt-based catalysts suffer from poor stability due to dissolution and aggregation of Pt nanoparticles during long-term operation of fuel cells. The stability of $Co@Co_3O_4@C-CM$ is evaluated by chronoamperometric measurement (Fig. 4.19). More than 90% of the relative current density of $Co@Co_3O_4@C-CM$ remains after 25000 s operation at 0.75 V. In contrast, only 68% of the relative current density of Pt/C remains, indicating better stability of $Co@Co_3O_4@C-CM$ than commercial Pt/C.

In practical fuel cells, Pt-based catalysts also suffer from crossover effect: methanol can permeate through the separator and reach the cathode, causing catalyst poisoning and leading to loss of energy output. The tolerance of Co@Co₃O₄@C-CM



and Pt/C towards methanol was evaluated by addition of methanol into the electrolyte during i–t testing (Fig. 4.20). No obvious change of current density is observed for $Co@Co_3O_4@C-CM$ upon addition of methanol, while a sharp jump causing by methanol oxidation appears for Pt/C, indicating much better catalytic selectivity of $Co@Co_3O_4@C-CM$ than commercial Pt/C.



4.3.2 Influence of Core-Bishell Structure on ORR Catalytic Performance

In order to explore the role of the Co core of $Co@Co_3O_4@C-CM$, a control sample $Co_3O_4@C-CM$ was synthesized by complete oxidation of $Co@Co_3O_4@C-CM$ at 150 °C for 96 h in air. XRD pattern of $Co_3O_4@C-CM$ shows no characteristic peaks of metallic Co, with all the sharp peaks matching well with standard Co_3O_4 (Fig. 4.21). Note that the sharp peak at 26.1° broadens after complete oxidation, which is attributed to the collapse of graphitic carbon shells.

HRTEM image of Co_3O_4 @C-CM shows that hollow Co_3O_4 polycrystals with obvious volume expansion are formed after complete oxidation of the metallic Co cores (Fig. 4.22). The carbon shells are completely destroyed, corresponding to the XRD analysis.

LSV curves of $Co@Co_3O_4@C-CM$ and $Co_3O_4@C-CM$ are compared in Fig. 4.23. The onset and half-wave potentials of $Co_3O_4@C-CM$ are slightly more negative, while the limiting current density is much lower than those of $Co@Co_3O_4@C-CM$, indicating the positive influence of the Co core. Considering that the Co core is wrapped by Co_3O_4 shell, so the enhancement of ORR catalytic performance may because of the modification of the electron density by Co core rather than direct contact and catalysis of the oxygen molecules. Similar effects have been reported and investigated in the case of Fe core wrapped by CNTs [21].

The carbon shell plays an important role in the ORR electrocatalysis. It derives from the benzimidazole ligands which is an aromatic precursor that has been proved to be effective to generate graphitic carbon with improved catalytic activity [8, 22]. Meanwhile, the N atoms in benzimidazole ligands are simultaneously doped in the graphitic carbon, which can improve the electrocatalytic activity for ORR. To verify the catalytic performance of the carbon shells, the Co@Co₃O₄ core in Co@Co₃O₄@C-CM was removed by acid washing to get carbon shell/CM



Fig. 4.22 HRTEM image of Co₃O₄@C-CM. Figure adapted from [6] with permission of the Royal Society of Chemistry

Fig. 4.23 LSV curves of $Co@Co_3O_4@C-CM$ and $Co_3O_4@C-CM$. Figure adapted from [6] with permission of the Royal Society of Chemistry

composite, denoted as C-CM. C-CM exhibits better electrocatalytic performance than the pristine CM, indicating the contribution of the carbon shell to the ORR electrocatalytic activity (Fig. 4.24).

The effect of the carbon shell in $Co@Co_3O_4@C-CM$ was verified by control synthesis of $Co@Co_3O_4-CM$ without carbon shell through a conventional wetimpregnation method: 0.210 g of $Co(NO_3)_2$ was dissolved in 50 mL of ethanol/water (w:w = 1:4), followed by addition of 0.050 g of modified CM. After sonication and stir for 1 h, the solvent was dried at 80 °C in air and then at 120 °C under vacuum. The resultant solid was treated at 500 °C under H₂/Ar (5% H₂) and at 90 °C in air to obtain the final product $Co@Co_3O_4-CM$. TEM images of $Co@Co_3O_4-CM$ show the


Fig. 4.24 LSV curves of C-CM and CM. Figure adapted from [6] with permission of the Royal Society of Chemistry



Fig. 4.25 TEM images of $Co@Co_3O_4$ -CM. Figure adapted from [6] with permission of the Royal Society of Chemistry

aggregation of the nanoparticles in the absence of the protection of carbon shells, leading to decreased exposed catalytic surface area (Fig. 4.25). In contrast, in the presence of the protection of the carbon shells, $Co@Co_3O_4@C-CM$ has much smaller nanoparticles even though the synthetic temperature is higher (700 °C). $Co@Co_3O_4-CM$ without carbon shells exhibits much poorer ORR performance than $Co@Co_3O_4@C-CM$, with 70 mV more negative onset potential and much lower limiting current density (Fig. 4.26).



In addition, the intimate contact between carbon shells and the $Co@Co_3O_4$ core can facilitate the electron transfer from CM substrate to the catalytic sites, promoting the ORR electrocatalysis.

4.3.3 Influence of the Highly Ordered Porous CM on ORR Performance

 $Co@Co_3O_4$ –C derived from pristine ZIF-9 without CM shows much poorer ORR performance than $Co@Co_3O_4@C$ -CM, with onset and half-wave potentials of 0.85 and 0.70 V, respectively, both of which are much more negative than those of $Co@Co_3O_4@C$ -CM (Fig. 4.27).



