Chapter 4
Supercapacitors

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4.1 Introduction

With the rapid development of modern economy, coal, oil, diesel, and other non-renewable energy resources are increasingly in short supply. At the same time, the use of these energies causes PM2.5, haze, greenhouse effect, and other environmental problems. To solve these urgent environmental problems, the development of renewable and clean energy has become a feasible way [1–5]. Electrochemical energy storage systems, such as fuel cells, supercapacitors (SCs), and second-generation lithium batteries, show great promise in harnessing new energy sources such as solar and wind power. Therefore, the research of electrochemical energy conversion and storage system is urgent [6–8]. Among them, SCs has good cycle stability, high power density, and good electrochemical reversibility, so it has great application potential in portable electronic products, standby power storage, electric vehicles and so on [9–13]. SCs have been widely used in the national economy, science and technology, and daily life. It has an important impact on alleviating energy and environmental crisis and improving people's living standards. What's more, it has become a new field of research and public attention [14–23]. Since the performance of SCs is mainly determined by its electrode materials, the research of high-performance materials has already been the focus of attention in this field.

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Metal–organic frameworks (MOFs) are a new kind of porous crystalline materials constructed in three-dimensional (3D) space with metal ions/clusters and organic bridging ligands as ligands [24]. Over the past few years, MOFs have attracted a lot of attention and are now one of the most rapidly growing areas of research. To date, there are more than 20,000 MOFs with different compositions, crystal structures, and morphologies been reported [25]. MOFs have great potential in SCs due to their customizable structure and function, high porosity, and large internal surface area. In this section, original MOF and MOF-derived materials are mainly discussed as electrode materials for SCs.

4.2 Pristine MOF for Supercapacitors

The use of pristine MOF materials as electrodes for supercapacitor (SC) has been the subject of much attention due to their great surface area and intrinsic redox properties. In this context, many metal ions such as Ni, Fe, Co, Mn, Cu, Zn, Ce, V, Cr, Al, Zr, and organic linkers like big families of terephthalic acids, imidazolates, and carboxylic acids, various types of bipyridine, benzoic acids, and phenylene have been employed in the production of pure MOFs for such application. Common good organic linkers are 1,4-benzenedicarboxylic acid (1,4-H_2bdc), 2-methylimidazole, 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), etc., as shown in Fig. 4.1. Worthwhile mentioning, that most of these kinds of ligands show weak

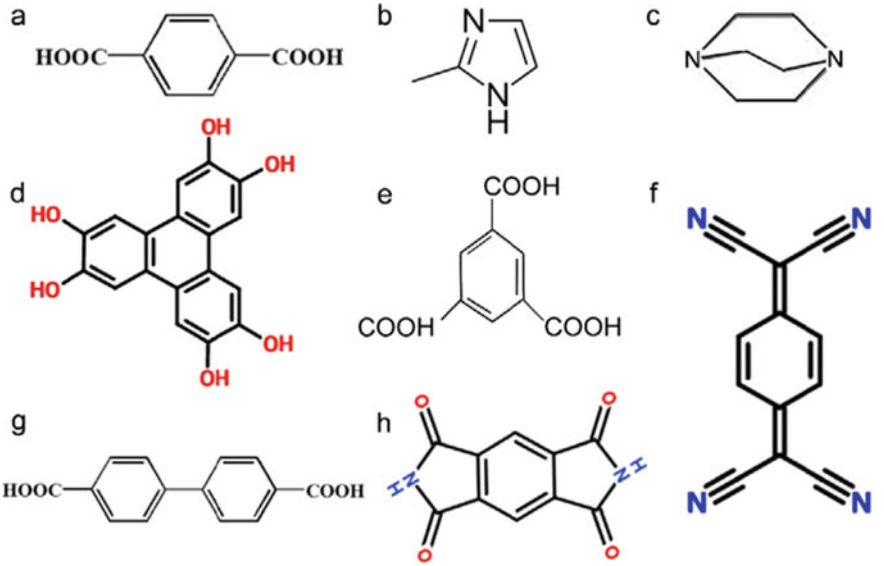

Fig. 4.1 Schematic representation of 1,4-H_2bdc (**a**), $C_4H_6N_2$ (**b**), $C_6H_{12}N_2$ (**c**), $C_{18}H_{12}O_6$ (**d**), H_3BTC (**e**), $C_{12}H_4N_4$ (**f**), 4,4'-H_2bpc (**g**) and $C_{10}H_4O_4N_2$ (**h**)

electron-withdrawing property which leads to act as a redox center. However, the direct application of MOFs as SC electrode materials is mainly faced with poor conductivity and mechanical/chemical stability. Besides, short cycle life at higher rates due to the increase in resistance and inadequate faradaic redox reactions at higher current densities as well as low electrode surface area, resulting in a small contact area between the electrolyte and the electrode material. In SCs, the use of MOFs has only been widely reported by researchers in recent years.

Early trials to use pristine MOFs as electrode materials for SCs have been reported via Díaz and co-workers [26]. Co_8-MOF-5 was selected to be combined with polytetrafluoroethylene and carbon black to construct electrode. Result exhibited a very low capacitance value of 0.3 F g^{-1}, which might be restricted via specific MOF and electrolyte. Meanwhile, Lee et al. explored Co-MOF as a promising material for SCs and opened the door to further research various MOFs as an electrode material [27]. The Co-MOF as electrode materials demonstrated capacitance of 206.76 F g^{-1} and good pseudocapacitor behavior (7.18 Wh kg^{-1}). In addition, three similar carboxylic acids with different molecular lengths were utilized as organic ligands to synthesize different morphology and pore sizes of Co-MOFs have been reported by Lee and co-workers [28]. Among the three Co-MOFs, the longer linkers have larger surface areas and larger pores. According to the surface area and pore diameter, the specific capacitance, power density, and energy density of the three Co-MOFs electrodes were detected to be ranging from 131.8 to 179.2 F g^{-1}; from 3.88 to 5.64 kW kg^{-1}; and from 20.7 to 31.4 Wh kg^{-1}, respectively. To achieve electrode materials with higher capacitance for SCs from two-dimensional (2D) layered MOFs, Liu and co-workers reported the syntheses of a 2D Co-MOF (Co-LMOF, $\{[Co(Hmt)(tfbdc)(H_2O)_2]\cdot(H_2O)_2\}_n$; H_2tfbdc = 2,3,5,6-tetrafluoroterephthalic acid; Hmt = hexamethylenetetramine) and its electrochemical performances as the electrode materials of SCs and found that Co-LMOF showed considerably high specific capacitance (1978 F g^{-1}) and can also retain 94.3% of the original capacitance over 2000 cycles [29]. Meanwhile, another Co-MOF material with conductive networks frames and a layer structure was synthesized via Wei and co-workers [30]. This material delivered a remarkable capacitance of 2564 F g^{-1} and can keep at 95.8% after 3000 cycles. In addition, Zheng et al. prepared ultra-thin 2D Co-MOF nanosheets and detected its supercapacitive behaviors [31]. Result showed and it achieved 1159 F g^{-1}, which might originate from the short ion diffusion length. Abazari et al. reported a novel Co-based MOF, (NH_2-TMU-53, $[Co(2\text{-}ATA)_2(4\text{-}bpdb)_4]_n$; 2-ATA = 2-aminoter ephthalic acid, 4-bpdb = N,N-bis-pyridin-4-ylmethylene-hydra zine) and evaluated its supercapacitive performance. It presented an upper capacitance, as well as good cycling stability (92.03% after 6000 cycles). When assembled asymmetric supercapacitor (ASC) device from NH_2-TMU-53 and AC, it delivered the high power and energy density [32].

