# Two-dimensional Metal-organic Frameworks and Derivatives for Electrocatalysis

WEN Jinguli, LI Yuwen and GAO Junkuo\*

Institute of Functional Porous Materials, School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, P. R. China

**Abstract** The most important topics in the world today are environmental and resource issues. The development of green and clean energy is still one of the great challenges of social sustainable development. Two-dimensional(2D) metal-organic frameworks(MOFs) and derivatives have exceptional potential as high-efficiency electrocatalysts for clean energy technologies. This review summarizes various synthesis strategies and applications of 2D MOFs and derivatives in electrocatalysis. Firstly, we will outline the advantages and uniqueness of 2D MOFs and derivatives, as well as their applicable areas. Secondly, the synthetic strategies of 2D MOFs and derivatives are briefly classified. Each category is summarized and we list classic representative fabrication methods, including specific fabrication methods and mechanisms, corresponding structural characteristics, and insights into the advantages and limitations of the synthesis method. Thirdly, we separately classify and summarize the application of 2D MOFs and derivatives in electrocatalytic water splitting, oxygen reduction reaction(ORR), CO<sub>2</sub> reduction reaction(CO<sub>2</sub>RR), and other electrocatalytic applications. Finally, the development prospects and existing challenges to 2D MOFs and derivatives are discussed.

Keywords Two-dimensional; Metal-organic framework; Derivative; Synthesis strategy; Electrocatalysis

# 1 Introduction

Two-dimensional(2D) materials are one of the cores of current low-dimensional materials research. In 2004, Novoselov et al.[1] successfully stripped graphene from graphite with adhesive tape. Since then, graphene has opened the mysterious door of 2D nanomaterials. Graphene, graphene oxide, boron nitride, chalcogenide, phosphorus, layered metal oxide, layered double hydroxide and other related 2D nanomaterials have been developed<sup>[2-4]</sup>. 2D nanomaterials exhibit unique physical and chemical properties and their advantages are as follows: (1) 2D nanomaterials have a high proportion of lateral size structures and a higher reaction rate. (2) 2D nanomaterials are flexible, which facilitates further structural modification. (3) 2D nanomaterials are designable, and can be used as basic materials for composite design with other functional materials to form multifunctional composite materials. Based on these advantages, 2D nanomaterials have become emerging materials in biomedicine<sup>[5]</sup>, capacitive energy storage<sup>[6]</sup> and energy catalysis<sup>[7,8]</sup>.

Metal-organic frameworks(MOFs) are a new type of porous materials composed of metal ions or clusters coordinated with organic ligands<sup>[9]</sup>. MOFs have high porosity, large surface area and adjustable coordination structure<sup>[10–12]</sup>. The metal ions in MOFs structure are usually Zn, Co, Fe, Ni, Cu, Cr, Mn ions and other transition metals<sup>[13,14]</sup>. At present, MOFs have shown promising applications, such as gas separation and storage<sup>[15,16]</sup>, chemical sensing<sup>[17]</sup>, biomedicine<sup>[18]</sup>, capacitor energy storage<sup>[19-22]</sup> and other applications<sup>[23-27]</sup> through the coordination of pore structure and functional sites. However, when MOFs are used as electrocatalysts, the metal nodes are surrounded by organic linking groups, resulting in poor conductivity<sup>[28]</sup>, which is a fatal flaw. In recent years, there have been many reports of combining MOFs with highly conductive materials(such as nickel foam and carbon cloth) to form composite materials to overcome the low conductivity of MOFs.

Traditional electrocatalysts are designed based on precious metal materials. However, due to the high price of precious metals and the scarcity of resources, it is necessary to look for electrocatalysts that can replace precious metals with high efficiency. Transition metals have abundant reserves in the earth, and the price is relatively low. Therefore, transition metals have become the most potential substitutes for precious metal catalysts. In recent years, transition metal-based MOFs have been widely used in catalyst fabrication strategies<sup>[29–31]</sup>. From low-dimensional nanotubes, nanofibers and nanosheets to complex three-dimensional structures and composites, they have demonstrated excellent electrocatalytic potential in electrocatalytic hydrogen evolution reaction(HER), oxygen evolution reaction(ORR), CO<sub>2</sub>

<sup>\*</sup>Corresponding author. Email: jkgao@zstu.edu.cn

Received May 28, 2020; accepted June 12, 2020.

Supported by the Zhejiang Provincial Natural Science Foundation, China(No.LY20E020001), the National Natural Science Foundation of China(Nos.51602301, 51672251), and the Fundamental Research Funds of Zhejiang Sci-Tech University, China (No.2019Q007).

<sup>©</sup> Jilin University, The Editorial Department of Chemical Research in Chinese Universities and Springer-Verlag GmbH

reduction reaction(CO<sub>2</sub>RR) and N<sub>2</sub> reduction reaction  $(NRR)^{[32,33]}$ .

Low-dimensional MOFs combined the characteristics of MOFs with the unique physical and chemical properties of low-dimensional materials<sup>[34,35]</sup>. Designing MOFs into 2D nanostructures is an effective strategy for manufacturing high-performance electrocatalysts, because they have the following advantages as electrocatalysts. (1) Nanometer thickness can improve mass transfer and electron transfer rate<sup>[36]</sup>. (2) Highly unsaturated metal active sites are exposed through a higher specific surface area, which has high catalytic activity<sup>[37]</sup>. (3) The surface structure can be selectively adjusted and designed to improve catalytic performance. In addition, ultra-thin MOFs are more conducive to industrial production and manufacturing of MOFs because of their good flexibility, which can further expand the commercial application value of MOFs in the future. At present, low-dimensional MOFs have good performance applications in chemical sensing<sup>[38]</sup> and supercapacitor<sup>[39]</sup>.

Although the exploration of 2D MOFs and derivatives in electrocatalytic reactions is insufficient systematization and deepening, some outstanding research results have been obtained. Especially in the two aspects of structural optimization and catalytic activity improvement in the direction of electrocatalysis. In this article, we introduce classic representative fabrication strategies for 2D MOFs and derivatives, including specific fabrication methods and mechanisms, corresponding structural features, insights into the advantages and limitations of synthetic methods. Subsequently, the application of 2D MOFs and derivatives in electrocatalysis is summarized, mainly including electrocatalytic water splitting, ORR, CO<sub>2</sub>RR and other catalytic reactions. This article aims to provide a brief and comprehensive theoretical summary of relevant aspects for the future optimization design of 2D MOFs and derivatives(Fig.1).



Fig.1 Schematic summary of 2D MOFs and derivatives for electrocatalysis

OER, Copyright(2018) Wiley-VCH<sup>[40]</sup>; HER, Copyright(2018) Wiley-VCH<sup>[41]</sup>; ORR, Copyright(2019) Wiley-VCH<sup>[42]</sup>; NRR, Copyright(2019) Wiley-VCH<sup>[43]</sup>; CO<sub>2</sub>RR, Copyright(2018) The Royal Society of Chemistry<sup>[44]</sup>; Others, Copyright(2019) American Chemical Society<sup>[45]</sup>.

# 2 Synthesis Strategy

In recent years, the urgent need for high-performance 2D MOF nanosheets has greatly promoted the rapid development in the field of fabrication and synthesis methods. The fabrication methods of 2D MOF nanosheets are generally divided into

two categories, top-down and bottom-up<sup>[46—48]</sup>. Top-down synthesis is mainly to delaminate the layered MOFs that have been synthesized through external force-assisted exfoliation or chemical solvent-induced exfoliation, and strip out the MOF nanosheets. Bottom-up synthesis is the direct synthesis of 2D MOF nanosheets through the control of solvothermal synthesis or interface-mediated synthesis. Different synthetic methods have their own advantages and disadvantages. The 2D MOF nanosheets fabricated by different synthetic methods also exhibit different chemical properties. Next, we will summarize each category and enumerate classic representative fabrication methods, including specific fabrication methods and mechanisms, corresponding structural features, and insights into the advantages and limitations of the synthesis methods.

#### 2.1 Top-down Synthesis

#### 2.1.1 External Force-assisted Exfoliation

MOFs are crystal structures composed of metal ions and organic ligands, but not all crystals form atomic bonds in three dimensions<sup>[49]</sup>. According to the phenomenon that graphite can be peeled and layered to produce ultra-thin atomic graphene, some MOFs with a layered crystal structure can be physically peeled off<sup>[50-53]</sup>. In 2008, Nielsen et al.<sup>[54]</sup> reported for the first time that metal-organic compounds can be peeled off a single layer of nanosheets by ultrasonic vibration. They used a classic solvothermal method to prepare  $Zn(C_{12}H_{14}O_4)$ , and the crystallographic analysis proved that the compound was a metal-organic layered structure(MOLS). Moreover, there was only weak van der Waals force between layers and was no strong chemical bond. It was observed through Atomic Force Microscope(AFM) images that ultrasonic treatment with different solvents(acetone, ethanol, toluene and 2-propanol) can peel off a single layer about 2 nm thick. Therefore, by simply adding the external force-assisted exfoliation method, the weak interlayer interaction can be easily overcome, and the MOFs can be delaminated into 2D MOF nanosheets.

Cliffe et al.<sup>[55]</sup> discovered hcp UiO-67, which was a ligand-deficient layered analogue. 3D hcp UiO-67 can form 2D metal-organic nanosheets hxl UiO-67 by plane shear layering. First, hcp UiO-67 was fabricated by solvothermal reaction, after 30 min of ultrasonic treatment, the supernatant was evaporated after precipitation to obtain 2D hxl UiO-67 sheets. Comparing XRD patterns, it can be proved that 2D hxl UiO-67 sheets are formed from hcp UiO-67 by breaking metal-bpdc<sup>2-</sup> bonds rather than the cleavage of the  $\mu_2$ -OH bonds between the clusters. In the next experiment, they also found that when washed in hot N,N-dimethylformamide(DMF, 70 °C), 2D hxl UiO-67 sheets could be re-coordinated with the remaining small amount of ligands to form hcp UiO-67. This further indicated that the Hf-carboxylate bonds between the 3D hcp UiO-67 layers could not only be broken by external force-assisted, but also be re-bonded after a second reaction. This report revealed that there might be some MOFs that could complete the bidirectional reversible transition process from 3D to 2D to 3D under certain conditions, and proposed a new method for the structural regulation of MOFs in the future.

In addition to the classic solvothermal method for ultrasonic peeling, Jayaramulu *et al.*<sup>[40]</sup> proposed a new method for preparing a large number of stacked Co-ZIF-9(III) nanosheets by fully mixing and grinding[Fig.2(A)]<sup>[40]</sup>. Through infrared spectroscopy analysis, it was found that hydrophobic benzimidazole groups were distributed on the layer and layer surface of the stacked Co-ZIF-9(III) nanosheets. Therefore, by placing the stacked Co-ZIF-9(III) nanosheets in ethanol dispersant for full ultrasonic dispersion, the weak van der Waals force could be overcome, and Co-ZIF-9(III) nanosheet with a thickness of only 2 nm was peeled off. From fabrication to peeling of nanosheets, the whole process was very simple and fast. An effective and feasible method was proposed for the future industrial mass production of 2D metal-organic frameworks and their derivatives.

Tian *et al.*<sup>[56]</sup> used an electric field to assist *in situ* hydrolysis of MOFs into ultra-thin metal oxyhydroxide nanosheets[Fig.2(B) and (C)]<sup>[56]</sup>. By reacting 2,5-di(1*H*-1,2,4-triazol-1-yl)terephthalic acid(H<sub>2</sub>BTTA) ligands with Fe clusters or Co-doped Fe clusters, two isomers of MOF(FJI-H25Fe and FJI-H25FeCo) with different chemical stability were fabricated. Under the assistance of electric field, FeCo-MOF(FJI-H25FeCo) was hydrolyzed to produce FeCo-hydroxy oxide

(FeCo-MOF-EH) nanosheets with a thickness of 3 nm. Further research showed that the formation of nanosheets came from the following two key processes. (1) FeCo-MOF was easily hydrolyzed into FeCo-MOF-H blocks under alkaline conditions. (2) The electric field promoted the reorganization of FeCo-MOF-H blocks into FeCo-MOF-EH nanosheets. This article proposed a new method for preparing metal oxyhydro-xide nanosheets with good crystallinity and morphology.