Fig. 4.28 TEM images and structural models of **a** $Co@Co_3O_4$ –C and **b** $Co@Co_3O_4@C$ -CM. Figure adapted from [6] with permission of the Royal Society of Chemistry

ORR takes place at the triple-phase boundary of oxygen, electrolyte, and the solid catalysts. More facile exchange of oxygen and electrolyte on the surface of the catalysts can promote the ORR electrocatalysis. In the case of $Co@Co_3O_4$ –C derived from pristine ZIF-9, only disordered slit pores are presented, which results in low mobility of oxygen and electrolyte (Fig. 4.28a). Also, most of the catalytically active metal oxide nanoparticles are embedded inside the carbon matrix, which are not exposed to the oxygen and electrolyte. In contrast, the introduction of CM leads to highly ordered open structure that ensure the full contact between the $Co@Co_3O_4@C$ nanoparticles and the oxygen as well as the electrolyte (Fig. 4.28b). Moreover, the transport of oxygen and electrolyte throughout $Co@Co_3O_4@C$ -CM is greatly improved because of the reduced diffusion resistance.

4.4 Summary

In this chapter, $Co@Co_3O_4@C$ nanoparticles with core-bishell structure uniformly embedded in highly ordered porous CM was synthesized, which exhibit excellent ORR performance with onset and half-wave potentials of 0.93 and 0.81 V respectively as well as good durability and tolerance towards methanol. The excellent ORR performance of Co@Co₃O₄@C-CM can be attributed to the unique core-bishell structure of the metal oxide nanoparticles and the highly ordered open frameworks of the CM substrate as well as the synergistic effects between these two components.

Not only a new earth-abundant electrocatalyst for ORR is provided, this chapter also expands the application of MOFs to fabricate efficient metal oxides electrocatalysts for ORR. Also, it is found that nanostructured materials derived from pristine MOFs is not always good for heterogeneous catalysis because of the hindered mass transport through the slit pores. A highly ordered porous template CM is introduced to obtain composite with open structure that promote the mass transport during catalysis in this chapter, which provides a new design idea to fabricate MOF-derived nanomaterials with unique structures and properties.

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Chapter 5 Formation of Hollow Metal Oxide Nanoparticles for ORR



5.1 Introduction

Metal oxides have been widely employed in various electrochemical energy storage and conversion applications including Li-ion batteries, supercapacitors and fuel cells [1, 2]. Designing the microstructure of metal oxide nanomaterials is important for advanced energy storage and conversion devices due to the pronounced size/shape effect on the reaction pathway and durability [3, 4]. Porous metal oxide nanomaterials can be synthesized through pyrolysis of MOFs, however, the structure and morphology are difficult to precisely tune due to the absence of induction force during structure transformation at elevated temperature [5]. The regular pores of MOFs tend to collapse and irregular slit pores that limit the mass transport will form upon heat treatment [6]. In this chapter, graphene aerogel is introduced to assist the formation of uniformly dispersed metal oxides nanoparticles with hollow structure and abundant edges and defects, leading to excellent ORR electrocatalytic performance (Fig. 5.1).

5.2 Formation of Metal Oxide Hollow Nanoparticles

5.2.1 Synthesis of Co-MOF/Nitrogen Doped Graphene Aerogel Composite

The synthetic process of the composite of nitrogen doped graphene aerogel (NG-A) and Co-MOF (Co-MOF@NG-A) is shown in Fig. 5.2. Nitrogen doped graphene hydrogel was first synthesized through a hydrothermal reaction, which was added into the precursor solution of the Co-MOF (methanol solution of $Co(NO_3)_2$ and 2-methylimidazole), leading to in situ grown of Co-MOF on the graphene hydrogel. After supercritical drying, Co-MOF@NG-A with color of dark purple was obtained.

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Fig. 5.1 Schematic illustrations of monodispersed metal oxide nanoparticles derived from MOFs. Figure adapted from [7] with permission of the American Chemical Society



Fig. 5.2 Synthetic process of Co-MOF@NG-A. Figure adapted from [7] with permission of the American Chemical Society

SEM image of Co-MOF@NG-A reveals the presence of both the Co-MOF nanocrystals of 300 nm and crumpled graphene sheets (Fig. 5.3). The Co-MOF nanocrystals are uniformly distributed on the surface of the nitrogen doped graphene sheets, which are interconnected to form a 3D framework structure.



Fig. 5.3 SEM image of Co-MOF@NG-A. Figure adapted from [7] with permission of the American Chemical Society

5.2.2 Synthesis and Characterizations of the Hollow Metal Oxide Nanoparticles

The final product $CoO_x/NG-A$ was synthesized through simple heat treatment of Co-MOF@NG-A. $CoO_x/NG-A$ shows extremely low density of 0.010–0.012 g/cm³, only nine times higher than that of air, and can be supported by a feather (Fig. 5.4a). SEM image of $CoO_x/NG-A$ shows the 3D framework structure of the interconnected graphene sheets, which has a large amount of voids and pores (Fig. 5.4b).

Specific surface area of CoO_x/NG -A calculated from nitrogen sorption isotherms is 1359 m²/g (Fig. 5.5a), which is much higher than that of the Co/NC derived from pristine Co-MOF (386 m²/g, Fig. 3.15). The total pore volume of CoO_x/NG-A is 7.2 cm³/g. The pore size distribution is shown in Fig. 5.5b, indicating the presence of micro-, meso-, and macropores in CoO_x/NG-A.

XRD pattern of $CoO_x/NG-A$ exhibits mainly characteristic peaks of Co_3O_4 , with weak signals from metallic Co (Fig. 5.6). Note that the intensities of the XRD peaks are weak along with obvious broadening, which indicates the sizes of metal oxide particles in $CoO_x/NG-A$ are small.

The SEM images of Co/NC and $CoO_x/NG-A$ are compared in Fig. 5.7. Without graphene, Co/NC inherits the rhombic dodecahedron shape of the parent Co-MOF, while uniformly distributed CoO_x nanoparticle of 25 nm are formed in the presence of graphene.

High-angle annular dark-field scanning TEM (HAADF-STEM) image of $CoO_x/NG-A$ is shown in Fig. 5.8a. CoO_x nanoparticles with high brightness are



Fig. 5.4 a Digital photograph and b SEM image of $CoO_x/NG-A$. Figure adapted from [7] with permission of the American Chemical Society



Fig. 5.5 a Nitrogen sorption isotherms and b corresponding pore size distribution of $CoO_x/NG-A$. Figure adapted from [7] with permission of the American Chemical Society

uniformly distributed on the surface of the crumpled graphene sheet network. Note that the brightness of the surface of the CoO_x nanoparticle is higher than the interior, revealing hollow structure of these CoO_x particles. The EDS profile of the CoO_x particle further proves the hollow nature, with void width of ~10 nm (Fig. 5.8b).

