

Review

## Metal Organic Frameworks Derived Nano Materials for Energy Storage Application

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Metal organic frameworks (MOFs) and derived Nano-materials have attracted much attention due to their various controllable nanostructures with large surface area and high porosity. MOFs are usually used as precursors or template to prepare various derived Nano-materials. This paper reviews the development of typical MOFs derived material design and synthesis progresses when they are used as electrodes material for energy storage such as lithium-ion batteries (LIBs), sodium-ion batteries (SIBs) and super-capacitor (SCs). Porous carbon, metal oxide, carbon matrix hybrid, mixed metal and two dimensional MOFs derived material (Zn, Co, Cu) are mainly presented. Besides, the major challenges and perspectives are mentioned in the end of review.

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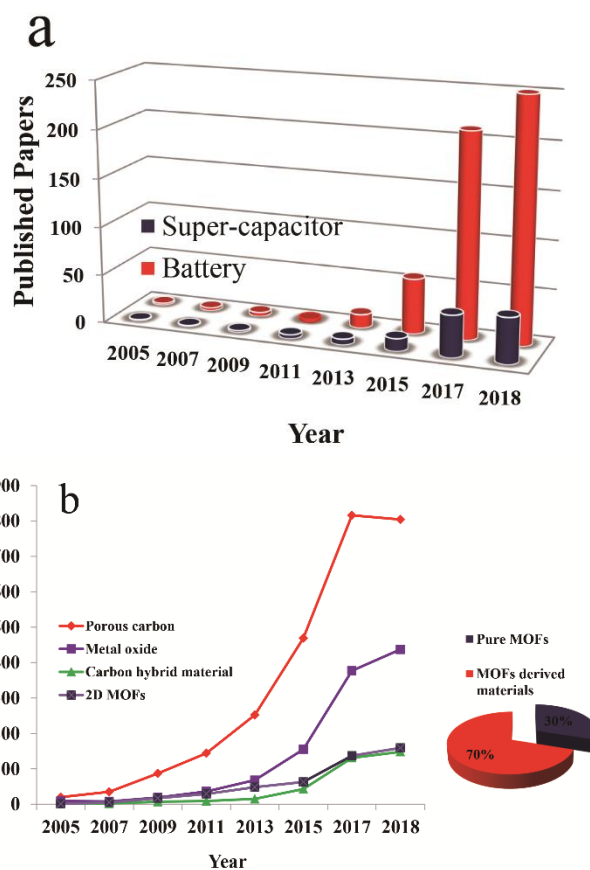
**Keywords:** MOFs, Lithium-ion batteries, Super-capacitors, Sodium-ion batteries

### 1. INTRODUCTION

Energy issue is an important topic all over the world. More efficient energy strategies and challenges are mentioned in the past [1-4]. Among them, Main development trend is that the high capacity green battery is used as the substitute of decreasing fossil fuels and other low efficient energy. Besides, the SCs with high energy density also become hot research topic in recent years. At the present, the research and study of ion batteries is increasing [5-6]. Traditional electrode material shows low capacity, unstable or poor cycling performance. New electrode materials with excellent properties need to be researched. As a result, the MOFs which connected by metal ions/clusters and organic linkers arouse strong interest of experienced materials experts. It was first prepared by Yaghi and his partners in 1990s [7-8]. It has high surface area, tunable pore volume and pore size [9]. Various microstructures

can be prepared by changing the correspond combinations or adding various functional groups. They were applied in many fields including the gas separation/adsorption, energy storage/conversion and catalysis [10-13].

MOFs were used as precursors or sacrificial templates to prepare derived Nano-materials, which were proven to be a versatile strategy, such as porous carbon, metal oxide or hybrid nanostructures [14-15]. The derived material can retain the morphologies and the properties of the pristine MOFs. Besides, the synthesis of MOFs derived materials is simple, such as the facile aqueous solution method, hydrothermal method and thermolysis [16]. Particularly, heteroatom doping can enhance the electrical conductivity and electrochemical activity of MOFs derived material, such as the nitrogen doped and sulfur doped [17-18, 22]. In this paper, we summarize and give a typical review of the MOFs derived material in the fields of energy storage in recent years. As shown in Fig.1a, the published papers on MOFs derived material in the field of energy storage over the last ten years were summarized. The MOFs derived porous carbon, metal oxide, carbon matrix metal oxide and hybrid Nano-materials research progresses are reviewed as shown in Fig. 1b. Besides, the 2D-MOFs material and structure progresses were also introduced in the last, which shows the MOFs derived material towards more thinner, more active sites and more applications. At the same time, the main challenges and personal insights of MOFs-derived material are highlighted in the last.



**Figure 1.** Chart of MOFs derived materials for SCs and ion-batteries in recent ten years. b) MOFs derived materials research trend for energy storage in recent ten years.

