



Metal-organic framework-derived nanomaterials in environment related fields: Fundamentals, properties and applications

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ABSTRACT

Metal-organic frameworks (MOFs) as a new class of crystalline porous materials, composing of metal nodes and organic linkers, have been extensively used as versatile precursors or sacrificial templates for the preparation of numerous nanomaterials. The advantages of these MOF-derived nanomaterials such as controllable composition, tunable structure and high porosity endow them with enormous potential in many areas, including catalysis, sensors, energy storage and conversion. Herein, MOF derivatives in environment related fields are highly emphasized. The fundamental properties and general background of these nanomaterials are summarized. The primary strategies involved in compositional manipulation, pre-synthetic modulation, morphology control and post-synthetic treatment to improve the performance of MOF-derived nanomaterials are highlighted. In addition, we systematically discuss their recent progress in environmental cleaning and monitoring, especially for the wastewater treatment, air purification and target-specific sensing. Finally, the challenges and prospects of MOF-derived nanomaterials are also proposed. This article gives a comprehensive overview of MOF-derived nanomaterials for environmental applications and is expected to shed light on the further study in this highly exciting area.

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1. Introduction

Over the past decades, the booming modern science and technology has caused serious threats and challenges to human survival and development such as energy shortage, ecological destruction and environmental deterioration. In order to mitigate these ever-increasingly severe issues, the utilization of advance technology is of great significance. Nanomaterials have aroused widespread research interest owing to the inherent superiorities including large surface area to volume ratio, stability, easy to fabrication as well as distinct electrical, optical and magnetic behaviors [1–4]. These novel features related to their molecular level state are generally not observed in conventional and macro-scale materials, motivating great potential for many applications no matter in emerging or the traditional domains [5–9]. Typically, environmental pollution as a long-term problem has been evidently alleviated because of the development of nanomaterials [10–13]. Exploiting more new types of functional nanomaterials for contaminant removal and detection are critically needed in environmental field [14–19].

Metal-organic frameworks (MOFs, also known as porous coordination polymers (PCPs)), constructing from metal-containing nodes (i.e. metal ions or clusters) and organic linkers, have attracted a great deal of concerns and emerged as one of the most fascinating advanced materials for both academia and engineering due to their intrinsic properties. The compositions and structures of MOFs can be facile tuned by adjusting the well-designed organic and inorganic building blocks or changing the synthetic conditions, and their morphologies can be carefully tailored to display ultrahigh surface area and porosity, high intensity and desirable chemical activity. Moreover, MOFs can serve as excellent supports to combined with other active species to form MOF composites due to their favorable surface area and porous structure [20–25]. However, the instability in water or other harsh conditions resulted from the weak coordination bonding between organic ligands and metal nodes as well as the weak conductivity restricts the practical utilization of many MOFs [26,27]. For instance, when MOF-5 exposed to atmospheric environment, its structure begins to collapse over 10 min, let alone at humid conditions [28]. With studies progressed, researchers found that when employed as sacrificial templates/precursors, MOFs can be transformed to nanomaterials (carbon materials, metal oxides, metal phosphides, metal carbides, metal chalcogenides as well as their hybrids) with much better stability [29–31]. Using MOFs as starting materials to fabricate carbon/metal-based porous nanomaterials has sparked considerable research interest. These nanoporous materials converted from MOFs, namely MOF derivatives, show synergistic effect by combining metallic and carbonaceous characters due to the hierarchical structures and metallic contents [32]. In addition, MOF derivatives could inherit the strengths and maintain original

morphology of parent MOFs, which endows them with superior functional properties such as extremely highly specific surface area, tailored porosity, tunable pore size and diverse composition, enabling them as highly attractive candidates for chemical sensing, gas storage, energy conversion, catalysis, etc [33–36].

Actually, the derivation of MOFs creates new opportunities for the preparation of novel diversified nanomaterials with many attracting properties, mainly as following points: (i) facile preparation process without extra templates; (ii) controllable pore size and ordered/uniform distribution pore structure; (iii) accurate adjustment of active sites; (iv) enough choices for synthetic product in virtue of the diversity of metal nodes and ligands in pristine MOFs; (v) simple heteroatom doping and hybridization with other functional materials [37–40]. Thus, MOF-derived nanomaterials with ultrahigh porosity, large surface area and tailored texture open up an avenue to various applications.