As mentioned above, Co-based MOF can be applied in SCs as electrode materials. For SCs, Ni-MOFs as supercapacitive electrode materials are also very common. Liao et al. successfully prepared a series of Ni-MOF for electrochemical SCs by mixing isonicotinic acid and nickel nitrate in N, N-dimethylformamide (DMF) at 140°C for 96 h in a high-pressure tank [33]. Electrochemical test results showed good capacitance performance (634 F g^{-1} at 5 mV s^{-1}) and cycle stability (84% for 2000 cycles). Kang and colleagues studied a novel pseudocapacitor material Ni-MOF, $Ni_3(BTc)_2 \cdot 12H_2O$ [34]. The experimental results show that Ni-MOF has excellent performance of 726 F^{-1} pseudocapacity and excellent cycling stability. However, Yang and colleagues obtained layered nanostructured Ni-MOF by mixing terephthalic acid (PTA) and nickel chloride in DMF at 120 °C for different times [35]. The material exhibits high capacitance at 0.5 A g^{-1} (1127 F g^{-1}) and cycle stability (90% after 3000 cycles). This excellent electrochemical performance is due to the inherent properties of Ni-MOF, such as preferred exposure surfaces and layered structures. Qu and co-workers successfully prepared novel, nickel-based, pillared MOFs of similar topology using 9,10-anthracenedicarboxylic acid (ADC), 2,3,5,6-tetramethyl-1,4-benzenedicarboxylic acid (TM), 1,4-naphthalene-dicarboxylic acid (NDC) as carboxylate ligands, and 1,4-diazabicyclo[2.2.2]-octane (DABCO) as pillar ligands [36]. As the electrode material of SCs, DMOF capacitor shows excellent electrochemical performance. Compare with the other two, Ni-DMOF-ADC had better cycling stability (98% after 16,000 cycles). Sheberla et al. reported $Ni_3(HiTP)_2$ (Ni_3(2,3,6,7,10,11-hexaamine triphenyl)$_2$) with high conductivity as the sole electrode material for double-layer electrical capacitors (EDLCs) [37]. As shown in Fig. 4.2h, $Ni_3(HITP)_2$ is composed of stacked π-conjugated two-dimensional layers, which are penetrated by one-dimensional cylindrical channel with a diameter of about 1.5 nm. The surface area normalized capacitance of $Ni_3(HITP)_2$ is up to about 18 μF cm^{-2}, which is higher than that of other carbon materials except porous graphene (Fig. 4.2j). As shown in Fig. 4.2i, the $Ni_3(HiTP)_2$ electrode shows high reliability in 10,000 cycles with a capacitance retention rate greater than 90%. Therefore, highly conductive porous MOF ($Ni_3(HiTP)_2$) is a promising active electrode material for EDLC. In addition to the above results, other Ni-MOFs used as SCS electrode materials have also been reported [38, 39].

Apart from Co- and Ni-based MOFs, other MOFs utilized in SCs have also been reported. Three Fe-based MOFs (MIL-88(Fe), MIL-53(Fe), and MIL-100(Fe)) synthesized by campagnol and co-workers was used as electrode materials for SCs [40]. They showed the effects of pellet thickness, pore size, and cations of different sizes on performance. Experimental results display that MIL-100 (Fe) has better performance than that of a combination of carbon and nanotubes in the same solution. However, the dissolution of the reduction process strongly limits the cycle stability of the electrode.

In addition, Choi et al. constructed a coin-type supercapacitor (SC) device based on nMOFs electrodes [41]. A series of 23 MOF compounds were successfully synthesized and examined with various organic ligands and central metal ions, including MOF-74 structures (multi-metallic metal oxide mixing units and 1D pores), zirconium (IV) MOF of different lengths and shapes of links and nanocrystalline sizes, MOF-5 structures (with multiple mixing functions and three-dimensional pores) and MOF containing metal units of different nucleity. In particular, a zirconium based MOF (nMOF-867, $Zr_6O_4(OH)_4$(2,2'-bipyridine-5,5'-dicarboxylate)$_6$) exhibited abnormally high volume and area-specific capacitances (0.64 F cm_{stack}^{-3} and 5.09 mF cm_{areal}^{-2}) and its performance can also maintain at least 10,000 cycles

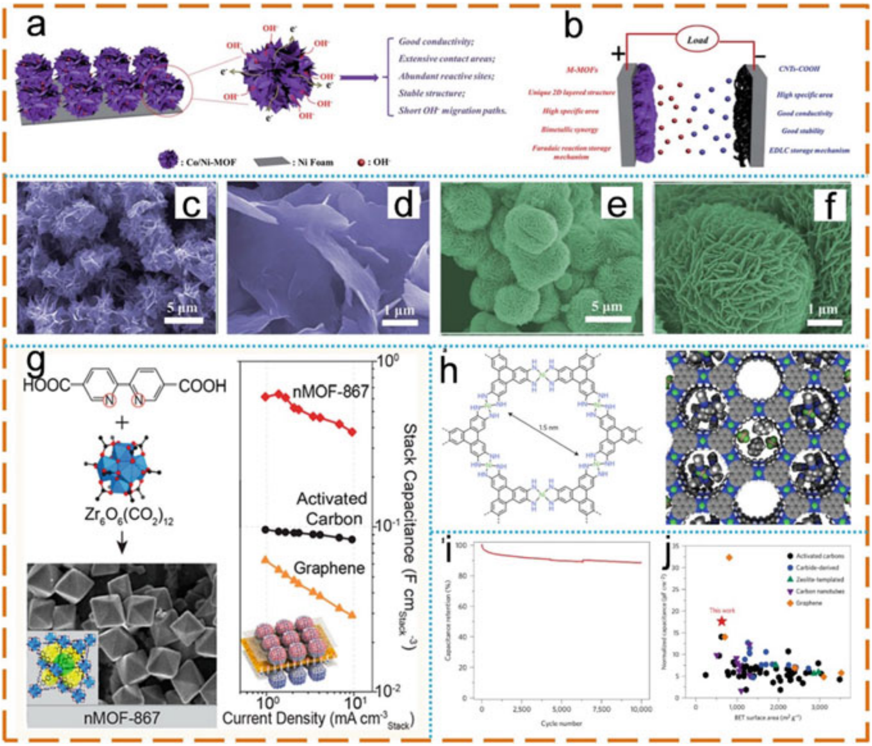

Fig. 4.2 **a** Schematic diagram of ion and charge transfer in the Co/Ni-MOF electrode. **b** An abstract illustration of hybrid supercapacitors. **c, d** SEM images of the as-synthesized Co/Ni-MOF and **e,f** Zn/Ni-MOF. **g** Structure of MOF-867 and the construction and performance of the nMOF SCs. **h** Structural schematics of $Ni_3(HITP)_2$. **i** Capacitance retention under repeated cycling at 2 A g^{-1} for 10,000 cycle. **j** Comparison of areal capacitances among various EDLC materials. **a–f** Reprinted with permission from Ref. [42]. Copyright 2016, The Royal Society of Chemistry. **g** Reprinted with permission from Ref. [41]. Copyright 2014, American Chemical Society. **h–j** Reprinted with permission from Ref. [37]. Copyright 2016, Nature

