

MOFs together with derivatives for supercapacitor applications

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Abstract. With the continuous progress of science and technology, the demand for energy of new scientific and technological products is higher and higher. However, with the development of large developing countries such as China, the fossil energy on the earth is almost exhausted. In order to solve this problem, people began to develop new clean energy. In order to use new energy more reasonably and efficiently, people must develop a high-performance Supercapacitor is a new energy storage device developed at the end of last century. However, the biggest obstacle to the development of supercapacitors is that their energy density is far lower than that of traditional energy storage devices. However, the biggest obstacle to the development of supercapacitors is that their energy density is far lower than that of traditional energy storage devices. The ideal supercapacitor electrode material has the characteristics of uniform pore size distribution, high specific surface area and high porosity. As a new organic-inorganic material, MOFs have a variety of spatial porous network structures, and the derivatives synthesized with MOFs as precursors can still maintain their original porous This review mainly introduces the examples of preparing electrode materials with reasonable structure with MOFs as electrode materials or MOFs and their derivatives as electrode materials were summarized and prospected.

Keywords: Supercapacitor; MOFs; Energy; Density; Clean

1. Introduction

The 21st century has seen a new transformation in the way we live our lives. On a global scale, technological advances have allowed new insights into productive life. During this time, a plethora of new brand applications and technologies have emerged: hybrid cars, solar cells, electric smart grids, communication devices, and artificial hearts. At the same time, new technologies have raised the demand for energy like never before. The spread of technology has exacerbated the global consumption of fossil fuels, which will one day run out of supply. This energy crisis has led to the development of new energy storage and conversion devices that can solve this problem and can meet the energy needs of new technologies[1,2]. Considering the mentioned problems above, rechargeable batteries and fuel cells are promising energy storage devices that are widely used in the field of energy storage. Another leading energy storage technology is electrochemical capacitors, also known as supercapacitors (SCs), which can store more power than conventional capacitors and can deliver power faster than batteries[3].

SCs can be divided into three categories according to their electrode materials: double electric layer supercapacitors (EDLCs), Faraday pseudocapacitors (PCs) and hybrid supercapacitors (HSCs)[4,5]. The electrode material of the double-layer supercapacitor is mainly a carbon-based material[6,7], which stores energy through the process of physical adsorption and detachment of ions realized on the contact surface of the electrode and electrolyte. The electrode materials of Faraday pseudocapacitors are mainly conducting polymers and metal oxides. Faraday pseudocapacitors rely on redox reactions at the contact surface of the electrode material and electrolyte for energy storage[8,9]. Another widely used SCs are hybrid supercapacitors. The electrode material of hybrid supercapacitor can be prepared by combining the electrode material of conventional double-layer supercapacitor with that of Faraday pseudocapacitor. Therefore, the energy storage mechanism of hybrid supercapacitors is a hybrid Faraday and non-Faraday mechanism, and the synergistic effect of the composite materials can result in SCs with both high power density and high energy density.

High performance SCs materials have tunable pore size distribution, high specific surface area, intentional electrochemical activity and electrical conductivity[10,11,12]. Carbon-based materials

have high specific surface area, electrochemical activity and good chemical stability, but relatively low specific capacity and energy density prevent them from being ideal electrode materials[13,14]. For pseudocapacitive materials, the lower specific surface area and porosity inhibit the dissociation of active components and ions in the electrolyte, slowing down the transfer of electrons and ions, resulting in the lower power density of pseudocapacitive materials. In addition, the redox reaction of the electrode material cannot react completely during the rapid charge/discharge process, which reduces the multiplicative performance of the electrode material[15]. The new SCs materials have to solve the problems of the existing electrode materials based on the excellent performance of the ideal electrode materials.