## 2. BRIEF OVERVIEW OF MOF MATERIAL

MOFs have drawn more attention in recent years since its applications in many fields [19-20]. MOFs are connected by organic ligands and metal ions, which have the advantages of porous, large surface area. The metal clusters or ions are always the transition metals or some lanthanides [21-22]. And the organic ligands contain pyridyl/cyano groups, crown ethers, polyamines, phosphonates or carboxylates [22-26]. Besides, the MOFs can be prepared with various structures, size, shape and morphologies. They are synthesized through the coordination reaction between different metal clusters/ions and different organic ligands. Until now, more than 20000 kinds of MOFs have been made in various fields [22, 27]. MOFs synthesis approaches must be taken into consideration as well. It can be prepared by using synthesis methods such as solvo-thermal, microwave-assisted heating, electrochemical and mechanic-chemical methods [22, 28]. However, the solvo-thermal synthesis of MOFs is regarded as an inefficient way, which takes few hours to several days in one synthesis process. New synthesis approaches have been developed to prepare MOFs more efficiently. Such as the microwave assisted heating, electrochemical and mechanic-chemical method [29-30]. MOFs materials are usually acted as the template or sacrifice material to prepare corresponding MOF-derived materials [31-34]. Various MOFs derived nanostructures for energy storage or other fields such as the purification, gas separation and catalysis [35-40]. In this review, the discussion focuses on the energy storage (LIBs SIBs SCs) of these very promising novel MOFs derived materials [14, 41-58]. Some typical promising MOFs derived materials applied for energy storage in recent years is showed as follows (Table1). It also has large porous volume which can avoid the volume expansion during charging or discharging when used for the electrode of the batteries or SCs. The preparation process always includes facile steps calcination of the pristine MOFs. By controlling the calcination temperature, various MOFs derived nanostructures have been made.

## 3. Zn BASED MOF DERIVED MATERIAL

### 3.1. Porous Carbon Material

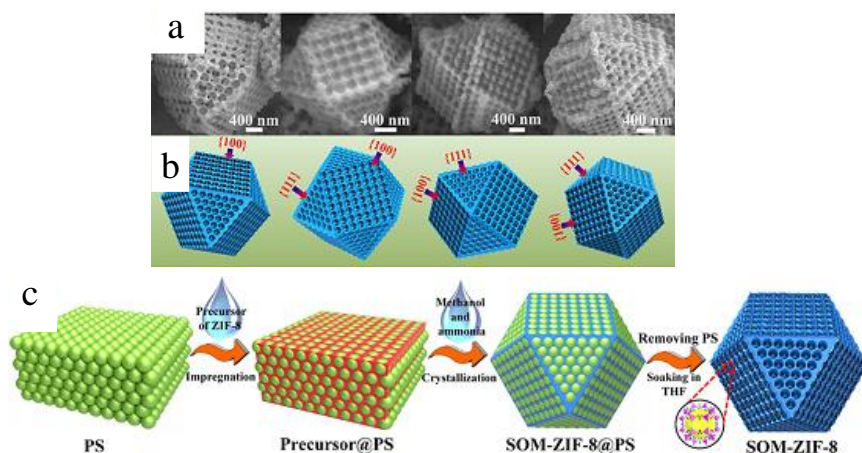
In the past, porous carbon materials or hollow carbon structures always require expensive templates and complicated processing technology [72]. For example, the Nanofibers, N-doped grapheme, nanotubes and hollow carbon spheres are always used as the templates to prepare porous carbon materials [73-76]. Besides, the heteroatom-doping technology always needs hazardous chemical reactions [77-78]. These disadvantages largely hinder the practical applications of carbon based materials. MOFs derived porous carbon has advantages of large surface area, controllable structures, easy preparation process, high electric conductivity and well structural stability [79-81]

**Table 1.** Summary of typical MOF-derived material as well as their preparation and applications

MOF derived material		Preparation strategies	Applications	Ref
<b>Porous Carbon</b>	ZIF-8 derived porous carbon polyhedrons (ZDPC)	KOH activation method followed by calcination	SCs	[59]
	Micro/meso porous carbon nanorod (MPCN)	Calcination of Zn-MOF	LIBs	[60]
	N-doped porous P@N-MPC	Calcination of Zn-MOF followed by removing Zn with HCl and P vaporization	NIBs	[61]
	Hollow (HPCNFs-N)	Embedding ZIF-8 into electrospun followed by calcination	SCs	[41]
<b>Metal Oxide</b>	hollow tetrahedral $\text{Co}_3\text{O}_4$	Calcination of ZIF-67	LIBs	[63]
	Spindle-like $\text{Fe}_2\text{O}_3$	Two-step calcination	LIBs	[51]
	$\text{CuO}/\text{Cu}_2\text{O}@/\text{CeO}_2$	Immersing Cu-MOFs into NaOH solution	LIBs	[52]
	$\text{Co}_3\text{O}_4/\text{TiO}_2$	Cation-exchange	LIBs	[66]
	$\text{Ni}_x\text{Co}_{3-x}\text{O}$	Calcination of Ni-Co MOF	SCs	[58]
<b>Metal Oxide Carbon Matrix</b>	$\text{CoP}@/\text{C-RGO-NF}$	In-situ low temperature phosphidation of $\text{Co}@/\text{C}$	NIB Porous s	[67]
	MWCNTs/ $\text{Co}_3\text{O}_4$	Calcination of MWCNT/ $\text{Co}_3\text{O}_4$	LIBs	[68]
	$\text{ZnO}/\text{ZnFe}_2\text{O}_4/\text{C}$	Calcination of hollow Zn-MOF	LIBs	[14]
	$\text{Cu-MOF}/\text{rGO}$	Ultra-sonication of Cu-MOF crystals with graphene oxide (rGO)	SCs	[71]