Ball mill grinding is also one of the methods of external force-assisted exfoliation. For example, Peng *et al.*<sup>[57]</sup> fabricated a layered Zn<sub>2</sub>(Bim)<sub>3</sub> by solvothermal reaction, and successfully peeled off ultra-thin 2D Zn<sub>2</sub>(Bim)<sub>3</sub> nanosheets after low-speed grinding with a ball mill and ultrasound in a water bath. Wu *et al.*<sup>[58]</sup> hydrothermally synthesized Ni(Im)<sub>2</sub> with a 2D layered structure, and then ultrasonically stripped out 2D Ni(Im)<sub>2</sub> nanometers with various thicknesses(5, 15, 65 and 140 nm) sheets. This fully exposed the shortcomings of the external force-assisted exfoliation method. (1) The thickness of the exfoliated 2D MOF nanosheets cannot be selectively controlled<sup>[59]</sup>. (2) The external force-assisted exfoliation method is only applicable to MOFs with weak interlayer interaction<sup>[57]</sup>. (3) The spalling yield is relatively low<sup>[60]</sup>.



Fig.2 Schematic representation of 2D Co-ZIF-9(III) nanosheets exfoliated in liquid phase from bulk Co-ZIF-9(III)(A), the possible evolution process from FeCo-MOF bulk to FeCo-MOF-EH nanosheets(B) and SEM image of FeCo-MOF-EH(C)

(A) Copyright(2018) Wiley-VCH<sup>[40]</sup>; (B) and (C) Copyright(2020) Wiley-VCH<sup>[56]</sup>.

# 2.1.2 Chemical Solvent-induced Exfoliation

In order to effectively and accurately peel off the single-layer nanosheets, the researchers have proposed a fabrication method that can regulate the interaction force of the chemical bonds between the layers through a controlling chemical reaction, and can specifically peel off the single-layer 2D nanostructure<sup>[61-64]</sup>. For example, Chandrasekhar *et al.*<sup>[65]</sup> found that solvents, such as ethanol and dimethyl sulfoxide(DMSO) could break the hydrogen bonds between the layers, causing Cd tris(2-pyridylmethyl)amine(Cd-TPA) to exfoliate into 2D nanosheets. This improves the potential for structural damage and the incompleteness caused by external force-assisted exfoliation, a physical stripping method. Au *et al.*<sup>[66]</sup> reported a layered Cu(II)-MOF with Kagome lattice[Fig.3(A)]. When the layered Cu(II)-MOF was put into an aprotic polar solvent[DMF or tetrahydrofuran(THF)] and gradually expanded, the cross-section remained unchanged and the longitudinal stretch was elongated[Fig.3(B)]. When the interlayer distance of Cu(II)-MOF expanded to a certain extent, adding some external force to assist stirring can completely peel off the double-layer and single-layer mixed nanosheets. In addition to solvents, such as ethanol, DMF and DMSO, Ding *et al.*<sup>[67]</sup> found that diphenyl disulfide(DPDS) could be inserted into layered MOF crystals, increasing the interlayer distance from 0.98 nm to 2.26 nm, while retaining the layered MOFs crystal structure[Fig.3(C) and (D)]. Then excessive trimethylolpropane(TMP) was added to the ethanol solution containing  $Zn_2(PdTCPP)(DPDS)_2$  crystals, and the ultra-thin nanosheets were successfully peeled off under the action of reduction reaction and external stirring. This proves that the embedded DPDS can effectively strip MOFs

into 2D MOF nanosheets through chemical reaction. Moreover, the peeling of the nanosheets may be due to the significant reduction of the interlayer interaction after removing part of the intercalator. 2D MOF nanosheets can be synthesized at a high yield(57% yield of 1 nm ultra-thin nanosheets) by controlling the peeling of MOFs crystals through intercalator.



Fig.3 Synthesis of kgm<sup>SMe</sup> and a microscopic image of its green hexagonal crystals(A), snapshots of kgm<sup>SMe</sup> upon expansion in DMF(B), schematic illustration of the overall process developed to produce 2D MOF nanosheets *via* an intercalation and chemical exfoliation approach(C) and experimental PXRD patterns of Zn<sub>2</sub>(PdTCPP) before and after insertion of DPDS along with simulated results considering the preferred orientation in the (001) direction(D)

(A) and (B) Copyright(2019) American Chemical Society<sup>[66]</sup>; (C) and (D) Copyright(2017) American Chemical Society<sup>[67]</sup>.

In contrast to the use of solvents for chemical reactions, Liu *et al.*<sup>[44]</sup> reported a new strategy for thermal stripping[Fig.4(A) and (B)]. First, hexamethylenetetramine(HMT) and transition metal clusters(Ni, Co and Cd) were coordinated to form metal-hexamine framework(MHF), which was a layered topological framework structure. Then, pyrolysis in Ar atmosphere resulted in the thermal exfoliation of the layered MHF, which was further converted into carbon-based nanosheets with a thickness of only 6 nm. By comparing the conditions of the control variables, it was found that NO, CH<sub>2</sub>O and NH<sub>3</sub> would be produced during the pyrolysis process. When these gases were released, a larger gas pressure was generated, which was enough to break the interaction force between the MHF layer and the weak hydrogen bond in the layer. Moreover, the carbon-based nanosheets exfoliated by pyrolysis have been uniformly dispersed in the metal nanoparticles, and the N-doping amount was also very high, which was beneficial to further improve the electrochemical performance of MHF.



Fig.4 SEM images of Ni-HMT MHFs annealed at 200(a), 300(b), and 400 °C(c), respectively, at a heating rate of 10 °C/min(A), the schematic of the thermal exfoliated process(B), selective pillar removal and exfoliation of a pillared-layer MOF(C) and SEM images of 2D-Co-NS(a) and the corresponding height profile of 2D-Co-NS(b)(D)

(A) and (B) Copyright(2018) The Royal Society of Chemistry<sup>[44]</sup>; (C) and (D) Copyright(2018) Wiley-VCH<sup>[68]</sup>.

Huang *et al.*<sup>[68]</sup> found that when 3D columnar MOF was used as an electrocatalyst for water oxidation(pH 13), columnar ligands were removed by *in-situ* oxidation to form 2D-Co nanomaterials[Fig.4(C) and (D)]. Through the control experiment, it was further found that 3D-Co nanomaterials could be con-

verted into 2D-Co nanosheets(NS) only in the electrolyte solution under  $O_2$  saturation, which showed that the conversion of 3D-Co nanomaterials was closely related to the oxidizing environment atmosphere. Comparing the difference in crystal structure between the two, it was found that the concentration of 2D-Co-NS active site was 15.1 mol/kg, which was 4 times that of 3D-Co nanomaterials. This was because all metal ions in 2D-Co-NS had two monodentate water ligands, thus significantly improving OER performance.

Although the fabrication method of top-down synthesis is simple and convenient, there are also inevitable disadvantages. (1) This method is applicable to limited and partially MOFs with layered structure, and structural damage may occur during the peeling process. (2) The peeling is limited to lower concentration, because the high concentration peeling may cause the problem of re-stacking of 2D MOFs. (3) The yield of 2D MOF nanosheets generally obtained by top-down synthesis is relatively low. Therefore, for the industrial fabrication of 2D MOF nanosheets with uniform thickness, high quality and high output, top-down synthesis method is obviously not feasible.

#### 2.2 Bottom-up Synthesis

#### 2.2.1 Solvothermal Synthesis

Early research has indicated that the shape change of MOFs can be adjusted and controlled by adding surfactants<sup>[69–71]</sup>. Similarly, by adding surfactants that can inhibit crystal growth in the vertical direction during the fabrication process, 2D MOFs can be successfully fabricated with a controllable thickness<sup>[72,73]</sup>. The inhibitors commonly reported include polyvinylpyrrolidone(PVP)<sup>[72–75]</sup>, pyridine<sup>[76]</sup>, 4,4'-bipyridine(BPY)<sup>[77]</sup>, monocarboxylic acids(formic acid, acetic acid, lauric acid and oleic acid)<sup>[78]</sup>, cationic surfactants cetyl trimethyl ammonium bromide(CTAB)<sup>[79]</sup> and ethyl trimethyl ammonium bromide<sup>[80]</sup>. Moreover, more and more surfactants have been proved through experiments to selectively inhibit crystal growth. For example, Zhao *et al.*<sup>[81]</sup> found that the carboxyl functional groups in 4,4'-biphthalic acid(BPDC) and benzoic acid(BA) could selectively combine with zinc ions, increase the steric hindrance, and limit the growth of Zn-TCPP MOF[Fig.5(A)].

Pham et al.<sup>[82]</sup> synthesized MOF { $[Cu_2(ndc)_2(dabco)]_n$ } with different sizes and shapes by adjusting the growth of crystals in different directions by using acetic acid and pyridine. The comparative experimental results showed that pyridine could inhibit the crystal growth in the [001] direction, and acetic acid hindered the crystal growth in the [100] direction. Similarly, Lin et al.[83] obtained 2D MOF hexagonal nanoplate(defined as HXP) with hexagonal cross-sections but uniform thickness changes by adjusting the concentration of pyridine[Fig.5(B)]. Through control variates, it was found that the higher the concentration of pyridine was, the smaller the thickness of HXP would be. This was because the original interlayer structure of MOF was linked by triethylenediamine(DABCO) molecules. Due to the similar molecule size of pyridine and DABCO, the pyridine molecule occupied the original coordination position of the DABCO molecule, which hindered the growth of MOF. Zhao et al.<sup>[84]</sup> reported a smooth ultra-thin Zn(bim)(OAc)MOF nanosheets with an average thickness of about 5 nm[Fig.5(C)]. The synthesis mechanism of Zn(bim)(OAc)MOF nanosheets was analyzed in combination with Fourier transform infrared(FTIR) spectroscopy. First, Zn<sup>2+</sup> was coordinated with gluconate in the solvent. Since the ligand had stronger coordination ability with Zn<sup>2+</sup>, when adding the ligand, the gluconate group was occupied by the ligand substitution. However, a small amount of unsubstituted gluconate continued to occupy the Zn<sup>2+</sup> coordination sites, thereby hindering the growth of crystals in the [100] plane direction.



Fig.5 Synthesis of 2D metal-organic framework nanodisk(A), schematic illustration for the HXP preparation and TEM image of the HXP(B) and schematic illustrations of the synthesis of Zn(bim)(OAc) and UT-Zn(bim)(OAc)(C)

(A) Copyright(2018) The Royal Society of Chemistry<sup>[81]</sup>; (B) Copyright(2020) American Chemical Society<sup>[83]</sup>;

(C) Copyright(2018) The Royal Society of Chemistry<sup>[84]</sup>.

Li *et al.*<sup>[85]</sup> used an appropriate mixed solvent(DMF and  $H_2O$ ) to perform solvothermal reaction to synthesize ultra-thin Ni-Fe-MOF nanosheets with only 1—2 nm[Fig.6(A) and (B)]. Through comparative experiments, it was found that when the solvent was only  $H_2O$ , the hydrothermal product was

Ni-Fe-MOF with nano flower structure. When the solvent was only dimethylacetamide(DMAC), the hydrothermal product had a fluffy structure with a certain thickness. The article explained that  $H_2O$  in the mixed solvent occupied the metal coordination on the surface of the nanosheet, which limited the

structure growth of Ni-Fe-MOF. However, there is still much room for exploring the specific mechanism of the formation of nanosheets in the hydrothermal method of mixed solvents, which needs further investigation.



Fig.6 Synthetic procedure for the production of ultra-thin MOF nanosheets and their utilization for the OER(A), TEM images of Ni-Fe-MOF nanosheets(B), schematic illustration of the 2D oxide sacrifice approach(2D OSA) conversion of M-ONS with H<sub>4</sub>dobdc ligand to form M-MNS(C) and TEM images of FeCo-MNS(D) (A) and (B) Copyright(2019) Wiley-VCH<sup>[85]</sup>; (C) and (D) Copyright(2019) Wiley-VCH<sup>[86]</sup>.

The surfactant is generally attached to the surface of MOF nanosheets or directly combined with metal ions to achieve the effect of inhibiting crystal growth. Therefore, the use of surfactants may reduce the catalytic activity of some active sites. Yao's team<sup>[86]</sup> proposed a method for preparing ultra-thin 2D MOF nanosheets without adding surfactants[Fig.6(C) and (D)]. Using metal oxide nanosheets(including single metal oxides Co, Ni, Cu and bimetallic FeCo, NiFe, CoCu oxides) as templates, a quantitative amount of 2,5-dihydroxyterephthalic acid (H<sub>4</sub>dobdc) was added to synthesize MOF-74 nanosheets by solvothermal method. Among them, the thickness of the MOF precursor metal oxide nanosheets FeCo-ONS was only 1.2 nm, and the thickness of the synthesized FeCo-MOF-74 nanosheets was only 2.6 nm, which was one thousandth of the thickness of MOF-74 particles synthesized by ordinary solvothermal method. In addition, through TEM images, it can be observed that FeCo-MOF-74 nanosheets had a smooth surface with relatively uniform thickness and good dispersion. Without the hindrance of surfactant and the structural destruction of exfoliation, the structural defects of FeCo-MOF-74 nanosheets on the outer surface were reduced to a certain extent, the utilization of Fe and Co ions was increased, and the catalytic activity of the metal active center was increased.