As far as we know, MOF derivatives have been extensively investigated in the energy related area, such as supercapacitors, water splitting, lithium-ion batteries and hydrogen storage [41–46]. Their utilization in environmental field is extremely promising as well. Although several reviews about adsorption and catalysis are reported [47–49], the review with comprehensive emphasis on this field is rare. There is still lack of a comprehensive and systematic summary of these newly emerged MOF-derived nanomaterials in the environmental application. Providing a focus review to summarize MOF-derived nanomaterials with versatile components and/or sophisticated architectures for environmental related application is highly expected. This would give researchers a deep understanding of the recent progress in various applications (e.g. adsorption, catalysis and sensing) of these functional materials derived from MOFs as well as the relationship between their enhanced performance and well-designed structures.

In this article, fundamental properties and general background of MOF derivatives are briefly summarized. The primary strategies to enhance the performance of nanomaterials derived from MOFs especially for the environmental remediation and monitoring are highlighted. Most importantly, this overview emphasizes the promising applications of MOF-derived nanomaterials for air purification (CO₂ capture and separation, volatile organic compounds (VOCs) degradation, and radionuclide adsorption and separation), wastewater treatment (adsorption and catalytic degradation), and target-specific sensing (gaseous pollutants sensing, organic pollutants sensing, and heavy metal ions sensing). The research scope mainly focuses on the excellent achievements in the past ten years. Finally, the bottlenecks and perspectives for future work of MOF-derived nanomaterials in this highly significant area are critically proposed. In short, this overview aims at providing a new insight into the elaborate design and potential application of advanced MOF-derived nanomaterials in environmental field.

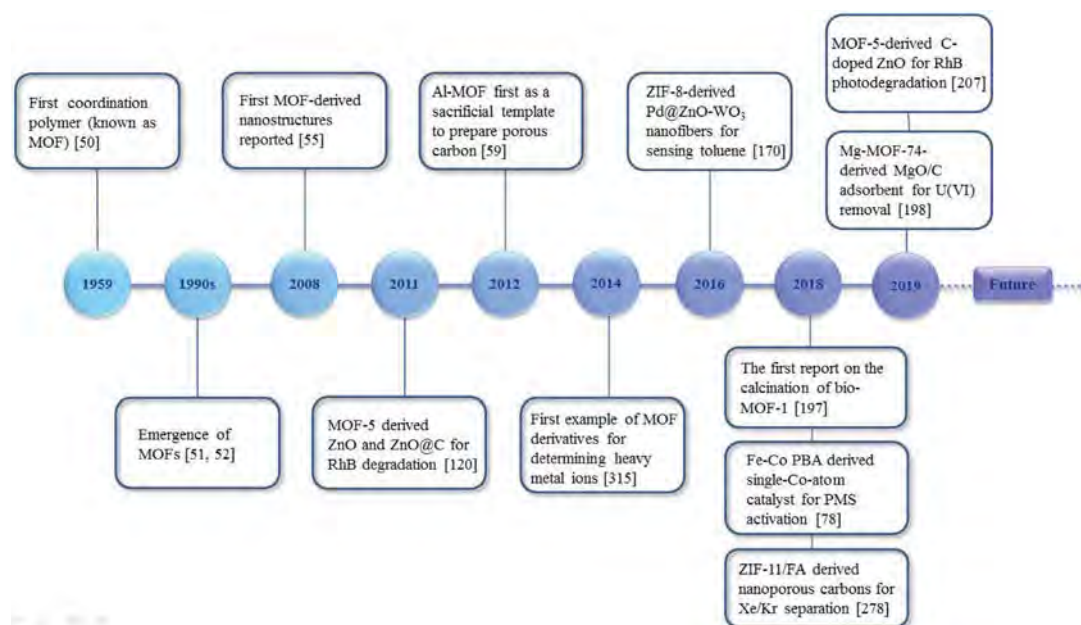


Fig. 1. Timeline of the important breakthroughs of MOF-derived nanomaterials in the environmental field.

