Metal-organic framework nanocrystal-derived hollow porous materials: Synthetic strategies and emerging applications

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GRAPHICAL ABSTRACT

PUBLIC SUMMARY

- MOFs have garnered multi-disciplinary attention due to their unique inherent properties
- Various synthetic strategies of MOFs-derived hollow porous materials are summarized
- Emerging applications of MOFs-derived hollow porous materials are reviewed
Metal-organic frameworks (MOFs) have garnered multidisciplinary attention due to their structural tailorability, controlled pore size, and physicochemical functions, and their inherent properties can be exploited by applying them as precursors and/or templates for fabricating derived hollow porous nanomaterials. The fascinating, functional properties and applications of MOF-derived hollow porous materials primarily lie in their chemical composition, hollow character, and unique porous structure. Herein, a comprehensive overview of the synthetic strategies and emerging applications of hollow porous materials derived from MOF-based templates and/or precursors is given. Based on the role of MOFs in the preparation of hollow porous materials, the synthetic strategies are described in detail, including (1) MOFs as removable templates, (2) MOF nanocrystals as both self-sacrificing templates and precursors, (3) MOF@secondary-component core-shell composites as precursors, and (4) hollow MOF nanocrystals and their composites as precursors. Subsequently, the applications of these hollow porous materials for chemical catalysis, electrocatalysis, energy storage and conversion, and environmental management are presented. Finally, a perspective on the research challenges and future opportunities and prospects for MOF-derived hollow materials is provided.

INTRODUCTION

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs), which consist of inorganic metal nodes linked by organic linkers via coordination bonds, represent a new class of crystalline porous materials. During the past few decades, MOF materials have allowed extraordinary achievements in both the synthesis of novel nanostructures and a wide variety of potential applications, such as energy storage and conversion, sensing, catalytic reaction, environmental management, and so on. MOFs have highly ordered crystalline framework structures, and these structures are durable enough to remove the contained guest species and yield permanent pores. In particular, through the rational design and/or control of organic ligands, metal nodes, and synthesis environment, the structure and related peculiarity of MOFs can be conveniently adjusted and modified to meet specific requirements. These attractive advantages are particular to MOFs and not easily accessible in most of the other traditional porous nanomaterials.

Due to their excellent intrinsic attributes, MOFs can be used as precursors or templates to fabricate MOF-derived secondary hollow porous nanomaterials (HPMs): metal carbides, metal oxides, metal sulfides, layered double hydroxides, porous carbon materials, and their hybrid composites. MOF-derived porous nanomaterials have also played a significant role in photocatalysis, energy storage and conversion, and particularly electrocatalysis, owing to their superior attributes, such as large specific surface area, micro- or mesoporosity for efficient electron and mass transport during the reaction, inherited structural versatility, high tolerance to acid/alkaline environments, and electrical conductivity, as well as diverse chemical components.

Among these MOF-derived hollow nanomaterials, discrete, hollow structures have garnered considerable attention. In most cases, the synthesis of MOF-derived HPMs essentially relies on a decomposition of the MOF or its composites under a certain condition or chemical reaction with desirable reagents: (1) hollow SiOx derived from a secondary constituent of MOF/shell composite, (2) hollow porous carbon materials derived from the organic components of the MOF and its shell or guest molecules, and (3) hollow metal oxides, sulfides, carbides, supported MNPs, etc., derived from the metallic components of the MOF or MOF composite. Traditional synthetic methods for HPMs require a hard template, for example, SiO2, and polystyrene (PS), while a significant drawback is that harsh conditions are required for template removal. Compared with the traditional hard template method, the conditions of preparing hollow porous materials from MOFs as a template and precursor system are mild, and there is no need to remove the template. Furthermore, in contrast to the traditional molecular sieve and amorphous porous materials, hollow nanomaterials derived from MOFs demonstrate numerous advantages, including uniform hollow morphology and chemical constituents, tunable distribution of chemical and structural compositions, and tunable porosity. Benefiting from these attributes, MOF-derived hollow nanomaterials exhibit excellent performance in chemical catalysis, electrocatalysis, energy storage and conversion, and other applications.

Although several reviews have summarized the MOF-derived hollow nanomaterials and their potential applications, most of these review articles are mainly focused on MOF-derived hollow materials and their applications in energy storage and conversion. Up to now, a comprehensive summary of the synthetic strategies and emerging applications of hollow porous materials derived from MOF-based templates and/or precursors is lacking in the literature. In this context, we aim to provide a systematic and detailed overview of the most recent achievements of MOFs as templates and/or precursors for fabricating hollow nanomaterials and their application in chemical catalysis, electrocatalysis, environmental management, energy storage, and energy conversions. Finally, this review concludes with some personal insights that we hope open a broad new avenue for future directions in this attractive research field.

DESIGN STRATEGIES FOR MOF-DERIVED HOLLOW POROUS MATERIALS

For this part, we will provide various detailed synthetic strategies for fabricating HPMs, such as hollow porous carbons and their composites, hollow layered double hydroxides, hollow metal-based compounds, and their composites (Table S1).

MOF nanocrystals as removable templates

Usually, the sacrificial template controls the size and morphology of the hollow inorganic nanostructures. He and co-workers proposed a synthetic route for SiO2-based hollow nanocrystals with tunable components. As shown in Figure 1A, a layer of SiO2 was uniformly coated on ZIF nanocrystals from a soluble TEOS precursor through the Stöber method. This produces a ZIF-8@SiO2 core-shell material. Subsequently, hollow SiO2-based materials were obtained from the ZIF-8@SiO2 core-shell composite by different ways of treatment: (1) a ZnO@SiO2 yolk-shell composite was formed by calcination in the air or (2) a ZnO@SiO2 yolk-shell composite and a hollow SiO2 polyhedron were formed by thermal treatment in acidic solution at 100 °C for 2 and 24 h, respectively. Inspired by the above research, we proposed a route to prepare hollow TiO2 using ZIF nanocrystals as a removable template and gave rare examples of hollow cubic and polyhedral morphologies (Figure 1B). It was particularly interesting to see that the surface of ZIF-8 can promote the growth of TiO2 coatings. The ZIF-8 core could be removed completely and quickly without affecting the integrity of the TiO2 shells. The sacrificial ZIF-8 template controls the shape and size of the obtained hollow TiO2 structure. These TiO2 materials demonstrated exceptional textural properties. Upon using ZIF-8 nanocrystals injected with Pt nanoparticles (NPs) as templates, the Pt NPs were successfully encapsulated into the hollow TiO2 cubes. Brinker and colleagues also proposed a novel concept for the functionalization of the surface of MOFs based on the direct coordination of a phenolic-inspired lipid molecule, DPPE (Figure 1C). Consequently,
MIL-88 nanocrystals and UiO-66 were also used as a removable template for the production of the hollow polymer.\textsuperscript{12}

Taken together, when an MOF is used as a template to fabricate hollow materials, the shape and size of the obtained hollow structures are controlled by the sacrificial MOF template. And the other advantage is that the MOF template can be completely and rapidly eliminated without affecting the integrity of the hollow shells.

**MOF nanocrystals as both self-sacrificing templates and precursors**

In addition to the removable templates, MOF nanocrystals can be used as both self-sacrificing templates and precursors for fabricating hollow nanostructures. Many approaches have been developed to synthesize MOF derivatives, for instance, hollow metal hydroxides, metal sulﬁdes, metal oxides, metal phosphides, hollow carbon matrices, and so on.\textsuperscript{13–16} ZIF-8 (Zn) and ZIF-67 (Co) were applied as self-sacrificial template and precursor to prepare M-Co-LDH (M = Mg, Ca, Ni) nanocages with hollow structures (Figure S1A).\textsuperscript{14} Control of the simultaneous reactions, the precipitation of the shells, and the template etching is extremely crucial to the preparation of perfect nanocages. Subsequently, similar synthesis strategies were used for producing other LDH and metal hydroxide nanocages, such as Mg-Co LDH\textsuperscript{15,17} and Ni-Co LDH\textsuperscript{14} by thermal treatment under air conditions.\textsuperscript{27} Those synthetic approaches were further applied to fabricate other hollow multicomponent metal oxides, such as Ni$_x$Co$_{3-x}$O$_4$ and Ni$_x$Zn$_{1-x}$O$_x$ hollow spheres,\textsuperscript{28}; hollow porous CuO-Cu$_2$O@Co$_3$O$_4$ core-shell nanocages,\textsuperscript{29}; hollow NiO/Co$_3$O$_4$ hollow core-shell nanocages,\textsuperscript{30} and hollow NiO/Co$_3$O$_4$.\textsuperscript{31} Guan et al. utilized a practical and versatile strategy to fabricate multicomponent metal oxides, including Co-Ni, Co-Mn, Mn-Ni, Zn-Mn, and Co-Mn-Ni structures (Figures 2A and 2B).\textsuperscript{31,32}

To prepare hollow porous carbon, MOF precursors are usually pyrolyzed under an Ar or N$_2$ atmosphere, and metal species will experience evaporation and/or subsequent leaching in the pyrolysis process. For example, Zhang et al. utilized ZIF-8 as a sacrificial template and precursor for fabricating a hollow carbon matrix (Figure 2C).\textsuperscript{14} First, the inner parts of the ZIF-8 template were etched with a tannic acid solution, and then hollow ZIF-8 was treated at 873 K under an inert atmosphere, with subsequently etching of the obtained sample with acid solution to eliminate the remaining Zn species, and the hollow carbon matrix was acquired. In addition, Wang et al. proposed a host-guest strategy to fabricate a hollow N-doped porous carbon electrocatalyst with Fe-Co dual sites.\textsuperscript{33}

Reasonable introduction of other species into MOFs and then pyrolysis can provide an excellent opportunity to manufacture the targeted hollow material with the desired compositions. For example, Wu et al. proposed an MOF-assisted strategy for synthesizing Mo$_x$C$_y$ NPs confined within hollow nano-octahedrons of porous carbon (Figure 2D).\textsuperscript{35} They first prepared [Cu$_2$(BTC)$_2$]$_{0.5}$(H$_2$O)$_{0.5}$[H$_3$PMo$_12$O$_{40}$] nanocrystals and then pyrolyzed this sample at 1,073 K to prepare Mo$_x$C$_y$Cu in an in situ carbonization process involving the Cu-MOF host framework and the guest H$_3$PMo$_12$O$_{40}$ components. FeCl$_3$ solution is used to selectively etch the Cu species to generate hollow Mo$_x$C$_y$ octahedrons (Figures 2E and 2F). Many research groups extended the fabrication method to other hollow nanostructures, such as hollow metal sulfides, metal selenides, and metal phosphides, that were synthesized by using MOF nanocrystals as both sacrificial templates and precursors.