It is also a widely used fabrication method to construct 2D MOF nanosheets crystals by *in-situ* solvothermal growth of MOFs arrays on a conductive substrate(*e.g.*, carbon cloth, Ni foam)<sup>[41,87,88]</sup>. For example, Wei *et al.*<sup>[89]</sup> added Ni foam during the reaction of Zn ion, Ni ion, Fe ion and terephthalic acid, and the petal-like ultra-thin 2D MOF nanosheets were successfully *in situ* grown on the foam Ni under the action of ultrasonic stirring. By adjusting the ratio of Ni and Fe ions, it

was found that the presence of Ni ions would make MOF tend to form the shape of fluffy nanosheets, while the presence of Fe ions would make MOF tend to agglomerate nanoparticles or amorphous structures. Therefore, when the ratio of Ni ions to Fe ions was 7:3, the MOF presented uniformly dispersed fluffy petal-shaped ultra-thin nanosheets. Through comparative experiments, it was further proved that the addition of Zn ions was conducive to the uniform dispersion of MOF nanosheets and the growth of MOF nanosheets, improving the surface area of MOF nanosheets and the catalytic performance. Compared with the traditional method of electrocatalysis using a binder to load 2D MOF nanosheets on a glassy carbon electrode, this integrated electrocatalyst showed greater application potential. (1) The metal active centers on this integrated conductive catalyst are more evenly distributed and the catalytic effect is better. (2) The use of surfactants and the binders to prepare electrodes will cause catalysts to lose part of its catalytic activity. (3) It can be directly used for electrocatalytic testing without secondary electrode fabrication, which further simplifies the experimental process. (4) The practical application of 2D MOF nanosheets electrocatalysis is further promoted and is moving closer to the flexible functional application.

#### 2.2.2 Interface-mediated Synthesis

The chemical reaction in the two-phase interface region is more unique than the reaction in the bulk phase, and can also limit the nucleation and growth of crystals<sup>[90,91]</sup>. Therefore, 2D MOF nanosheets can also be synthesized by controlling the crystal morphology and structure through interface-mediated synthesis. According to the synthesis method of different interfaces, it can be divided into liquid-liquid interface<sup>[92,93]</sup>, gas-liquid interface<sup>[94]</sup>, gas-solid interface<sup>[95]</sup>, liquid-solid interface<sup>[96]</sup>, etc.

When two components with different solubility react with each other, the liquid-liquid interface synthesis method is usually selected. For example, Rodenas *et al.*<sup>[92]</sup> fabricated dispersible copper 1,4-phthalate MOF nanosheets by kinetic diffusion of a three-layer liquid medium. According to the different density of the three liquids, the metal ions and the ligand solution were placed in the top and bottom solvent layers, separated from each other by the solvent layer in the middle. Through the slow diffusion of molecules, MOF nanosheets were formed in the intermediate solvent layer. Tsukamoto *et*   $al.^{[93]}$  synthesized multiple coordination nanosheets(CONASHs) with a large sheet size(centimeter level) at the liquid/liquid interface[Fig.7(A) and (B)]. The fabrication strategy was to dissolve the ligand in CH<sub>2</sub>Cl<sub>2</sub> and place it on the bottom of the bottle, then the ligand solution was covered with pure water to form a water/oil interface. Then, by slowly pipetting, the aqueous solution of Zn(BF<sub>4</sub>)<sub>2</sub> was added to the aqueous phase, and a film could be formed at the interface after 5 days. Many different nanosheets, such as Cu-BHT<sup>[97]</sup>, Cu-3(btc)<sup>[98]</sup> and Co-THT<sup>[99]</sup> have been successfully fabricated through the liquid-liquid interface synthesis method.



Fig.7 1-Zn generated at the liquid/liquid interface between Zn(BF<sub>4</sub>)<sub>2</sub> in water(1.3×10<sup>-2</sup> mol/L) and ligand 1 in dichloromethane(1.0×10<sup>-4</sup> mol/L) after 5 days(A), appearances of 1-Zn on a quartz substrate under ambient(a), TEM image of 1-Zn(b) and AFM image and its cross-section analysis of 1-Zn on a Si substrate(c)(B), schematic illustration of sublimation-vapor phase transformation mechanism of LDH-MOF NS(C) and SEM images of pristine LDH-MOF@NF(D)

(A) and (B) Copyright(2017) American Chemical Society<sup>[93]</sup>; (C) and (D) Copyright(2019) Wiley-VCH<sup>[95]</sup>.

The gas-liquid interface can be used in the synthesis of insoluble reactants<sup>[100]</sup>. The hydrophilic group of the reactant in the liquid solvent is combined with the solvent molecule to ensure that they are fully spread on the solvent surface, while the relatively hydrophobic part faces the reactant in the gas<sup>[101]</sup>. A classic example is that Makiura et al.<sup>[94]</sup> grew 2D molecular thin crystal MOF nanosheets composed of porphyrin building blocks and metal ion junctions(NAFS-13) on the air/liquid interface. The fabrication strategy was to disperse the PdTCPP solution of the molecular building unit directly on the pure water subphase, and then the copper ion metal joint solution was gently injected into the subphase. Through comparative experiments, it was proved that the necessary conditions for film formation were that the PdTCPP molecules were packed closely and stood vertically at some angle to the air/liquid interface.

The gas-solid interface is a novel fabrication method of 2D MOF nanosheets. Chen *et al.*<sup>[95]</sup> fabricated a vertically aligned, uniform and controllable NiFe-based MOF nanosheet array(LDH-MOF@NF) using the sublimation-vapor phase pseudocrystal transformation(SVPT) method[Fig.7(C) and (D)]. First, NiFe-LDH@NF was fabricated by the hydrothermal method of metal salt mixed urea. Then terephthalic acid(BDC) was added to the crucible and NiFe-LDH@NF was added above the crucible to avoid direct contact with the ligand. After sealing the crucible, it was heated at 350 °C for 1 h under N<sub>2</sub>

atmosphere. When the temperature reached the sublimation point of BDC, the BDC powder would sublimate into gas, and the rising BDC gas would fully react with NiFe-LDH@NF to finally obtain LDH-MOF@NF. This fabrication scheme can be universally applied to the synthesis of many different metal ions and ligands.

In addition to the three fabrication strategies of liquid-liquid interface, gas-liquid interface and gas-solid interface, liquid-solid interface can also synthesize 2D MOF nanosheets. Kitagawa *et al.*<sup>[96]</sup> reported the successful fabrication of  $Fe(py)_2[Pt(CN)_4](py=pyridine)$  by the liquid-solid interface method. Using 4-mercaptopyridine as the raw material, ethanol solvent mixed with metal ions could form a 2D MOF layer on the liquid-solid interface of each cycle. After 30 cycles, a film with a thickness of 16 nm could be fabricated. Infrared spectroscopy analysis results showed that this fabrication strategy could achieve cycle control of film growth.

#### 2.3 Other Synthesis Method

The template method can effectively limit the growth of MOFs and control the structural changes. By properly designing the template to adjust the synthesis of MOFs, successful fabrication of 2D MOF nanosheets can be achieved. For example, Huang *et al.*<sup>[102]</sup> for the first time combined ZIF with inorganic salt templates to prepare ultra thin ZIF-67 nanosheets.

The synthesis of ZIF-67 nanosheets was divided into two parts. First, NaCl powder was added during the synthesis of ZIF-67 at room temperature, and NaCl@ZIF-67 nanosheets were obtained by evaporating methanol solvent. Then, after carbonization under the protection of N2 atmosphere, a stable 2D MOF derivative carbon nanosheet was obtained, and subsequently the NaCl template was removed by repeated washing with deionized water. Successful fabrication of ultra-thin 2D nanomaterials required two key conditions, a limited volume of solvent and an appropriate ratio of precursor to salt. The solvent was confined in the salt crystallite gap, which effectively limited the growth space and direction of ZIF-67. The precursor was limited, only enough to supply ZIF-67 nanoparticles' growth along the salt crystallite plane. Consequently, ZIF-67 particles could not be formed. In addition to this, the pyrolysis temperature was particularly important. If the pyrolysis temperature was not high enough, graphitization would be incomplete. Therefore, Co ions could not be reduced to Co nanoparticles, and some active sites would be lost in the post-processing process, which would reduce the catalytic performance. However, if the pyrolysis temperature was too high and exceeded the crystal melting point of NaCl, the full fusion of NaCl would reunite the Co nanoparticles, which was not conducive to play the catalytic role of Co nanoparticles. Therefore, a suitable pyrolysis temperature(800 °C) was conducive to Co ion reduction and carbon encapsulation, which could prevent agglomeration, achieve the purpose of uniform dispersion, and maximize the utilization of active sites.

Zhu *et al.*<sup>[42]</sup> used chemical solvent-induced exfoliation method to remove large  $MoS_2$  in *n*-butyl lithium solution to strip  $MoS_2$  nanosheets, and then the Co-BDC/MoS<sub>2</sub> hybrid nanosheets were fabricated by reacting the  $MoS_2$  nanosheets with ligands and metal ions through ultrasonic assisted solution method. Recently, Cai *et al.*<sup>[103]</sup> successfully fabricated a 2D CoFe-MOF by combining 2D layered double hydroxide(LDH) with ligands. In addition, graphene oxide(GO)<sup>[104,105]</sup>, K<sub>0.5</sub>Mn<sub>2</sub>O<sub>4</sub><sup>[106]</sup>, Ni(OH)<sub>2</sub><sup>[107]</sup>, etc. have also been reported as templates for the coordinated synthesis of 2D MOF nanosheets.

# 3 Electrocatalytic Applications

Because 2D MOFs have a highly exposed surface area and good flexibility, they have shown potential application prospects in many fields<sup>[108—110]</sup>. Especially in the field of electrocatalysis, the structure and function of 2D MOFs can be adjusted by combining various metal ions and ligands, thus providing specific excellent performance for electrocatalysis<sup>[111,112]</sup>. The carbonization, oxidation, sulfidation or doping of 2D MOFs produces 2D MOF-derivative materials that have more unique advantages than 2D MOFs, further improving electrocatalytic performance<sup>[113—115]</sup>. In this part, we mainly summarize the application of 2D MOFs and derivatives in electrocatalysis, including electrocatalytic water splitting, ORR, CO<sub>2</sub>RR, NRR and other electrocatalytic applications.

# 3.1 2D MOFs for Electrocatalysis

The important materials of electrocatalysts are precious

metals and their oxides(Pt, RuO<sub>2</sub>, IrO<sub>2</sub>, etc.). However, due to the high price of precious metals and the scarcity of resources, it is necessary to look for electrocatalysts that can replace precious metals with high efficiency. 2D MOFs have abundant unsaturated metal sites and a high specific surface area, which has attracted the attention of researchers<sup>[37,116]</sup>. After years of research and exploration, it has successfully opened up a new world of 2D MOFs in the field of electrocatalysis.

#### 3.1.1 Electrocatalytic Water Splitting

Electrolyzed water is an efficient and sustainable way to produce hydrogen and is considered to be an effective method for renewable energy production in the future. Electrolyzed water consists of two half reactions, HER and OER. HER is a two-electron transfer reaction, and OER is а four-electron-proton coupling reaction, which requires a higher overpotential<sup>[117,118]</sup>. The design and synthesis of high-efficiency OER catalysts is the key to improving the efficiency of hydrogen production from electrolyzed water. At present, the most effective OER catalysts are RuO<sub>2</sub> and IrO<sub>2</sub>, but they are expensive, scarce in resources and poor in stability, and are not ideal catalysts<sup>[119]</sup>.

Transition metals have the advantages of abundant reserves and low cost. Most MOFs are composed of transition metals. For example, Rui et al.[120] anchored Fe-MOF nanoparticles to NiCo-MOF nanosheets and used the synergistic effect between NiCoFe to directly catalyze OER without annealing. Similarly, Li et al.<sup>[85]</sup> used bottom-up solvothermal methods to prepare Ni-M-MOF nanosheets(NSs) with a thickness of only a few atomic layers(M=Fe, Al, Co, Mn, Zn and Cd), and can be used directly for OER. Among them, Ni-Fe-MOF NSs had the best OER performance, and the overpotential was only 221 mV at a current density of 10 mA/cm<sup>2</sup>. Through X-ray photoelectron spectroscopy(XPS) comparative analysis, it was found that the peaks of  $Ni_{2p}$  and  $Fe_{2p}$  of Ni-Fe-MOF NSs moved to a higher binding energy compared to Ni-MOF NSs, which indicated that the introduction of Fe improved the electrocatalytic performance. The following density functional theory(DFT+U) calculations showed that the overpotential of Fe site on OER was significantly lower than that of Ni site, which further proved that high-active Fe might replace part of Ni site and Ni-Fe-MOF NSs showed higher electrocatalysis active.