TEM image of $CoO_x/NG-A$ shows that the CoO_x nanoparticles are of hollow structure (Fig. 5.9a). Lattice spacings obtained from HRTEM image of $CoO_x/NG-A$ correspond to (220) and (311) planes of Co_3O_4 , in accordance with XRD analysis.



Fig. 5.6 XRD pattern of $CoO_x/NG-A$. Figure adapted from [7] with permission of the American Chemical Society



Fig. 5.7 SEM images of a Co/NC and b CoO_x/NG-A. Figure adapted from [7] with permission of the American Chemical Society

It is worth noting that the CoO_x nanoparticles possess highly defective surfaces with abundant edges and corner sites, which may improve the ORR electrocatalytic performance by promoting the adsorption and activation of oxygen (Fig. 5.10). Recently, great efforts have been devoted to design and synthesis of nanocatalysts with abundant edges to afford enhanced catalytic performance. For example, Ptbased nanoframes was designed and synthesized, which exhibited excellent catalytic activity due to the abundant edges [8]. However, the control synthesis of metal oxides with similar defective structure is still a big challenge [9, 10]. Herein, hollow metal



Fig. 5.8 a HAADF-STEM image and b corresponding EDS profile of $CoO_x/NG-A$. Figure adapted from [7] with permission of the American Chemical Society

oxide nanoparticles with abundant edges are reported for the first time. The hollow nature of the particles reduces the unfunctional interior atoms, while the abundant edges can improve the electrocatalytic ORR performance.

XPS spectrum of $CoO_x/NG-A$ reveals the presence of C, N, O, and Co on the surface (Fig. 5.11a). High-resolution XPS spectrum of Co2p indicates the coexistence of Co^{3+} and Co^{2+} (Fig. 5.11b) [11]. The Co sites of cobalt oxide, especially the Co^{3+} , have been suggested as active donor-acceptor reduction sites [12]. The content of Co in $CoO_x/NG-A$ is ~17.1 wt% according to TG analysis. The content of N is 5.34 at% from XPS analysis, with the most active pyridinic N accounting for the largest proportion (39.6%, Fig. 5.11c, d).

5.2.3 Formation Mechanism of Hollow Metal Oxide Nanoparticles

The formation of the hollow CoO_x nanoparticles with abundant edges is mainly influenced by three factors:

First, the introduction of the diffusion barrier graphene can assist the MOFs to form monodispersed CoO_x . Graphene is an emerging advanced 2D material that has been intensively studied in various fields because of its unique physical and



Fig. 5.9 a TEM and b HRTEM images of $CoO_x/NG-A$. Figure adapted from [7] with permission of the American Chemical Society

chemical properties. Herein, a new function of graphene is proposed: graphene can serve as diffusion-assisted medium to help the MOFs to diffuse along the surface of graphene at elevated temperature. It is evidenced by the complete disappearance of the rhombic dodecahedra resulting from the diffusion of metal and carbon atoms along the surface of graphene. CNT aerogel [13], another advanced carbonaceous material that can be considered as bended graphene, is used to further demonstrate the diffusion process. CoO_x hollow nanoparticles can be uniformly loaded on the surface of the CNTs ($COO_x/CNT-A$) using the same synthetic method, indicating the universality of the strategy (Fig. 5.12).

Second, suitable heating temperature is necessary for the formation of uniformly distributed CoO_x nanoparticles. When a low temperature is employed in the thermal activation process (e.g. 450 or 600 °C), the rhombic dodecahedron shape is maintained, while a very high temperature (e.g. 900 °C) would lead to aggregated particles with large size (Fig. 5.13).

Third, the Co-core-C-shell intermedium plays an important role on the formation of the hollow CoO_x nanoparticles with abundant edges and corner sites. Without the carbon shell, regular hollow structures are usually obtained through the Kirkendall effect [14, 15]. In our case, Co-core-C-shell intermedium is first formed (Fig. 5.14).



Fig. 5.10 HRTEM images of CoO_x/NG-A. Figure adapted from [7] with permission of the American Chemical Society

As the Co core is oxidized in air, voids are formed inside the nanoparticle due to the different diffusion rates of the O and Co atoms along the CoO_x phase. The large density difference between CoO_x and Co leads to volume expansion that extrudes and then destroys the carbon shell to form irregular CoO_x nanoparticles with abundant edges.

The formation process of hollow CoO_x nanoparticles with defective surface and abundant edges can be described as follow (Fig. 5.15): At suitable temperature (750 °C), Co-MOF loaded on graphene decomposes with reduction of Co cations to metallic Co and carbonization of ligands. The resultant Co and C atoms diffuse along the surface of graphene and form Co nanoparticles wrapped by carbon shells. When the Co-core-C-shell nanoparticles are exposed to air, the highly active Co is oxidized to CoO_x and void is generated inside the particle due to Kirkendall effect. The density difference between Co and CoO_x results in great volume expansion, leading to extrusion of CoO_x through the carbon shell and formation of irregular hollow nanoparticles with defective surface and abundant edges (Fig. 5.15).



Fig. 5.11 a XPS spectrum and high-resolution **b** Co2p and **c** N1 s XPS spectra of $CoO_x/NG-A$. **d** Schematic illustration of N-doped graphitic sheet. Figure adapted from [7] with permission of the American Chemical Society

5.3 ORR Performance of the Hollow Metal Oxide Nanoparticles

5.3.1 CV and LSV Measurements of the Hollow Metal Oxide Nanoparticles

CV curves of CoO_x/NG-A, Co/NC, and Pt/C with loading of 0.1 mg/cm² tested in O₂-/N₂-saturated 0.1 M KOH are shown in Fig. 5.16. Obvious cathodic peaks for ORR are observed in CV curves of all these three samples. For Co/NC derived from pristine Co-MOF, the peak potential centers at 0.734 V along with relatively low current density. In contrast, CoO_x/NG-A derived from Co-MOF/NG-A composite exhibits more positive peak potential of 0.786 V with much higher current density



Fig. 5.12 Characterizations of CoO_x/CNT -A: **a** Digital photograph and structural model, **b** SEM and **c** TEM images. Figure adapted from [7] with permission of the American Chemical Society





Fig. 5.14 a–**e** TEM images and **f** structural model of Co@C@N-GA. Figure adapted from [7] with permission of the American Chemical Society



Fig. 5.15 Formation process of hollow CoO_x nanoparticles with abundant edges. Figure adapted from [7] with permission of the American Chemical Society

even higher than that of commercial Pt/C, indicating excellent electrocatalytic activity for ORR.