**MOF@secondary-component core-shell composites as precursors**

The growth of MOF@secondary-component core-shell structures is very popular for fabricating MOF-derived hollow porous materials. Hu et al. provided some excellent opportunities to manufacture the targeted hollow material with different MOF@secondary-component core-shell structures.
utilized phenolic acids as surface functionalization and etching reagents to prepare hollow MOFs (Figure 3A). Metal-phenolic networks (MPNs) were formed on the MOF surfaces by the coordination of phenolic acid and metal ions and finally functionalized the surface of the resulting hollow MOFs. As a seminal study, we proposed the synthetic routes toward the first N-HPC capsule, and then the N-HPC capsules encapsulated NPs with tunable components employing ZIF-8 nanocrystals as a template (Figure 3B). First, ZIF-8@K-TA was prepared by coating the metal-phenolic coordination (K-TA) as an auxiliary material on the surface of the ZIF-8 crystal. Afterward, ZIF-8@K-TA was pyrolyzed under an Ar atmosphere at 900°C. It is worth noting that this process converted the organic components of ZIF-8@K-TA into hollow microcapsules with the shape of the ZIF-8 templates. During the pyrolysis process, the Zn species vaporized and escaped from the material to form N-HPC capsules. Interestingly, post-synthetic ion exchange of the K⁺ ions in the K-TA shell by Co(II) or Ni(II) could be realized by facilely immersing ZIF-8@K-TA in a methanolic solution of Co(NO₃)₂ or Ni(NO₃)₂, respectively. Subsequently, monometallic Co or Ni NPs encapsulated in N-HPC capsules could be achieved by heating ZIF-8@Co-TA or ZIF-8@Ni-TA, respectively, under an Ar atmosphere. We further extended this strategy to synthesize supported multicomponent metal NPs. The heating of ZIF-8/Pt@M-TA or ZIF-8/Pt@Mmix-TA results in N-HPC capsules with Pt-based alloyed NPs embedded in the capsule walls. This approach can be extended to prepare NPs composed of four different metals. Inspired by the above successes, we subsequently fabricated a series of atomically dispersed metal catalyst-decorated hollow carbon capsules, including H₂Fe-Nₓ-C, H₂Co-Nₓ-C, H₂FeCo-Nₓ-C, H₂FeNi-Nₓ-C, H₂FeCoNi-Nₓ-C, etc.

ZIF-8@ZIF-67 nanocrystals to prepare hollow composites of Co/P NPs embedded in N-doped CNTs through a continuous pyrolysis-oxidation-phosphorylation process. In addition, various hollow carbon and hollow carbon-supported metal-based materials, including metals, metal oxides, metal sulfides, metal phosphides, and metal selenides, can be easily produced through the reaction of MOF@secondary-component templates with the corresponding thermolysis.

**Hollow MOF nanocrystals and their composites as precursors**

Similarly to the previously mentioned design strategy, direct thermolysis of hollow MOFs is a facile route to fabricate functional hollow porous materials. Pan and co-workers fabricated NIO/Ni/graphene composites with hierarchical hollow structure through annealing of Ni-MOF with hierarchical hollow structure (Figure 3D). After pyrolysis under N₂ atmosphere and subsequent etching treatment, double-shelled NC@Co/NGN nanocapsules with surface-anchored carbon nanotubes (CNTs) were obtained. It should be noted that the formation of hollow nanostructures can be attributed to surface-stabilized shrinkage of core-shell ZIF-8@ZIF-67 nanocrystals at high temperatures. Similarly, Pan and colleagues used core-shell materials to stabilize the growth of hollow MOFs and their composites as precursors.

**Figure 2. Schematic illustrations of strategies for using MOF nanocrystals as sacrificial templates and precursors**

(A) The synthesis of multicomponent metal oxides. (B) FESEM images of multicomponent metal oxides: (B1) Co-Ni, (B2) Co-Mn, (B3) Mn-Ni, (B4) Zn-Mn, and (B5) Co-Mn-Ni. (C) A hollow carbon matrix. (D) Porous Co₃O₄ nano-objects. (E) FESEM image of porous Co₃O₄ nano-cage. (F) XRD pattern spectra of Co₃O₄/Cu and Co₃O₄ nano-cage. Copyright John Wiley & Sons, Royal Society of Chemistry, and Springer Nature.

Similarly, the synthetic route toward an N, P, S-co-doped carbon shell (NPS-HCS) was reported. They first prepared ZIF-8 nanocrystals and then deposited a cross-linked PZS layer on the surface of ZIF-8 to obtain a ZIF-8@PZS core-shell structure (Figure 3C). After heat treatment in Ar and acid etching, NPS-HCCs were obtained (Figure 3D). Inspired by the study, Fe single atoms supported on an N, P, S-co-doped hollow carbon polyhedron were fabricated. They revealed that the long-range interaction of the active metal center with sulfur and phosphorus facilitated the formation of a hollow structure and improved catalytic performance.
also employed Zn/Ni-MOF-5 and nanocubes as the precursor to prepare Zn/Ni-MOF-2 nanosheet with hierarchical hollow nanocubes.56

External templates can also be used to construct hollow porous materials derived from MOF nanocrystals. Su and co-workers reported a multicavity hollow Au@ZIF-8 nanoreactor (Figure 4C) produced via the exterior template method.51 As depicted in Figure 4D, silica was employed as the template source coating on the surface of Au NPs to produce Au NP@silica core-shell composites. Subsequently, the growth of ZIF-8 led to packaging of multiple Au NP@silica particles embedded in its surface to form “raisin bun”-like structures. Then, multicavity hollow Au NP@ZIF-8 nanoreactors were formed after etching the silica. The hollow products feature intrinsic monodispersed micropores and introduced macropores, and each microvoid unit structure has only one Au NP inside. NP@MOF57 and yolk-shell nanocrystal@ZIF-858 were also synthesized with a similar process.

Figure 3. Schematic illustrations of strategies for using MOF nanocrystals as sacrificial templates (A–C and E) the formation of (A) hollow MOFs,37 (B) porous carbon capsules,38 (C) N, P, S-doped carbon shells,39 and (E) double-shelled NC@Co-NGC nanocages.40 (D) TEM image of NPS-HCS.39 Copyright John Wiley & Sons and American Chemical Society.
Moreover, hollow MOF nanocrystals and their composites have also been applied for synthesizing periodic hollow porous MOF structures. For instance, 3D hollow SOM-ZIF-8 with oriented and ordered macro-micropores were acquired by packaging ZIF-8 and PS spheres (PSs) as a well-assembled “precursor@PS” template (Figure 4E). Specifically, PSs were assembled into a highly ordered 3D opal structure, and then ZIF-8 precursors filled the PS monolith interstices to form “precursor@PS.” It was immersed in the CH₃OH and NH₄H₂O₂ solution to reach a balanced process between the growth of the ZIF-8 crystal and the removal of the PSs. As a result, the highly oriented and ordered macropores SOM-ZIF-8 were obtained (Figure 4F). Subsequently, Guo et al. synthesized Zn-N-HOPCPs with ordered pores through confined growth and pyrolysis of ZIF-8 crystalline template voids. As shown in Figure S2A, in the preparation of ZIF-8, SiO₂ CCT was added for the preparation of SiO₂-CCT/ZIF-8 precursors. The obtained SiO₂-CCT/ZIF-8 was pyrolyzed under N₂ conditions and then SiO₂-CCT was removed in 1 M NaOH to obtain the final products.

In addition, multishelled hollow MOFs can be fabricated by controlling crystal production and etching or self-assembly strategies. As shown in Figure S2B, Liu et al. developed a rational method to prepare single-, double-, and triple-shelled hollow MIL-101 with single-crystalline shells by step-by-step crystal growth and subsequent etching processes. The cavity size and shell thickness of each layer can be tailored by rational regulation of MOF nucleation and crystallization. Choe and colleagues demonstrated the process of a solid UMOM-1 (MOP) transformed to a hollow MOP with controlled layers of shells through self-assembly (Figure S2C). First, they immersed solid UMOM-1 (MOP) in DABCO solution to generate a core-shell structure. The external surface of the MOP crystal was coordinated with the linker, thus, the center of the MOP can be retained even if the reaction was stopped halfway. Due to the difference in solubility, the core was selectively dissolved in methanol solution and formed a single-crystal hollow MOF with a single shell. By repeating the above process, a single-crystal hollow MOF with multiple shell layers can be obtained. Similarly, Liu and co-workers synthesized a multishelled ZIF-8 by selectively dissociating ZIF-67 from the multilayered ZIF-67@ZIF-8 (Figure S2D).

APPLICATIONS OF MOF NANOCRYSTAL-DERIVED HOLLOW POROUS MATERIALS

Chemical catalysis

Chemical catalysis is a widespread phenomenon and a central topic for modern industry. To date, tremendous efforts have been committed to preparing and constructing excellent chemical catalysts. Recently, various novel MOF-derivative constructions have been reported and used in selective hydrogenation, goal-directed oxidation, CO₂ reduction reaction, and so on.