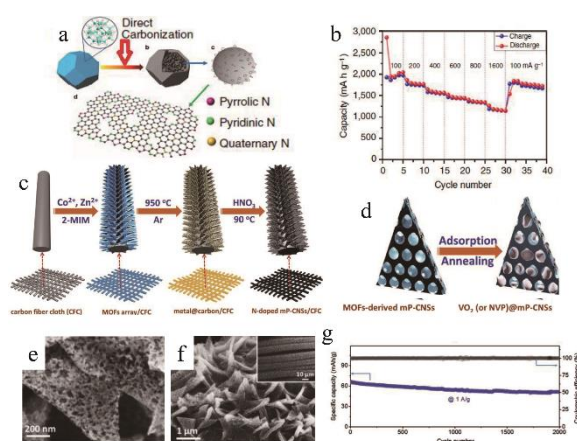
It also pointed that the increase of calcination temperature can lead to the increases of specific surface area and the number of mesopores and large pores. Besides, MOFs derived porous carbon with novel morphologies and specific hierarchical porous structures are beneficial for electrochemical properties. For instance, Wang reported two kinds of ZIF-8 derived porous carbon polyhedrons (ZDPC) and the battery-like  $\text{MoS}_2$ -ZIF composite [82]. The porous carbon polyhedrons have a continuous 3D porous network with an extremely high surface and a well-controlled pore size distribution, and the  $\text{MoS}_2$ -ZIF composite shows a three-dimensional (3D) nanostructure with an open framework [82]. When they used for the electrode of capacitors, this hybrid system exhibits a large energy density and a high power density of  $20,000\text{W kg}^{-1}$ [82]. The author claims that it shows the best properties of current hybrid

SCs with respect to energy, power and cycling life [82]. Shen constructed highly oriented and ordered macropores within Zn-MOF single crystals, opening up the area of 3D ordered porous materials in single-crystalline form [83]. The strategy relies on the shaping effects of a polystyrene nanosphere monolith template and a double-solvent induced heterogeneous nucleation approach (Fig.2a, b and c) [83]. Heteroatom doping (N, S, B, P) is more important in MOFs applications, which enhance the electrochemical, storage and thermal performances [84]. Among them, nitrogen-doped porous carbon by calcination of MOFs under specific condition is one of the main ways applied for the electrodes material and studies have proved that the N source comes from  $N_2$  atmosphere or the organic ligands.



**Figure 2.** ZIF-8 derived porous carbon,  $MoS_2$ -ZIF composite and 3D ordered materials synthesis. a) Synthesis of  $MoS_2$ -ZIF composite and ZIF-8 derived porous carbon. b) and c) SEM images of porous carbon and  $MoS_2$ -ZIF. d) Rate capability of  $MoS_2$ -ZIF electrodes. e) Designing schematic of ZIF-8 derived 3D ordered porous materials. f) SEM images of individual crystals at different directions.

For example, Fan reported an amorphous carbon nitride composite (ACN) based on Zn-MOF as anode material for SIBs [85]. It was synthesized by heat treatment of Zn-MOF particles under  $N_2$  flow. It exhibits an excellent  $Na^+$  storage performance with a reversible capacity of  $430 \text{ mAhg}^{-1}$  and  $146 \text{ mAhg}^{-1}$ . The ACN composite exhibits excellent thermal stability with low self-heating rate and high onset temperature. Similarly, Zuo prepared 3D porous carbons by annealing treatment of MOF-5 at  $900^\circ\text{C}$  in  $N_2$  [87], The 3D porous structure of the carbon material not only provided more binding sites for  $Li^+$  insertion/extraction but also provided the channels for charge and ionic transport. The porous carbon exhibited high reversible capacity of  $1015 \text{ mAh g}^{-1}$  over 100 cycles. Zheng prepared Zn-MOF derived graphene particle analogues with nitrogen content of up to 17.72 wt% (Fig.3a) [88]. The N-doped graphene analogous particles exhibit excellent electrochemical performance as an anode material for LIBs (Fig.3b) [88]. Xu designed and prepared Na-ion capacitors constructed by 2D MOFs array [89]. The MOFs array is converted to porous carbon Nanosheets, which are then uniformly encapsulated with  $VO_2$  and  $Na_3V_2(PO_4)_3$  (NVP) nanoparticles as the cathode and anode materials respectively (Fig.3c-f). This hybrid device delivers high energy density and power density as well as good cycle stability (Fig.3g). This is the first report of flexible quasi-solid-state SCs.



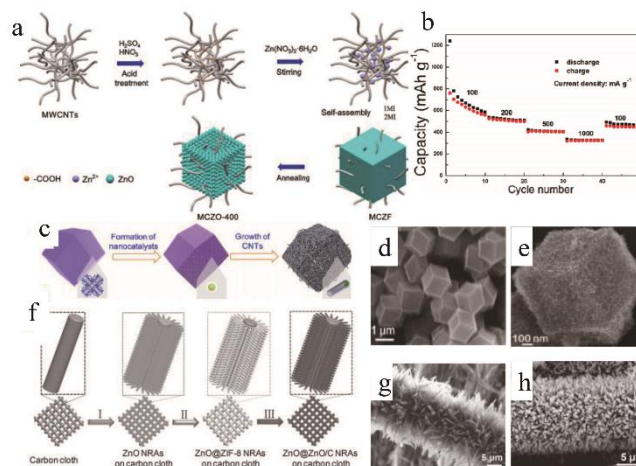
**Figure 3.** Schematic illustration of graphene analogous and porous carbon nanosheets. a) Schematic illustration of N-doped graphene analogous particles. b) Cycling performance of N-C-800 at current density of  $50 \text{ mA g}^{-1}$ . c) Schematic illustration of mesoporous graphitic carbon nanosheets. d)  $\text{VO}_2@ \text{mp-CNS}$ s and  $\text{NVP}@ \text{mp-CNS}$ s. e-f) FESEM images of nitrogen-doped mesoporous graphitic carbon nanosheets. g) Cycling performance at  $1 \text{ A g}^{-1}$ .