Fig. 5.17 LSV curves of CoO_X/NG-A, Co/NC, and Pt/C. Figure adapted from [7] with permission of the American Chemical Society

The electrocatalytic activities of $\text{CoO}_x/\text{NG-A}$, Co/NC, and Pt/C are further compared by LSV measurement (Fig. 5.17). The onset potential of $\text{CoO}_x/\text{NG-A}$ (potential at which current density reaches -0.1 mA/cm^2) is 1.019 V, much more positive than that of Co/NC (0.872 V). Moreover, $\text{CoO}_x/\text{NG-A}$ exhibits half-wave potential that is 54 mV more positive than that of Co/NC and comparable to that of Pt/C. In the mixed kinetic- and diffusion-controlled zone (0.6–0.9 V), the current density of $\text{CoO}_x/\text{NG-A}$ is even higher than that of Pt/C.



Fig. 5.18 a LSV curves at different rotation rates and b corresponding Koutechy-Levich plots of $CoO_x/NG-A$. Figure adapted from [7] with permission of the American Chemical Society

5.3.2 Kinetic Current Density and Electron Transfer Number of the Hollow Metal Oxide Nanoparticles

LSV curves at different rotation rates of $CoO_x/NG-A$ are shown in Fig. 5.18a, from which the kinetic current density (J_k) can be calculated. The corresponding Koutechy-Levich plots are shown in Fig. 5.18b, which exhibit excellent linearity and near coincidence, indicating first-order reaction kinetics and similar electron transfer number at different potentials. Electron transfer number at different potentials can be calculated from Koutechy-Levich plots.

The kinetic current densities and electron transfer numbers at 0.75 V of CoO_x/NG -A, Co/NC, and Pt/C are compared in Fig. 5.19. CoO_x/NG -A has the highest J_k of 32.5 mA/cm², which is 8.2 and 2.3 times higher than those of Co/NC and Pt/C respectively, indicating higher intrinsic activity of CoO_x/NG -A. The electron transfer number of CoO_x/NG -A is calculated to be 3.8, revealing an efficient 4 electron process during ORR electrocatalysis similar to Pt/C. In contrast, the electron transfer number of Co/CN is only 2.7, displaying an inefficient 2 electron process.

5.3.3 Durability of the Hollow Metal Oxide Nanoparticles

Durability for ORR electrocatalysis is evaluated by chronoamperometric measurement and accelerated durability test (ADT).

The I-t curves of $CoO_x/NG-A$ and Pt/C tested at 0.764 V in O_2 -saturated 0.1 M KOH are shown in Fig. 5.20. For $CoO_x/NG-A$, 82% of the relative current can remain after continuous operation for 30,000 s, while less than 50% of the relative current survives in the case of Pt/C, indicating higher stability of $CoO_x/NG-A$ than Pt/C.



In ADT, the samples are cycled between 0.561 and 1.164 V for 3000 cycles and then LSV curves tested before and after cycles are compared (Fig. 5.21). For $CoO_x/NG-A$, there is no obvious change between LSV curves tested before and after ADT, indicating excellent cycling durability. In contrast, the LSV curve of Pt/C shows a 26 mV negative shift of half-wave potential after cycles, revealing poor cycling stability.



Fig. 5.21 LSV curves of **a** CoO_x/NG-A and **b** Pt/C tested before and after 3000 cycles between 0.561 and 1.164 V. Figure adapted from [7] with permission of the American Chemical Society



5.3.4 Tolerance of Hollow Metal Oxide Nanoparticles Against Methanol Crossover Effect

The results of tolerance of $CoO_x/NG-A$ and Pt/C against methanol crossover effect are shown in Fig. 5.22. The current density of $CoO_x/NG-A$ remains stable after addition of methanol into the electrolyte, while a dramatic change in current density is observed for Pt/C, indicating better tolerance towards methanol poisoning of $CoO_x/NG-A$ than Pt/C.

5.4 Summary

In this chapter, unusual structure transformation is observed during pyrolysis of Co-MOF in the presence of graphene, which leads to hollow CoO_x nanoparticles of ~25 nm with defective surface and abundant edges. The structure transformation is closely related to three factors: (a) graphene serves as diffusion medium to assist the diffusion of Co and C atoms along its surface; (b) suitable pyrolytic temperature activates and drives the diffusion of Co and C atoms; (c) the intermedium Co-core-C-shell nanoparticles help generate abundant edges and defects in the CoO_x nanoparticles. The unique structure of CoO_x/NG-A leads to excellent ORR electrocatalytic performance, exhibiting higher activity than Co/NC derived from pristine Co-MOF without graphene and better durability as well as tolerance towards methanol poisoning than commercial Pt/C.

Not only a new efficient and durable earth-abundant electrocatalyst for ORR is provided, this chapter also proposes a concept of surface-assisted diffusion, that is, the framework structure of MOFs can be "cut" into monodispersed metal oxide nanoparticles with the help of graphene or CNTs at elevated temperature. It provides a new way to load monodispersed hollow metal oxide nanoparticles on the surface of advanced carbonaceous materials, which can be employed in various energy storage and conversion applications such as electrocatalysis, Li-ion batteries, and supercapacitors.