Selective hydrogenation. Hollow MOF composites with noble metals possess remarkable selectivity in hydrogenation reactions. Tsung and co-workers fabricated Pd on ZIF-8, yolk-shell Pd@ZIF-8, and core-shell Pd@ZIF-8 by utilizing Pd nanocrystals and hollow ZIF-8. Through the gas-phase hydrogenation reaction of ethylene, cyclohexene, and cyclooctene, the molecular size selectivity of the prepared catalysts was studied. Experimental results revealed that all of the catalysts demonstrated superior activity for ethylene hydrogenation, while only the Pd on the ZIF-8 catalyst exhibited excellent catalytic performance for the cyclooctene. This is because ethylene molecules (2.5 Å) can diffuse through the pore size (3.4 Å) of the ZIF-8 shell, while cycloalkene molecules (5.5 Å) are much larger than the pore size of the ZIF-8 shell (Figure S4A). Similarly, Yang et al. fabricated hollow Pd@ZIF-8 nanosphere catalysts with different thicknesses and studied their selectivity in liquid-phase hydrogenation. As shown in Figure 5B, when Pd@ZIF-8 was applied to the hydrogenation reactions of 1-hexene, trans-stilbene, and tetrastylene, experimental results showed that the smaller the size of the reactant, the higher the conversion. Moreover, Pd@ZIF-8 catalysts with thicker shells (Pd@ZIF-8(S)) possessed lower conversion efficiency. A similar conclusion was obtained when void@HKUST-1/Pd@ZIF-8 was applied for synthesizing periodic hollow porous MOF structures. For instance, 3D hollow SOM-ZIF-8 with oriented and ordered macro-micropores were acquired by packaging ZIF-8 and PS spheres (PSs) as a well-assembled “precursor@PS” template (Figure 4E). Specifically, PSs were assembled into a highly ordered 3D opal structure, and then ZIF-8 precursors filled the PS monolith interstices to form “precursor@PS.” It was immersed in the CH₃OH and NH₄H₂O₂ solution to reach a balanced process between the growth of the ZIF-8 crystal and the removal of the PSs. As a result, the highly oriented and ordered macropores SOM-ZIF-8 were obtained (Figure 4F). Subsequently, Guo et al. synthesized Zn-N-HOPCPs with ordered pores through confined growth and pyrolysis of ZIF-8 crystalline template voids. As shown in Figure S2A, in the preparation of ZIF-8, SiO₂ CCT was added for the preparation of SiO₂-CCT/ZIF-8 precursors. The obtained SiO₂-CCT/ZIF-8 was pyrolyzed under N₂ conditions and then SiO₂-CCT was removed in 1 M NaOH to obtain the final products.

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was used as a hydrogenation reaction catalysis. Moreover, hollow PAuDNP@HKUST-1 petalous heterostructures also exhibited excellent performance in the hydrogenation of olefin. Noble-metal catalysts exhibited remarkable activity in selective hydrogenation, but the high cost limited their practical application in the hydrogenation reaction. One strategy is to combine noble metals with low-cost non-noble metals, which can reduce costs and maintain activity and selectivity. Analogously, yolk-shell PdCu@FeIII-MOF-5, yolk-shell (PTA) @CdCu@MOF-5, and hollow Pd@Zn-Co ZIF exhibited excellent selective hydrogenation performance.

**Goal-directed oxidation.** MOF-derived hollow porous materials have demonstrated remarkable performance in goal-directed oxidation of organic matters. Shen et al. reported a single-crystalline SOM-ZIF-8 with the 3D ordering of macro-micro pores. They investigated the catalytic performance of SOM-ZIF-8 in the Knoevenagel reaction of benzaldehyde and malononitrile. As shown in Figures 5C and 5D, SOM-ZIF-8 catalysts possessed significantly enhanced performance compared with the other catalysts and exhibited superior structural stability and enhanced recyclability. Doping heteroatoms can significantly improve the catalytic ability of hollow porous materials in various organic reac-

| Reaction Time (h) | Conversion (%) |
|------------------|---------------|
| 2                | 92            |
| 4                | 96            |
| 6                | 99            |
| 8                | 99            |

**Electrocatalysis**

**ORR.** Fuel cells and metal-air batteries have garnered extensive attention owing to their being a possible solution to the fossil energy shortage and increasing environmental pollution. ORR is important for fuel cells and metal-air batteries. The precious metal Pt is applied as an outstanding and effective four-electron transfer electrocatalyst for ORR. However, the low abundance and preciousness limit its widespread applications. Among all of the reported electrocatalysts, MOF-derived nanomaterials with high specific surface area, an abundance of accessible active sites, and improved mass/charge transfer rate have been viewed as highly beneficial for the ORR process (Table 1).

| Catalyst | Eonset (V) | E1/2 (V) |
|----------|------------|----------|
| Pt@C     | 1.03       | 0.92     |
| SOM-ZIF-8| 0.95       | 0.87     |
| PH-ZIF-8 | 0.90       | 0.78     |

Among the studied non-noble metals, Fe and Co are the most active metal species for ORR. A lot of excellent studies about Fe and Co as efficient cathode electrocatalysts have been reported. Tang and co-workers reported carbonized Fe NPs derived from MOFs (MIL-88B-NH2), which showed excellent ORR property with Eonset and E1/2 reaching 1.03 and 0.92 V (versus RHE), respectively, in alkaline medium. In real ADMFC, carbonized Fe NPs possessed high output power density and were even 1.7 times higher than the 20% Pt/C. Guo and colleagues fabricated Co@Co3O4@C-bishell NPs derived from MOFs into a highly ordered porous CM to prepare the catalyst Co@Co3O4@C-CM used for ORR. This work created a solid interaction between the metal oxide and the carbon shell linked to the porous CM, which is significant for facilitating the

**Figure 5.** The application of MOF-derived hollow porous materials in chemical catalysis (A) The molecular sizes of ethylene, cyclohexene, cyclooctene, and the ZIF-8 pore aperture. (B) Catalytic performance of Pd@ZIF-8 nanospheres for the liquid-phase hydrogenation of 1-hexene, trans-stilbene, and tetraphenylethylene with different ZIF-8 shell thicknesses. (C) Benzaldehyde conversion over various samples as a function of reaction time. (D) Recyclability tests of SOM-ZIF-8 and PH-ZIF-8. (E) Catalytic CO2 methanation performance of Ni@C version of endothermic CO2. Meanwhile, single Zn atoms act as a Lewis acid site, and a Lewis base site can cooperate to boost substrate activation. Moreover, the carbon shell with hierarchically porous character accelerated CO2 enrichment and improved the transport rate of reactants/products. That was the first report on integrating the photothermic effect into endothermic CO2 conversion. Briefly, hollow porous materials derived from MOFs have the following advantages as catalysts in industrial catalytic processes: (1) the porous MOF shell can serve as a host matrix to prevent NP aggregation and (2) be applied to realize selective catalysis, and (3) the presence of porosity allows for promoting mass transport of chemical species. It is noteworthy that the thickness of the shell has a certain degree of influence on the catalytic performance.
electron transfer rate between NPs and the porous CM and improving mass transport of O2 and electrolytes, making the NPs hard to detach from the porous CM support. It was found that, in alkaline medium, Co@Co3O4@C-CM displayed almost identical catalytic performance but enhanced stability and better methanol tolerance for ORR relative to the 20% Pt/C.

In addition to MOF-derived composites, MOF-derived materials with an M-N-C structure (M represents a metal atom) have also demonstrated supernormal electrocatalytic performance for ORR and have attracted widespread attention.92 For instance, Wan et al. prepared a concave-shaped Fe-N-C SAC (TPI@Z8(SiO2)-650-C) with enhanced surface area and dense Fe-N4 sites (Figure S3A).79 Further investigation revealed that TPI@Z8(SiO2)-650-C has the special properties of additional mesoporosity, high surface area, and high exposure to Fe-N4 active sites (Figures S3B and S3C). Density functional theory (DFT) calculations proved the single-atom dual sites can decrease the cleavage energy of O-O bonds and realize excellent performance toward ORR and high selectivity for the four-electron reduction path (Figure S3I). Recently, we reported on CrN@H-Cr-Nx-C derived from ZIF-8@Cr-TA core-shell nanocrystals (Figure S4A).80 Due to the synergies between CrNNPs and single-atomic-site CrNx, the enriched CrNx sites, discrete CrNNPs, and affluent micro/mesopores, as an electrocatalyst, CrN@H-Cr-Nx-C displayed superior electrocatalytic performance for ORR in an acidic medium with outstanding OCV, and excellent current power densities were also observed when used as a cathode electrocatalyst applied in PEMFC (Figure S4B). The CrN@H-Cr-Nx-C also showed enhanced stability, proved by durability tests (Figure S4C). In addition, Ce-SAS/HPNC with a hierarchically macro/meso/microporous structure derived from MOFs can also be applied as an electrocatalyst for ORR (Figure S4A).81 XAS analysis results verified that the Ce sites were stabilized by four coordinated N atoms and six O atoms (Ce-SAs/NC (Figures S3G and S3H). Density functional theory (DFT) calculations proved the single-atom dual sites can decrease the cleavage energy of O-O bonds and realize excellent performance toward ORR and high selectivity for the four-electron reduction path (Figure S3I).