Now, it still remains challenging and attractive to prepare 1D carbon nanostructures [89-93]. For instance, Chen prepared hollow particle-based carbon Nanofibers (HPCNFs-N). By embedding ZIF-8 nanoparticles into electrospun polyacrylonitrile (PAN), the Nanofibers are carbonized into hierarchical porous Nanofibers composed of interconnected nitrogen-doped carbon hollow nanoparticles [94]. Owing to its unique structural feature and the desirable chemical composition it exhibits enhanced electrochemical properties.

### 3.2. Carbon Matrix Material

Derived metal oxides material usually suffers from drastic volume change and particles aggregation during charging or discharging process, which can result in capacity decay and inferior cycling stability [31]. The carbon matrix and metal oxide were usually combined to avoid this problem [95, 96]. For example, Zhang designed and prepared MOF-5 derived  $\text{ZnO}/\text{ZnFe}_2\text{O}_4/\text{C}$  hollow octahedrons, in which nanoparticles ( $\sim 5 \text{ nm}$ ) are well dispersed within carbonaceous matrix [14]. It delivers the capacity of  $762 \text{ mAh g}^{-1}$  and showing an outstanding rate performance when used for LIBs. Zou designed and prepared MWCNTs/ $\text{ZnO}$  (MCZO) nanocomposites (Fig.4a and b) [97]. It delivers reversible capacity of  $419.8 \text{ mAh g}^{-1}$ . ZIF-8 polyhedrons with MWCNTs inserted and intertwined are prepared by in situ self-assembly method. The good rate capability and cycling stability could be attributed to the synergetic effect between the MWCNTs and the porous  $\text{ZnO}$  polyhedron structure. Meng et al. designed and prepared CNT assembled hollow materials by low temperature pyrolysis process (Fig.4c-e). This method also can extend to obtain various oriented CNT materials [98]. Zhang obtained  $\text{ZnO}@ \text{ZnO}$  QDs/C core-shell nanorod arrays (NRAs) on flexible carbon cloth (CC) substrate based on a facile and scalable in situ ion exchange process (Fig.4f-h) [99]. The author claims that the

ZnO@ZnO QDs/C NRAs electrodes without any auxiliary materials are expected to open up new opportunities for ZnO-based material to power flexible electronic devices.



**Figure 4.** MOFs derived carbon matrix material synthesis illustration. a) Schematic of MOF-derived ZnO/MWCNTs nano-composite synthesis. b) Cycling performance of the ZnO/MWCNTs at a current density of 200 mA g<sup>-1</sup>. c) Formation process of N-CNTs. d-e) Low and high magnifications of CNT/Co-MOF. f) Schematic illustrating the synthesis procedures of ZnO@ZnO QDs/C core-shell NRAs. g-h) Low and high magnifications of core-shell ZnO@ZnO QDs/C NRAs grown on flexible carbon cloth.

## 4. Co BASED MOF DERIVED MATERIAL

### 4.1. Porous Carbon material

Except for the Zn-MOFs derived porous carbon, the Co-MOFs can also be used as precursor or template to prepare derived porous carbon materials. Zhang prepared 3D graphitic carbon networks by pyrolysis of nano-sized ZIF-67 [102]. The experiment shows that the carbon networks require small ZIF-67 particle size of less than 100 nm, which can realize a high-fraction of Co nanoparticles near the particle surface. It is found that a reduction in the size of the ZIF-67 particles can lead to a spontaneous welding of the resulting carbon particles, thereby giving rise to the formation of 3D porous carbon networks with highly graphitized structures. Wei prepared cobalt porous carbon composite Co/ZIF-67 [101]. It maintains the structure of ZIF-67 and the cobalt porous carbon composites has the carbon-shell/cobalt-core architecture. The performance should be ascribed to the pseudo-capacitor behavior of cobalt metal particles as well as the partially graphitized carbon.

### 4.2. Metal Oxide Material

Transition metal oxide shows the characteristics of high thermal capacities, chemical stability and well controlled size and tape in energy storage [102-104]. MOFs are provided as template for various morphology of metal oxide which has large surface area and better cycling stability [104-106]. The metal oxide material is mostly prepared by one step direct calcination of MOFs. Other strategies are also

researched to prepare metal oxide material instead of calcination. For example, Song prepared two kinds of novel CuO with 3D urchin-like and rods-like superstructures composed of nanoparticles, nanowires and nanosheets were both obtained by immersing the corresponding Cu-MOFs into NaOH solution [64].