(Fig. 4.2g). In order to improve the electrical conductivity of MOFs, Jiao et al. successfully obtained mixed MOFs (M-MOFs) by partially replacing Ni^{2+} in Ni-MOF with Co^{2+} or Zn^{2+} [42]. According to the SEM images of Co/Ni-MOF and Zn/Ni-MOF (Fig. 4.2c-f), it can be clearly observed that Co/Ni-MOF flower-like structures are composed of many nanosheets (average thickness of 30 nm) and the morphology of Zn/Ni-MOF is similar to that of Co/Ni-MOF. As a battery-type electrode material, M-MOFs have a unique two-dimensional layered structure (Fig. 4.2b), which can provide enough space for OH^- insertion and disinsertion (Faraday Reaction). This special hybrid SC combines the advantages of capacitive and Faraday reactions to improve the power density and energy density. Compared with Ni-MOF, 2D M-MOF shows excellent electrochemical performance. M-MOF has excellent electrochemical properties for the following reasons. First, as shown in Fig. 4.2a, the flower-like M-MOF structure, as the conduction pathway and backbone, provides a strong support for the structural integrity and efficient charge transfer of the faraday reaction. In addition to broadening the application of MOFs, their research could open up new ways to bridge the performance gap between batteries and SCs.

4.3 MOF-Derived Materials for Supercapacitors

In recent years, in addition to directly use pure MOFs, more and more researchers have used MOFs as a sacrificial template to prepare highly controllable nanostructured materials and apply them to electrochemistry [24]. Some recent reports have shown that pure MOF has problems such as low conductivity, poor electrolyte ion transport performance, and low conversion efficiency, which limit its application in energy storage. Compared with pure MOFs materials, MOF-derived materials have superiority in electrochemical energy storage. MOF is a highly porous crystalline material that can be transformed into the desired product through a one-step calcination process, which promotes the fact that MOF is used for the development of nanostructured materials, which enhances their practical applications on pilot and industrial scales. Due to these advantages, MOF materials have been successfully used to develop porous carbon, metal compounds, and composite materials (M/MO@C) [43]. In this section, the application of MOF-derived materials in supercapacitors is reviewed.

4.3.1 MOF-Derived Porous Carbon Materials for Supercapacitors

As a common electrode material, carbon materials have the characteristics of high electrical conductivity, low thermal expansion coefficient, and low density, and have been widely used in the field of electrochemical energy storage. However, the storage capacity of conventional carbon materials is small, so it is difficult to increase power density and energy density. Recently, the preparation of carbon materials with microporous, mesoporous, and macroporous structures using MOF precursors as templates has attracted widespread attention. This is mainly because the preparation of porous carbon materials largely maintains the specific surface area of the precursor MOF. The uniform distribution of the pore size of the carbon material and the effective contact of the electrolyte help it improve the electrochemical performance of the supercapacitor.

Without adding any other precursors, the porous carbon material obtained by directly carbonizing the MOF will have excellent electrochemical performance when used in supercapacitors.

Three-dimensional porous carbon materials are favored by many scientific researchers due to their simple preparation process. Amali et al. used the ultrasonic method to prepare the microporous framework ZIF-8, and assembled the microporous particles into medium/large pores as the secondary structure [44]. After simple carbonization, ZIF-8 forms a three-dimensional layered porous carbon framework with micropores, mesopores, and macropores, and has excellent supercapacitor electrode performance (Fig. 4.3a–c). Similarly, Torad et al. used cobalt-containing zeolite imidazole framework 67 (ZIF-67) to directly carbonize highly graphitized three-dimensional NPCs [45]. Their NPCs have high specific surface area, large pore volume, and inherent electrical conductivity. It is expected to become a high-efficiency electrode for high-performance supercapacitors. Compared with the previous carbon-based double-layer capacitors, the maximum specific capacitance obtained by using this NPC as the electrode material of the supercapacitor is very high. Salunkhe et al. designed a new type of symmetrical supercapacitor based on NPC by directly carbonizing zinc-based MOF without controlling the reaction conditions to synthesize two NPCs with different particle sizes [46]. The results show that the NPC material has excellent electrochemical properties, and the maximum specific capacitance in 1 M H_2SO_4 electrolyte is 251 $F{\cdot}g^{-1}$. Research shows that these high-efficiency electrodes have good capacitance, high stability, and good rate capability. As the electrode material of supercapacitors, carbon derived from Al-PCP has ideal capacitor performance. Porous carbon polyhedron and other materials are used as different electrodes to synthesize supercapacitors to obtain better electrochemical performance. Yi et al. constructed an asymmetric supercapacitor based on the core–shell structure of porous carbon materials derived from MOF and CNT@NiO composite materials [47]. The main component of the anode material is polyhedral porous carbon obtained by carbonizing ZIF-8 at a high temperature of 1000 °C. This kind of porous carbon has uniform pore size, no large defects on the surface, and large specific surface area (1980 m^2 g^{-1}), which is very helpful

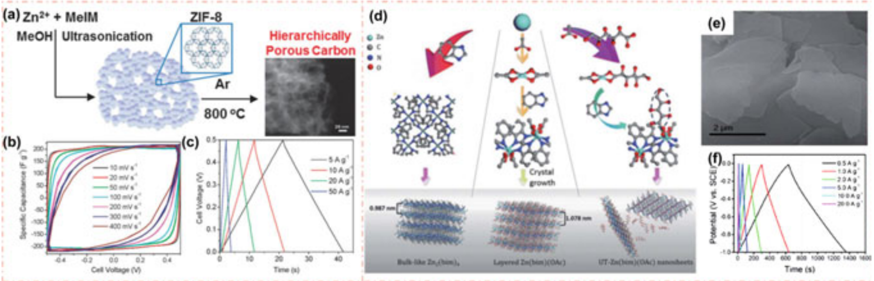

Fig. 4.3 **a** Schematic illustration for the preparation of hierarchically porous carbon from an assembly of ZIF-8 particles. **b** Cyclic voltammograms at different sweep rates of AS-ZC-800 for an electrochemical capacitor in 1.0 M H_2SO_4 electrolyte. **c** galvano static charge–discharge curves at high current densities. **d** Schematic illustrations of the synthesis of $Zn_2(bim)_4$, Zn(bim)(OAc), and UT-Zn(bim)(OAc). **e** SEM image of the UT-Zn(bim)(OAc) nanosheets. **f** Galvanostatic charge–discharge profiles of the UT-CNS electrode at different current densities