### Table 1: Summary of ORR performance of MOF-derived hollow porous electrocatalysts

| Material       | Performance | Electrolyte | PEMFC/Zn-air battery | Stability          | Reference       |
|----------------|-------------|-------------|----------------------|--------------------|-----------------|
| A-CoNC         | E1/2 = 0.79 V | 0.1 M KOH   | peak power density 144.0 mW cm−2 | –                  | Zhong et al.76  |
|                 | Eonset = 0.91 V |            | capacity 612.3 mAh g−1 (Zn-air battery) | –                  |                 |
| CNPs           | E1/2 = 0.92 V | 0.1 M KOH   | power density 22.7 mW cm−2 | –                  | Zhao et al.77   |
|                 | Eonset = 1.03 V |            | –                    | –                  |                 |
| Co@Co3O4@C-CM  | E1/2 = 0.7 V  | 0.1 M KOH   | –                    | –                  | Xia et al.78    |
|                 | Eonset = 0.85 V |            | –                    | –                  |                 |
| TPI@Z8(SiO2)-650-C | –          | –           | power density 1.18 W cm−2 at 0.8 V_{Erfree} | –                  | Wan et al.79    |
|                 |             |             | current density 0.047 A cm−2 at 0.88 V_{Erfree} | –                  |                 |
| CrN@H-Cr-Nx-C  | E1/2 = 0.72 V | 0.1 M HClO4 | current density 0.888 A cm−2 | 110 h retain 77%   | Yang et al.80   |
|                 | Eonset = 0.85 V |            | peak power density 0.382 W cm−2 at 0.43 V |                    |                 |
|                 | Tafel slope = 55 mV dec−1 |        | –                    | –                  |                 |
| Ce SAS/HPNC    | E1/2 = 0.862 V| 0.1 M HClO4 | circuit voltage 0.95 V | –                  | Zhu et al.81    |
|                 | Eonset = 2.673 mA cm−2 |        | power density 0.525 W cm−2 at 2.0 bar | –                  |                 |
| PSTA-Co-T      | E1/2 = 0.878 V| 0.1 M KOH   | –                    | –                  | Wei et al.82    |
| HNCSs          | E1/2 = 0.82 V | 0.1 M KOH   | –                    | –                  | Chai et al.83   |
|                 | Eonset = 0.92 V |            | 10 h retain 96.5%    |                    |                 |
| N-HPCs         | E1/2 = 0.92 V | 0.1 M KOH   | power density 158 mW cm−2 (Zn-air battery) | –                  | Kong et al.84   |
|                 | Eonset = 1.06 V |            | power density 486 mW cm−2 (H2-O2 fuel cell) | –                  |                 |
| Fe/NC-700      | E1/2 = 0.854 V| 0.1 M KOH   | –                    | 8 h retain 97.7%   | Zhang et al.85  |
| (CoSx/N, S-HCS)700 | E1/2 = 0.87 V| 0.1 M KOH   | –                    | 60,000 s retain 59.6% | Xiao et al.86  |
|                 | Eonset = 0.93 V |            | –                    |                    |                 |
| C-PANI-MIL-2   | E1/2 = 0.87 V | 0.1 M KOH   | –                    | –                  | Yang et al.87   |
|                 | Eonset = 1.0 V |            | –                    | –                  |                 |
| C-FeHZ8@g-C3N4-950 | E1/2 = 0.845 V| 0.1 M KOH | – 80,000 s retain 91.6% | Deng et al.88 |                 |
|                 | Eonset = 0.97 V |            | –                    |                    |                 |
| H-Fe-Nx-C      | E1/2 = 0.92 V | 0.1 M KOH   | –                    | –                  | Yang et al.89   |

According to EXAFS results, the dual metal center was named NiFeCoN3 in Figure S3F. The catalyst with Fe-Co dual active sites exhibited remarkable ORR performance under acidic conditions with E1/2 (0.863 V versus RHE) and enhanced stability compared with 20% Pt/C, individual Fe Sas/Nc, and Co Sas/Nc (Figures S3G and S3H). Density functional theory (DFT) calculations proved the single-atom dual sites can decrease the cleavage energy of O-O bonds and realize excellent performance toward ORR and high selectivity for the four-electron reduction path (Figure S3I). Recently, we reported on CrN@H-Cr-Nx-C derived from ZIF-8@Cr-TA core-shell nanocrystals (Figure S4A).80 Due to the synergies between CrNNPs and single-atomic-site CrNx, the enriched CrNx sites, discrete CrNNPs, and affluent micro/mesopores, as an electrocatalyst, CrN@H-Cr-Nx-C displayed superior electrocatalytic performance for ORR in an acidic medium with outstanding OCV, and excellent current power densities were also observed when used as a cathode electrocatalyst applied in PEMFC (Figure S4B). The CrN@H-Cr-Nx-C also showed enhanced stability, proved by durability tests (Figure S4C). In addition, Ce-SAS/HPNC with a hierarchically macro/meso/microporous structure derived from MOFs can also be applied as an electrocatalyst for ORR (Figure S4A).81 XAS analysis results verified that the Ce sites were stabilized by four coordinated N atoms and six O atoms (Ce-N4/O6) (Figures S4E and S4F). Remarkably, the Ce-SAS/HPNC displayed an outstanding ORR performance with E_{onset} of 1.04 V, E_{1/2} of 0.862 V, and J_{0} of 2.673 mA cm−2 at 0.9 V compared with the referenced catalysts (Figures S4G and S4H). In addition, the doping of heteroatoms (such as S, P, or O) would change...
the intrinsic performance of M-N-C catalysts. In this regard, P-doped P-CNC-20°° and N/P-doped Co-NP2-°° were also reported to have enhanced ORR performance. In addition, MOF-derived hollow heteroatom-doped carbon materials also displayed outstanding electrocatalytic ORR activity.83

As an attractive study, a N-doped carbon electrocatalyst with a negligible amount (0–0.08 wt %) of Fe (N-HPC) was synthesized. Such N-HPCs feature a hollow and hierarchically porous architecture, which shows excellent ORR activity and durability.84 When used as cathode catalysts, the N-HPCs demonstrated distinguished power densities of 486 and 158 mW cm−2 for PEMFCs and Zn-air batteries, respectively. Interestingly, Fe sites do not contribute to ORR. The results indicated that the non-covalent-bonded N-decorated materials being one of them (Table S2).94

HER. Like the OER, HER is an essential reaction for water splitting. Although the overpotential of HER is much lower than OER, electrocatalysts are still needed to improve the HER reaction.102 Recently, earth-abundant transition metal carbides, especially MoC, have been extensively studied as high-efficiency HER catalysts under acidic and basic conditions. Mesoporous molybdenum carbide nano-octahedrons (MoCn, nano-octahedrons) were prepared through confined carbonization in an MOF.35 The unique nanostructure MoCn, nano-octahedrons exhibited promising durability in acidic and alkaline media (Figure 8A). Stabilty tests are demonstrated in Figure 8B. The current density of MoCn nano-octahedrons is generally stable for more than 10 h in 0.5 M H2SO4 with slight degradation observed during long-term operation in 1 M KOH. A TEM image conveyed that the nanostructure and crystallinity after degradation measurement are well retained, further confirming its good stability in an acidic environment (Figure 8B). The HER activity under basic conditions is also superiorly favorable for many HER catalysts, such as graphene and CNTs, and even state-of-the-art β-Mo2C-based electrocatalysts. Subsequently, hollow Ni-decorated molybdenum-carbide was also synthesized through a similar strategy.104 Benefiting from the advantages of combined composition (MoC and Ni NPs) and unique structure, the obtained catalysts showed superior OER performance and a high Cdl value compared with the single-shelled ones (Figure 7G).

Figure 8. Stabilty of HER (A) Stability tests of MoCn nano-octahedrons. (B) Current stability of MoCn nano-octahedrons for HER over 10 h. (C) Polarization and power density plots of PEFC using N-HPCs as cathode catalysts under HER and OER conditions. (D) Integration of MOF-derived materials and their application in HER.

Figure 6. MOF-derived hollow porous materials and their application in ORR. (A) Schematic of the primary configuration of H2-O2 cells. (B) Discharge polarization and the corresponding power density curves of ZABs using N-HPCs or Pt/C catalyst as the air cathode. (C) Polarization and power density plots of PEMFC using N-HPCs as cathode catalysts under H2-O2 conditions (60 °C, 100% RH, 1 bar HzO2). (D) Interfacial electron transfer schematics in bilayer model (N-HPCs). (E) The reaction pathway of ORR in acidic solution. (F) Free energy diagrams for ORR at U = 0 on a double-layer structure in the whole pH range.84 Copyright Springer Nature.

Figure 7. MOF-derived LDH materials also showed excellent OER properties. Zhang et al. fabricated Ni-Fe LDH nanocages with tunable shells that used MIL-88A particles as sacrificial templates (Figure 7F).88 By mixing different proportions of ethanol and water, Fe-Ni LDH single-shelled nanocages (SSNCs) and double-shelled nanocages (DSNCs) were easily acquired. Owing to more Fe elements in the outer shell, the obtained Ni-Fe LDH DSNCs with effective surface area exposure showed superior OER performance and a high Cdl value compared with the single-shelled ones (Figure 7G).
structure host prevents the ultrasmall Pt3Co NPs from aggregating, thus ensuring long-term durability. In a fascinating study, Huang et al. synthesized a series of hollow Co-based bimetallic sulfide (MxCo3−xS4, M = Zn, Ni, and C) polyhedrals by using MOFs as self-templates. Zn0.30Co2.70S4 exhibited outstanding electrolytic HER activity over a wide pH range, with overpotentials of 80, 90, and 85 mV at 10 mA cm−2 and 129, 144, and 136 mV at 100 mA cm−2 in 0.5 M H2SO4, 0.1 M phosphate buffer, and 1 M KOH, respectively. Zn0.50Co2.50S4 further exhibited photocatalytic HER activity when working with an organic photosensitizer (Eosin Y) or semiconductors (TiO2 and C3N4). This study provides a reference for the synthesis of transition metal sulfides used for HER.