MOFs are novel organic-inorganic materials synthesized by self-assembly of metal ions and organic ligands. Compared with traditional porous materials, MOFs have the advantages of diverse grid structures, tunable pore sizes, high specific surface areas and abundant active sites[16,17]. Currently, MOFs have been widely used in gas adsorption and separation, drug delivery, catalysis, imaging and sensors. In recent years, MOFs and their derivatives have been frequently used in electrochemical energy storage, such as lithium-ion batteries, fuel cells and SCs. However, since the electrical conductivity of MOFs is much lower than that of carbon-based materials. Therefore, the synthesis of MOFs and MOFs derivatives with good stability and high conductivity is an urgent task for the development of SCs [18,19,20,21].

2. MOFs and their derivatives as electrodes for supercapacitors

2.1. MOFs directly as supercapacitor electrodes

Since the energy density of SCs is $E = \frac{1}{2}CV^2$, so increasing the specific capacitance can effectively increase the energy density of the electrode material.

Tan et al.[22] synthesized Zr-MOFs by the solvothermal method (Figure 1). The particle sizes were Zr-MOF_{s1} (100 nm), Zr-MOF_{s2} (200 nm), Zr-MOF_{s3} (450 nm), and Zr-MOF_{s4} (500 nm), and the temperature was controlled at 50 °C for the smallest particle size (Figure 2). The adsorption-desorption experiments of nitrogen in a nitrogen atmosphere at 200 °C for 16 h yielded a high specific surface area of 1047 m² g⁻¹ for Zr-MOF_{s1}, which was higher than the other three groups. The specific capacitance of Zr-MOF_{s1} was as high as 1144 F/g at a scan rate of 5 mV/s.

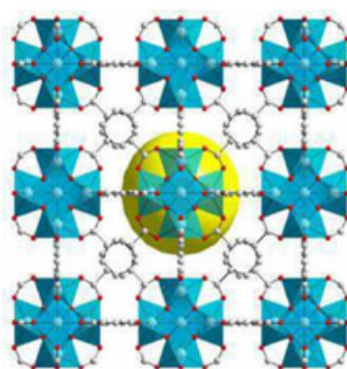


Figure 1 Crystal structure of Zr-MOFs (O in red, C in gray, Zn polyhedra in blue)

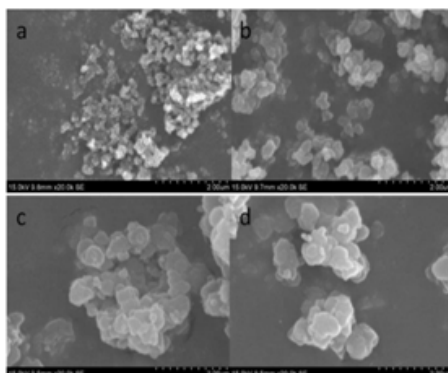


Figure 2 SEM images of Zr-MOFs at different temperatures

Lee et al. [23] synthesized Co-MOFs using cobalt nitrate and benzoic acid at 100°C. Co-MOFs films with a uniform thickness of 5 μm were successfully synthesized by using MOFs ions with particle sizes ranging from 50 to 100 nm (Figure 3a). The maximum pseudocapacitance of Co-MOFs in LiOH electrolyte was up to 206.76 F g⁻¹ (Figure 3c) at a current density of 0.6 A g⁻¹, the capacity remained 98.5% of the initial capacity after 1000 cycles, with a very good cycling stability. This is mainly attributed to the good crystal structure of the MOFs, which makes the MOFs stable in any electrolyte (Figure 3b).

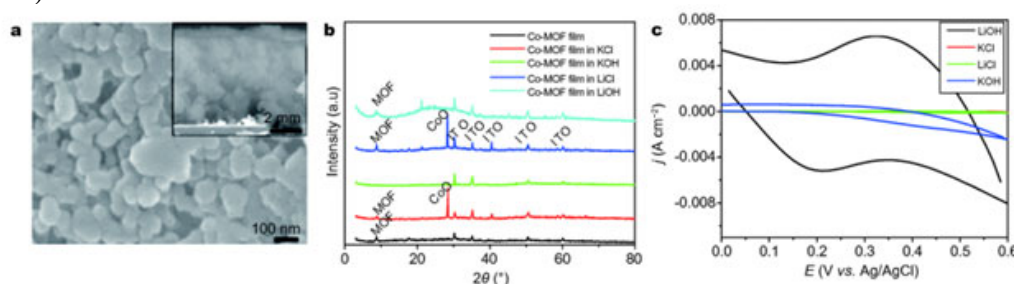


Figure 3 (a) SEM image of Co-MOFs film (b) XRD image of Co-MOFs film after 1000 cycles in different electrolytes (c) CV curves of Co-MOFs film in different electrolytes