Co-oxide stands out as an electrode material for ion-batteries, owing to its high theoretical capacity. For example, Tian prepared porous hollow tetrahedral  $\text{Co}_3\text{O}_4$  as anode material for LIBs [63]. A double-walled tetrahedral MOF is selected as the precursor to prepare hollow  $\text{Co}_3\text{O}_4$ . Profiting from the highly porous hollow structure, the obtained material exhibited a large lithium storage capacity, superior rate performance, and cyclic stability. Similarly, Shao prepared  $\text{Co}_3\text{O}_4$  hollow dodecahedrons for LIBs with controllable interiors by pyrolysis of ZIF-67 [107]. Two different types of hollow structures are obtained through facile several steps calcination of ZIF-67. For application as the anode material of LIBs, the ball-in-dodecahedron  $\text{Co}_3\text{O}_4$  delivers high reversible capacity of  $1550 \text{ mA h g}^{-1}$  and excellent cycling stability. The low electron conductivity and volume change when the process of charging and discharging limit  $\text{Co}_3\text{O}_4$  energy storage application. Qiu designed and prepared  $\text{Co}_3\text{O}_4$  nanoparticles coated with a thin carbon shell via a carbonization process [108]. Carbon matrix material is widely used to obtain excellent electrochemical performances of MOFs derived materials and release the strain during the charging/ discharging processes.

#### 4.3. Carbon Matrix Hybrid Material

There is an increasing trend of utilizing Co-MOFs as precursors to get carbon matrix composite nanostructures. Ge designed and prepared MOFs derived core/shell structured CoP@C polyhedrons anchored 3D reduced graphene oxide (RGO) on nickel foam (NF) as binder-free anode for SIBs, through an in-situ low-temperature phosphidation process [67]. The CoP@C-RGO-NF exhibits a remarkable electrochemical performance with outstanding cycling stability and high rate capability. The excellent properties can be attributed to synergistic effects between core/shell CoP@C polyhedrons and RGO networks [67]. Similarly, Huang prepared hierarchical porous MWCNTs/ $\text{MCo}_2\text{O}_4$  ( $\text{M}=\text{Zn}, \text{Co}$ ) nanocomposite synthesized by thermal treatment [109]. The MWCNTs are inserted in the  $\text{MCo}_2\text{O}_4$  polyhedra, forming a hierarchical porous structure with nano-sized building blocks. MWCNTs/ $\text{MCo}_2\text{O}_4$  exhibits superior lithium storage performances. Chen [110] designed and prepared CNT/ $\text{Co}_3\text{O}_4$  by several steps of thermal treatment of ZIF-67. PAN-cobalt acetate  $\text{Co}(\text{Ac})_2$  composite nanofibers are used as the functional template. Through a facile chemical transformation process and subsequent removal of the core, tubular-like structures of ZIF-67 nano-crystals are obtained. A two-step annealing process is applied to convert these ZIF-67 tubulars into hierarchical CNT/ $\text{Co}_3\text{O}_4$  microtubes. The nanocomposite delivers a high reversible capacity and excellent cycling properties.

## 5. Cu BASED MOF DERIVED MATERIAL

### 5.1. Metal Oxide Material

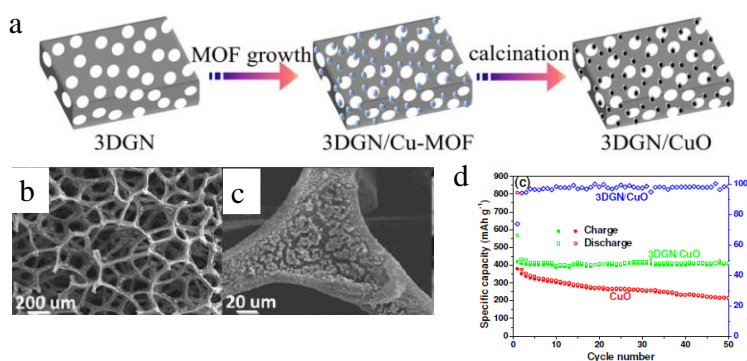
Copper oxide material is always researched as electrode material for LIBs because of its high theoretical capacity, low cost, high safety and environmental friendly [111-112] For instance, Wu



prepared porous CuO hollow architecture with perfect octahedral morphology which is synthesized by annealing Cu-based-MOF templates [53]. In view of this unique structural, these CuO octahedra evaluated as electrodes exhibit excellent performance in LIBs with good rate capability. The low cost and convenient method in this work can be extended to the fabrication of other anisotropic hollow metal oxides with well-defined structures that may have potential applications in energy storage and conversion. However, copper oxide also suffers from low electronic conductivity and large volume variation during charge and discharge cycling, resulting in severe mechanical strains and rapid capacity decay.

## 5.2. Metal Oxide-Carbon Matrix Material

More recently, Xu designed and prepared 3D graphene network (3DGN/CuO) (Fig.5a-d) [70]. The obtained 3DGN/CuO composites are utilized as binder-free anodes of LIBs for the first time, yielding a high reversible gravimetric capacity of  $409 \text{ mAhg}^{-1}$  [70]. The remarkable performance can be reasonably attributed to the synergistic interaction between octahedral CuO nanoparticles and the conductive 3D graphene network [70]. Similarly, saraf prepared Cu-MOF/rGO by simple ultrasonication of Cu-MOF crystals with chemically synthesized reduced graphene oxide (rGO) [71]. It is the first time that the dual application of Cu-MOF/rGO hybrid (i) SCs electrode material and (ii) electrochemical nitrite sensor. The noteworthy improvement in the performance of SCs can be expected as the highly porous Cu-MOF crystals provide high surface area and the combination of rGO serves to synergistically enhance the conductivity of the hybrid.