to improve the energy storage performance of combined supercapacitors. The electrochemical test results show that at a certain current density, the electrode made of porous carbon has a high specific capacitance. The charge and discharge test of asymmetric supercapacitors of CNT@NiO composite and porous carbon showed that the power density and energy density are both high within a certain voltage range. In addition, asymmetric supercapacitors also have excellent cycle stability. This is due to the synergy between porous carbon and CNT@NiO, which makes asymmetric supercapacitors have high energy density and power density as well as good cycle stability. In addition to pure porous carbon, N-doped porous carbon also has excellent performance when applied to electrode materials of supercapacitors. N doping not only introduces pseudocapacitance, but also improves surface wettability, making it easier for electrolyte ions to enter the electrode material, thereby increasing capacitance. Too much N will cause the conductivity to decrease, so it is necessary to explore a suitable synthesis method to control the nitrogen content within a reasonable range. Nune et al. used N-containing isoreticular metal–organic framework (IRMOF-3) as a template to prepare a series of N-doped carbon materials with different structures, and by adjusting the carbonization temperature, the nitrogen content and porosity can be changed [48]. For a carbonization temperature of 950 °C, N-doped porous carbon has an extremely high capacitance of 239 $F \cdot g^{-1}$. In contrast, similar N-free carbons have a low capacitance of 24 $F \cdot g^{-1}$, which indicates the importance of nitrogen dopants in the charge storage process. Since it is easy to produce small amounts of N-doped porous carbon, this route can be extended. N-doped carbon materials synthesized from MOF-8 have low electrical conductivity due to their high nitrogen content. Due to graphitization, the nitrogen content and specific surface area of porous carbon prepared by ZIF-67 are reduced. On this basis, Yamauchi et al. used a seed method to grow ZIF-67 on the surface of ZIF-8 to prepare ZIF-8@ZIF-67 core–shell composites, and then heat-treated them in flowing nitrogen to obtain N-doped carbon (NC) is the core of carbon nanotubes, graphitic carbon (GC) is the shell, and nanopore NC@GC composites have a core–shell structure [49]. The research results show that the specific surface area of the obtained composite carbon material is 127 $m^2 g^{-1}$, the nitrogen content is moderate, and the pore structure distribution ranges from micropores to mesopores. At the same time, NC@GC electrode has excellent electrochemical performance. When tested at a higher current density of 2 $A \cdot g^{-1}$, the capacitance value is as high as 270 $F \cdot g^{-1}$, which is due to the synergy of NC's high nitrogen content and highly graphitized GC. The researchers also found that gaps of different sizes in carbon materials can be connected to each other, resulting in a relatively large specific surface area, which can promote the transport of electrolyte ions.

However, the three-dimensional porous carbon material has a small specific surface area and low pore utilization rate, which easily causes slow electrochemical capacitors and electrochemical catalytic reaction kinetics and poor long-term stability, which limits its application in the field of electrochemical energy storage. In contrast, two-dimensional porous carbon materials have the advantages of ultrathin morphology, large specific surface area, high aspect ratio, continuous layering, etc., so they have better electrochemical performance when applied to supercapacitors. Yan et al. directly carbonized Al-PCP to obtain a two-dimensional porous carbon material with a higher BET surface area [50]. Similarly, nitrogen doping can also be used to change the electrochemical properties of two-dimensional porous carbon materials. Zhao et al. reported a low-cost, bottom-up synthesis of ultra-thin Zn(bim)(OAc) MOF nanosheets and their derived N-doped porous ultra-thin (2.5–0.8 nm) carbon nanosheets (UT-CNS) synthesis method, and applied it to supercapacitors, to study it [51]. The capacitance of UT-CNS at high current density is higher than that of most of the reported electrode carbon materials of MOF supercapacitors (Fig. 4.3d–f).

Sometimes, porous carbon materials obtained by indirect carbonization can also obtain better performance. In the indirect carbonization process, first, an external carbon source (such as furan alcohol, ethylenediamine, tetraethyl chloride, and phenolic resin) is penetrated into the pores of the MOF by impregnation or gas phase methods and then carbonized in an inert atmosphere. Zhang et al. prepared a series of ZIF-derived porous carbon materials by co-carbonizing ZIF-7 with carbon sources such as glucose, ethylene glycol, glycerol, and furfuryl alcohol [52]. The results show that the ZIF-7/glucose composite carbon L-950 as an electrode for electrochemical capacitors exhibits ultra-high specific capacitance under alkaline conditions and has good stability. In addition, no conductive agent (such as acetylene black) is needed in the preparation process of the working electrode, which not only reduces the preparation cost, but also benefits the stability and performance. Jiang et al. used zeolite-like metal–organic framework as the precursor and template, and furfuryl alcohol as the precursor to prepare porous carbon materials with very high surface area (3405 $m^2 \cdot g^{-1}$, BET method) for electric double-layer capacitors [53]. The electrode material has high hydrogen storage capacity (2.77% by weight at 77 K and 1 atm) and good electrochemical performance.

In contrast, because the use of MOF as a template and carbon source for direct carbonization does not require an additional carbon source, but only involves a simple calcination step, and the carbon content in MOF is higher, so it is simpler and more practical in industrial-scale preparation.

The above research shows that MOF is an excellent template for preparing porous carbon materials. Due to its ultra-thin morphology and large specific surface area, the two-dimensional structure of carbon materials can obtain excellent electrochemical performance when applied to electrode materials of supercapacitors. The conductivity of the electrode material will affect the capacitance, and the balance between porosity and graphitization is also an important factor affecting electrochemical performance. In addition, additives, carbonization temperature, and treatment methods all affect the porosity or conductivity of the carbon material. In addition, in the process of synthesizing MOF, introducing heteroatoms or other templates on the ligand is also a way to increase the capacitance of the capacitor. This method can effectively improve the surface wettability of carbon materials while providing additional redox reaction centers.

4.3.2 *MOF-Derived Metal Compounds Materials for Supercapacitors*

Metal compounds store energy in the form of Faraday pseudocapacitors. At present, the metal compounds used in the field of supercapacitors mainly include metal oxides/hydroxides, metal sulfides, etc [54].

Metal oxides have attracted extensive attention from researchers due to their rich reserves, controllable morphology, reversible redox reaction, and higher theoretical specific capacitance. Among many metal oxides, Co_3O_4 electrode materials are considered to be ideal pseudocapacitance materials due to their excellent electrical conductivity, good chemical stability, and high specific capacitance.