Yan et al. [24] synthesized accordion-like Ni-MOFs by hydrothermal method using nickel nitrate hexahydrate, N,N-dimethylformamide (DMF), and sodium hydroxide. 3 mol L⁻¹ of KOH solution at a current density of 1.4 A g⁻¹, and the specific capacitance of Ni-MOFs was found to be up to 988 F g⁻¹ by three-electrode test, and the initial value was maintained after 5000 cycles of 96.5% of the initial value after 5000 cycles.

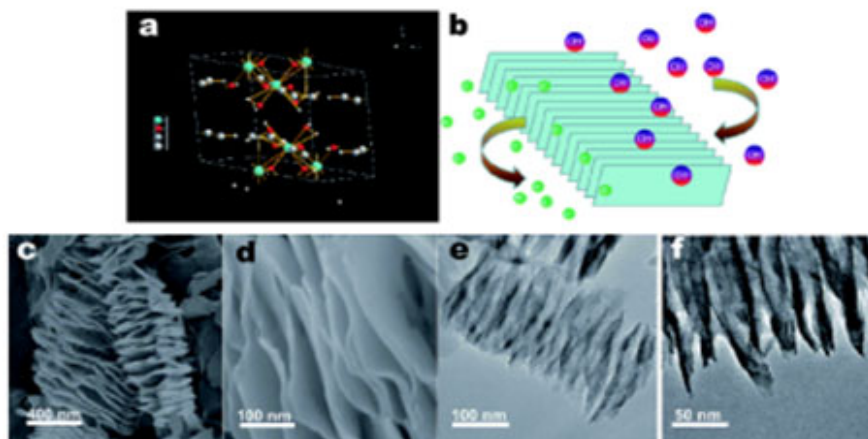


Figure 4 (a) Crystal structure of Ni-MOFs (b) Illustration of charging and discharging process (c, d) SEM image of Ni-MOFs (e, f) TEM image of Ni-MOFs

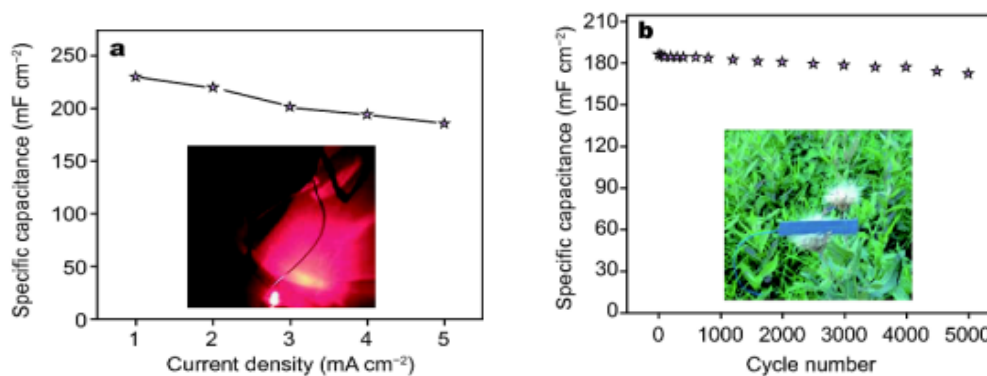


Figure 5 (a) Specific capacitance of supercapacitor at different current densities (b) Performance of the device at a current density of 5.0 mA cm⁻² for 5000 cycles

2.2. MOFs derivatives as supercapacitor electrodes

Derivatives of MOFs usually consist of three categories, which are prepared in different ways. Broadly, they can be summarized into the following three categories: (1) porous carbon materials obtained by pyrolysis of MOFs in an inert gas atmosphere (2) calcination of MOFs in multiple temperature zones to obtain the corresponding excess metal oxides (3) carbonization of MOFs to obtain metal oxide/porous.