Bifunctional electrocatalysts. Electrocatalysis, as an important process in energy conversion, usually involves more than one process. Specifically, water splitting includes HER and OER, and metal-air batteries involve ORR and OER. The OER is also the fundamental electrochemical reaction for fuel cells. The performance of the catalyst plays an important role in energy conversion efficiency. Although MOF-derived catalysts have made great achievements in electrocatalytic reactions owing to their hierarchical porous structures, accessible active sites, high chemical stability, and good electron conductivity. Electrocatalytic reactions such as ORR, HER, and OER are crucial reaction steps in energy conversion and require catalysts to accelerate their slow kinetics. The performance of the catalyst plays an important role in energy conversion efficiency. Although MOF-derived catalysts have made great achievements in electrocatalytic reactions, several problems and challenges still exist, such as device durability, stability, cost issues, catalytic performance, structure-activity relationships, etc. Therefore, the above issues should be considered when designing electrocatalysts.

Energy storage and conversion. MOF-derived hollow nanostructures with extremely porous structures, low density, robust architecture, large surface area, and high redox reactions of metal ions have verified their unique capabilities and exhibited improved energy storage and conversion performance. Recently, MOF derivatives have been extensively applied in energy storage, especially for LIBs, SIBs, and supercapacitors, and showed high reversible capacity, superior rate, and cycling performance.

Heteroatom-doped carbon nanomaterials are considered to be promising electrocatalysts for the electrocatalytic reaction process. Direct formation of NCNTFs (figures 9C and 9D) derived from MOFs could be achieved through control of the pyrolysis atmosphere. The as-prepared NCNTFs demonstrated superior electrocatalytic properties for the OER. As shown in Figure 9F, they gave a current density of 10 mA cm−2 at 1.60 V (versus RHE), which compared favorably with reported nanocarbon-based catalysts and was lower by ~180 mV than the 20% Pt/C (10 mA cm−2, about 1.78 V). The advantageous traits of NCNTFs, such as hierarchical shells of interconnected crystalline NCNT, optimum graphitic degree, and N-doping level, are the source of the excellent electrocatalytic activity of both ORR and OER.

In summary, MOF-derived hollow nanostructures are promising candidates for applications in electrocatalytic reactions owing to their hierarchical porous structures, accessible active sites, high chemical stability, and good electron conductivity. Electrocatalytic reactions such as ORR, HER, and OER are crucial reaction steps in energy conversion and require catalysts to accelerate their slow kinetics. The performance of the catalyst plays an important role in energy conversion efficiency. Although MOF-derived catalysts have made great achievements in electrocatalytic applications, several problems and challenges still exist, such as device durability, stability, cost issues, catalytic performance, structure-activity relationships, etc. Therefore, the above issues should be considered when designing electrocatalysts.
The sluggishness of the LiPSs redox reactions is a great challenge in the large-scale practical application of Li-S cells. Aiming at the above problems, Li and co-workers constructed a hollow N-doped porous carbon (Ni-N5/HNPC) with an optimal Ni-Nx active moiety, which acted as an ideal host for a sulfur cathode under the guidance of theoretical simulations. First, the Ni-N5/C structure (x = 3–5) with the highest cathode performance was selected by first-principles calculations. The energy calculation results of the reaction step indicated that the Ni-N5/C structure is the best cathode candidate. Therefore, they fabricated Ni-Nx/HNPC with Ni-Nx active sites using MOFs as self-sacrificing templates. As cathode of Li-S batteries, Ni-Nx/HNPC exhibited outstanding rate performance and long-term cycling stability.

Recently, SIBs have been proposed as a potential alternative to LIBs due to the advantage of the high abundance and low cost of the sodium source, high system safety, and wide distribution, as well as storage mechanisms and components similar to those of lithium. Similar to LIBs, MOF-derived hollow metal materials can also be applied as electrodes with remarkable rate capability, cycling stability, and reversible capacity to SIBs. Liu et al. reported on NiS2@Co9S8/N-doped carbon composites via carbonization and sulfurization of binary Ni/Co MOFs (Ni-Co-MOF). Due to the integrated merits of ultrathin NiS2 and Co9S8 NPs (∼7 nm), hollow porous structure, and an ultrathin N-doped carbon coating, the final composite material exhibited excellent performance when used as an anode in SIBs. Experiments showed that a reversible specific capacity of 419.9 mAh g⁻¹ was achieved after 100 cycles at 0.1 A g⁻¹, and a superior capacity retention rate of 98.6% was achieved. In addition, excellent rate performance was observed: at a current density of 2 A g⁻¹, an average capacity of 323.2 mAh g⁻¹ can be reached. The formation of metal sulfide and N-doped carbon layers provides larger capacity and enhanced conductive surface coating. With these virtues, NiS2/Co9S8/N-doped carbon composite materials possess fast sodium storage kinetics and high conductivity, thereby achieving high rate properties.

The construction of composite nanomaterials can effectively alleviate the huge volume expansion/contraction of antimony-based materials when used in sodium-ion batteries, resulting in low cycle life. For instance, Huang and co-workers proposed a NiN-Sb2Se3@C composite with a hierarchical nanodot-in-nanofiber structure in which antimony selenide (Sb2Se3) nanocrystals are confined by both 0D and 1D carbon layers. As expected, the NiN-Sb2Se3@C composite anode achieved enhanced capacity and exceptional cycle lifespan for over 10,000 cycles at 2.0 A g⁻¹ (Figure S5A). Figure S5B demonstrates the process of the structure evolution of micro-Sb2Se3@C composite during electrochemical processes. It is seen that the NiN-Sb2Se3@C composite can bear the volume-change-induced strain and avoid aggregation of Sb2Se3 NPs. Similarly, the (CoS NP@HNC)@MXene composite manifests distinguished electrochemical performance when used as electrode material for all of the LIBs, SIBs, and PIBs, which benefit from the synergistic effect of the components (Figure S5C).

**Supercapacitors.** Supercapacitors have become an ideal choice of energy storage device for their various advantages such as low internal resistance, high power density, and excellent cycle life. The surface area and chemical composition of the electrode have a great influence on the properties of the supercapacitor. In this regard, MOF-derived porous hollow structures meet requirements such as affording rich redox chemistry with abundant active sites, inducing the hollow structures for larger capacitance, forming carbon-based nanomaterials for improving surface areas, and enhancing conductivity. (Table S3). Until now, hollow-structured metal oxides (MnO2, NiO/ZnO, CoO2, NiO/CoO2, CoO2/NiO/CoO2, and metal sulfides (NiCo-LDH/NiO) have been utilized in supercapacitors. Furthermore, MXene-based materials such as CoNiO MXene, CoS-NiS–CoN, and NiCoMoS2@NiO/Cu have been explored for high-performance supercapacitors. (Figure 8A).

**Figure 8. MOF-derived hollow porous materials and their application in electrocatalytic reaction** (A and B) HER performance of porous MoCx nano-octahedrons. (A) Polarization curves after continuous potential sweeps at 50 mV s⁻¹ in 0.5 M H2SO4 (left) and 1 M KOH (right). (B) Time-dependent current density curves in 0.5 M H2SO4 and 1 M KOH (insets: TEM images and SAED pattern after 5,000 potential sweeps in 0.5 M H2SO4). (C–F) (C) TEM and (D) SEM images of NCNTFs. LSV curves of Pt/C and NCNTFs for (E) ORR and (F) OER. Copyright Springer Nature.
widespread use as anode materials for supercapacitors. For instance, Ni₃Co₄₋ₓOₓ with a hollow structure was used as anode material in supercapacitors and demonstrated outstanding specific capacitance of 2,870.8 F g⁻¹ at 1 A g⁻¹ and excellent cyclic stability with 81% capacitance retention after 5,000 cycles. 136 In addition, Ho and colleagues fabricated hybrid NiCo₉LDH/Co₅S₄(Cr/LDH/S) with outstanding performance in supercapacitors. 141 As Figure SSD shows, galvanostatic CD indicated excellent capacitive behavior with highly reversible and rapid reaction kinetics of C/LDH/S. In addition, it exhibited excellent cycle stability and 95.4% retention capacitance after 3,000 cycles. They found that the uniform combination of multiple metal species, the production of hetero-oxifide-hydroxide, and the arrangement of the hollow structure optimize the catalytic site and enhance conductivity and hydrogen adsorption of NiCo₉LDH/Co₅S₄.

Pang and co-workers proposed a general approach for preparing hollow 3D Mxene/MOF composites (TiₓCᵧZₓ/ZIF-67/COₓOₓ) by in situ growth of MOFs and subsequent ion exchange. 150 TiₓCᵧZₓ/ZIF-67/COₓOₓ overcomes the disadvantage of poor conductivity of traditional MOFs. 145,146 Notably, the TiₓCᵧZₓ/ZIF-67/COₓOₓ electrode demonstrated excellent performance with a high specific capacitance of 253.8 F g⁻¹ at 5 A g⁻¹ and a high coulombic efficiency of 94.4% after 4,000 GCD cycles at 3 A g⁻¹.

Composite materials can overcome the defects of a single material and integrate the advantages of different nanomaterials, thus facilitating the performance of the target application. Therefore, a composite could obtain neoteric physical and chemical properties that cannot be achieved by a single component.