**Figure 5.** a) Schematic synthesis of 3DGN/CuO; (b,c) 3DGN/CuO at different magnifications; d) Cycling performances of 3DGN/CuO; e) Schematic synthesis of Cu-MOF/rGO hybrid; f) The SCs performances of Cu-MOF/rGO.

## 6. OTHER TYPICAL MOF DERIVED MATERIAL

### 6.1. Other Metal (Fe Ni Mn Ti ) MOF Derived Material

Many other metal oxide nano-materials have been designed [113-116]. Typical MOFs derived materials (Fe, Ni, Ti, Mn) applied for energy storage in recent years are discussed as follows. (Table 2)

Xu obtained spindle-like mesoporous  $\text{Fe}_2\text{O}_3$  for high rate LIBs [117]. This spindle-like porous  $\alpha\text{-Fe}_2\text{O}_3$  shows greatly enhanced performance of Li storage. When cycled at 10 C, comparable capacity of  $424 \text{ mAh g}^{-1}$  could be achieved. Han prepared porous hollow double-shelled NiO nanoparticle architecture by calcining a novel Ni-MOF in air (Fig.6a-b) [118].

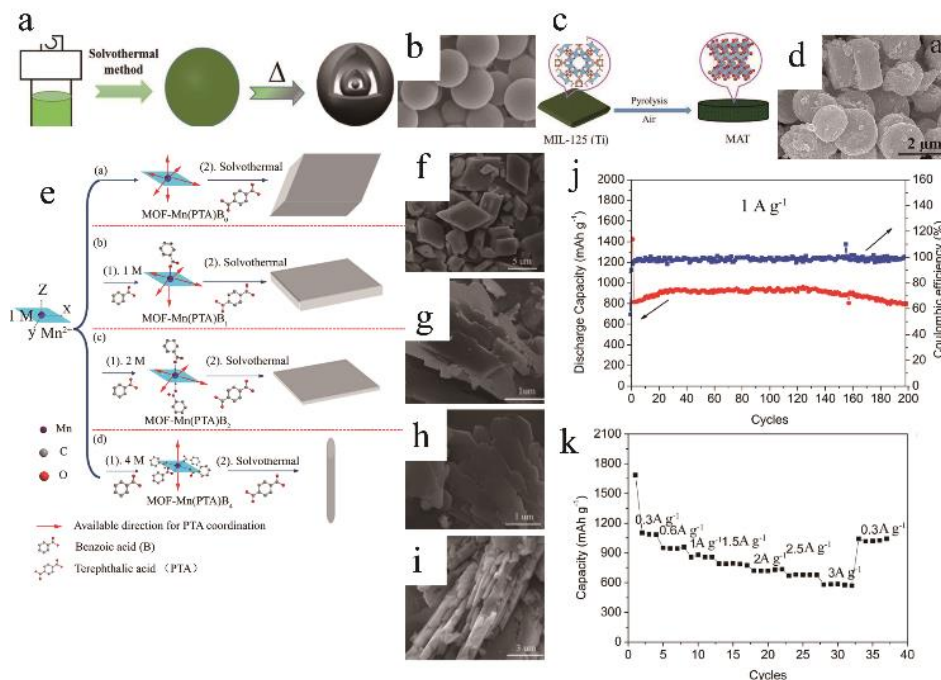
**Table 2.** Summary of other MOF-derived material as well as their preparation and applications

MOF derived material		Preparation strategies	Applications	Ref
<b>Other Metal</b>	spindle-like $\text{Fe}_2\text{O}_3$	Cacination	LIBs	[117]
	NiO	Cacination	SCs	[118]
	$\text{TiO}_2$ (MAT)	Cacination	LIBs	[119]
	MnO/C hybrids	Cacination	LIBs	[120]
<b>Mixed Metal</b>	$\text{Co}_3\text{O}_4/\text{TiO}_2$	Cation exchange method in MOF	LIBs	[66]
	ZnO/NiO	Solid-state calcination of heterobimetallic MO	LIBs	[121]
	$\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$ nanorod	Cacination and cation exchange	LIBs	[122]
	$\text{Ni}_{0.62}\text{Fe}_{2.38}\text{O}_4$	Cacination and cation exchange	SCs	[123]
<b>Two Dimensional</b>	$\text{CoS}_{1.097}$ /nitrogen-doped carbon	sulfidation and carbonization	SCs	[55]
	2D h- $\text{MoO}_3$	Top-down method	SCs	[124]