2.1.1. Porous carbon

Due to the low boiling point of the central metal ion in MOFs materials (907 °C for Zn in Zn-MOFs), NPCs can usually be obtained by carbonization or acid treatment of MOFs.

Hao et al. [25] obtained nitrogen referenced porous carbon materials by carbonization and activation of ZIF-11. During the synthesis, ammonium hydroxide was added to the reactant solution. The specific surface area of the nitrogen-crosslinked carbon nanomaterials synthesized by this method is 2188 m² g⁻¹. The specific capacitance can reach 307 F g⁻¹ at a current density of 1 A g⁻¹ in 1 mol L⁻¹ of H₂SO₄ electrolyte.

Yang et al. [26] obtained porous carbon materials by direct carbonization of MOFs using Zn-MOFs synthesized with zinc nitrate and different organic ligands, such as H₂BDC, H₂BPDC, H₃BTC, and H₃BTB as precursors. The porous carbon material using H₂BDC as organic ligand had the highest specific surface area of 2816 m² g⁻¹. The specific capacity of the material was measured at a scan rate of 1 mV s⁻¹ in 6 mol L⁻¹ of KOH solution with a capacitance retention of 98% after 5000 cycles⁻¹.

2.1.2. Transition metal oxides

Transition metal oxides are ideal electrode materials for SCs because of their rich oxidation state structure, redox active sites and high specific capacity [27,28,29]. The metal oxides obtained by MOFs method can maintain the unique structure of MOFs and thus have higher cycling stability compared to the transition metal oxides obtained by other methods.

Sun et al. [30] used cobalt nitrate hexahydrate and dimethylimidazole as raw materials to synthesize ZIF-67. Co₃O₄ was synthesized by calcining ZIF-67 directly in air at 450 °C and 750 °C, respectively, using the synthesized ZIF-67 as precursors, with specific capacitance up to 706 F g⁻¹ and capacitance retention up to 71.5% after 1000 cycles. Li et al. [31] obtained Co₃O₄ nanotubes by calcining Co-MOF-74 to obtain Co₃O₄ nanotubes. The specific capacitance of Co₃O₄ nanotubes could reach 647 F g⁻¹ at a current density of 1 A g⁻¹, and there was no significant decay of the capacitance after 1500 cycles at a current density of 2 A g⁻¹. In addition, Wu et al. [32] prepared NiO with hollow double-shell layer structure by calcining Ni-MOFs precursors at a suitable temperature. NiO synthesized at

400 °C had the highest specific capacitance of 473 F g⁻¹ at a current density of 0.5 A g⁻¹ and a capacitance retention of 94% after 3000 cycles.

Li et al. [33] synthesized Co₃O₄ /NiO/Mn₂O₃ mixed metal oxides by calcining CoNiMn-MOF at different temperatures. The energy density of the asymmetric supercapacitor with graphene and Co₃O₄ /NiO/Mn₂O₃ as electrode materials can be 65.7 Wh kg⁻¹ at a window voltage of 1.7 V.

Chen et al.[34] synthesized NiCo mixed metal oxides using NiCo-MOF as precursors (Fig. 6a). When the ratio of Ni²⁺ /Co²⁺ is 1:2 (NiCo₂O₄), the specific capacitance can reach 797 F g⁻¹ at 6 mol L⁻¹ of KOH solution and a current density of 1 A g⁻¹ (Fig. 6b). This may be due to the presence of multiple metal ions that increase the active sites of the electrode material. In addition, the specific capacitance can be maintained at 500 F g⁻¹ after 10,000 cycles (Figure 6c).