2. Brief overview of MOF-derived nanomaterials

First coordination polymer (known as MOF) was reported in 1959 [50]. Then, MOF constructions and functionalization were pioneered and emphasized in the 1990s [51–53]. Until now, over 70,000 MOFs have been discovered [54], but just a limited species have been selected as suitable templates/precursors and utilized successfully, such as MOF-5, MOF-74, UiO-66 (UiO stands for University of Oslo), MILs (Mat riel Institut Lavoisier), ZIFs (Zeolitic Imidazolate Frameworks), etc. Consequently, great attention has been paid to MOF-derived nanomaterials due to their diverse compositions and they have been regarded as outstanding substitutions in many areas. In 2008, pristine porous carbons as the first reported MOF-derived nanostructures were prepared by carbonization of MOF-5 precursors [55]. Later, the same group also prepared the nanomaterials by heating ZIF-8 with furfuryl alcohol (FA) [56]. Since then, a variety of metal-based nanoscale materials were obtained using MOFs as the starting materials [57,58]. Versatile metal compounds containing Zn(II), Cu(II), Al(III), Fe(III) or Zr(IV) can be constructed due to the diversity of metal nodes of parent MOFs [59–61]. MOF-derived nanoporous carbons with more heteroatomic doping, reactive sites and favorable structural stability can be ascribed to the diversiform of organic ligands, including amines, carboxylates, phosphates and sulfonates. The nanostructured architectures synthesized by this novel MOF-templated pathway possess much superiority compared with the traditional methods. Fig. 1 summarized the breakthrough of MOF-derived nanomaterials in the environmental field.

Through the meticulous control of chemical/thermal conversion, various nanomaterials with structural and compositional merits derived from MOFs such as metal compounds, carbonaceous nanomaterials, and metal/carbon hybrids [62–64] can be gained. Apart from the extra acquired advantages (e.g. water stability) after heating, MOF-derived nanocomponents can effectively retain the highly BET surface area, porous architecture and basic morphology of parent MOFs [65–67]. Meanwhile, the common equipment for the production process offers much more possibilities for the large-scale industrial preparation for the MOF-derived nanomaterials, which involved in a furnace responsible for the high-temperature calcination and a gas supply system capable of providing predetermined pyrolysis atmosphere (e.g. N₂, Ar, air).

In the fabrication process, thermolysis conditions (e.g. heating rate, pyrolysis temperature, annealing parameters and gaseous condition) greatly govern the composition and shape of MOF derivatives and further influence their properties in relevant applications [68,69]. Owing to the thorough consumption of MOF templates in the fabrication of nanoparticles, only carbon and/or nanoparticles were reserved at last [70]. With the extensive investigation of employing MOFs as sacrificial templates/precursors to acquire versatile materials in recent years, several reviews on the synthesis of porous nanostructures derived from MOFs are available [21,29,32]. Therefore, for a more comprehensive and systematic overview on the preparation of the MOF-derived porous materials, we refer readers to these publications.

Over the recent years, researchers have bended to develop more excellent nanomaterials derived from MOFs for overcoming the energy shortage. It is worthy to note that removing/detecting environmental pollutants is also of great potential. For instance, with the large specific surface areas, MOF-derived materials display a large density of active sites and thus can be employed as remarkable heterogeneous catalysts, co-catalysts, or catalyst supports for numerous reactions [71,72]. Moreover, the controllable pore size and high porosity endow them with the excellent adsorption ability for target pollutants [73]. In addition, MOF-derived metal oxide semiconductors with inherited advantages from original precursors can concentrate and capture more analytes with suitable pore diameter and configuration, further achieving high sensing performances [74,75]. Taking into account these intrinsic characteristics, MOF-derived nanomaterials are a class of promising next-generation material with superb efficiencies for wastewater treatment, air purification and detection for specific pollutants. Inevitably, however, derivatives obtained from directly pyrolyzing pristine MOFs also have some disadvantages, and therefore much more efforts have been devoted to enhancing their performance to adapt for environment-related applications. The details will be discussed in next section.