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Chapter 6 Synthesis of 3D Porous Carbon and Its Application in Li–S Batteries



6.1 Introduction

It's feasible to synthesize porous carbon materials from MOFs since MOFs can act as a porous template and carbon source at the same time, which simplifies the traditional process for preparing porous carbon. Moreover, the MOF-derived porous carbons possess extraordinarily high surface area and rich porosity that cannot be achieved from conventional method, contributing to enhanced performance in electrochemical energy storage/conversion, gas adsorption/separation or sensing [1, 2]. However, there exist some limitations in this method. Generally speaking, the growth process of MOF crystals is quite long while the output is very limited. The pore texture in MOF-derived carbons is monotonous, mostly microporous structure, which is a disadvantage for mass diffusion inside the materials. In this chapter, an extended MOF structure, metal–organic gel, is introduced to facilitate the preparation of 3D porous carbon with large quantity and higher efficiency. The obtained carbon possesses hierarchically porous structure, which is beneficial for the application as sulfur host for lithium-sulfur batteries.

6.2 Metal–Organic Aero/Xerogel

6.2.1 Formation of Metal–Organic Aero/Xerogel

Metal–organic gel (MOG) was first synthesized by mixing aluminum nitrate and 135-benzentricarboxylic acid in ethanol. The mixed solution was sealed in a Teflon container and heated at 120 °C for 1 h, producing a light yellow gel with the same shape as the container (Fig. 6.1).

The as-formed MOG possesses a hierarchical architecture, as shown in Fig. 6.2. The primary structure units are the Al–O clusters built by the octahedrally coordinated Al(III) with four carboxyl oxygen atoms and 1,3,5-benzentricarboxylic acid ligands. The primary structure are assembled into the secondary structure units, a similar MIL-100(Al) substructure [4]. MIL-100(Al) has the MTN topology which

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Fig. 6.1 Digital image of metal–organic gel and its precursors. Figure adapted from [3] with permission of the Royal Society of Chemistry



Fig. 6.2 Structure model of MOG. Figure adapted from [5] with permission of the Nature Publishing Group

can be usually found in zeolites and possesses two types of cages (2.9 and 2.5 nm in diameter). The tertiary 3D network is constructed from the interconnected MIL-100(Al) nanoparticles.

A great number of mesopores and macropores are formed at the interspaces among the packed nanoparticles of MOG, however are filled by residual solvent. These pores, particularly the macropores, tend to collapse under conventional ambient drying because of the strong capillary force, which leads to the shrinkage of MOG and the formation of dense metal organic xerogel (MOX) particles with a density of ~0.56 g/cm³. A supercritical carbon dioxide drying technology was adopted to treat the as-formed MOG sample. The solvent in pores were exchanged by carbon dioxide supercritical fluid, which brought little damage to the pore texture in dried sample [6]. As shown in Fig. 6.3, the dried sample kept the original shape of MOG. The empty space of the dried gel (named as metal–organic aerogel, MOA) was filled by air, leading to a low density in the sample (~0.12 g/cm³).

Moreover, MOX and MOA displayed different colors in spite of the same composition. MOX showed dark yellow while MOA is light yellow. The difference in color



Fig. 6.3 Photographs of MOA and MOX samples. Figure adapted from [5] with permission of the Nature Publishing Group

is a reflection of distinct microstructures in the samples [7], which will be discussed in the SEM and TEM results.

6.2.2 Characterization of Metal–Organic Aero/Xerogel

The MOA and MOX samples were first characterized by XRD, which displayed low crystallinity with several broad peaks in the obtained patterns (Fig. 6.4). Although the broad peaks suggested amorphous structure in both samples, they located in the same position as the XRD pattern of MIL-100(Al) crystal reference, suggesting the identical basic structure.

The microstructures of MOA and MOX were revealed by SEM and TEM images (Fig. 6.5), verifying that both samples consist of interconnected nanoparticles as displayed in the structure model (Fig. 6.2). The size of the nanoparticles is around 10–20 nm. In comparison, the MOA samples displayed higher porosity with obvious macropores and mesopores. MOX showed closely packed nanoparticles without obvious pores or cracks.

The pore textures are further studied by nitrogen sorption experiment. Figure 6.6 shows the nitrogen isotherms of MOA and MOX at 77 K, which displayed different sorption behaviors. MOA exhibited type-II isotherms in which a nearly vertical tail at the relatively high pressure was found, indicating the existence of macropores [8]. However, MOX displayed type-IV isotherms with a typical hysteresis loop between the adsorption and desorption branches at the relative pressure of P/P₀ = 0.4–0.8 showing the presence of mesopores in MOX. In addition, both samples demonstrated considerable nitrogen adsorption at the relatively low pressure, which suggests the presence of a high degree of microporosity in them. The detailed pore textures were



Fig. 6.5 SEM (a) and TEM (b) images of MOA; SEM (c) and TEM (d) images of MOX. Figure adapted from [5] with permission of the Nature Publishing Group

given by the pore size distribution based on the Quenched Solid Density Functional Theory (Fig. 6.6). MOA showed a broad pore size distribution from micropores to



Fig. 6.6 Nitrogen sorption isotherms and pore size distributions of MOA (a) and MOX (b). Figure adapted from [5] with permission of the Nature Publishing Group

large mesopores, which is consistent with the SEM/TEM results. MOX displayed relatively narrow pore size distribution with two main peaks at 1.0 and 3.4 nm. Moreover, both samples possess high BET specific surface areas that are 1795 and 1761 m²/g, respectively. The similar high surface areas in MOA and MOX arise from the same basic structure, that is, the porous MIL-100(Al) units. In addition, they showed distinct pore volumes due to the different drying method. The pore volume of MOA is up to $4.5 \text{ cm}^3/\text{g}$ while it decreases to $1.3 \text{ cm}^3/\text{g}$ in MOX due to the severe pore contraction caused by capillary force in ambient drying. However, the pore volume of MOX is still higher than that of most MOF crystals.

6.3 Formation of 3D Porous Carbon

6.3.1 MOG Derived 3D Porous Carbon

The MOA sample was carbonized at 800 °C and washed by acid, resulting in a 3D carbon with hierarchically porous structure (named as MOA-C). XRD pattern of the MOA-C product displayed a broad peak at around 26°, indicating the amorphous nature (Fig. 6.7a). The purity of MOA was verified by ICP and TGA measurements.