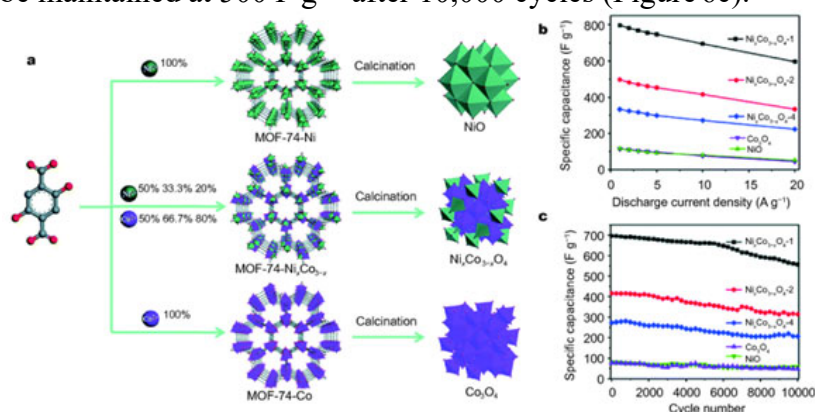


Figure 6 (a) Schematic diagram of NiCo oxide manufacturing process (b) Specific capacitance of different NiCo oxides at different current densities (c) Cycling stability of NiCo oxides at a current density of 10 A g⁻¹.

2.1.3. MOFs-derived porous carbon/metal oxide composite electrode materials

Porous carbon and transition metal oxides are ideal electrode materials for bilayer and pseudocapacitance, respectively, and carbon/metal oxide composite electrode materials prepared by MOFs have excellent bilayer and pseudocapacitance properties, thus attracting much attention in recent years.

Sinha et al.[35] obtained a mixture of TiO₂ and carbon (TiO₂ /C) by pyrolysis of MIL-125 (Ti-MOF) in an argon atmosphere (Figure 7). The SCs prepared using two parts of TiO₂ /C of equal mass had a power density of 865 W/kg and an energy density of up to 43.5 Wh/kg.

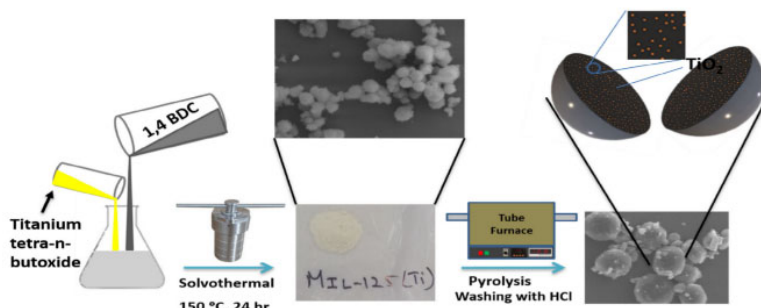


Figure 7 Schematic diagram of the synthesis of MIL-125-derived TiO₂ /C composite nanostructures

Chen et al. [36] grew in situ manganese oxide nanoparticles (MnO_x -CSs) with mixed valence states on ultrathin carbon sheets by calcination using Mn-MOF as a precursor. Thanks to the unique structure, the MnO_x -CSs-600 obtained by calcination at 600 °C has excellent properties. The specific capacity can reach 220 F g⁻¹ at a current density of 1 A g⁻¹.

2.3. Mixtures of MOFs and derivatives

The addition of surfactants and ionic doping is an effective strategy to build a stable system. Conductive materials such as carbon materials and conducting polymers are widely used to dope MOFs[37]. Through our research, composites can be obtained by direct doping during the synthesis of MOFs.