Meng et al. used cobalt-based metal organic framework (Co-MOF) crystals to prepare porous Co_3O_4 materials through a solid phase conversion process (Fig. 4.4a) [55]. The results show that the prepared Co_3O_4 has crystallinity and clear porous properties (Fig. 4.4b). The electrochemical results showed that the porous Co_3O_4 particles exhibited a high specific capacitance of 150 $F{\cdot}g^{-1}$ at a current density of 1 $A{\cdot}g^{-1}$, and maintained a slightly higher capacitance after 3400 cycles, which can be attributed to Due to higher specific surface area and accessible channel structure characteristics (Fig. 4.4c–d). Therefore, the method is simple, controllable, and repeatable. Importantly, this specific solid-state thermal conversion strategy can be easily extended to prepare other porous metals and/or metal oxide nanomaterials with specific surface textures and morphologies. In addition to the solid-state conversion strategy, Co_3O_4 nanostructures can also be prepared by directly calcining the MOF precursor. Pang et al. synthesized dendritic Co_3O_4 nanostructures by calcining Co-8-hydroxyquinoline coordination structure [56]. As an electrode material for supercapacitors, they found that the nanostructured Co_3O_4 electrode has high specific capacitance and long cycle life. By adjusting the reaction conditions, porous carbon materials, and Co_3O_4 nanostructures can be synthesized simultaneously. Salunkhe et al. used ZIF-67 as a precursor to calcinate porous C and Co_3O_4 under different temperature conditions [57]. The characterization of structure and morphology showed that the porous carbon prepared by derivatization has a large specific surface area (350 m^2 g^{-1}); at the same time, the derivative Co_3O_4 has high purity without obvious carbon impurities, and the specific surface area can reach 148m^2 g^{-1}. The electrochemical performance test results of the electrodes composed of these two derivatives show that the specific capacitances of porous C and porous Co_3O_4 are 272 $F{\cdot}g^{-1}$ and 504 $F{\cdot}g^{-1}$, respectively, at a scanning speed of 5 $mV{\cdot}s^{-1}$. They further constructed an asymmetric supercapacitor based on two electrodes, and the asymmetric supercapacitor showed a higher energy density (15 $Wh{\cdot}kg^{-1}$) and power density (8000 $W{\cdot}kg^{-1}$). Moreover, after 2,000 charge–discharge cycle tests, asymmetric supercapacitors can still maintain high stability. On the one hand, the reason is that the porous Co_3O_4 has a larger porosity, which provides a better channel for ion transfer, so that the electrolyte can completely contact the electrode material. On the other hand, the good conductivity of porous carbon effectively improves the charge transfer speed of asymmetric supercapacitors.

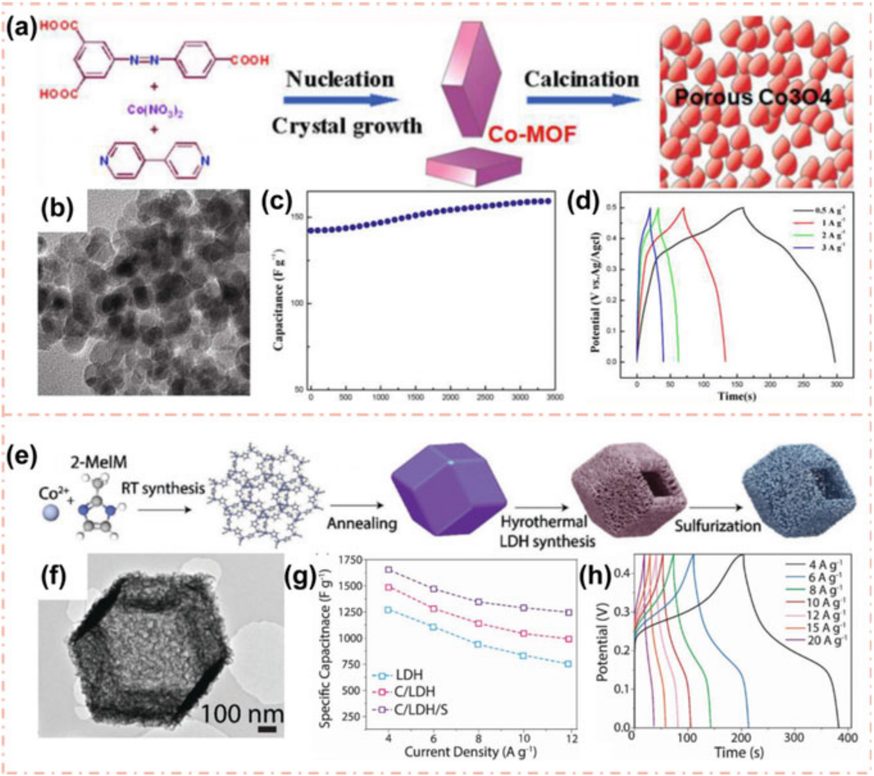

Fig. 4.4 **a** Schematic illustration of the formation process for porous Co_3O_4 aggregates. **b** HRTEM image of porous Co_3O_4 material. **c** Average specific capacitance versus cycle number of porous Co_3O_4 electrode at a galvanostatic charge/discharge current density 1 A g^{-1}. **d** Galvanostatic charge/discharge curves of porous Co_3O_4 electrode material at various charge/discharge current densities of 0.5, 1, 2, and 3 A g^{-1}, respectively, the potential window was ranged from 0 to 0.5 V. **e** Schematic illustration for the synthesis process of hollow NiCo-LDH/Co_9S_8 hybrid. **f** TEM images of C/LDH/S. **g** Specific capacitances as a function of current density. **h** charge–discharge profiles at various current densities for C/LDH/S

In addition to Co_3O_4, other metal oxides can also be applied to supercapacitors. For example, the use of manganese oxide as a supercapacitor electrode material can obtain good electrochemical performance. Maiti et al. reported that 1,3,5-benzoic acid manganese metal–organic framework (Mn-BTCMOF) formed a well-crystallized Mn_2O_3 mesoporous nanomaterial through simple heat treatment [58]. When tested as a pseudocapacitor electrode in a three-electrode configuration, a specific capacitance of 250 F·g^{-1} can be obtained at 0.2 A·g^{-1}. In addition, in order to prove its practicality, a two-electrode asymmetric supercapacitor pouch battery was assembled. It uses Mn_2O_3 as the positive electrode and commercially available activated carbon as the negative electrode. In the case of a power density of 1004 Wh·kg^{-1}, it shows an ultra-high energy of 147.4 Wh·kg^{-1}. The current work shows the potential of the MOF-derived route, which can be used to obtain metal oxides with nanostructures required for high-performance electrochemical applications. In addition, cesium oxide has also been used in supercapacitor materials with similar good results. Maiti et al. reported the use of [Ce(1,3,5-BTC)(H_2O)$_6$] (1,3,5-BTC = 1,3,5 phenyl tricarboxylate) MOF as the sacrificial template [59]. This method is simple and convenient to synthesize CeO_2. At 0.2 A·g^{-1}, the pseudocapacitance of CeO_2 produced by MOF is 1204 F·g^{-1}, which far exceeds its theoretical capacitance (560 F·g^{-1}). This study shows that controllable nanostructures can potentially alleviate the low energy density and capacitance attenuation problems that plague current metal oxide electrostatic precipitators.