Recently, Cai *et al.*<sup>[103]</sup> successfully fabricated a 2D CoFe-MOF by combining 2D layered double hydroxide(LDH) with ligands[Fig.8(A)]. Because of the synergistic effect of Co ions and Fe ions, and the structural advantages of 2D CoFe-MOF, 2D CoFe-MOF has excellent performance in electrocatalytic water oxidation[Fig.8(B)]. In addition, NiFe<sub>0.2</sub>Co<sub>0.3</sub>-ZIF<sup>[121]</sup>, NiFe-UMNs<sup>[122]</sup>, NiCo-UMOFNs<sup>[123]</sup> and Ni<sub>0.75</sub>Fe<sub>0.25</sub>BDC<sup>[124]</sup> have all used binary, even ternary metals to increase the active site to improve OER performance.

In recent years, reports about the combination of 2D MOF nanosheets and conductive carriers to improve the low conductivity of MOFs have emerged as a new strategy for synthesizing high-efficiency electrocatalysts. Typically, Sun *et al.*<sup>[41]</sup> used solvothermal methods to grow MIL-53(Fe) *in situ* on Ni foam[Fig.8(C)]. However, due to the addition of ligand BDC,

the mixed solution was weakly acidic(pH 5). The Ni metal in the Ni foam was etched into Ni and Fe ions to react with the ligand to form a tightly stacked Ni foam MIL-53(FeNi) nanosheets array. XRD, XPS and FTIR spectroscopy could fully prove that MIL-53(FeNi) was successfully loaded on Ni foam. At a high current density of 50 mA/cm<sup>2</sup>, MIL-53(FeNi)/NF only had an overpotential of 233 mV, and the Tafel slope was only 31.3 mV/dec[Fig.8(D)]. In addition, after 1000 cycles of cyclic voltammetry(CV) in 1.0 mol/L KOH electrolyte, the polarization curve was basically unchanged, showing excellent stability. Compared with the traditional method of electrocatalysis using a binder to load 2D MOF nanosheets on a glassy carbon electrode, this integrated electrocatalyst showed greater application potential.



Fig.8 Schematic illustration for the ligand-assisted transformation to prepare 2D-MOFs(A), polarization curves(a) and corresponding Tafel(b)(B), schematic illustration of the fabrication procedure of MIL-53(FeNi)/NF(C) and polarization curves(D)

(A) and (B) Copyright(2020) The Royal Society of Chemistry<sup>[103]</sup>; (C) and (D) Copyright(2018) Wiley-VCH<sup>[41]</sup>.

The other half reaction of electrolyzed water is HER, and there are few reports on the high performance of MOFs in the HER catalytic reaction, which indicates that the application of MOFs in HER is still in a preliminary stage to be explored. The precious metal Pt is considered to be the current highly effective HER catalyst. Rui *et al.*<sup>[45]</sup> deposited Pt on 2D Ni-MOF nanosheets to obtain Ni-MOF@Pt[Fig.9(A)]. The surface of Ni-MOF nanosheets contained a large amount of oxygen atoms with unpaired electrons, which provided sufficient favorable conditions for Pt deposition. Therefore, the loading of Pt in Ni-MOF@Pt reached 20%(mass fraction). Both the 0.5 mol/L  $H_2SO_4$  acid electrolyte and the 1 mol/L KOH alkaline electrolyte showed better HER electrocatalytic performance than standard Pt/C electrode[Fig.9(B)].

Recently, Zhu *et al.*<sup>[42]</sup> used MoS<sub>2</sub> nanosheets as templates to react with ligands and metal ions to prepare Co-BDC/MoS<sub>2</sub> hybrid nanosheets[Fig.9(C)]. It could be clearly observed from scanning electron microscope(SEM) images that Co-BDC/MoS<sub>2</sub> hybrid nanosheets perfectly inherited the original morphology of MoS<sub>2</sub> nanosheets[Fig.9(D)]. XRD also further proved that Co-BDC was successfully fabricated on the basis of MoS<sub>2</sub> nanosheets. In electrochemical tests, the HER



Fig.9 Schematic illustration for the preparation of the 2D MOF@Pt heterostructure(A), polarization curves of electrocatalysts in 0.5 mol/L H<sub>2</sub>SO<sub>4</sub>(a) and 1 mol/L KOH(b)(B), schematic of the synthesis process for Co-BDC/MoS<sub>2</sub> hybrid nanosheets(C), TEM image of Co-BDC/MoS<sub>2</sub> nanosheets(D), and LSV curves of electrocatalysts in 1 mol/L KOH(a) and LSV curves of Co-BDC/MoS<sub>2</sub> recorded before and after 2000 CV cycles(inset: the chronopotentiometric response of Co-BDC/MoS<sub>2</sub> at a constant current density of -10 mA/cm<sup>2</sup> for 15 h)( b)(E)

(A) and (B) Copyright(2019) American Chemical Society<sup>[45]</sup>; (C) and (D) Copyright(2019) Wiley-VCH<sup>[42]</sup>.

performance of Co-BDC/MoS2 hybrid nanosheets was much higher than that of Co-BDC and MoS<sub>2</sub>, with good stability [Fig.9(E)]. This proved that the composite fabrication of Co-BDC and MoS<sub>2</sub> could enhance the electrocatalytic activity, and proposed a creative strategy for the composite fabrication MOFs. MoS<sub>2</sub> and various other Similarly, of Au/CoFe-MOFNs<sup>[125]</sup>, THAT-Co/G<sup>[126]</sup>, AB&CTGU-5<sup>[127]</sup> and NiBTC/Ni foam<sup>[88]</sup> were all compounded with MOFs and highly conductive materials to improve HER performance. Recently, Ji et al.[128] used the first-principles calculations and screened out 6 of 36 2D *n*-conjugated metal-organic nanosheets(Rh-N, Ir-N, Ru-O, Rh-O, Co-S and Pd-S) HER potential catalyst. This provided an important theoretical basis for the future design of single-atom catalyst synthesis.

Catalysts with HER and OER catalytic functions can be used as both cathode and anode catalytic materials. When assembled, they can form a complete electrolytic cell<sup>[89,118]</sup>. Duan *et al.*<sup>[87]</sup> reported a fabrication strategy for depositing MOFs on Ni foam to form 2D MOF nanosheets[Fig.10(A)]. Electrochemical tests were carried out in 0.1 mol/L KOH electrolyte environment. Compared with Fe-MOF/NF, Ni-MOF/NF and

calcined NiFe-MOF/NF, it was found that the original NiFe-MOF/NF had the best performance. When using NiFe-MOF/NF as the cathode and anode, only a voltage of 1.55 V was needed to achieve a current density of 10 mA/cm<sup>2</sup>, which was better than the standard noble metal electrode for water electrolysis[Fig.10(B)]. Xu et al.[43] found that ultra-thin Ni-ZIF/Ni-B nanosheets could be easily synthesized by a simple room temperature boronization of Ni-based ZIF[Fig.10(C)]. OER and HER tests were carried out in the 1.0 mol/L KOH electrolyte environment and Ni-ZIF/Ni-B nanosheets only required 234 and 67 mV overpotentials to achieve a high current density of 10 mA/cm<sup>2</sup>. In the alkaline electrolytic cell, Ni-ZIF/Ni-B@NF could be directly used as the anode and cathode of the overall water splitting without secondary sample fabrication. It only needed 1.54 V to complete the high current density work of 10 mA/cm<sup>2</sup>[Fig.10(D)], which was better than the overall water splitting catalyst materials of transition metal-based MOF reported so far. Although, 2D MOF nanosheets have made some research progress on the overall water splitting catalytic performance, but there is still a long way to go for the practical application of clean energy.





(A) and (B) Copyright(2019) Nature Publishing Group<sup>[87]</sup>; (C) and (D) Copyright(2017) Wiley-VCH<sup>[43]</sup>.

#### 3.1.2 Oxygen Reduction Reaction(ORR)

Different from OER, ORR is a catalytic process that reduces  $O_2$  to produce  $H_2O_2$  or  $H_2O$ . In this process, not only the four-electron reduction reaction, but also the inevitable two-electron reduction reaction occurred<sup>[129]</sup>. The presence of the two-electron reduction reaction reduces the ORR reaction efficiency, and the intermediate product  $H_2O_2$  will destroy the catalyst activity and accelerate the aging of the fuel cell. The advantages of MOFs in structure and physicochemical properties coincide with the necessary conditions for enhancing the catalytic activity of ORR. ORR electrocatalysts can be designed by pyrolyzing MOFs, adding graphene oxide and other compounds. But there are few reports on 2D MOF nanosheets<sup>[117,130]</sup>.

Recently, it was reported that Zhong et al.[131] synthesized a new type of 2D conjugated MOF by solvothermal method with 2,3,9,10,16,17,23,24-octahydroxyphthalocyaninato copper and cobalt ions. The large amount of exposed Co was defined as the efficient ORR active site of PcCu-O8-Co. In addition, the ORR performance of the composite material after mixing PcCu-O8-Co and carbon nanotubes was further improved. In addition to metal active sites. Ni-N₄ in Ni<sub>3</sub>(hexaiminotriphenylene)<sub>2</sub> 2D MOF has also shown to be an active catalyst for ORR<sup>[132]</sup> and can be used in zinc-air battery devices, providing efficient discharge functions.

#### 3.1.3 CO<sub>2</sub> Reduction Reaction(CO<sub>2</sub>RR)

 $\mathrm{CO}_2$  is one of the main products produced by the burning of fossil fuels and the source of contemporary global

greenhouse environmental problems. The development of clean energy is still urgently needed to be explored, but the use of fossil fuels to cause large amounts of CO<sub>2</sub> emissions is still inevitable. If CO<sub>2</sub> can be captured and converted into available carbon resources, this will maximize the recycling of energy. CO<sub>2</sub>RR is the reduction of CO<sub>2</sub> to CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, alcohols and other reusable carbon resources through catalytic reactions<sup>[99,133–135]</sup>. CO<sub>2</sub> reduction involves more complex multielectron reactions, and correspondingly, a greater energy barrier needs to be overcome<sup>[136]</sup>. Using the advantages of the porous structure and high specific surface area of MOFs to design 2D MOF nanosheets catalysts can expose more active sites and improve the efficiency of CO<sub>2</sub> reduction<sup>[137,138]</sup>.

For example, Wu *et al.*<sup>[58]</sup> reported a 2D Ni(Im)<sub>2</sub> nanolayered structure based on Ni ions and imidazole ligands synthesized under hydrothermal conditions[Fig.11(A) and (B)]. 2D

Ni(Im)2 nanosheets with different thicknesses were peeled off with ultrasonic vibration. By electrolyzing 2D Ni(Im)<sub>2</sub> nanosheets with different thicknesses at different potentials, it was proved that the thinner the 2D Ni(Im)2 nanosheets were, the higher the electron transfer exchange rate would be. Correspondingly, the larger the carbon monoxide partial current densities were, the better the CO2RR performance would be[Fig.11(C)]. Analogously, Wu et al.[139] designed cathodized copper porphyrin MOF nanosheets with Cu ions and porphyrin ligands, which could selectively and efficiently reduce formic acid and acetic acid. In addition to Ni and Cu, there were also reports on the use of Ag with high active sites to construct efficient  $CO_2$ electroreduction highly catalysts [Fig.11(D)-(F)]<sup>[140]</sup>. However, based on the problem of permanent use of catalytic materials, the catalytic stability of 2D MOF nanosheets needs to be further explored and improved.



# Fig.11 Scheme of the liquid exfoliation process(A), TEM image of 2D Ni(Im)<sub>2</sub>-5 nm(B), potential-dependent faradaic efficiencies of CO(a) and potential-dependent CO partial current densities(b)(C), schematic illustration of Ag<sub>2</sub>O/layered ZIF synthesis(D), TEM images of the Ag<sub>2</sub>O/layered ZIF(E) and LSV curves of different catalysts in CO<sub>2</sub>-saturated 0.25 mol/L K<sub>2</sub>SO<sub>4</sub> at the scan rate of 50 mV/s(F)

(A)—(C) Copyright(2019) The Royal Society of Chemistry<sup>[58]</sup>; (D)—(F) Copyright(2017) The Royal Society of Chemistry<sup>[140]</sup>.