Meng et al.[38]synthesized spun Fe-MIL-88B-NH₂ using polymeric surfactant F127 as a structural guide and template. Fe₃O₄ /carbon composites were prepared using a well-controlled incomplete annealing process (Fig. 8a, b, c, d). The SSA of Fe₃O₄/carbon composites reached 37.7 m² g⁻¹. At a current density of 1 A g⁻¹, at 0, 20°C, 40°C and 60°C, using 1 mol L⁻¹KOH as electrolyte, the specific capacitance of this Fe₃O₄ /carbon was calculated to be 86, 128, 138, 162 F g⁻¹. The specific capacitance of the electrode slowly decreased to 88% of the initial value for 1000 cycles at 20°C, which implies a more stable electrode structure at 20°C. However, it was observed that the specific capacitance decreases rapidly as the temperature increases to 40°C due to the decrease in the internal resistance of the electrolyte (Figure 8f). After 1000 cycles at 40°C, the temperature was reduced to 0°C using an ice bath and then 1000 charge/discharge cycles were performed. The temperature was then restored to 20°C and after a further 1000 cycles (4000 cycles in total), the capacitance value of the electrode dropped to 83.3% of its initial capacity (Figure 8f).

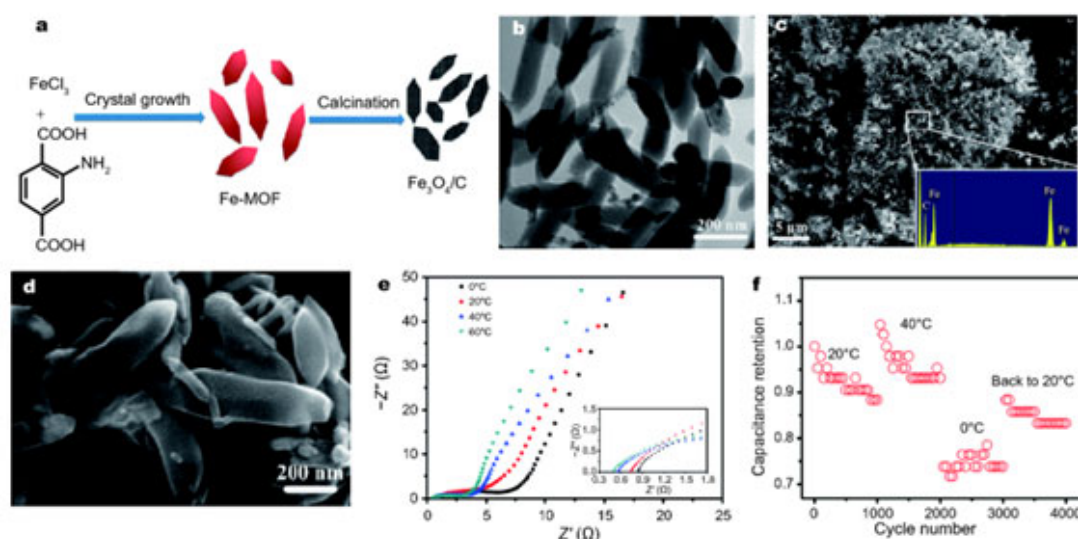


Figure 8 (a) Flow chart of Fe₂ O₃ /C composite preparation (b) TEM image of Fe-MIL-88B-NH₂ (c) SEM and EDS images of Fe₂ O₃ /C composite (d) SEM image of Fe₂O₃ /C (e) EIS measurement of Fe, O content (f) Cycling stability of Fe₂O₃ /C composite at different temperatures

Cao et al.[39]added PVP during the synthesis of PPF-3 (Figure 9). Then 2D CoSNC nanocomposites were formed by simultaneously carbonizing and sulfiding the resulting 2D PPF-3 nanosheets (Figure 9e). In the prepared CoSNC nanocomposites, CoS_{1.097} nanoparticles were uniformly dispersed in the nitrogen-doped carbon matrix during the heat treatment.