In recent years, metal sulfides have played an important role in energy storage fields such as solar cells, lithium-ion batteries, and supercapacitors. Compared with metal oxides and hydroxides, sulfides have lower electronegativity, rich redox reactions, and higher electrochemical activity. Recent studies have found that the MOF-derived metal sulfide nanostructure has a high specific surface area and a large number of pores, which is very helpful to improve the capacitance performance of supercapacitors.

Le et al. used MOF as a sacrificial template to prepare a layered core–shell hollow iron cobalt sulfide-cobalt sulfide nanoarray, which was supported on conductive nickel foam (Fe-Co-S/NF) (Fig. 4.4e) [60]. The etching/ion exchange reaction between Co-MOF and $FeSO_4$ and subsequent solvothermal vulcanization resulted in the formation of layered core–shell hollow nanostructures, in which $FeCo_2S_4$-nanosheets and shells were assembled on Co_3O_4 hollow nanoarrays (Fig. 4.4f). Due to its complex composition and unique structure, Fe-Co-S/NF has rich electroactive potential, shorter charge/ion diffusion path, rich redox reaction, and good structural robustness, which help to improve the super Electrochemical performance of capacitor electrodes. Therefore, the obtained Fe-Co-S/NF electrode has a specific capacitance of 2695 F·g^{-1} at 1 A·g^{-1}, and a capacitance retention rate of 69.8% at 10 A·g^{-1}. 84% of the life is maintained in 84 cycles. In addition, Fe-Co-S/NF and rGO were used as cathode and anode respectively to assemble asymmetric supercapacitors. The obtained equipment provides a high energy density of 43.6 Wh·kg^{-1} at a power density of 770 W·kg^{-1}, while still maintaining a capacity retention rate of 89.6% after 5000 cycles (Fig. 4.4g–h). The strong electrochemical performance shows that Fe-Co-S/NF can be used as a promising electrode material in high-performance supercapacitor applications. Yilmaz et al. reported the in-situ quasi-crystal transformation of the hollow rhombohedral dodecahedron template derived from MOF and the interlayer metal sulfide (NiCo-LDH/NiCo-LDH/ Co_9S_8) system construction [61]. The intergranular metal sulfide (Co_9S_8) in LDH provides the best interface for mixed components and material stability. The NiCo-LDH/Co_9S_8 hybrid system together provides an ideal porous structure, rich redox chemicals, and high conductivity matrix. This leads to a significant improvement in its complementary electrocatalytic hydrogen release and supercapacitor energy storage performance. This work established the potential of MOF-derived SC scaffolds in the design of new hybrid inorganic-inorganic functional materials for electrochemical applications and other fields.

These outstanding research results all show that MOF can be used as a template for preparing metal compounds, and these metal compounds have good electrochemical performance when used in supercapacitor electrodes. In order to make the actual capacitance as close to the theoretical capacitance as possible in the application process, the surface area of the MOF should be as large as possible. Therefore, metal compounds derived from MOF have become popular materials due to their suitable ion transport channels and large contact area.

4.3.3 MOF-Derived Metal Metal/metal Compounds and Carbon Materials for Supercapacitors

Different types of electrode materials have different characteristics. Carbon-based materials have good electrical conductivity, but their specific capacitance is relatively small. Metals and their compounds have higher theoretical capacity, but their conductivity is poor. In order to obtain better electrochemical performance, it is necessary to use the advantages of different materials to make up for their respective defects, so that composite materials came into being. In short, a composite material is a material with new characteristics, which combines two or more materials with different characteristics through physical or chemical methods. The composite material can not only maintain the advantages of a single electrode material, but also can compensate for its own defects through the composite material, thereby achieving the purpose of improving electrochemical performance. The advantages of nanomaterials with a hybrid electrode structure composed of graphene sheets and inorganic substances include: (1) Effectively improve the electrical connectivity between the various electroactive materials, and shorten the ion transport path through the electrolyte path; (2) Two-phase The dense mixing makes them have a synergistic effect, which greatly improves the overall electrochemical performance.

Recent studies have found that MOF-derived metal and carbon composite materials can be used in supercapacitors. Metal has good conductivity and capacitance, while carbon material has ordered holes and conductivity. These characteristics give MOF specific functions to improve the electrochemical performance of supercapacitors. Wen et al. synthesized Ni-MOF@CNT composite material by a two-step method and applied it in the field of electrochemical energy storage. The results show that when the current density is 0.5 $\mathrm{A \cdot g^{-1}}$, the specific capacitance of Ni-MOF@CNT reaches 1765 $\mathrm{F \cdot g^{-1}}$ [62]. In addition, an asymmetric supercapacitor was constructed by combining Ni-MOF@CNT electrode and oxidized GO/CNT electrode. When the power density is 480 $\mathrm{W \cdot kg^{-1}}$, its energy density can reach 36.6 $\mathrm{Wh \cdot kg^{-1}}$. In addition, after 5000 charge and discharge tests, Ni-MOF@CNT still retains 95% of the capacitance. This is mainly due to the large amount of electrocatalytically active Ni metal ions exposed on the surface of the MOF itself, which facilitates the occurrence of redox reactions. At the same time, CNT can effectively improve the conductivity of the entire composite capacitor and accelerate the electron transfer process, so that the composite capacitor exhibits excellent electrochemical performance. Lin et al. prepared a mixed material of CNT and Mn-MOF and used it as an electrode material for Mn-based supercapacitors. After adding CNT to Mn-MOF, the conductivity and specific capacitance are greatly improved [63]. This work has opened up a new direction for the development of manganese-based supercapacitor materials and provided an effective way to improve the capacitance performance of MOF materials. Some people also synthesize bimetal-loaded carbon nanosheets for use as electrode materials for supercapacitors. Because of the synergy between the bimetals and can change the electronic structure, the electrochemical properties of the material can be improved. Xia et al. used a solvothermal method to improve the conductivity and electrochemical activity of MOF materials by adjusting their morphology and composition [64]. The hollow structures of Ni/Co-MOF nanosheets and Ni-MOF nanosheets were assembled in supercapacitors for electrochemical performance optimization. The results show that in 1 M LiOH aqueous solution, the specific capacitance of Ni/Co-MOF nanosheets is 530.4 F·g^{-1} and the specific capacitance is 530.4 F·g^{-1}, which is much higher than Ni-MOF (306.8 F·g^{-1}) and ZIF-67 (168.3 F·g^{-1}), has good rate and rate performance and has good cycle performance after 2000 cycles, and capacity degradation occurs. This work emphasizes the important role of adjusting Ni/Co-MOF two-dimensional nanosheets in accelerating electron and charge transport to optimize energy storage and conversion devices (Fig. 4.5a–d).