#### 3.1.4 Other Electrocatalytic Applications

In addition to the electrocatalysis of OER, HER, ORR and CO2RR summarized above, 2D MOF nanosheets are also involved in other electrocatalytic reactions, including alcohol oxidation<sup>[141]</sup>, glucose oxidation<sup>[142]</sup>, urea oxidation<sup>[143]</sup> and so on<sup>[144,145]</sup>. Recently, Xu et al.<sup>[146]</sup> used solvothermal methods to grow Ir-doped Ni-MOF ultra-thin nanosheets on Ni foam in situ. The NiIr-MOF/NF composite electrode can be directly used in the electrocatalytic reaction of urea oxidation without secondary electrode fabrication. In addition, Ir and Ni on the Ni foam were evenly distributed, which increased the active area and the electron transfer rate. Wang et al.<sup>[144]</sup> have developed a trimetallic 2D MOF(NiCoFe-CAT), whose electrocatalytic oxidation performance for benzylamine was currently the best among the known MOF-based catalysts. A high yield of benzonitrile[0.058 mmol/(mg·h)] and Faraday efficiency (ca. 87%) were achieved in the 1.45 V benzylamine electro-oxidation reaction. This was mainly due to the multi-metal ions(Ni, Co and Fe) in NiCoFe-CAT, which provided abundant active sites.

#### **3.2 2D MOF-derivatives for Electrocatalysis**

Although 2D MOF nanosheets have abundant unsaturated metal sites and high specific surface area, the disadvantages of poor conductivity and low mass permeability severely limit their use in electrocatalysis for cycle stability<sup>[28]</sup>. The research in recent years has shown that 2D MOF-derivatives obtained by carbonizing, oxidizing, vulcanizing and doping 2D MOFs can improve the inherent disadvantages of 2D MOFs<sup>[113–115]</sup>. 2D MOF-derivatives not only have the advantages of high specific surface area and structural designability of MOF precursors, but their carbon-based structure is also more conducive to improving the durability of the catalyst and optimizing the electrocatalytic performance of the catalyst. In this section, 2D MOF-derivatives for electrocatalysis are classified and summarized using classic catalytic reactions.

#### 3.2.1 Electrocatalytic Water Splitting

Electrochemical water splitting presents new possibility for the industrial mass production of green new energy hydrogen. Due to the poor water stability of most MOFs, structural collapse occurs during the process of electrolyzing water, which affects the later catalytic efficiency of MOFs electrocatalysts. In 2008, Xu *et al.*<sup>[147]</sup> first pyrolyzed MOFs to produce porous nanocarbons with high specific surface area and excellent electrochemical performance, and proposed an innovative MOF-derivative material fabrication strategy. Since then, the door of MOF-derivatives in the direction of electrocatalytic water splitting has been opened.

High temperature calcination in an inert atmosphere can reduce a large number of metal atoms to metal NP, optimize the electronic structure, and enhance the electrocatalytic activity of MOF-derivatives. For example, Gao's team<sup>[148,149]</sup> used pyrolysis and oxidation of multi-metal MOF to form nanoflowers stacked with carbon-based nanosheets. The nanoflowers had ultra-thin nanosheet petals and showed a high specific surface area. The carbonized and oxidized nanosheets also showed a porous structure, which was beneficial to expose more active sites. Assuredly, MOFs could also be grown in situ on a conductive carrier template(such as carbon cloth, Ni foam, etc.), and then they were pyrolyzed to form a carbon-based nanosheet array<sup>[150-153]</sup>. This integrated electrocatalyst had excellent flexibility and plasticity. After carbonization, it could still maintain high electrocatalytic performance after 20 h of stability test, which indicated that the electrocatalyst had better stability.

MOFs usually introduce some heteroatoms before pyrolysis. During pyrolysis, heteroatoms are directly and uniformly doped into the carbon matrix of MOF-derivatives through organic ligands. The doping of heteroatoms will cause the electronic structure of metal atoms in MOFs to change, resulting in highly conductive and stable compounds, such as nitrides and phosphides, which will help to improve the activity and stability of electrocatalysis. At present, the heteroatoms reported for doping include N<sup>[83,152,154]</sup>, S<sup>[76,152]</sup>, P<sup>[155]</sup>, B<sup>[43]</sup>, metal elements<sup>[156,157]</sup> and so on. Typically, Jiang et al.<sup>[155]</sup> produced ultra-thin 2D MOF nanosheets by interfacial diffusion[Fig.12(A)]. P-Doped 2D MOF nanosheets were pyrolyzed in Ar atmosphere at 300 °C, and a 2D bimetallic phosphorus-doped ultra-thin carbon nanosheet was successfully synthesized. By adjusting the ratio of bimetallic Co and Fe, the authors found that adding a certain amount of Fe ions could make nanosheets thinner, which could promote the oxidation of CoP nanoparticles and improve the catalytic performance of OER. But when the added Fe ion exceeded a certain proportion, it would cause the metal ion to agglomerate, which was not conducive to the uniform dispersion of the active sites. Therefore, when the ratio of Co to Fe was 7:3, the OER performance of the carbonized MOF-derivatives reached the best(current density  $j=10 \text{ mA/cm}^2$ , overpotential of 270 mV, and the Tafel slope of 27 mV/dec)[Fig.12(B)]. The 2D MOF nanosheets after carbonization successfully maintained the ultra-thin nanosheet structure of the MOF precursor, which was conducive to the rapid exchange of electrons in the electrolyte and improved the conductivity.



Fig.12 Photographs of a glass test tube at the initial stage of MOF synthesis and after 24 h(layers labeled as 1, 2, and 3 corresponding to the solution of  $\text{Co}^{2+}/\text{Fe}^{2+}$  ions, the spacer layer and the BDC solution, respective-ly)(a), schematic illustration of the MOF assembling process at layer 2(b) and schematic illustration of the preparation of  $\text{Co}_{1-x}\text{Fe}_x\text{P/C}$  nanosheets(c)(A), LSV curves(a) and the corresponding Tafel plots(b) of  $\text{Co}_{1-x}\text{Fe}_x\text{P/C}$  nanosheets and commercial RuO<sub>2</sub> catalyst in 1 mol/L KOH solution(B), schematic illustration of the preparation strategy of 2D N-doped Ni-Ni<sub>3</sub>S<sub>2</sub>@carbon nanoplates from Ni-based MOFs precursor(C) and LSV curves of Py-1@SNC600 and Py-1.5@SNC600 at a scan rate of 5 mV/s(D) (A) and (B) Copyright(2018) The Royal Society of Chemistry<sup>[155]</sup>; (C) and (D) Copyright(2019) Wiley-VCH<sup>[76]</sup>.

Recently, Lin *et al.*<sup>[76]</sup> synthesized 2D Ni-Ni<sub>3</sub>S<sub>2</sub> carbon nanoplates using 2D Ni-based MOF nanosheets as templates[Fig.12(C)]. In the process of synthesizing MOFs, NiSO<sub>4</sub> not only provided Ni ions, but  $SO_4^{2-}$  was also used as a source for the internal supply of S during pyrolysis of 2D Ni-based MOF nanosheets. The 2D Ni-based MOFs used 4,4'-bipyridine as the ligand. During the carbonization process, the N atoms in 4,4'-bipyridine were evenly anchored in the carbon matrix to form a small amount of N-doping. In 1 mol/L KOH electrolyte, Ni-Ni<sub>3</sub>S<sub>2</sub> carbon nanoplates required an overpotential of 284.7 mV to achieve a high current density of 10 mA/cm<sup>2</sup>[Fig.12(D)]. Wang *et al.*<sup>[154]</sup> reported a Zn-based bimetallic MOF

fabricated by a solvent-free molten salt method. Zn-based bimetallic MOF was carbonized at 900 °C to obtain bifunctional N-doping monometallic porous carbon nanosheet materials with HER and ORR. In the ORR test, the initial overpotential of Fe-NC was -0.963 V, which was 6 mV lower than the initial overpotential of Pt/C. In 0.1 mol/L KOH electrolyte, Co-NC only needed an overpotential of -255 mV to achieve a current density of -10 mA/cm<sup>2</sup>. Moreover, after continuous 20000 s electrocatalytic cycle, Fe-NC and Co-NC could still maintain more than 90% of the electrocatalytic activity. The excellent electrocatalytic performance of single-metal nitrogen-doped porous carbon nanosheet materials was inseparable from the support of the following aspects. (1) The complete escape of Zn ions under high temperature pyrolysis made the surface of carbon nanosheets uniformly distributed in a 15-nm hole. These abundant nanopores increased the specific surface area, so that more active sites were fully exposed, which was conducive to improving the electron transfer rate. (2) There were both zero-valent metals and multiple metal oxides in single-metal nitrogen-doped porous carbon nanosheet materials. This was a necessary condition for the carbon nanosheet material to have dual functions of HER and ORR. (3) The single-metal nitrogen-doped porous carbon nanosheet material contained N atoms with a doping content(mass fraction) of up to 4%, which provided abundant active sites for electrocatalysis. (4) The metal ions under the carbon encapsulation were evenly dispersed, which avoided the rapid loss under the initial catalysis and improved the stability and durability of the single metal nitrogen-doped porous carbon nanosheet material.

In addition to the nitrogen doping and phosphorus doping methods listed above, 2D MOF-derivatives can be combined with other low-dimensional carbon materials to design composite materials. For example, Srinivas et al.[158] reported a composite material of MOFs and carbon nanotubes[Fig.13(A)]. FeNi<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles were evenly dispersed on 2D MOF-derivatives and 1D carbon nanotubes by pyrolysis. OER and HER tests were carried out by glassy carbon electrodes. When the overpotentials were 234 and 108 mV for OER and HER, respectively, the current density could achieve 10 mA/cm<sup>2</sup>. Furthermore, after 20-h long-term electrolyzed water testing, it was proved that the stability of the 2D MOF-derivative composite was good. When this material was used as anode and cathode to construct an integral water-splitting electrolysis cell(the load is 0.28 mg/cm<sup>2</sup>), only 360 mV overpotential was required to achieve a current density of 10 mA/cm<sup>2</sup>. This is higher than the efficiency of electrolyzing water with noble metal Pt as the cathode and RuO<sub>2</sub> as the anode(overpotential of 393 mV at a current density of 10 mA/cm<sup>2</sup>)[Fig.13(B)]. This work proposed a novel 2D and 1D mutually assisted composite material, which provided sufficient evidence that MOF electrocatalysts could completely replace precious metal catalysts in the future.



Two-step fabrication process of FeNi<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub> NPs/MOF-CNT NPs(A), polarization curves of FeNi<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub> Fig.13 NPs/MOF-CNT and FeNi<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub> NPs/MOF as both the cathode and anode, and noble-metal catalyst combination(Pt/C and RuO<sub>2</sub>) for overall water splitting in 1.0 mol/L KOH(a) and amperometric j-t curve at the overpotential of 360 mV(b)(B), electric-field assisted in-situ hydrolysis of MOF bulk into ultra-thin MOOH nanosheets for efficient oxygen evolution(C) and LSV curves of electrocatalysts(a) and galvanostatic measurements of FeCo-MOF-EH and IrO<sub>2</sub> at a constant current density of 10 mA/cm<sup>2</sup>(b)(D)

(A) and (B) Copyright(2020) American Chemical Society<sup>[158]</sup>; (C) and (D) Copyright(2020) Wiley-VCH<sup>[56]</sup>. Recently, Tian *et al.*<sup>[56]</sup> fabricated FeCo-MOF-EH nano- morphology. This was a new way sheets in situ on Ni foam, showing excellent OER performance[Fig.13(C)]. At a current density of 10 mA/cm<sup>2</sup>, it showed an extremely low overpotential of 231 mV[Fig.13(D)]. The Tafel slope was only 42 mV/dec, and  $C_{dl}$  value was 105.8 mF/cm<sup>2</sup>. Concurrently, it had a long-term durability of more than 30 h. This work not only provided a new strategy for the ultra-fast and easy preparation of low-cost and efficient OER electrocatalysts, but also provided a new method for preparing metal oxyhydroxide nanosheets with good crystallinity and

morphology. This was a new way to mildly synthesize nanoscale derivatives from MOF materials.

#### 3.2.2 Oxegen Reduction Reaction(ORR)

Zinc-air battery has a higher energy density than Li ion, and the manufacturing cost is relatively low. It is the most potential green and efficient battery device in the future<sup>[159]</sup>. At present, one of the biggest challenges facing zinc-air batteries is that the efficiency of the air catalyst(ORR) is not high enough. In particular, the four-electron process in ORR mainly relies on highly exposed active sites. Therefore, the fabrication of high-performance ORR catalysts requires a combination of intrinsic(selecting appropriate MOFs as precursors) and extrinsic(design heteroatom doping)<sup>[160,161]</sup>.