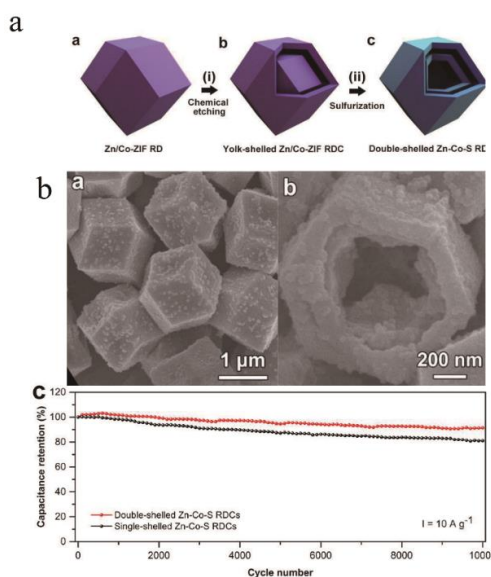
As synthesized NiO nano-spheres calcined at different temperatures have distinct surface areas and electrical conductivities. It possesses a reversible specific capacitance of  $324 \text{ F g}^{-1}$  after 1000 cycles. Besides, Xiu designed and prepared meso-porous anatase  $\text{TiO}_2$  (MAT) with a disk-like morphology [119], which was prepared by direct pyrolysis of MIL-125(Ti)-MOF in air (Fig.6c-d). The  $\text{TiO}_2$  electrode exhibited high reversible capacity, superior rate capability, and excellent long-term cycling stability. Recently, Sun prepared MnO/C hybrids by simple treatment of Mn-MOFs, as shown in Fig.6e [120]. It proposed a novel space constraint assembly approach to tune the morphology of Mn-MOFs (Fig.6f-k). As anodes for LIBs, these morphologies showed great influence on the electrochemical properties [120].

6.2. Mixed Metal MOF Derived Material

Metal oxides with different metal composites get more attention and researched [125-127]. For example, experiment shows that the Bi-metal porous oxide can improve the lithium storage performances [127, 128].



**Figure 6.** Schematic diagram of NiO, TiO<sub>2</sub> and Mn(PTA)-MOF precursors a) Schematic illustration of NiO b) SEM images of NiO c) Schematic illustration of TiO<sub>2</sub> d) SEM images of TiO<sub>2</sub> e) Schematic illustration of Mn(PTA)-MOF f-i) SEM images of Mn(PTA)-MOF precursors. j-k) Cycling and rate performances of spindle like Mn(PTA)-MOF precursors as anode for LIBs.



**Figure 7.** a) Schematic synthesis illustration of double-shelled Zn-Co-S RDCs. b) FESEM images of Zn/Co-ZIF RDs and yolk-shelled Zn/Co-ZIF RDCs. c) Cycling performances of Zn/Co-ZIF RDCs.

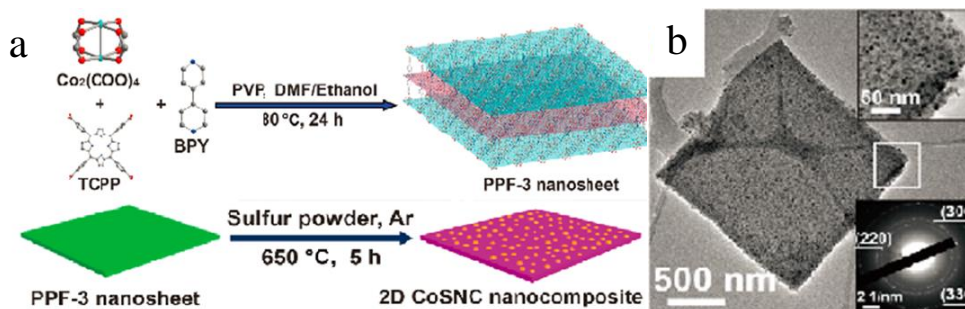
Various hetero-metallic nanostructures have been researched. For instance, Xu designed and prepared  $\text{Co}_3\text{O}_4/\text{TiO}_2$  hollow polyhedrons by cation-exchange approach [66]. The  $\text{Co}_3\text{O}_4/\text{TiO}_2$  composite hollow polyhedrons exhibits long cycling life and remarkable rate capability. It exhibits a high reversible capacity of 642mAh/g. Zhang designed and prepared porous ZnO/NiO micro-spherical structures by solid-state thermal decomposition [121].

The study explored an effective strategy for tuning the size and morphology of Ni (II)-doped Zn-based coordination polymer particles by changing the volume ratio of solution. Recently, Lou designed and prepared double shelled Zn-Co-S dodecahedral cages which deliver high specific capacitance ( $1266\text{Fg}^{-1}$ ) and good rate capacity (Fig.7b and c) [129]. Zinc-cobalt sulfide rhombic dodecahedral cages with a well-defined double-shelled hollow structure have been synthesized by a sequential chemical etching and sulfurization strategy. The schematic of formation illustration can be seen in Fig.7a. Li designed and prepared mesoporous  $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$  nanorods [130]. The sample prepared at low annealing temperature possesses more abundant meso-pores and higher specific surface area, and exhibits excellent SCs performances. Similarly, Xia prepared  $\text{Ni}_{0.62}\text{Fe}_{2.38}\text{O}_4$  nanotubes, which possess a specific surface area of  $134.3\text{m}^2\text{g}^{-1}$  and are composed of nano-sized primary particles [123]. It delivers a capacity of  $1184\text{mAhg}^{-1}$ . In addition to the MOFs derived Ni-Co, Fe-Ni bi-metal oxides, Zn and Ni oxides shows more attractive in energy storage applications.