**Environmental applications**

Environmental pollution has become a critical issue in human health and environmental protection. 151,152 Benefiting from their tunable configuration, controllable composition, permanent porosity, and larger specific surface area, MOF-derived hollow structures have displayed fascinating physiochemical properties and amassed extensive attention in catalytic degradation of pollutants in our environment. Li and colleagues fabricated ZnO@C-N-Co core-shell nanotubes that used a hollow Zn/Co-ZIF matrix as precursor toward efficient degradation of MO and displayed excellently improved performance and remarkable recyclability. 153 The CeO₂/Ag@SiO₂ hollow nanotubes obtained demonstrated high catalytic performance for 4-nitrophenol reduction. The kinetic reaction rate constant (k) of Ce-MOF/Ag@SiO₂ (0.71 min⁻¹) is higher than that of Ag@SiO₂ (typically 0.1 min⁻¹). Moreover, the catalytic activity was decreased by only ~17.6% after five successive cycles, indicating that the CeO₂/Ag@SiO₂ catalyst has superior stability and reusability. The outstanding catalytic performance was attributable to the unique and small size of the Au NPs, as well as the strong synergistic effect between the CeO₂ and the Au NPs. 154 In addition, hollow materials have abundant metal active sites and can also realize the elimination of organic pollutants by exciting free radicals with strong oxidizing properties. For example, the homogeneous bimetallic hollow C-Co-MH-HNC derived from a MOF achieves the effective removal of RbH by activating persulfate. 155 According to reports, similar studies have used MOF-derived hollow Co₉O₄/Carbon as an effective activator of PMPS and achieved the degradation of BPA. 156

Adsorption technology is widely used to purify environmental pollutants due to its advantages of simple operation, simple regeneration, and large-scale applications. 157–160 The inherent specialties of MOF nanomaterials, including higher surface area, abundant pore structures, and adjustable chemical composition, have been allowing them to serve as prospective candidates for supernormal adsorbents and demonstrated outstanding performance in supercapacitors. For example, Ma et al. 156 synthesized crystalline MoS₂@TiO₂ nanohybrids with MOFs as precursors through a simple hydrothermal method. The optimal material showed prominent catalytic activity for HER with a high hydrogen production rate of 10,046 μmol h⁻¹ g⁻¹ under visible light. The catalyst obtained also displayed excellent electrocatalytic activity. The extensive and close contact interface and synergistic effect of different components are regarded as the source of enhanced catalytic activity. Moreover, a novel ZnO@C-N-Co core-shell nanocomposite was also reported as a highly efficient photocatalyst for pollutant photodegradation. 162 The most significant advantage of this material is the recycling performance, which benefits from the assistance of magnetic Co NPs inside the material. Reducing CO₂ toward the generation of valuable chemicals is one of the important strategies to achieve the dual carbon goal. 177,178 Wang et al. presented a carbon-confined nitrogen oxide electrocatalyst for efficient CO₂ RR toward the direct production of formic acid. 179 Experimental results showed that the formaldehyde selectivity exceeds 90% in a wide potential window from ~0.8 to ~1.3 V versus RHE in a liquid-phase flow cell. The high selectivity and activity for CO₂ RR benefited from the carbon protective layer preventing the reductive corrosion of nitrogen oxide and the carbon layer, optimizing the adsorption of reaction intermediates.

**CONCLUSION AND OUTLOOK**

We have systematically summarized the design strategies of MOFs as precursors and/or soft templates in the fabrication of hollow porous materials, including hollow carbon, metals, metal oxides, metal carbides, metal sulfoxides, metal hydroxides, and their hybrid composites. Due to various favorable structural features, MOF-derived hollow nanomaterials are considered promising candidates for multifield applications: an enhanced surface area, low density, mesoporous structure, and advanced oxidation processes (AOPs) are a robust system to degrade refractory organic pollutants in environmental pollution management. MOF-derived SACs have been widely used due to the maximum utilization of metal atoms and the unique electronic properties of metal sites and ultralow metal loads. 163,164 Mi et al. reported that atomically dispersed Co-SA catalyst derived from MOFs applied to peroxynonsulfate (PMS) activation. 164 DFT calculations revealed that CoNₓOₓ was the definite active site (Figure 9A). 165 O₂ was the predominant reactive oxygen species, and the proportion was 98.89% (Figures 9B and 9C). The generated O₂ showed excellent degradation activity for organic pollutants in a wide pH range.

**Other applications**

In addition to the above-mentioned emerging applications, the unique properties of MOF-derived hollow structures enable their applications in gas storage/separation, 166 gas sensors, 167–169 extraction of uranium from seawater, 155,165,174 etc. Xu and co-workers synthesized ZnO/Fe₂O₃ hollow nanocages and used them as a sensing material for gas sensors. It demonstrated an improved response to acetone (25.8) with a detection limit of 1 ppm. 166 Moreover, MOF-derived Ag/Al HPNS@FO were used for electrochemical As(III) determination and exhibited high sensitivity (922.5 μA ppb⁻¹) and sustained stability. 175 Recently, our group applied the MOF-derived adsorption-electrocatalyst FeₙNₓ-C in uranium extraction from seawater and demonstrated considerable results. 176 Real seawater experiments showed that FeₙNₓ-C has a superior uranium extraction capacity of ~1.2 mg g⁻¹ in 24 h. Interestingly, we found that the isolated FeₙNₓ site first reduced UO₂²⁺ to UO₂⁺, and then oxidized U(VI) to U(VI) in the presence of Na₂O, finally obtaining the product Na₂O(UO₂-H₂O)ₓ (Figures 9D and 9E). To our knowledge, the developed system is the first to yield a U(VI) solid product (i.e., Na₂O(UO₂-H₂O)ₓ) in uranium extraction from seawater by an adsorption-electrocatalysis system. We further demonstrated that an ami-noxide-functionalized indium-nitrogen-carbon catalyst (InₙNₓ-C) offers a 5-fold higher uranium extraction capacity in seawater compared with our aforementioned FeₙNₓ-C system. X-ray absorption spectroscopy and in situ Raman spectroscopy allowed the relationship between the InₙNₓ-C-R structure and the adsorption-electrocatalytic mechanism for uranium extraction from seawater to be understood. 173 This provides meaningful clues for the study of uranium extraction from seawater. The adsorption-reduction of U(VI) to U(V) is an efficient technique for the extraction or preconcentration of U(VI) from aqueous solutions.

In addition to the above applications, MOF-derived porous hollow materials also exhibited excellent performance in photocatalytic and electrocatalytic CO₂ RR. For example, Ma et al. 176 synthesized crystalline MoS₂@TiO₂ nanohybrids with MOFs as precursors through a simple hydrothermal method. The optimal material showed prominent catalytic activity for HER with a high hydrogen production rate of 10,046 μmol h⁻¹ g⁻¹ under visible light. The catalyst obtained also displayed excellent electrocatalytic activity. The extensive and close contact interface and synergistic effect of different components are regarded as the source of enhanced catalytic activity. Moreover, a novel ZnO@C-N-Co core-shell nanocomposite was also reported as a highly efficient photocatalyst for pollutant photodegradation. 162 The most significant advantage of this material is the recycling performance, which benefits from the assistance of magnetic Co NPs inside the material. Reducing CO₂ toward the generation of valuable chemicals is one of the important strategies to achieve the dual carbon goal. 177,178 Wang et al. presented a carbon-confined nitrogen oxide electrocatalyst for efficient CO₂ RR toward the direct production of formic acid. 179 Experimental results showed that the formaldehyde selectivity exceeds 90% in a wide potential window from ~0.8 to ~1.3 V versus RHE in a liquid-phase flow cell. The high selectivity and activity for CO₂ RR benefited from the carbon protective layer preventing the reductive corrosion of nitrogen oxide and the carbon layer, optimizing the adsorption of reaction intermediates.
higher loading capacity, and shortened transport distance for mass and charge. Here, the promising applications of MOF-derived hollow structures for chemical catalysis, electrocatalysis, energy storage and conversion, environmental applications, and so on have been summarized. Despite the intriguing progress and great achievements that have occurred in the synthesis and extensive application of various MOF-derived HPMs, the study is at a burgeoning stage, and more effort is needed to deal with the issues that will be encountered in the future development process. Here, we propose several challenges and research directions that MOF-derived hollow materials may face in future development: (1) more effort should be focused on controllably synthesizing complex structures and regulating components of hollow MOFs and derivatives according to the needs of specific applications; (2) combination with other functional nanomaterials, for example, NPs, clusters, CNTs, and GO, etc., is an economical and facile strategy to regulate the properties of hollow MOFs and their derivatives; (3) the design of hollow MOFs or their derivatives with different sizes and geometrical structures will greatly enrich the storage of HPMs and ultimately affect their internal properties; (4) realizing the large-scale yield of hollow MOFs or derivatives is significant in practical applications; (5) strengthening the deep understanding of structure-activity relationships of hollow material structures is important; particularly, the mechanisms of various MOF-derived hollow materials in electrochemistry have not been thoroughly investigated; and (6) future work should combine experimental and computational methods to explore the interior reaction mechanisms, revealing the influence of structure-property-function and their synergistic interactions.