Classically, MOFs are grown in situ on layered double hydroxide(LDH), graphene oxide(GO) and other templates. Then pyrolysis is used to form a porous carbon-based MOF-derivative network structure<sup>[162-164]</sup>. The size of these MOF-derivative nanoplates is large, and the surface forms a rich and uniform honeycomb due to the escape of metal ions, which is conducive to improving the exchange rate of electrons. Huang et al.<sup>[102]</sup> combined ZIF with inorganic salt templates for the first time to prepare ultra-thin ZIF-67 nanosheets, and obtained stable 2D MOF-derivatives carbon-based nanosheets after pyrolysis. Comparing the ORR electrocatalytic activity at different pyrolysis temperatures, it was found that the pyrolysis products performed best at 800 °C. The  $E_{\text{onset}}$  and  $E_{1/2}$  of Co,N-C NS-800 were calculated to be 0.938 and 0.869 V, respectively, which had better catalytic performance than commercial precious metal standard Pt/C electrode. The methanol tolerance test was added in the 3000 cycles of durability test. The results showed that, compared with the standard Pt/C electrode, Co,N-C NS-800 had better resistance to methanol etching. In addition, Co,N-C NS-800 had excellent long-term stability, and the initial current density can still be maintained above 98% after continuous operation for 36000 s. The outstanding ORR catalytic performance of Co,N-C NS-800 was inseparable from the fabrication design strategy. The high specific surface area of the 2D structure, the rich porous structure, and the uniform distribution of carbon-encapsulated active sites all laid the foundation for improving the catalytic activity of the

catalyst.

Lately, Zhang et al.<sup>[165]</sup> proposed to use polydopamine(PDA) to optimize Zn and Co-ZIF pyrolysis to prepare hollow cactus-like CS/CNT electrocatalyst for ORR[Fig.14(A)]. The entire fabrication strategy was simple and easy to operate. A certain amount of PDA was added when stirring at room temperature to prepare Zn,Co-ZIF. Due to the limitation of PDA, a hollow cactus-like CS/CNT structure was formed during pyrolysis. By controlling the amount of added PDA, it was proved that increasing the amount of added PDA was conducive to controlling ZIF to form a large cavity, and the thicker outer layer of PDA could generate rich carbon nanotubes[Fig.14(B)]. These were conducive to accelerating the rate of electron conduction. The pyrolysis temperature condition was more important. The higher pyrolysis temperature was beneficial to the reduction of Co ions and the graphitization of the structure, but the structure was destroyed when the temperature exceeded 1000 °C. Therefore, the ORR performance of the pyrolyzed CS/CNT at 900 °C was the best, which could be comparable with the commercial standard Pt/C electrode [Fig.14(C)]. The article also used the rotating disk electrode(RRDE) test to calculate the yield of H<sub>2</sub>O<sub>2</sub> and explore the principle of the catalyst's oxygen reduction reaction. Among them, the H<sub>2</sub>O<sub>2</sub> yield of the 0.5-CS/CNTs-9 sample was the lowest, but higher than the Pt/C yield. This showed that the four-electron reduction reaction of 0.5-CS/CNTs-9 is favourable, but there is also two-electron reduction reaction. After 20000 s of stability test with 0.1 mol/L KOH electrolyte with saturated O2, 0.5-CS/CNTs-9 could still maintain 98% electrocatalytic activity.



Fig.14 Schematic illustration of the formation process of CS/CNTs(A), TEM images of ZIFs@PDA(a) and 0.5-CS/CNTs-9(b)(B) and polarization curves of electrocatalysts(a), long-term durability of 0.5-CS/CNTs-9 in O<sub>2</sub>-saturated 0.1 mol/L KOH solution(b) and methanol tolerance of 0.5-CS/CNTs-9 in O<sub>2</sub>-saturated 0.1 mol/L KOH solution(c)(C)

Copyright(2019) The Royal Society of Chemistry<sup>[165]</sup>.

Wang *et al.*<sup>[166]</sup> reported a method for directly converting 3D In-based MOF(CPM-5) into 2D Co,N-doped carbon nanosheets(NCNS-Co<sub>0.5</sub>In<sub>0.5</sub>) by pyrolysis. Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> ions were added before CPM-5 pyrolysis to obtain Co(NH<sub>3</sub>)<sub>6</sub>@CPM-5 because Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> ions could provide Co and N doping sources in the subsequent pyrolysis process. At 400 °C, CoIn<sub>2</sub> alloy was formed in the material. However, as the temperature

continued to increase, the amino and  $CoIn_2$  alloys in the structure evaporated and were taken away by the flow of inert gas. This caused the original MOF structure to collapse, and a large number of mesopores and micropores were formed, which was beneficial to increase the electron diffusion rate and the ORR electrocatalytic activity. In the report, the authors compared the ORR performance of NCNS-Co<sub>0.5</sub>In<sub>0.5</sub> with a commercial standard Pt/C electrode. NCNS- $Co_{0.5}In_{0.5}$  achieved a half-wave potential of 0.82 V, and the  $E_{onset}$  was only 0.91 V, which was 20 mV lower than the standard Pt/C electrode. Besides, after 20 h continuous catalytic testing, NCNS- $Co_{0.5}In_{0.5}$  still maintained more 92.76% of the electrocatalytic activity, which was over 10% more stable than Pt/C. The assembled Zn-air battery device could provide 25 diode lamps to emit power. In addition, the open circuit potential of NCNS- $Co_{0.5}In_{0.5}$  is comparable to commercial standard Pt/C electrodes. This report provided a new strategy for the conversion of other In-based MOFs into 2D MOF-derivatives with excellent electrocatalytic properties.

Consequently, compared with 2D MOFs, 2D MOFderivatives have some more unique advantages. (1) 2D MOF-derivatives not only retain the size structure and high specific surface area of MOF, but also further enrich the porous structure after carbonization<sup>[167]</sup>. (2) The carbon matrix pyrolyzed from organic ligands has high conductivity, which is conducive to improving the disadvantages of poor conductivity of 2D MOFs and the electron transfer efficiency during electrocatalysis<sup>[168–170]</sup>. (3) Various heteroatoms can be directly and uniformly doped into the carbon matrix of 2D MOF-derivatives after pyrolysis through organic ligands. The heteroatoms themselves can not only become catalytic active sites, but also interact with other metal ions, thereby generating more active sites<sup>[171]</sup>. (4) During the pyrolysis process, the metal ions are converted into metal nanoparticles coated with carbon, which is conducive to uniform distribution and prevents metal ions from agglomerating. In addition, the carbon encapsulation avoids the rapid loss of metal active sites in the initial stage of catalysis, and improves the stability and durability of 2D MOF-derivatives<sup>[73,172]</sup>.

### 4 Conclusions and Outlook

In summary, this paper reviews the research progress of 2D MOFs and derivatives for electrocatalysis in recent years, mainly including electrocatalytic water splitting, ORR, CO<sub>2</sub>RR and other catalytic reactions. It categorizes and summarizes classic representative fabrication methods, including specific fabrication methods, mechanisms, corresponding structural features, and insights into the advantages and limitations of the synthesis methods. The explosive development of MOFs in the past few years proves that 2D MOFs and derivatives are the most potential electrocatalysts. They may play an important role in the future of new energy and mitigate environmental problems.

In the past several years, although there are still some challenges, the application of 2D MOFs and derivatives in electrocatalysis has made great progress. By designing the chemical composition of MOFs, adjusting the ratio of non-noble metal ions or combining with a variety of conductive carriers to form composite materials, many highly efficient electrocatalysts based on non-noble metals have been developed. The electrocatalytic properties of various 2D MOFs and derivatives materials are comparable to those of commercial standard precious metal Pt/C electrodes. Some are even better than precious metal Pt/C electrodes. Great progress has been made in the design and fabrication of the bifunctional electrocatalysts of ORR and OER. However, during the charging and discharging process, the air electrode of the zinc-air battery would inevitably undergo a small amount of oxidation reaction, which is detrimental to the cycle stability of the zinc-air battery device. In addition, 2D MOFs and derivatives for electrocatalysis mostly focus on the application of the three aspects of HER, OER and ORR. For other aspects of electrocatalytic performance, the research needs to be further developed.

In brief, 2D MOFs and derivatives are excellent materials with unique advantages as low-dimensional materials. 2D MOFs and derivatives have excellent nano-cale size, large specific surface area, abundant active sites rich in metal ions, high-fficiency electron transport and transfer capabilities, making their development prospects in the field of electrocatalysis remarkable. Nevertheless, 2D MOFs and derivatives still have two challenges in future research. (1) The synthesis method of 2D MOFs and derivatives still requires the development of new strategies. The fabrication method of top-down synthesis is simple and convenient, but it also has the disadvantages of uneven thickness and size of the finished product. Bottom-up synthesis can flexibly control the thickness and size of the finished product during the fabrication process, but the synthesis rate is relatively low, which cannot meet the large-scale industrial demand. (2) The synthesis mechanism of 2D MOFs and derivatives needs to be revealed more completely and clearly. This will help the functional design of 2D MOFs and derivatives and explore the specific process and mechanism of catalytic reactions. Thereby, the functional application of 2D MOFs and derivatives can be raised to a new height.

#### References

- Novoselov K. S., Geim A. K., Morozov S. V., Jiang D., Zhang Y., Dubonos S. V., Grigorieva I. V., Firsov A. A., *Science*, 2004, 306(5696), 666
- [2] Novoselov K. S., Jiang D., Schedin F., Booth T. J., Khotkevich V. V., Morozov S. V., Geim A. K., *P. Natl. Acad. Sci. USA*, **2005**, *102*(30), 10451
- [3] Li H., Wu J., Yin Z., Zhang H., Acc. Chem. Res., 2014, 47(4), 1067
- [4] Yi M., Shen Z., J. Mater. Chem. A, 2015, 3(22), 11700
- [5] Li M., Luo Z., Zhao Y., Sci. China Chem., 2018, 61(10), 1214
- [6] Mendoza-Sanchez B., Gogotsi Y., Adv. Mater., 2016, 28(29), 6104
- [7] Choudhary N., Islam M. A., Kim J. H., Ko T.-J., Schropp A., Hurtado L., Weitzman D., Zhai L., Jung Y., *Nano Today*, 2018, 19, 16
- [8] Jin H., Guo C., Liu X., Liu J., Vasileff A., Jiao Y., Zheng Y., Qiao S. Z., Chem. Rev., 2018, 118(13), 6337
- [9] Li P., Cheng F.-F., Xiong W.-W., Zhang Q., Inorg. Chem. Front., 2018, 5(11), 2693
- [10] Sun T., Xie J., Guo W., Li D. S., Zhang Q., Adv. Energy Mater., 2020, 10(19), 1904199
- [11] Zhi Y., Wang Z., Zhang H. L., Zhang Q., Small, 2020, 2001070
- [12] Zhan X., Chen Z., Zhang Q., J. Mater. Chem. A, 2017, 5(28), 14463
- [13] Furukawa S., Reboul J., Diring S., Sumida K., Kitagawa S., Chem. Soc. Rev., 2014, 43(16), 5700
- [14] Lu G., Li S., Guo Z., Farha O. K., Hauser B. G., Qi X., Wang Y., Wang X., Han S., Liu X., DuChene J. S., Zhang H., Zhang Q., Chen X., Ma J., Loo S. C., Wei W. D., Yang Y., Hupp J. T., Huo F., Nat.