Compared with pure carbon, transition metal oxide as a redox-active electrode material provides higher energy density and specific capacitance, which depends on th65 and 1434.37 e reversible Faraday reaction at the interface, thus having higher

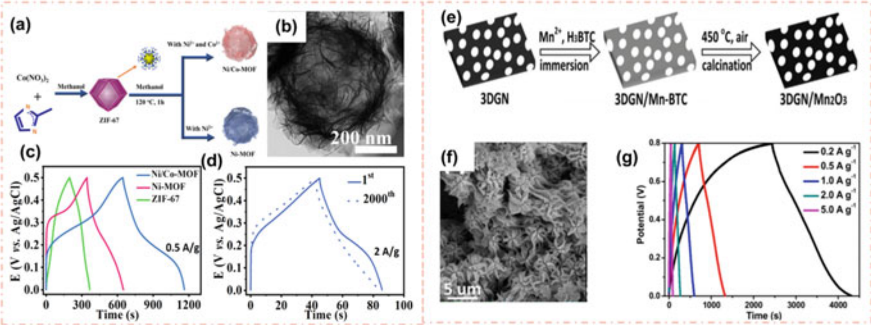

Fig. 4.5 **a** Schematic illustration of the synthesis of Ni/Co-MOF nanoflakes and Ni-MOF nanoflakes. **b** TEM images of Ni/Co-MOF nanoflakes. **c** Galvanostatic charge–discharge curves comparison of Ni/Co-MOF nanoflakes, ZIF-67, and Ni/Co-MOF nanoflakes at various current densities in 1 M LiOH solution. **d** Galvanostatic charge–discharge curves of Ni/Co-MOF nanoflake supercapacitor before and after 2000 cycles measured at 2 A g^{-1}. e Schematic illustration for the fabrication of 3DGN/Mn_2O_3. **f** High magnifications SEM image of 3DGN/Mn_2O_3. **g** GCD curves of the electrodes of Mn-BTC, Mn_2O_3, 3DGN/Mn-BTC and 3DGN/Mn_2O_3 at 0.2 A g^{-1}; **h** Specific capacitance as a function of the current density of the electrodes of Mn-BTC, Mn_2O_3, 3DGN/Mn-BTC and 3DGN/Mn_2O_3

energy density and specific capacitance, but pure transition metal The inherent high resistance and poor cycle stability of oxides greatly reduce their overall effectiveness. Therefore, the combination of pseudocapacitance materials and carbon-based conductive materials as electrodes has been widely used to realize high-efficiency supercapacitor devices to compensate for the inherent defects of metal oxides, increase overall energy density, and promote cycle stability.

Meng et al. reported a porous Fe_3O_4/carbon composite supercapacitor electrode material with excellent temperature resistance and long-term cycle stability [65]. Due to the poor annealing effect of the MOF template, the Fe-MOF template is easy to calcinate in one step. The template is composed of porous Fe_3O_4 nanoparticles and carbon, so the preparation of the material can be easily controlled. When this material is used as an electrode, it has excellent long-term cycle stability to temperature changes, which may be due to the porous structure and good conductivity of the composite material. This work provides a new method to prepare porous carbon/metal oxide electrodes derived from MOF with excellent conductivity and good capacitance characteristics. Ji et al. proposed a simple strategy to construct three-dimensional graphene networks (3DGN) and metal–organic materials, using MOF-derived metal oxide composites as free-standing electrodes for supercapacitors for the first time (Fig. 4.5e) [66]. The manganese-based MOF is first grown in situ on the 3DGN substrate by a simple solution immersion method, and then subjected to high-temperature treatment to form a 3DGN decorated by Mn_2O_3 with a flower-like stacked nanowire morphology (Fig. 4.5f). The designed 3DGN/Mn_2O_3 electrode material has ultra-high specific capacitance and excellent long-cycle stability, and will not decay after 1800 charge and discharge cycles (Fig. 4.5g). The excellent electrochemical performance is derived from the synergistic effect of the high conductivity and large surface area of 3DGN and the excellent pseudocapacitance activity of Mn_2O_3 nanowires. The results indicate that 3DGN/MOF-derived metal oxide composite materials are promising and effective binder-free electrode materials for high-performance supercapacitors. Jayakumar et al. prepared highly optimized mixed oxides of nickel and cobalt from the zeolite imidazole framework [67]. The mixed oxide is further used to produce a nickel–cobalt mixed oxide/graphene 3D hydrogel composite material to enhance electrochemical performance through a continuous and porous graphene conductive network. The electrode made of GNi:Co = 1:1 successfully obtained a higher specific capacitance of 2870.8 $F\cdot g^{-1}$ at 1 $A\cdot g^{-1}$, and also showed a capacitance retention rate of 81% after 5000 cycles. Thereby greatly improving the cycle stability. An asymmetric supercapacitor was also assembled using pure graphene 3D hydrogel as the negative electrode and GNi:Co = 1:1 as the positive electrode. With a 1.5 V potential window and a binder-free electrode, the capacitor can provide a high specific energy density of 50.2 $Wh\cdot kg^{-1}$ at a high power density of 750 W kg^{-1}. This may be due to the synergy between Co, Ni, and C and the electronic effects that increase the electrochemical performance. Xu et al. used GO/MOF as the precursor and obtained a variety of rGO/MOF-derived aerogels through a two-step calcination method [68]. The porous metal oxide composite material prepared by this method has the following advantages: on the one hand, the presence of graphene can effectively prevent the agglomeration of MOF and its derived porous metal oxide; on the other hand, the material has the high metal oxide properties. The specific capacitance performance has the high conductivity of graphene. At a current density of 1 A g^{-1}, its specific capacitance is as high as 869.2 F·g^{-1}, and there is no significant drop in performance after 5000 cycles. In addition, they found that the method can be used to prepare various graphene/MOF-derived metal oxide composite materials, such as rGO/ZnO, rGO/CuO, rGO/NiO/Ni, and rGO/Co_3O_4. This work provides a new and effective method to prepare MOF-derived porous composites using GO/MOF composites as precursors. Javed et al. report a convenient hydrothermal method for growing mesopore 2D Zn-Cobalt nanosheets directly at low temperatures on flexible carbon substrates (Zn-Co–O@CC) with an average thickness of 45 nm (Fig. 4.6a–b) [69]. The Zn-Co–O@CC electrode showed high capacitance of 1750, 1573.65, and 1434.37 F·g^{-1} in the neutral aqueous electrolyte LiCl, NaCl, and KCl at current densities of 1.5 A·g^{-1} and KCl, respectively. In up to 5000 cycles, it has excellent performance at high current densities and has good cycle stability (>94%) (Fig. 4.6c). In addition, highly flexible asymmetric supercapacitor devices have been fabricated using Zn-Co–O@CC as the positive electrode and NPC@CC (Zn-Co–O@CC//NPC@CC) as the negative electrode. Asymmetric supercapacitors can operate under a large potential window of 0.0–2.0 V, and provide an ultra-high energy density of 117.92 W h kg^{-1} and a power density of 1490.4 W kg^{-1}, showing excellent energy storage performance. The cycle stability after 5000 charge/discharge cycles is 94%. These results provide valuable insights for the preparation of asymmetric supercapacitors for high-efficiency energy storage devices using bimetal oxide and MOF-derived carbon. Metal oxide has attracted much attention due to its high theoretical capacitance, wide working potential range, low cost, natural abundance, and environmental friendliness, but the conductivity and ion diffusivity of simple metal oxide electrodes will lead to low specific capacitance. And the performance is poor. The multiplication performance of supercapacitors hinders its application. Zhou et al. reported a simple and cost-effective method to directly grow MIL-88-Fe-derived-Fe_2O_3@C on oxidized carbon nanotube fibers (S-Fe_2O_3@C/ OCNTF) [70]. The S-α-Fe_2O_3@C/OCNTF electrode has a high area capacitance of 1232.4 mF·cm^{-2} at a current density of 2 mA·cm^{-2}, and a considerable power ratio and capacitance retention rate at a current density of 20 mA·cm^{-2}. And it matches well with the Na-MnO_2 NSs/CNTF cathode of CNTF-doped MnO_2 nanosheets. Electrochemical test results show that the asymmetric supercapacitor S-α-Fe_2O_3@C/OCNTF//NaMnO_2NSs/CNTF has a high specific capacitance of 201.3 mF·cm^{-2} and an excellent energy density of 135.3 Wh·cm^{-2}. Therefore, the MIL-88-Fe-MOF derivative S-Fe_2O_3@C will become a promising anode for the next generation of wearable asymmetric supercapacitors.