### 6.3. Two Dimensional MOF Derived Material

2D nanostructures derived from MOFs attract more attention due to its unique physical and chemical properties [131-134]. Such as the transition-metal dichalcogenides black phosphorus and noble-metal nanosheets. The 2D nanostructures have the advantages of large surface area, highly flexible, ultrathin thickness, more accessible active sites and shortened ion-diffusion lengths compared to the other 1D and 3D nanomaterials [135]. More active sites on the surface of 2D nanomaterial can add the interactions, which can make the performances improved in the applications of electronics, energy storage/conversion, gas separation, photocatalysis and sensing platforms [136-138]. Cao designed and prepared  $\text{CoS}_{1.097}$ /nitrogen-doped carbon nano-composites by the simultaneous sulfidation and carbonization of PPF-3 MOF nanosheets (Fig.8a-b) [55]. Here, for the first time, the facile synthesis of 2D MOF nanosheets with thickness of 12-43 nm. Through the simultaneous sulfidation and carbonization, 2D nano-composite of  $\text{CoS}_{1.097}$  nanoparticles (NPs) and nitrogen-doped carbon are made, referred to as CoSNC. 2D CoSNC is used as an electrode material for SCs, which exhibits a specific capacitance of  $360.1\text{Fg}^{-1}$  and high rate capability. Generally, the preparation method of the 2D nanomaterial can divide into two ways which is the exfoliation of bulk MOF and direct bottom up synthesis respectively [132, 139-141]. Zhao designed and prepared 2D ultrathin carbon nano-sheets (UTCNSs) by using bottom-up synthesis and carbonization of ultrathin Zn-MOF nano-sheets [142]. It also exhibits a capacitance of  $278\text{Fg}^{-1}$  at a high current density and excellent rate performances when used for LIBs. The superior electrochemical properties are mainly due to their ultrathin morphology, large specific surface area, high conductivity, and suitable porous structure. This work provides a new strategy for the high-yield and low-cost synthesis of ultrathin MOF nano-sheets. Besides, some other methods

have also been researched for the fabrication. For example, Xiao prepared the 2D h-MoO<sub>3</sub> nanosheets by using the surfaces of water-soluble salt crystals as growth substrates or templates [143]. After dissolving the salt-template in water, the obtained 2D nanosheets could be reassembled into a binder- and additive free film by filtration [143-144].



**Figure 8.** Synthesis and physical characterization of typical 2D MOFs derived materials. a) Schematic synthesis illustrations of the PPF-3 nano-sheets, 2D CoS nanoparticles and nitrogen-doped carbon. b) TEM image of 2D CoS nanoparticles and nitrogen-doped carbon. c) Schematic synthesis illustration of ultrathin carbon nano-sheets. d) TEM of ultrathin carbon nano-sheets. e) Rate performance at current densities from 100 to 10000 mA g<sup>-1</sup>.

The low cost approach with inexpensive salts is applicable for both layered compounds and various binary transition metal oxides [145]. Despite the 2D nanomaterial has many excellent properties, some challenges are still remained in the road of nanomaterial development. High yield and easy green synthesis methods of the 2D nanomaterial is the target of the researchers. The development of the 2D nanomaterials is still in their infancy and the various nanocomposites derived from the 2D-MOFs-template are coming soon.

## 7. SUMMARY AND PROSPECTION

MOFs material has been proved to be a competitive electrode material for energy storage which is usually used as precursors or templates to prepare various derived material. This paper mainly introduces the development of MOFs derived material for energy storage in recent years. Meanwhile, the synthesis methods and references significances are briefly introduced. In recent few years, MOFs material with rich pores has been found in gasoline tanks of cars passing through the street, which may become a mile stone event of MOFs material boarding the commercial stage. During the worldwide mass researching of MOFs, it has got ready for commercial stage at many fields. Abundant adjustable pores and big specific surface area make MOFs stand out in gas adsorption (methane adsorption, hydrogen storage) and energy storage. At present, the stability and multiple rounds of chemical reactions tolerance limit MOFs development. Besides, low yield rare metal and expensive organic linkers increased their synthesis costs. In fact, a serious problem is that the number of MOFs is too large and dizzying. Researchers should be concentrating on MOFs which stability or activity has been verified. Another problem is that people realize the important of cost reduction when it competes with existing technologies such as molecular sieves. MOFs derived material can be simply synthesized by several

steps of calcination under specific temperatures and gas atmospheres. Compared to the traditional porous materials which include complex synthesis process and structure, the way of MOFs as template or precursor has obvious advantages. The structures of MOFs derived material can be controlled by adjusting the calcination temperature or combining various mature synthetic technologies. Currently, most research reports are focus on the design and application of MOFs powder materials. However, the inconvenience caused by powder materials in actual applications is not good for the optimization of materials properties, such as the phenomenon of materials agglomerate, loose, shedding, poor electrical mechanical stability and large mass transfer resistance. To solve such problems, the way of template guiding growth of various aligned MOFs array materials has been proposed. This material can grow metal oxide or hydroxide arrays of different structures on variety of substrates. The advantage of this strategy is not only that it can rationally change the conductive substrate of the array structure, MOFs type and array morphology but also realize that the MOFs grow only in heterogeneous nucleation on the corresponding template, thereby obtaining a high quality and neatly arranged array. After simple calcination, MOFs array can be converted to porous carbon based composite array materials. Although, many achievements of various MOFs derived material has been get, preparation of different nanostructures and different compositions still have many problems due to in-depth understanding of preparation process. Besides, theoretical modeling of MOFs derived material is still lacking for better understanding the connection of MOFs structures and their properties.

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