Chem., 2012, 4(4), 310

- [15] Adil K., Belmabkhout Y., Pillai R. S., Cadiau A., Bhatt P. M., Assen A. H., Maurin G., Eddaoudi M., Chem. Soc. Rev., 2017, 46(11), 3402
- [16] Gao J., Qian X., Lin R. B., Krishna R., Wu H., Zhou W., Chen B., Angew. Chem. Int. Ed., 2020, 59(11), 4396
- [17] Dolgopolova E. A., Rice A. M., Martin C. R., Shustova N. B., *Chem. Soc. Rev.*, **2018**, *47*(13), 4710
- [18] Wu M. X., Yang Y. W., Adv. Mater., 2017, 29(23), 1606134
- [19] Qu C., Jiao Y., Zhao B., Chen D., Zou R., Walton K. S., Liu M., *Nano Energy*, **2016**, *26*, 66
- [20] Zhao R., Liang Z., Zou R., Xu Q., Joule, 2018, 2(11), 2235
- [21] Wang K.-B., Xun Q., Zhang Q., EnergyChem, 2020, 2(1), 100025
- [22] Wu Z., Xie J., Xu Z. J., Zhang S., Zhang Q., J. Mater. Chem. A, 2019, 7(9), 4259
- [23] Zhao Y., Song Z., Li X., Sun Q., Cheng N., Lawes S., Sun X., Energy Storage Mater., 2016, 2, 35
- [24] Hou C. C., Xu Q., Adv. Energy Mater., 2018, 9(23), 1801307
- [25] Yan Y., Li C., Wu Y., Gao J., Zhang Q., J. Mater. Chem. A, 2020, doi:10.1039/D0TA03749D
- [26] Wu Y.-P., Wu X.-Q., Wang J.-F., Zhao J., Dong W.-W., Li D.-S., Zhang Q.-C., Crystal Growth & Design, 2016, 16(4), 2309
- [27] Qin Z.-S., Dong W.-W., Zhao J., Wu Y.-P., Zhang Q., Li D.-S., *Inorg. Chem. Front.*, 2018, 5(1), 120
- [28] Sun L., Campbell M. G., Dinca M., Angew. Chem. Int. Ed., 2016, 55(11), 3566
- [29] Cui X., Tang C., Zhang Q., Adv. Energy Mater., 2018, 8(22), 1800369
- [30] Tang C., Qiao S. Z., Chem. Soc. Rev., 2019, 48(12), 3166
- [31] Gao J., Cong J., Wu Y., Sun L., Yao J., Chen B., ACS Appl. Energy Mater., 2018, 1, 5140
- [32] Jahan M., Liu Z., Loh K. P., Adv. Funct. Mater., 2013, 23(43), 5363
- [33] Chen G. F., Ren S., Zhang L., Cheng H., Luo Y., Zhu K., Ding L. X., Wang H., Small Methods, 2018, 3(6), 1800337
- [34] Ashworth D. J., Foster J. A., J. Mater. Chem. A, 2018, 6(34), 16292
- [35] Liu W., Yin R., Xu X., Zhang L., Shi W., Cao X., Adv. Sci., 2019, 6(12), 1802373
- [36] Duan J., Li Y., Pan Y., Behera N., Jin W., Coordin. Chem. Rev., 2019, 395, 25
- [37] Jiao L., Wang Y., Jiang H. L., Xu Q., Adv. Mater., 2018, 30(37), 1703663
- [38] Campbell M. G., Liu S. F., Swager T. M., Dinca M., J. Am. Chem. Soc., 2015, 137(43), 13780
- [39] Li Y. L., Zhou J. J., Wu M. K., Chen C., Tao K., Yi F. Y., Han L., *Inorg. Chem.*, 2018, 57(11), 6202
- [40] Jayaramulu K., Masa J., Morales D. M., Tomanec O., Ranc V., Petr M., Wilde P., Chen Y. T., Zboril R., Schuhmann W., Fischer R. A., *Adv. Sci.*, 2018, 5(11), 1801029
- [41] Sun F., Wang G., Ding Y., Wang C., Yuan B., Lin Y., Adv. Energy Mater., 2018, 8(21), 1800584
- [42] Zhu D., Liu J., Zhao Y., Zheng Y., Qiao S. Z., Small, 2019, 15(14), 1805511
- [43] Xu H., Fei B., Cai G., Ha Y., Liu J., Jia H., Zhang J., Liu M., Wu R., Adv. Energy Mater., 2019, 10(3), 1902714
- [44] Liu S., Zhou J., Song H., Chem. Commun., 2018, 54(70), 9825
- [45] Rui K., Zhao G., Lao M., Cui P., Zheng X., Zheng X., Zhu J., Huang W., Dou S. X., Sun W., Nano Lett., 2019, 19(12), 8447
- [46] Sakamoto R., Takada K., Pal T., Maeda H., Kambe T., Nishihara H., *Chem. Commun.*, 2017, 53(43), 5781

- [47] Zheng C., Zhu J., Yang C., Lu C., Chen Z., Zhuang X., Sci. China Chem., 2019, 62(9), 1145
- [48] Wang J., Li N., Xu Y., Pang H., Chem. Eur. J., 2020, 26(29), 6402
- [49] Varoon K., Zhang X., Elyassi B., Brewer D. D., Gettel M., Kumar S., Lee J. A., Maheshwari S., Mittal A., Sung C. Y., Cococcioni M., Francis L. F., McCormick A. V., Mkhoyan K. A., Tsapatsis M., *Science*, 2011, 334(6052), 72
- [50] Foster J. A., Henke S., Schneemann A., Fischer R. A., Cheetham A. K., Chem. Commun., 2016, 52(69), 10474
- [51] Hernandez Y., Nicolosi V., Lotya M., Blighe F. M., Sun Z., De S., McGovern I. T., Holland B., Byrne M., Gun'Ko Y. K., Boland J. J., Niraj P., Duesberg G., Krishnamurthy S., Goodhue R., Hutchison J., Scardaci V., Ferrari A. C., Coleman J. N., *Nat. Nanotechnol.*, **2008**, *3*(9), 563
- [52] Li C., Wu C., Zhang B., ACS Sustain. Chem. Eng., 2019, 8(1), 642
- [53] Saines P. J., Tan J. C., Yeung H. H., Barton P. T., Cheetham A. K., Dalton T., 2012, 41(28), 8585
- [54] Nielsen R. B., Kongshaug K. O., Fjellvåg H., J. Mater. Chem., 2008, 18(9), 1002
- [55] Cliffe M. J., Castillo-Martinez E., Wu Y., Lee J., Forse A. C., Firth F. C. N., Moghadam P. Z., Fairen-Jimenez D., Gaultois M. W., Hill J. A., Magdysyuk O. V., Slater B., Goodwin A. L., Grey C. P., J. Am. Chem. Soc., 2017, 139(15), 5397
- [56] Tian J., Jiang F., Yuan D., Zhang L., Chen Q., Hong M., Angew. Chem. Int. Ed., 2020, 10.1002/anie.202004420
- [57] Peng Y., Li Y., Ban Y., Yang W., Angew. Chem. Int. Ed., 2017, 56(33), 9757
- [58] Wu J. X., Yuan W. W., Xu M., Gu Z. Y., Chem. Commun., 2019, 55(77), 11634
- [59] Tan J.-C., Saines P. J., Bithell E. G., Cheetham A. K., ACS Nano, 2012, 6, 615
- [60] Xu H., Gao J., Qian X., Wang J., He H., Cui Y., Yang Y., Wang Z., Qian G., J. Mater. Chem. A, 2016, 4(28), 10900
- [61] Brent J. R., Savjani N., Lewis E. A., Haigh S. J., Lewis D. J., O'Brien P., Chem. Commun., 2014, 50(87), 13338
- [62] Coleman J. N., Lotya M., O'Neill A., Bergin S. D., King P. J., Khan U., Young K., Gaucher A., De S., Smith R. J., Science, 2011, 331(6017), 568
- [63] Gallego A., Hermosa C., Castillo O., Berlanga I., Gomez-Garcia C. J., Mateo-Marti E., Martinez J. I., Flores F., Gomez-Navarro C., Gomez-Herrero J., Delgado S., Zamora F., *Adv. Mater.*, **2013**, *25*(15), 2141
- [64] Wang H.-S., Li J., Li J.-Y., Wang K., Ding Y., Xia X.-H., NPG Asia Mater., 2017, 9(3), 354
- [65] Chandrasekhar P., Mukhopadhyay A., Savitha G., Moorthy J. N., J. Mater. Chem. A, 2017, 5(11), 5402
- [66] Au V. K., Nakayashiki K., Huang H., Suginome S., Sato H., Aida T., J. Am. Chem. Soc., 2019, 141(1), 53
- [67] Ding Y., Chen Y. P., Zhang X., Chen L., Dong Z., Jiang H. L., Xu H., Zhou H. C., J. Am. Chem. Soc., 2017, 139(27), 9136
- [68] Huang J., Li Y., Huang R. K., He C. T., Gong L., Hu Q., Wang L., Xu Y. T., Tian X. Y., Liu S. Y., Ye Z. M., Wang F., Zhou D. D., Zhang W. X., Zhang J. P., *Angew. Chem. Int. Ed.*, **2018**, *57*(17), 4632
- [69] Cho W., Lee H. J., Oh M., J. Am. Chem. Soc, 2008, 130(50), 16943
- [70] Peng X., Manna L., Yang W., Wickham J., Scher E., Kadavanich A., Alivisatos A. P., *Nature*, 2000, 404(2), 59
- [71] Gao J., He M., Lee Z. Y., Cao W., Xiong W.-W., Li Y., Ganguly R., Wu T., Zhang Q., *Dalton T.*, **2013**, *42*(32), 11367

- [72] Jian M., Liu H., Williams T., Ma J., Wang H., Zhang X., Chem. Commun., 2017, 53(98), 13161
- [73] Zhan G., Zeng H. C., Adv. Funct. Mater., 2016, 26(19), 3268
- [74] Wang Y., Zhao M., Ping J., Chen B., Cao X., Huang Y., Tan C., Ma Q., Wu S., Yu Y., Lu Q., Chen J., Zhao W., Ying Y., Zhang H., *Adv. Mater.*, **2016**, *28*(21), 4149
- [75] Zhao M., Wang Y., Ma Q., Huang Y., Zhang X., Ping J., Zhang Z., Lu Q., Yu Y., Xu H., Zhao Y., Zhang H., *Adv. Mater.*, **2015**, *27*(45), 7372
- [76] Lin Y., Chen G., Wan H., Chen F., Liu X., Ma R., Small, 2019, 15(18), 1900348
- [77] Cao F., Zhao M., Yu Y., Chen B., Huang Y., Yang J., Cao X., Lu Q., Zhang X., Zhang Z., Tan C., Zhang H., J. Am. Chem. Soc., 2016, 138(22), 6924
- [78] He T., Ni B., Zhang S., Gong Y., Wang H., Gu L., Zhuang J., Hu W., Wang X., Small, 2018, 14(16), 1703929
- [79] Pustovarenko A., Goesten M. G., Sachdeva S., Shan M., Amghouz Z., Belmabkhout Y., Dikhtiarenko A., Rodenas T., Keskin D., Voets I. K., Weckhuysen B. M., Eddaoudi M., de Smet L., Sudholter E. J. R., Kapteijn F., Seoane B., Gascon J., *Adv. Mater.*, **2018**, *30*(26), 1707234
- [80] Xue F., Kumar P., Xu W., Mkhoyan K. A., Tsapatsis M., Chem. Mater., 2017, 30(1), 69
- [81] Zhao Y., Jiang L., Shangguan L., Mi L., Liu A., Liu S., J. Mater. Chem. A, 2018, 6(6), 2828
- [82] Pham M.-H., Vuong G.-T., Fontaine F.-G., Do T.-O., *Cryst. Growth Des.*, 2012, 12(6), 3091
- [83] Lin Y., Wan H., Wu D., Chen G., Zhang N., Liu X., Li J., Cao Y., Qiu G., Ma R., J. Am. Chem. Soc., 2020, 142(16), 7317
- [84] Zhao K., Liu S., Ye G., Gan Q., Zhou Z., He Z., J. Mater. Chem. A, 2018, 6(5), 2166
- [85] Li F. L., Wang P., Huang X., Young D. J., Wang H. F., Braunstein P., Lang J. P., Angew. Chem. Int. Ed., 2019, 58(21), 7051
- [86] Zhuang L., Ge L., Liu H., Jiang Z., Jia Y., Li Z., Yang D., Hocking R.
   K., Li M., Zhang L., Wang X., Yao X., Zhu Z., *Angew. Chem. Int. Ed.*, 2019, 58(38), 13565
- [87] Duan J., Chen S., Zhao C., Nat. Commun., 2017, 8, 15341
- [88] Jabarian S., Ghaffarinejad A., J. Inorg. Organomet. Polym., 2019, 29(5), 1565
- [89] Wei X., Li N., Liu N., Electrochim. Acta, 2019, 318, 957
- [90] Dong R., Zhang T., Feng X., Chem. Rev., 2018, 118(13), 6189
- [91] Tan C., Cao X., Wu X. J., He Q., Yang J., Zhang X., Chen J., Zhao W., Han S., Nam G. H., Sindoro M., Zhang H., Chem. Rev., 2017, 117(9), 6225
- [92] Rodenas T., Luz I., Prieto G., Seoane B., Miro H., Corma A., Kapteijn F., Llabres I. X. F. X., Gascon J., Nat. Mater., 2015, 14(1), 48
- [93] Tsukamoto T., Takada K., Sakamoto R., Matsuoka R., Toyoda R., Maeda H., Yagi T., Nishikawa M., Shinjo N., Amano S., Iokawa T., Ishibashi N., Oi T., Kanayama K., Kinugawa R., Koda Y., Komura T., Nakajima S., Fukuyama R., Fuse N., Mizui M., Miyasaki M., Yamashita Y., Yamada K., Zhang W., Han R., Liu W., Tsubomura T., Nishihara H., J. Am. Chem. Soc., 2017, 139(15), 5359
- [94] Makiura R., Konovalov O., Sci. Rep., 2013, 3, 2506
- [95] Chen J., Zhuang P., Ge Y., Chu H., Yao L., Cao Y., Wang Z., Chee M.
  O. L., Dong P., Shen J., Ye M., Ajayan P. M., *Adv. Funct. Mater.*, 2019, *29*(37), 1903875
- [96] Sakaida S., Otsubo K., Sakata O., Song C., Fujiwara A., Takata M., Kitagawa H., *Nat. Chem.*, 2016, 8(4), 377
- [97] Huang X., Sheng P., Tu Z., Zhang F., Wang J., Geng H., Zou Y., Di C.