In addition to metal oxides, other metal compounds (such as metal sulfides) and carbon composite materials can also exhibit excellent electrochemical performance. Qu et al. successfully synthesized a hierarchical porous hybrid electrode composed of R-NiS and rGO [71]. The electrode was directly sulfided with MOF-74/rGO hybrid material. When tested in supercapacitors, the R-NiS/rGO hybrid electrode has higher specific capacitance, excellent rate capability, and good cycle life, which is far

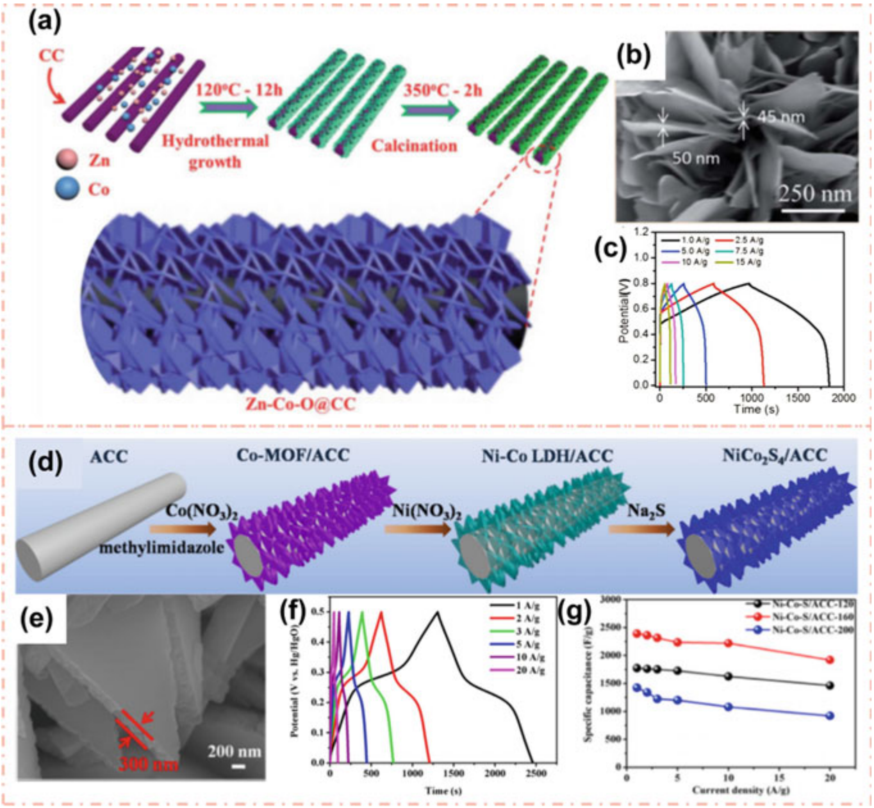

Fig. 4.6 **a** Schematic illustration of the strategy to directly grow the bimetallic nanosheets (Zn-Co–O@CC) on a flexible conductive carbon cloth substrate with a short-term post-annealing treatment at 350 °C in an oxygen atmosphere. **b** High-resolution FESEM images and the average thickness of nanosheets is about 47.5 nm as indicated. **c** Charge/discharge curves of the Zn-Co–O@CC electrode recorded at various current densities ranging from 1 to 15 A g^{-1}. **d** Schematic illustration for the synthesis of MOF-derived ultra-thin $NiCo_2S_4$ nanoarrays on electrochemical activated carbon cloth. **e** High magnification SEM images of Co-MOF/ACC. **f** GCD curves at different current densities of Ni-Co-S/ACC-160. **g** Specific capacitances calculate from GCD curves of all the Ni-Co-S electrodes, respectively

superior to other nickel-sulfur-based electrodes previously reported. The improvement of electrochemical performance is mainly attributed to the edge enrichment of (101) and (110) active sites of R-NiS/rGO hybrid materials. Through experimental measurement and DFT-based calculations, they have an effect on the OH in 2 M KOH electrolyte very strong affinity. In addition, especially when coupled with the capacitive electrode C/NG-A to construct a hybrid supercapacitor with R-NiS/RGO/electrolyte/C/NG-A, the hybrid device exhibits a very high energy density and power density. The developed layered porous hybrid electrode manufacturing method is suitable for the manufacture of other high-performance electrodes for various energy storage and conversion devices. Zhao et al. demonstrated the rational design and preparation of hollow and ultra-thin nickel cobalt sulfide nanocrystals (Ni-Co-S/ACC) for flexible hybrid supercapacitors on electrochemically activated carbon cloth, where Ni-Co-S nanosheets are extracted from the metal–organic framework by etching/ion exchange method (Fig. 4.6d) [72]. The Ni-Co-S/ACC electrode can provide very high specific capacitance at a current density of 1 A·g^{-1} and has good rate performance. The enhanced electrochemical performance should be attributed to the hollow and ultra-thin structure of electrochemically activated carbon cloth and Ni-Co-S nanosheets, resulting in hydrophilicity, good electrical conductivity, and abundant redox active sites (Fig. 4.6e). When Ni-Co-S/ACC is used as the positive electrode of a flexible hybrid supercapacitor and activated carbon is used as the negative electrode, it shows a high energy density of 30.1 W h·Kg^{-1} and excellent cycling at a power density of 800.2 W·Kg^{-1} stability (Fig. 4.6g–h). In addition, the excellent flexibility and wear resistance of hybrid supercapacitors can predict its application prospects in high-performance wearable energy storage devices.

Finally, this section will provide some personal insights into the future direction of this attractive research field. We hope that this article can summarize groundbreaking research and promote new developments based on MOF and MOFs-derived materials.

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