REFERENCES

1. Furukawa, H., Cordova, K.E., O’Keeffe, M., et al. (2013). The chemistry and applications of metal-organic frameworks. Science 341, 974.
2. Kitagawa, S., Kitaura, R., and Noro, S. (2004). Functional porous coordination polymers. Angew. Chem. Int. Edit. 43, 2334–2375.
3. Wang, C., Kim, J., Tang, J., et al. (2020). New strategies for novel MOF-derived carbon materials based on nanoarchitectures. Chem 6, 19–40.
4. Yang, H., and Wang, X. (2019). Secondary-component incorporrated hollow MOFs and derivatives for catalytic and energy-related applications. Adv. Mater. 31, 1800743.
5. Cai, Z.X., Wang, Z.L., Kim, J., et al. (2019). Hollow functional materials derived from metal-organic frameworks: synthetic strategies, conversion mechanisms, and electrochemical applications. Adv. Mater. 31, 1804903.
6. Liu, D., Wan, J., Pang, G., et al. (2019). Hollow metal-organic-framework micro/nanostructures and their derivatives: emerging multifunctional materials. Adv. Mater. 31, 1803291.
7. Yang, M., Zhang, C.H., Li, N.W., et al. (2022). Design and synthesis of hollow nanomaterials for electrochemical water splitting. Adv. Sci. 9, 2105135.
8. Azhar, A., Li, Y., Cai, Z., et al. (2019). Nanoarchitectonics: a new materials horizon for prussian blue and its analogues. Bull. Chem. Soc. Jpn. 92, 875–904.
9. Cai, G., Yan, P., Zhang, L., et al. (2021). Metal-organic framework-based hierarchically porous materials: synthesis and applications. Chem. Rev. 121, 12278–12326.
10. He, L., Li L., Zhang, L., et al. (2014). ZIF-8 templated fabrication of thombic dodecahedron-shaped ZnO@SiO2, ZIF-8@SiO2, yolk-shell and SiO2 hollow nanoparticles. CrystEngComm 16, 6534–6537.
11. Yang, H., Kruger, P.E., Telfer, S.G., et al. (2015). Metal-organic framework nanocrystals as sacrificial templates for hollow and exceptionally porous titania and composite materials. Inorg. Chem. 54, 9483–9490.
12. Zhu, W., Xiang, G., Shang, J., et al. (2021). Versatile surface functionalization of metal-organic frameworks through direct metal coordination with a phenolic lipid enables diverse applications. Adv. Funct. Mater. 28, 1705274.
13. Li, R., Che, R., Liu, Q., et al. (2017). Hierarchically structured layered-double-hydroxides derived by ZIF-67 for uranium recovery from simulated seawater. J. Hazard Mater. 338, 167–176.
14. Jiang, Z., Li, Z., Qin, Z., et al. (2013). LDH nanocages synthesized with MOF templates and their high performance as supercapacitors. Nanoscale 5, 11770–11775.
15. Du, Y., Li, G., Chen, M., et al. (2019). Hollow nickel-cobalt-manganese hydroxide polyhedra via MOF templates for high-performance quasi-solid-state supercapacitor. Chem. Eng. J. 378, 6534–6537.
16. Zhang, J., Yu, L., Chen, Y., et al. (2020). Designed formation of double-shelled NiFe-layered-double-hydroxides derived by ZIF-67 for lithium-ion batteries. Inorg. Chem. 59, 8159–8161.
17. Bai, X., Liu, J., Liu, Q., et al. (2019). MOF-derived hollow NiFe2O4/polypyrrole nanocoatings for efficient electrocatalysts for oxygen evolution. Electrochem. Acta 301, 238–266.
18. Bai, X., Liu, J., Liu, Q., et al. (2017). In-situ fabrication of MOF-derived Co-Co layered double hydroxide hollow nanocages/graphene composite: a novel electrode material with superior electrochemical performance. Chemistry 23, 14839–14847.
19. Zhang, J., Yu, L., Chen, Y., et al. (2020). Designed formation of double-shell NiFe-layered-double-hydroxides nanocoatings for efficient oxygen evolution reaction. Adv. Mater. 32, 1906432.
20. Wang, W., Yan, H., Anand, U., et al. (2021). Visualizing the conversion of metal-organic framework nanoparticles into hollow layered double hydroxide nanocages. J. Am. Chem. Soc. 143, 1854–1862.
21. Tian, D., Zhou, X.L., Zhang, Y.H., et al. (2015). MOF-derived porous Co3O4 hollow tetrahedra with excellent performance as anode materials for lithium-ion batteries. Inorg. Chem. 54, 8159–8161.
22. Guo, W., Sun, W., Lu, L.P., et al. (2017). Microwave-assisted morphology evolution of Fe-based metal-organic frameworks and their derived Fe3O4 nanostructures for Li-ion storage. ACS Nano 11, 4198–4205.
Li, G.C., Liu, P.F., Liu, R., et al. (2016). MOF-derived hierarchical double-shelled NiO/ZnO nanorods for high-performance ethanol gas sensor. J. Mater. Chem. C 2, 158–166.

Chen, G., Guo, Z., Zhao, W., et al. (2017). Design of porous/hollow structured ceria by partial thermal decomposition of Ce-MOF and selective etching. ACS Appl. Mater. Interfaces 9, 39594–39601.

Tao, K., Han, X., Yin, Q., et al. (2017). Metal-organic frameworks-derived porous In2O3 hollow nanorod for high-performance ethanol gas sensor. ChemSusChem 10, 10918–10925.

Cai, Y., Fang, G., Zhou, J., et al. (2018). Metal-organic framework-derived porous shuttle-like vanadium oxides for sodium-ion battery application. Nano Res. 11, 449–463.

Guo, Y., Sun, W., and Wang, Y. (2015). Multilayer CuO@NiO hollow spheres: microwave-assisted metal-organic-framework derivation and highly reversible structure-matched stepwise lithium storage. ACS Nano 9, 11462–11471.

Hu, H., Guan, B., Xia, B., et al. (2015). Designed formation of Co3O4@NiCo2O4 double-shelled nanocages with enhanced pseudocapacitive and electrocatalytic properties. J. Am. Chem. Soc. 137, 5590–5595.

Antony, R.P., Satpati, A.K., Bhattacharyya, K., et al. (2016). MOF derived nonstoichiometric NiCo2O4 hollow nanocubes for superior electrocatalytic oxygen evolution. Adv. Mater. 28, 1603623.

Li, G.C., Liu, P.F., Liu, R., et al. (2016). MOF-derived hierarchical double-shelled NiO/ZnO hollow spheres for high-performance supercapacitors. Dalton Trans. 45, 13311–13316.

Zhen, S.Y., Wu, H.T., Wang, Y., et al. (2019). Metal-organic framework-derived hollow porous CuCo2O4 dodecahedrons as a cathode catalyst for LiO2 batteries. RSC Adv. 9, 162288–162295.

Qu, F., Jiang, H., and Yang, M. (2016). Designed formation through a metal organic framework route of ZnO/ZnCo2O4 hollow core-shell nanocages with enhanced gas sensing properties. Nanoscale 8, 16349–16356.

Chen, X., Li, J.J., Chen, X., et al. (2018). MOF-templated approach for hollow NiOx/Co3O4 catalysts: enhanced light-driven thermocatalytic degradation of toluene. ACS Appl. Mater. Interfaces 10, 29771–29781.

Guan, B.Y., Kusuma, A., Yu, L., et al. (2016). Coordination polymers derived general synthesis of multishelled mixed metal-oxide particles for hybrid supercapacitors. Adv. Mater. 29, 1605902.

Zhang, W., Jiang, X., Zhao, Y., et al. (2017). Hollow carbon nanobubbles: monocrystalline CuO-CuCo2O4 dodecahedrons as a cathode catalyst for LiO2 batteries. RSC Adv. 7, 40882–40889.

Yu, L., Yang, J.F., and Lou, X.W.D. (2016). Formation of CoS2 nanobubble hollow prisms for highly reversible lithium storage. Angew. Chem. Int. Ed. 55, 12517–12521.

Liu, Y., Zhang, W., Li, S., et al. (2017). Designable yolk-shell nanoparticle@MOF patentet hull-carbon dioxide conversion. Angew. Chem. Int. Ed. 56, 5329–5333.

Lee, J., Kwak, J.H., and Choe, W. (2017). Evolution of form in metal-organic frameworks. Nat. Commun. 8, 14070.

Liu, X.Y., Zhang, F., Goh, T.W., et al. (2018). Using a multi-shelled hollow metal-organic framework as a host to switch the guest-to-host and guest-to-guest interactions. Angew. Chem. Int. Ed. 57, 2110–2114.

Guo, J., Yin, Q., Zhu, Y., et al. (2021). Metal-organic frameworks as catalytic selectivity regulators for organic transformations. Chem. Soc. Rev. 50, 5366–5396.

Yang, Y., Zhang, F., Yang, Q., et al. (2014). Hollow metal-organic framework nanospheres via emulsion-based interfacial synthesis and their application in size-selective catalysis. ACS Appl. Mater. Interfaces 6, 18163–18171.

Lin, X., Wang, S., Tu, W., et al. (2019). MOF-derived hierarchical hollow spheres composed of carbon-confined Ni nanoparticles for efficient CO2 methanation. Catal. Sci. Technol. 9, 731–738.

Yang, Q., Yang, C.C., Lin, C.H., et al. (2019). Metal-organic-framework-derived hollow N-doped porous carbon with ultrahigh concentrations of single Zn atoms for efficient carbon dioxide conversion. Angew. Chem. Int. Ed. 131, 3549–3553.

Wan, M., Zhang, X., Li, M., et al. (2017). Hollow Pt/MOF nanosphere with double shells as multimodal functional catalyst for hydrogenation reaction. Small 13, 1701395.

Zhang, Z., Chen, X., Yu, X., et al. (2014). Well-defined metal-organic framework hollow nanocages. Angew. Chem. Int. Ed. 53, 429–433.

Fang, X., Shi, Y., Wu, K., et al. (2017). Upgrading of palmic acid over MOF catalysts in supercritical fluid of n-hexane. RSC Adv. 7, 40581–40590.

Yang, J., Zhang, F., Lu, H., et al. (2015). Hollow Zn/Co ZIF nanocage derived from core-shell ZIF-67@ZIF-8 as selective catalyst for the semi-hydrogenation of acetylene. Angew. Chem. Int. Ed. 127, 11039–11043.

Zhao, J., Tang, Z., Dong, F., et al. (2019). Controlled porous hollow Co3O4 polyhedral nanocages derived from metal-organic frameworks (MOFs) for toluene catalytic oxidation. Mol. Catal. 463, 77–86.

Chen, H., Shen, K., Mao, Q., et al. (2018). Nanoreactor of MOF-derived yolk-shell Co@C-N: precisely controllable structure and enhanced catalytic activity. ACS Catal. 8, 1417–1426.

Fang, R., Luque, R., and Li, Y. (2016). Selective aerobic oxidation of biomass-derived HMF to 2,5-diformyfuran using a MOF-derived magnetic hollow Fe-Co nanocatalyst. Green Chem. 18, 3152–3157.

Sun, K.K., Chen, S.J., Li, Z.L., et al. (2019). Synthesis of a ZIF-derived hollow yolk-shell Co@C@N: catalyst for the oxidative esterification of 5-hydroxymethylfurural. Green Chem. 21, 1602–1608.

Zhou, M., Wang, H.L., and Guo, S. (2016). Towards high-efficiency nanoelectrocatalysts for oxygen reduction through engineering advanced carbon nanomaterials. Chem. Soc. Rev. 45, 1237–1307.