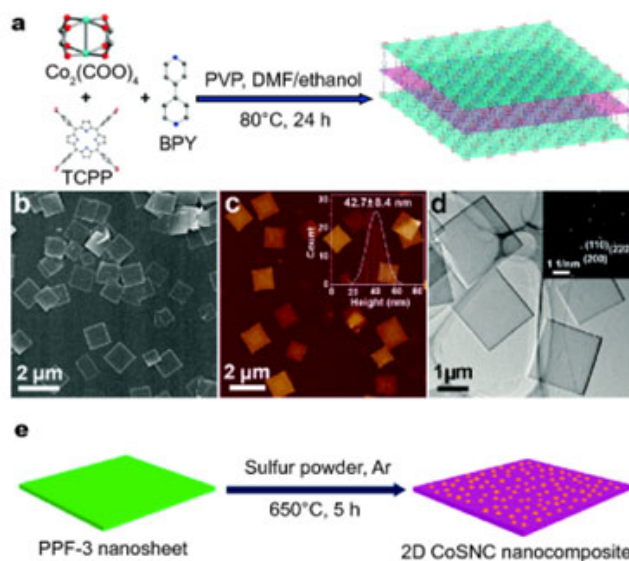


Figure 9 (a) Schematic diagram of the preparation process of PPF-3 nanosheets (b) SEM image of PPF-3 (c) Atomic force microscopy (AFM) image of PPF-3 (d) SEM image of PPF-3 (e) Schematic diagram of the synthesis process of two-dimensional CoSNC nanocomposites

3. Summary and Outlook

In conclusion, with the increasing demand for high-performance SCs electrodes, MOFs materials have attracted a lot of attention. In order to achieve the criteria of adjustable pore size distribution, high specific surface area, abundant active sites and excellent electrical conductivity of ideal electrode materials, various nano-MOFs structures and their derivatives have been explored by intensive research. Currently, MOFs are strong candidates for SCs electrodes due to their ordered porous structures and reversible intercalation of electrolyte ions. Although the introduction of pseudocapacitive materials in MOFs systems with porous structures can improve the capacitance more effectively, the low rate of Faraday reaction greatly prolongs the charging and discharging process. In addition, the low structural/chemical stability of most transition metal oxide active electrodes significantly shortens the cycle life of supercapacitors. Coating carbon materials on MOFs and constructing double-shell layer structures are common strategies to reduce the irreversible capacity loss incurred during the charging/discharging process. Numerous examples show that the ideal structure of MOFs obtained by laminating carbon-based materials with polymers is the way to obtain electrode materials with high specific capacitance and cycle life. Although most MOFs materials have poor electrical conductivity, compounding materials with good electrical conductivity in MOFs can accelerate the electron transport rate and thus improve the electrochemical performance of the electrode. Therefore, it is important to study the mechanism of electron transport in these materials and to design suitable conductive materials.

Hollow nanostructures are an important class of functional materials with low mass density, high surface area, and short diffusion length. These properties make it promising for a wide range of applications. The most popular method for synthesizing hollow nanostructures is the template-assisted growth method, in which new materials are grown on nanoparticles (NPs) with sacrificial templates, which are removed by gradual etching. The template-mediated method can overcome the low electrical conductivity and poor stability of MOFs by converting them into more stable and better conducting hollow bilayer-like double hydroxide nanostructures (LDHs), while maintaining the porous structure of MOFs. LDHs are a class of inorganic layered compounds consisting of a main layer and interlayer anions. The main layer consists of divalent and trivalent metal ions of octahedral coordination hydroxyl groups that form two-dimensional (2D) layers by sharing edges. The layers contain anions with balanced charges, such as NO_3^- , Cl^- , ClO_3^- and water molecules. MOFs can be converted into hollow LDH nanostructures by metal salt etching. The morphology of the final product

can be roughly tuned by controlling the concentration of the metal salt, the water content of the solvent can and adjusting the structure of the MOFs template. The doping of the synthesized LDHs with conductive substances such as nanocarbon can greatly improve their electrical conductivity. The synthesized hollow structures have better properties and can be used as electrode materials for SCs. However, the details related to the conversion of MOFs into LDHs are still to be solved: 1) Which surface locations such as angles and cut surfaces of MOFs templates are most susceptible to etching? What are the factors affecting the etching rate? 2) How the shell layer is formed and how the NPs are hollowed out during the conversion reaction. 3) How to adjust the morphology of the final product by controlling the reaction kinetics. Solving these questions will facilitate us to design supercapacitor electrode materials with more desirable structures and properties.

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