As shown in Fig. 6.7b, the MOA sample showed obvious volume shrinkage after carbonization, but the original monolith can still be maintained. The bulk density of MOA-C is as low as 0.0952 g/cm³, reflecting a highly porous structure in it. The microstructure of MOA-C was characterized by SEM and TEM. As shown in the SEM images of Fig. 6.8a, b, the microstructure of MOA-C is similar to that of MOA. It is assembled from interconnected carbon nanoparticles, forming a 3D network. Marcopores and mesopores were also observed at the interspaces among the packed nanoparticles with smaller size than that in MOA. TEM Fig.s revealed richer



Fig. 6.7 XRD patterns (**a**) and photograph (**b**) of the MOA and MOA-C samples. Figure adapted from [5] with permission of the Nature Publishing Group



Fig. 6.8 SEM (a, b) and TEM (c, d) images of MOA-C. Figure adapted from [5] with permission of the Nature Publishing Group

mesoporosity in MOA-C than that in MOA due to the contraction of macropores and large mesopores during the heating process.

Figure 6.9a shows the nitrogen sorption isotherms of MOA-C that are identical to that of MOA, indicating the similar pore texture in MOA-C and MOA that both possess hierarchical pores. The BET specific surface are of MOA-C is up to $1820 \text{ m}^2/\text{g}$, surpassing most of the carbon powder samples obtained from conventional synthesis methods with specific surface areas in the range of $1000-2000 \text{ m}^2/\text{g}$. The specific



Fig. 6.9 Nitrogen sorption isotherms (**a**) and pore size distribution (**b**) of MOA-C. Figure adapted from [5] with permission of the Nature Publishing Group

surface areas for 3D carbon materials are even lower. For example, carbon aerogel assembled from graphene sheelts (theoretical specific surface area: $2630 \text{ m}^2/\text{g}$) only show the surface area value in the range of 400–700 m²/g. In addition, the pore volume of MOA-C reaches $3.22 \text{ cm}^3/\text{g}$, which is higher than that of most porous carbon materials. The detailed pore texture of MOA-C was given in Fig. 6.9b, demonstrating a close relationship to MOA. Similar to MOA, MOA-C also displayed broad pore size distribution from micropores to mesopores. The micropore volume of the carbonized sample is identical to that of the MOA precursor, but the volume of mesopores larger than 7 nm obviously decreases while the volume of mesopores smaller than 7 nm increases after carbonization. The phenomena is related to the origin of the pores. The micropores mainly come from the void space between the interconnected nanoparticles that tend to shrink or collapse and form smaller mesopores during the heat treatment process.

6.3.2 MOX Derived Porous Carbon

The MOX sample was first carbonized at 800 °C and washed by acid to remove metal components. Then the sample was mixed with KOH and activated at 700 °C for 1 h, leading to the final product (denoted as MOX-C).

Figure 6.10 shows the nitrogen sorption isotherms of the MOX-C sample before KOH activation, revealing a similar shape to that of MOX and the coexistence of micropores and mesopores. The BET specific surface area and pore volume are $2131 \text{ m}^2/\text{g}$ and $1.63 \text{ cm}^3/\text{g}$, respectively, higher than that of the precursor ($1761 \text{ m}^2/\text{g}$ and $1.31 \text{ cm}^3/\text{g}$). It can be read from the pore size distribution curve that the pore size of the carbon intermediate is identical to the precursor and the corresponding pore volume is a little bit higher. It showed little pore contraction caused by thermal treatment, demonstrating the higher stability in MOX structure.



The porosity of the carbon intermediate was enhanced by KOH activation. The mechanism for this process is displayed by Eq. (6.1) [9].

$$6\text{KOH} + 2\text{C} \leftrightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3 \tag{6.1}$$

In this process, carbon is oxidized to carbonate, and the potassium complex is embedded in the carbon skeleton. After a following acid was process, the inorganic impurities are removed forming new pores in the carbon product. Nitrogen sorption measurement showed remarkable nitrogen adsorption by the KOH activated sample (Fig. 6.11). The BET specific surface area and pore volume reached 3770 m²/g and 2.62 cm³/g, respectively. To the best of our knowledge, these parameters, particularly the BET surface area, are among the best results for all carbon materials and far exceed that of other MOF-derived carbons (Table 6.1).

In all the reported MOF-derived carbons, only PCP-800 sample showed higher specific surface area than MOX-C. It should be noted that the yield of PCP-800 was

Sample	BET specific surface area (m ² /g)	Pore volume (cm ³ /g)	Reference
NPC	2872	2.06	[8]
WMC	2587	3.14	[10]
NPC530	3040	2.79	[11]
MC	1812	2.87	[12]
C1000	3405	2.58	[13]
CNF	90	0.23	[14]
Al-PCP-FA	513	0.84	[15]
BF-1000	1131	0.69	[16]
IRMOF-1	3447	1.45	[17]
PCP-800	5500	4.40	[18]
Z-1000	1110	0.62	[19]
6c	1820	1.84	[20]
C-70	1510	1.75	[21]
MOX-C	3770	2.62	This work
MOA-C	1820	3.22	This work

Table 6.1 Summary of the pore textures of some MOF-derived carbons

Figure adapted from [5] with permission of the Nature Publishing Group

relatively low, which was in a milligram scale. Moreover, the surface area of PCP-800 decreased drastically in a scaled-up synthesis [18]. In comparison, the MOX-C sample demonstrated easier synthesis procedure and higher yield than can reach gram level, showing a better prospect.

The microstructure of MOX-C was further investigated by SEM and TEM. As shown in Fig. 6.12, the sample displayed dense structure without noticeable micropores or mesopores, which was in consistence with the pore size distribution result.