Zhong, L., Huang, Q., Ding, J., et al. (2021). Abundant Co-Nx sites onto hollow MOF-Derived framework single crystals. Science 370, 8–11.

Zhao, Y., Huang, C., Li, M., et al. (2014). Carbonized nanoscale metal-organic frameworks as high performance electrocatalyst for oxygen reduction reaction. ACS Nano 8, 12660–12667.

Sun, K.K., Chen, S.J., Li, Z.L., et al. (2019). Synthesis of a ZIF-derived hollow yolk-shell Co@C@N: catalyst for the oxidative esterification of 5-hydroxymethylfurural. Green Chem. 21, 1602–1608.

Zhou, M., Wang, H.L., and Guo, S. (2016). Towards high-efficiency nanoelectrocatalysts for oxygen reduction through engineering advanced carbon nanomaterials. Chem. Soc. Rev. 45, 1237–1307.

Zhong, L., Huang, Q., Ding, J., et al. (2021). Abundant Co-Nx sites onto hollow MOF-Derived framework single crystals. Science 370, 8–11.
81. Zhu, M., Zhao, C., Liu, X., et al. (2021). Single atomic cerium sites with a high coordination number for efficient oxygen reduction in proton-exchange membrane fuel cells. ACS Catal. 11, 3923–3929.

82. Wei, X., Zheng, D., Zhao, M., et al. (2020). Cross-linked polyphosphazene hollow nanopores derived from NiP-coated porous carbon with single nonprecious metal atoms for the oxygen reduction reaction. Angew. Chem. Int. Ed. 132, 14747–14754.

83. Chai, L., Zhang, L., Wang, X., et al. (2019). Bottom-up synthesis of MOF-derived hollow N-doped carbon materials for enhanced ORR performance. Carbon 146, 248–256.

84. Kong, F., Cui, X., Huang, Y., et al. (2022). N-doped carbon electrocatalyst: marked ORR activity in acidic media without the contribution by metal sites? Angew. Chem. Int. Ed. 61, e2100370.

85. Zhang, S.L., Guan, B.Y., and Lou, X.W.D. (2019). CoFe alloy/N-doped carbon hollow spheres derived from dual metal-organic frameworks for enhanced electrocatalytic oxygen reduction. Small 15, 1805324.

86. Xiao, J., Zhao, C., Hu, C., et al. (2017). Pudding-typed cobalt sulfides/nitrogen and sulfur double-doped hollow carbon spheres as a highly efficient and stable oxygen reduction electrocatalyst. J. Power Sources 343, 163–192.

87. Yang, L., Feng, H., and Liang, J. (2018). Self-sacrificial template synthesis of a nitrogen-doped microstructured carbon tube as electrocatalyst for oxygen reduction. ChemElectroChem 5, 3731–3740.

88. Deng, Y., Chi, B., Tian, X., et al. (2019). g-C3N4 promoted MOF derived hollow carbon nano-particles for boosting oxygen evolution reaction. Chem. Soc. Rev. 48, 1874–1904.

89. Liu, Z., Wang, X., and Li, X. (2016). Metal-organic framework derived hollow polyhedron metal oxide positioned graphene for energy storage applications. Chem. Commun. 52, 946–949.

90. Hu, W., Zheng, M., Xu, B., et al. (2021). Design of hollow carbon-based materials derived from metal-organic frameworks for electrocatalysis and electrochemical energy storage. J. Mater. Chem. 9, 3880–3917.

91. Xu, B., Zhang, H., Mel, H., et al. (2020). Recent progress in metal-organic framework-based supercapacitor electrode materials. Chem. Rev. 120, 213438.

92. Wu, R., Qian, X., Yu, F., et al. (2013). MOF-templated formation of porous CuO hollow octahedra for lithium-ion battery anode materials. J. Mater. Chem. 1, 11126.

93. Liu, H., Huang, Y., Zhang, F., et al. (2013). CuO/Cu2O composite hollow polyhedrons fabricated from metal-organic framework templates for lithium-ion battery anodes with a long cycling life. Nanoscale 5, 4186–4190.

94. Ramaraju, B.L., Li, H., Prakash, S., et al. (2016). Metal-organic framework derived hollow polyhedron metal oxide positioned graphene for energy storage applications. Chem. Commun. 52, 946–949.
138. Li, H., Yue, F., Yang, C., et al. (2016). Porous nanotubes derived from a metal-organic framework as high-performance supercapacitor electrodes. Chem. Int. Ed. 42, 3121–3129.

139. Jayakumar, A., Antony, R.P., Wang, R., et al. (2017). MOF-derived hollow cage NOxCo3O4 and their synergy with graphene for outstanding supercapacitors. Small 13, 1603102.

140. Ren, X., Fan, H., Ma, J., et al. (2018). Hierarchical Co3O4/PANI hollow nanocages: synthesis and application for electrode materials of supercapacitors. Appl. Surf. Sci. 441, 194–203.

141. Yilmaz, G., Yam, K.M., Zhang, C., et al. (2017). In situ transformation of MOFs into layered double hydroxide embedded metal sulfides for improved electrocatalytic and supercapacitive performance. Adv. Mater. 29, 1606814.

142. Zhang, P., Guan, B.Y., Yu, L., et al. (2017). Formation of double-shelled zinc-cobalt sulfide dodecahedral cages from bimetallic zeolitic imidazolate frameworks for hybrid supercapacitors. Angew. Chem. Int. Ed. 129, 7247–7251.

143. Li, G.C., Liu, M., Wu, M.K., et al. (2016). MOF-derived self-sacrificing route to hollow Ni/ ZnS nanospheres for high performance supercapacitors. RSC Adv. 6, 103517–103522.

144. Cao, F., Zhao, M., Yu, Y., et al. (2016). Synthesis of two-dimensional CoS1.097/nitrogen-doped carbon nanocomposites using metal-organic framework nanosheets as precursors for supercapacitor application. J. Am. Chem. Soc. 138, 6924–6927.

145. Huang, C., Gao, A., Yi, F., et al. (2021). Metal-organic framework derived hollow NiS2C with S-vacancies to boost high-performance supercapacitors. Chem. Eng. J. 419, 129643.

146. Wang, J., Huang, H., Han, X., et al. (2021). Construction of hierarchical Co3S4/NIO synergistic microstructure for high-performance asymmetric supercapacitor. J. Colloid Interface Sci. 603, 440–449.

147. Kang, C., Ma, L., Chen, Y., et al. (2022). Metal-organic framework derived hollow rod-like NiCo2O4 dendritic metal sulfide for high-performance asymmetric supercapacitors. Chem. Eng. J. 427, 131033.

148. Hu, H., Guan, B., and Lou, X. (2016). Construction of complex CoS hollow structures with enhanced electrochemical properties for hybrid supercapacitors. Chem. 1, 102–113.

149. Liu, C., Bai, Y., Li, W., et al. (2022). In situ growth of three-dimensional MXene/Metal-organic framework composites for high performance supercapacitors. Angew. Chem. Int. Ed. 61, e202116282.

150. Sheberla, D., Bachman, J.C., Elias, J.S., et al. (2017). Conductive MOF electrodes for stable supercapacitors with high areal capacitance. Nat. Mater. 16, 220–224.

151. Xiao, X., Zou, L., Pang, H., et al. (2020). Synthesis of micro/nanoscale metal-organic frameworks and their direct electrochemical applications. Chem. Soc. Rev. 49, 301–331.

152. Cai, Y., Zhang, Y., Lv, Z., et al. (2022). Highly efficient uranium extraction by a piezo catalytic reduction-oxidation process. Appl. Catal. B. Environ. 310, 121343.

153. Chen, T., Yu, K., Dong, C., et al. (2017). MOF-derived carbon-based electrocatalysts for molecular sieving membranes. Science 358, 1336–1339.

154. Wang, X., Zhang, S., Shao, M., et al. (2017). Fabrication of ZnO/ZnFe2O4 hollow nanocages as a high-performance multifunctional nanozyme catalyst for bio- oxidation. J. Colloid Interface Sci. 506, 252–259.

155. Chen, J., Lv, H., Bai, X., et al. (2021). Synthesis of hierarchically porous Co3O4/Biomass carbon composites derived from MOFs and their highly NO2 gas sensing performance. Microporous Mesoporous Mater. 321, 111108.

156. Li, H., Yue, F., Yang, C., et al. (2016). Porous nanotubes derived from a metal-organic framework composites derived from MOFs and their highly NO2 gas sensing performance. Coord. Chem. Rev. 445, 214073.

157. Liu, X., Xie, Y., Chen, Z., et al. (2022). Highly efficient electrocatalytic uranium extraction from seawater over a flexible amidoxime–functionalized In–N–C catalyst. Adv. Sci. 9, 2201735.

158. Zhao, Z., Zhang, Z., Li, C., et al. (2018). MOF-derived iron oxide-based smart plasmonic Ag/ Au hollow and porous nanoshells “ultra-microelectrodes” for ultra-sensitive detection of arsenic. J. Mater. Chem. 6, 16164–16169.

159. Ma, B., Guan, P.Y., Li, G.Y., et al. (2016). MOF-derived flower-like MoS2@TiO2 nanohybrids with enhanced activity for hydrogen evolution. ACS Appl. Mater. Interfaces 8, 26794–26800.

160. Wang, Z., Zhou, Y., Liu, D., et al. (2022). Carbon-confined iodine oxides for efficient carbon dioxide reduction in a solid-state electrolyte flow cell. Angew. Chem. Int. Ed. e20200552. https://doi.org/10.1002/anie.202022.

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AUTHOR CONTRIBUTIONS

X.L. wrote the entire manuscript. G.V., Z.C., B.H., and Q.H. polished the article. H.Y., S.M., and X.W. revised and improved the entire article.

DECLARATION OF INTERESTS

The authors declare no competing interests.

SUPPLEMENTAL INFORMATION

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