A., Yi Y., Sun Y., Xu W., Zhu D., Nat. Commun., 2015, 6, 7408

- [98] Wang Z., Gui M., Asif M., Yu Y., Dong S., Wang H., Wang W., Wang F., Xiao F., Liu H., *Nanoscale*, **2018**, *10*(14), 6629
- [99] Ning H., Mao Q., Wang W., Yang Z., Wang X., Zhao Q., Song Y., Wu M., J. Alloys Compd., 2019, 785, 7
- [100] Wang L., Sahabudeen H., Zhang T., Dong R., NPJ 2D Mater. Appl., 2018, 2(1), 26
- [101] Murray D. J., Patterson D. D., Payamyar P., Bhola R., Song W., Lackinger M., Schluter A. D., King B. T., J. Am. Chem. Soc., 2015, 137(10), 3450
- [102] Huang L., Zhang X., Han Y., Wang Q., Fang Y., Dong S., J. Mater. Chem. A, 2017, 5(35), 18610
- [103] Cai M., Liu Q., Xue Z., Li Y., Fan Y., Huang A., Li M.-R., Croft M., Tyson T. A., Ke Z., Li G., J. Mater. Chem. A, 2020, 8(1), 190
- [104] Kukulka W., Cendrowski K., Mijowska E., Electrochim. Acta, 2019, 307, 582
- [105] Li Y., Liu H., Wang H., Qiu J., Zhang X., Chem. Sci., 2018, 9(17), 4132
- [106] Yao S., Jiao Y., Sun S., Wang L., Li P., Chen G., ACS Sustain. Chem. Eng., 2020, 8(8), 3191
- [107] Zhu D., Liu J., Wang L., Du Y., Zheng Y., Davey K., Qiao S. Z., Nanoscale, 2019, 11(8), 3599
- [108] Zhao M., Huang Y., Peng Y., Huang Z., Ma Q., Zhang H., Chem. Soc. Rev., 2018, 47(16), 6267
- [109] Dhakshinamoorthy A., Asiri A. M., Garcia H., Adv. Mater., 2019, 31(41), 1900617
- [110] Li Y.-Z., Fu Z.-H., Xu G., Coordin. Chem. Rev., 2019, 388, 79
- [111] Khan K., Tareen A. K., Aslam M., Zhang Y., Wang R., Ouyang Z., Gou Z., Zhang H., *Nanoscale*, **2019**, *11*(45), 21622
- [112] Zhu Y., Peng W., Li Y., Zhang G., Zhang F., Fan X., Small Methods, 2019, 3(9), 1800438
- [113] Du L., Xing L., Zhang G., Sun S., Carbon, 2020, 156, 77
- [114] Lu X. F., Xia B. Y., Zang S. Q., Lou X. W. D., Angew. Chem. Int. Ed., 2020, 59(12), 4634
- [115] Wang H. F., Chen L., Pang H., Kaskel S., Xu Q., Chem. Soc. Rev., 2020, 49(5), 1414
- [116] Morozan A., Jaouen F., Energy Environ. Sci., 2012, 5(11), 9269
- [117] Zhang K., Guo W., Liang Z., Zou R., Sci. China Chem., 2019, 62(4), 417
- [118] Zhu B., Xia D., Zou R., Coordin. Chem. Rev., 2018, 376, 430
- [119] Wang T., Xie H., Chen M., D'Aloia A., Cho J., Wu G., Li Q., Nano Energy, 2017, 42, 69
- [120] Rui K., Zhao G., Chen Y., Lin Y., Zhou Q., Chen J., Zhu J., Sun W., Huang W., Dou S. X., *Adv. Funct. Mater.*, **2018**, *28*(26), 1801554
- [121] Ding M., Chen J., Jiang M., Zhang X., Wang G., J. Mater. Chem. A, 2019, 7(23), 14163
- [122] Hai G., Jia X., Zhang K., Liu X., Wu Z., Wang G., Nano Energy, 2018, 44, 345
- [123] Zhao S., Wang Y., Dong J., He C.-T., Yin H., An P., Zhao K., Zhang X., Gao C., Zhang L., Lv J., Wang J., Zhang J., Khattak A. M., Khan N. A., Wei Z., Zhang J., Liu S., Zhao H., Tang Z., *Nat. Energy*, **2016**, *1*(12), 1038
- [124] Hao Y., Liu Q., Zhou Y., Yuan Z., Fan Y., Ke Z., Su C. Y., Li G., Energy Environ. Mater., 2019, 2(1), 18
- [125] Wang S. S., Jiao L., Qian Y., Hu W. C., Xu G. Y., Wang C., Jiang H.
   L., Angew. Chem. Int. Ed., 2019, 58(31), 10713
- [126] Dong R., Zheng Z., Tranca D. C., Zhang J., Chandrasekhar N., Liu S., Zhuang X., Seifert G., Feng X., *Chem. Eur. J.*, **2017**, *23*(10), 2255

- [127] Wu Y. P., Zhou W., Zhao J., Dong W. W., Lan Y. Q., Li D. S., Sun C., Bu X., Angew. Chem. Int. Ed., 2017, 56(42), 13001
- [128] Ji Y., Dong H., Liu C., Li Y., Nanoscale, 2019, 11(2), 454
- [129] Lions M., Tommasino J. B., Chattot R., Abeykoon B., Guillou N., Devic T., Demessence A., Cardenas L., Maillard F., Fateeva A., *Chem. Commun.*, 2017, 53(48), 6496
- [130] Li L., He J., Wang Y., Lv X., Gu X., Dai P., Liu D., Zhao X., J. Mater. Chem. A, 2019, 7(5), 1964
- [131] Zhong H., Ly K. H., Wang M., Krupskaya Y., Han X., Zhang J., Zhang J., Kataev V., Buchner B., Weidinger I. M., Kaskel S., Liu P., Chen M., Dong R., Feng X., *Angew. Chem. Int. Ed.*, **2019**, *58*(31), 10677
- [132] Miner E. M., Fukushima T., Sheberla D., Sun L., Surendranath Y., Dinca M., Nat. Commun., 2016, 7, 10942
- [133] Feng X., Pi Y., Song Y., Brzezinski C., Xu Z., Li Z., Lin W., J. Am. Chem. Soc., 2020, 142(2), 690
- [134] Ji L., Chang L., Zhang Y., Mou S., Wang T., Luo Y., Wang Z., Sun X., ACS Catal., 2019, 9(11), 9721
- [135] Yin Z., Yu C., Zhao Z., Guo X., Shen M., Li N., Muzzio M., Li J., Liu H., Lin H., Yin J., Lu G., Su D., Sun S., *Nano Lett.*, **2019**, *19*(12), 8658
- [136] Varela A. S., Ju W., Strasser P., Adv. Energy Mater., 2018, 8(30), 1703614
- [137] Ding M., Flaig R. W., Jiang H. L., Yaghi O. M., Chem. Soc. Rev., 2019, 48(10), 2783
- [138] Lei Z., Xue Y., Chen W., Qiu W., Zhang Y., Horike S., Tang L., Adv. Energy Mater., 2018, 8(32), 1801587
- [139] Wu J. X., Hou S. Z., Zhang X. D., Xu M., Yang H. F., Cao P. S., Gu Z. Y., Chem. Sci., 2019, 10(7), 2199
- [140] Jiang X., Wu H., Chang S., Si R., Miao S., Huang W., Li Y., Wang G., Bao X., J. Mater. Chem. A, 2017, 5(36), 19371
- [141] Yang L., Cao L., Huang R., Hou Z. W., Qian X. Y., An B., Xu H. C., Lin W., Wang C., ACS Appl. Mater. Interfaces, 2018, 10(42), 36290
- [142] Li Q., Shao Z., Han T., Zheng M., Pang H., ACS Sustain. Chem. Eng., 2019, 7(9), 8986
- [143] Zhu D., Guo C., Liu J., Wang L., Du Y., Qiao S. Z., Chem. Commun., 2017, 53(79), 10906
- [144] Wang Y., Xue Y. Y., Yan L. T., Li H. P., Li Y. P., Yuan E. H., Li M., Li S. N., Zhai Q. G., ACS Appl. Mater. Interfaces, 2020, 5(6), 5094
- [145] Yang L., Ma F. X., Xu F., Li D., Su L., Xu H. C., Wang C., Chem. Asian. J., 2019, 14(20), 3557
- [146] Xu Y., Chai X., Ren T., Yu S., Yu H., Wang Z., Li X., Wang L., Wang H., Chem. Commun., 2020, 56(14), 2151
- [147] Liu B., Shioyama H., Akita T., Xu Q., J. Am. Chem. Soc., 2008, 130(16), 5390
- [148] Li Y., Lu M., He P., Wu Y., Wang J., Chen D., Xu H., Gao J., Yao J., *Chem. Asian. J.*, **2019**, *14*(9), 1590

- [149] Li Y., Lu M., Wu Y., Xu H., Gao J., Yao J., Adv. Mater. Interfaces, 2019, 6(12), 1900290
- [150] Guan C., Liu X., Ren W., Li X., Cheng C., Wang J., Adv. Energy Mater., 2017, 7(12), 1602391
- [151] Sun H., Lian Y., Yang C., Xiong L., Qi P., Mu Q., Zhao X., Guo J., Deng Z., Peng Y., *Energy Environ. Sci.*, **2018**, *11*(9), 2363
- [152] Zhang X., Liu S., Zang Y., Liu R., Liu G., Wang G., Zhang Y., Zhang H., Zhao H., *Nano Energy*, **2016**, *30*, 93
- [153] Zhou J., Dou Y., Zhou A., Shu L., Chen Y., Li J.-R., ACS Energy Lett., 2018, 3(7), 1655
- [154] Wang Y., Pan Y., Zhu L., Yu H., Duan B., Wang R., Zhang Z., Qiu S., Carbon, 2019, 146, 671
- [155] Jiang M., Li J., Cai X., Zhao Y., Pan L., Cao Q., Wang D., Du Y., Nanoscale, 2018, 10(42), 19774
- [156] Li Y., Zhao T., Lu M., Wu Y., Xie Y., Xu H., Gao J., Yao J., Qian G., Zhang Q., Small, 2019, 15(43), 1901940
- [157] Lu M., Li Y., He P., Cong J., Chen D., Wang J., Wu Y., Xu H., Gao J., Yao J., J. Solid State Chem., 2019, 272, 32
- [158] Srinivas K., Lu Y., Chen Y., Zhang W., Yang D., ACS Sustain. Chem. Eng., 2020, 8(9), 3820
- [159] Li Y., Dai H., Chem. Soc. Rev., 2014, 43(15), 5257
- [160] Shah S. S. A., Najam T., Aslam M. K., Ashfaq M., Rahman M. M., Wang K., Tsiakaras P., Song S., Wang Y., *Appl. Catal. B: Environ.*, 2020, 268(18), 118570
- [161] Zhu B., Liang Z., Xia D., Zou R., Energy Storage Mater., 2019, 23, 757
- [162] Li Z., Shao M., Zhou L., Yang Q., Zhang C., Wei M., Evans D. G., Duan X., *Nano Energy*, **2016**, *25*, 100
- [163] Li Z., Shao M., Zhou L., Zhang R., Zhang C., Wei M., Evans D. G., Duan X., Adv. Mater., 2016, 28(12), 2337
- [164] Zhong H. X., Wang J., Zhang Y. W., Xu W. L., Xing W., Xu D., Zhang Y. F., Zhang X. B., Angew. Chem. Int. Ed., 2014, 53(51), 14235
- [165] Zhang M., Wang C., Yan X., Kwame K. P., Chen S., Xiao C., Qi J., Sun X., Wang L., Li J., *J. Mater. Chem. A*, **2019**, 7(35), 20162
- [166] Wang X., Zhu Z., Chai L., Ding J., Zhong L., Dong A., Li T.-T., Hu Y., Qian J., Huang S., *J. Power Sources*, **2019**, 440, 227158
- [167] Dang S., Zhu Q.-L., Xu Q., Nat. Rev. Mater., 2017, 3(1), 17075
- [168] Chen Y. Z., Wang C., Wu Z. Y., Xiong Y., Xu Q., Yu S. H., Jiang H. L., Adv. Mater., 2015, 27(34), 5010
- [169] Shen K., Chen X., Chen J., Li Y., ACS Catal., 2016, 6(9), 5887
- [170] Zhang S. L., Guan B. Y., Lou X. W. D., Small, 2019, 15(13), 1805324
- [171] Ren Q., Wang H., Lu X. F., Tong Y. X., Li G. R., Adv. Sci., 2018, 5(3), 1700515
- [172] Zhang S. L., Guan B. Y., Wu H. B., Lou X. W. D., Nano-Micro Lett., 2018, 10(3), 44