6.4 MOG-Derived 3D Porous Carbon for Li–S Battery

6.4.1 Synthesis of 3D Porous Carbon/Sulfur Composite Cathode

The MOA-C/S composites were synthesized by a melt-diffusion method. MOA-C was first mixed with sulfur powder with the same weight and sealed in a vacuumed tube. Then the mixture was heated at 155 °C for 12 h and 300 °C for another 12 h before cooling down to room temperature. The two-step heating process is critical to the formation of uniform carbon/sulfur composites. Sulfur becomes a liquid state at



Fig. 6.12 SEM (**a**, **b**) and TEM (**c**, **d**) images of MOX-C. Figure adapted from [5] with permission of the Nature Publishing Group

155 °C with the lowest viscosity. The liquid sulfur can be adsorbed into the micropores and mesopores of MOA-C by capillary force. In the second heating process, the surface adsorbed sulfur would sublimate, leaving behind sulfur nanoparticles confined in the pores. Due to the large pore volume in MOA-C, most of the sulfur could enter the pores after the first heating process. Few were adsorbed on the surface, resulting in little sulfur crystal formed on the inner wall of the tube after the second heat treatment.

The same method was applied to construct MOX-C composite. The same amount of sulfur can't be completely adsorbed by MOX-C due to the smaller pore volume. Obvious sulfur crystals appeared inside the tube. Thus, the practical sulfur loading in MOX-C was lower than that in MOA-C.

6.4.2 Characterizations of 3D Porous Carbon/Sulfur Composites

Figure 6.13 shows the XRD patterns of the mixture of MOA-C and sulfur before and after the melt-diffusion treatment. In the physically mixed sample, sharp peaks corresponding to the sulfur appeared in the XRD pattern. These peaks disappeared upon thermal treatment, indicating sulfur impregnation in the pores and lack of bulk



Fig. 6.14 Nitrogen sorption isotherms (**a**) and corresponding pore size distributions (**b**) of MOA-C before and after sulfur impregnation. Figure adapted from [5] with permission of the Nature Publishing Group

crystalline sulfur on the surface. Pore-filling was also confirmed by nitrogen sorption experiment. Figure 6.14a compares the nitrogen sorption isotherms of MOA-C before and after sulfur impregnation. The isotherms of MOA-C/S have the same shape as MOA-C, but locate in a lower position, which indicates a similar pore structure but lower specific surface area and pore volume due to the impregnation of sulfur. The BET specific surface area of MOA-C dropped to 200 m²/g from the initial value of 1820 m²/g, while the pore volume decreased to 0.78 from 3.22 cm³/g. Figure 6.14b reveals an obvious change in the pore size distribution before and after sulfur impregnation. Most of the mocropores and mesopores were filled by sulfur.

The practical sulfur loading in the MOA-C/S composites was 50.9 wt% given by TGA (Fig. 6.15), which was consistent with the sulfur content in the reactants, further confirmed the efficient sulfur impregnation in MOA due to the large pore volume. Pure sulfur was also tested by TGA for comparison, which displayed dramatic weight loss starting from ~150 °C and completing at ~280 °C. However, the





MOA-C/S composites started to lose weight at ~190 °C and finished at ~420 °C. The broader weight loss temperature range in MOA-C sample reflected a strong interaction between the carbon host and the confined sulfur that are beneficial for a high stability in the cycle performance as cathode material in Li–S battery. The sulfur content in MOX-C/S was tested as 30.3%. It was much lower than that in the reactants, indicating the smaller pore volume in MOX.

The MOA-C/S composites were also examined by SEM measurement. Random observations of several large regions at low magnification were conducted but didn't show any aggregated sulfur particles. The surface of carbon particles was smooth without noticeable sulfur residue (Fig. 6.16). Single MOA-C/S particle was further studied by EDS mapping in order to investigate the sulfur distribution inside the MOA-C host. The obtained sulfur and carbon elemental maps clearly displayed the homogeneous distribution of sulfur in the carbon particles.

6.4.3 Electrochemical Tests of the 3D Porous Carbon/Sulfur Composites as Cathode

Figure 6.17 shows the initial two charge-discharge curves of the MOA-C/S composites as cathode material in a coin-Cell (Li metal as anode). The charge-discharge profiles were recorded as a current density of 400 mA/g. The capacity values were calculated based on the mass of sulfur. The discharge curve of MOA-C/S displayed two plateaus at around 2.0 and 2.3 V which are typical for Li/S cells. The discharge curve can be divided into three sections based on the different discharge depths. Section I corresponds to the transition from solid sulfur (mainly S₈ molecules) to soluble polysulfides (S_x, $x \ge 4$), while section II is related to the formation of insoluble Li₂S₂ from polysulfides and section III corresponds to the transition from Li₂S₂ to the final discharge product, solid Li₂S. As shown in Fig. 6.17, side reactions



Fig. 6.16 EDS elemental mapping of MOA-C/S. Figure adapted from [5] with permission of the Nature Publishing Group



took place at the surface of electrode in the first cycle within the voltage range of 1.0–1.2 V, which contributed extra capacity to the electrode and resulted in the initial discharge capacity of 1694 mAh/g that was higher that the theoretical value of sulfur (1675 mAh/g). The side reactions were not observed in the second cycle but the capacity still reached 1240 mAh/g that is 74% of the theoretical value, showing a high utilization of the sulfur nanoparticles confined in the pores of MOA-C. The charge-discharge profiles of MOX-C/S composites are displayed in Fig. 6.18. The discharge capacities of the first two cycles were 1512 mAh/g and 1087 mAh/g, which were lower than that of the MOA-C/S sample.

The cycle performance of C/S composite was recorded at a current density of 400 mA/g and displayed in Fig. 6.19. For comparison, reference cathode made from pure sulfur and conducting carbon was prepared and demonstrated very low



capacities. The discharge capacity was only 450 mAh/g in the first cycle and dropped to 396 mAh/g in the second cycle, revealing the low atom utilization in bulk sulfur. Moreover, the capacity decreased to only 202 mAh/g after 20 cycles, indicating a poor stability in the pure sulfur cathode. The cycle performance was remarkably improved in the MOA-C/S and MOX-C/S composite cathodes with the capacities of 790 mAh/g and 608 mAh/g after 20 cycles, respectively, demonstrating the effectiveness of nanoconfinement in proving the stability of sulfur cathode.

It is noteworthy that the proportion of sulfur in MOA-C/S composites was 50.9% which exceed that in MOX-C/S (30.3%). Although the former sample contained a higher ratio of sulfur, it demonstrated higher sulfur utilization and better battery performance. When the sulfur ratio in MOA-C/S composites was reduced to the same level as MOX-C, the performance of the corresponding cathode was further improved, with a capacity of 967 mAh/g after 20 cycles, indicating that the filling
state of sulfur in the pores of carbon host is of great significance. The addiction of free macropores and mesopores in the electrode could enhance the overall performance.

The above results demonstrated the advantages of the hierarchically porous structure for sulfur hosting in Li–S battery. On the one hand, the macropores can work as reservoirs for electrolyte while mesopores can act as mass transport paths. On the other hand, the micropores and mesopores can be used to confine sulfur. Thus the hierarchically porous structure can promote fast mass exchange and meanwhile prevent loss of active materials, leading to high capacity and stability even at high current densities.

6.5 Summary

This chapter introduces an extend MOF structure—metal–organic gel. For the first time, a three-dimensional carbon material with hierarchically porous structure was prepared from the metal–organic gel, which filled the blank of MOF-derived three-dimensional carbons. The synthesis of metal–organic gel is quite simple with mild reaction condition and short reaction time. The derived three-dimensional carbon materials have high surface area nd large pore volume of up to 1820 m²/g and 3.22 cm^3 /g, respectively, exceeding most of the reported carbons from MOFs. Moreover, carbon powder with rich micropores and mesopores was also synthesized from the metal–organic gel. The material has a specific surface area of 3770 m²/g and a pore volume of 2.62 cm³/g. The surface area is higher than most porous carbon materials. The performance of these carbons as sulfur host in Li–S battery was also studied, revealing the effectiveness of pore confinement in improving the utilization and stability of sulfur and the advantages of coexistence of micro-, meso and macropores in the carbon host.

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Chapter 7 Summary



The thesis mainly discusses the design and controlled synthesis of MOF precursors, and investigates the methods for tuning the microstructure of MOF-derived nanomaterials. The applications of the obtained MOF derivatives in electrochemical energy storage and conversion related systems such as oxygen reduction catalysis and lithium-ion/lithium sulfur batteries are demonstrated, which leads to the following conclusions:

- (1) The growth kinetics of a Co-based MOF is revealed and applied to construct samples with tunable size, morphology and composition for the first time. The obtained MOF precursors are later converted into nitrogen doped porous carbons through a one-step thermal treatment process. The ORR catalytic activities of these samples are systematically studied and the size effects of the MOF precursor toward the catalytic performance of the derived catalyst is revealed. As the particle size decreases, the catalytic activity increases remarkably. Sample obtained from the smallest MOF nanoparticles (300 nm) demonstrates the highest catalytic activity and outperforms most the non-precious catalysts in acid electrolyte, which can attributed to the fully exposed active sites and excellent mass and electron transport properties. Moreover, the derived carbons display excellent lithium storage properties due to the rich nitrogen dopants in the framework and shorten lithium diffusion length. The idea of using nano MOF here opens new avenues for the design of MOFs in electrochemistry and catalysis applications.
- (2) The influence of the microstructure of MOF-derived materials on the catalytic activity is studied, which reveals the existence of non-interconnected slit pores in materials obtained from direct heat treatment as a conventional strategy. This structure is a disadvantage for ORR catalysis due to the low mass exchange efficiency and the shield of active sites. In this work, a structure-directing agent is introduced to optimize the microstructure of MOF-derived materials, leading to the formation of Co@Co₃O₄@C core-shell nanoparticles uniformly embed in carbon support with interconnected ordered channels that can provide better transport pathway of O₂ and electrolyte. In this structure, the ORR active metal oxide cores are connected to the porous host through the nitrogen-doped carbon

shell, creating a strong interaction/contact between the cores and the carbon host and thus contributing to enhanced electron conductivity and stability. Benefiting from these properties, the new system displays identical catalytic activity but superior stability for ORR relatively to the commercial Pt/C catalyst. This work fully takes advantage of the coexistence of metal nods and nitrogen/carbon rich ligands, and produces highly active metal oxide-carbon composite structures for ORR catalysis for the first time. Due to a wide choice of metals and ligands in constructing MOF precursors, more composite structures can be anticipated through the strategy introduced in this work.

- (3) Following the idea introduced in Chap. 4, other structure-directing agents such as graphene and carbon nanotube are used to tune the microstructure of MOFderived materials. Co-MOF crystals are grown on graphene or carbon nanotube and pyrolyzed at elevated temperatures. It's interesting to find that the Co and C atoms from the Co-based MOF can diffuse through the carbon surface upon thermal activation and assemble into ultra-small Co@C nanoparticles that are converted into fancy CoO_x hollow nanoparticles through the Kirkendall effect. The ORR catalysis performance of the MOF-derived material is further enhanced, which surpass the commercial Pt/C catalyst in activity as well as in stability. The strategy is believed to be effective in constructing metal oxide hollow structures from other MOFs, such as Fe or Ni-based MOFs. The applications of these structures in supercapacitors or fast-charge type lithium ion batteries can be anticipated.
- (4) It's feasible to synthesize porous carbon materials from MOFs since MOFs can act as a porous template and carbon source at the same time. However, the conventional method in preparing MOF-derived carbons is of quite low efficiency and high cost. A new route based on an extended MOF structure, metal–organic gel, is developed to produce porous carbon materials with large quantity and simplified process. The obtained carbon materials inherit the highly porous nature of MOF and combine the integrated character of gel, leading to a hierarchically porous architectures in the derived 3D carbons with ultra-high surface area and large pore volumes. It's found that the new structure is beneficial for sulfur hosing in Li-S batteries, which can contribute improved utilization of active materials and cycle performance due to the nano-confinement effect of the porous carbon products.

It is demonstrated though this thesis that the microstructure and active center of MOF-derived materials can be precisely tuned through MOF precursor design and optimized thermal activation process in order to meet the demands from particular electrochemical reactions. Two aspects should be considered in further improving the performance of the MOF-derived nanomaterials in the later research. One is to construct hybrid MOF precursors with multi metals nodes or various heteroatom dopants in ligands. The other is to fabricate advanced composite systems. Moreover, a deep investigation of the phase conversion or structure evolution of MOFs during thermal activation process would be meaningful in understanding the design, formation and properties of MOF-derived materials.