3. Strategies to improve the performance of MOF-derived nanomaterials

At an early stage, studies revealed that some MOF derivatives tend to undergo structural collapse and serious particle aggregation

in high-temperature pyrolysis. The inevitable damage to original morphologies of MOFs result in featureless morphologies of bulk materials [76]. Additionally, active metal species leached from MOF-derived nanoporous carbon materials can cause secondary pollution to water system [77]. These above-mentioned shortcomings may hinder their extensive application in environment. So far, there are four popular routines to accomplish the improvement of performance: (i) judiciously manipulating the components of MOF-derived nanomaterials; (ii) precisely controlling the morphology/structure of the derivatives; (iii) pre-synthetic modulation of MOF precursors; (iv) post-synthetic treatment for calcined MOFs. In some cases, these pathways are adopted simultaneously.

3.1. Compositional manipulation

Multiple selections of component of MOFs bring infinite potential to the diversity of their derivatives, enabling them with the desirable physico-chemical properties in various fields. Through ingenious manipulation of metal nodes/ organic ligands and the conversion conditions such as pyrolytic atmospheres and temperature, MOFs as excellent sacrificial precursors/templates can be converted to metal compounds (e.g. metal oxides/chalcogenides/phosphides/carbides and their composites), carbons, and their hybrids. Rational selection of suitable precursors is of great importance because of the diversity of metal nodes and organic ligands. Specifically, metal complex contained Fe, Co, Cu or their hybrids derived from MOFs with changeable valence state can be employed as the catalyst directly or co-catalyst in Fenton system and persulfate (PS)/peroxymonosulfate (PMS) activation [78–80]. Ti-based metal compounds are regarded as a potential alternative to improve the photocatalytic activity [81]. Aside from metal nodes, organic linkers in MOFs are important for the thermal stability, which mainly depend on the metal–ligand bond strength, and thus avoid structure collapse under high-temperature calcination. As is well-known, the bond strength is positively related to charges of metal cations and negatively associated with the ionic radius. High-valent metal ions like Zr^{4+} , Ti^{4+} , Fe^{3+} , Al^{3+} and Cr^{3+} with high charge densities could generate powerful coordination bonds and thereby a more stable network [82–84]. In addition, the stable framework of MOFs also can be assembled by soft divalent metal ions (e.g. Ag^+ , Cu^{2+} , Zn^{2+} , Mn^{2+} and Ni^{2+}) and soft azolate ligands (e.g. pyrazolates, tetrazolates, triazolates, and imidazolates) [85].

By careful selection and design of the MOF precursors, their derivatives with distinct features show outstanding activity for specific environmental applications. Metal compounds with versatile chemical components like bi-/tri-metallic compounds and complex heterojunction can be constructed for enhanced performance in catalysis and sensing [86,87]. The prepared carbonaceous nanomaterials possess ultrahigh surface area, favorable porosity and tunable pore size, which could benefit the adsorption ability and extremely improve the accessibility of the target molecules into the active locations, further ensuring the rapid diffusion of the target molecular for catalysis [88]. In view of the simultaneous existence of metal components and organic in MOFs, metal/carbon hybrids can be easily fabricated. The composites composed of metal and carbon successfully combine the strengths of each composition and trigger the synergic action between them. In the next sections, the fundamental synthetic approaches of MOF derivatives in terms of compositional manipulation are summarized.

3.1.1. MOF-derived metal compounds

Metal compounds involved in metal oxides, metal phosphides, metal chalcogenides (MX, X = S, Se, Te) and metal carbides are a crucial kind of materials with great promise in many applications. The release of internally formed CO_2 and H_2O during the oxidative decomposition of organic linkers in MOFs eventually results in the

generation of metal compounds [89]. Among these metal-based materials derived from MOFs, metal oxides have received particular interest owing to their ultrahigh surface area and ample pore structures inherited from the parent MOF. Generally, direct pyrolysis of MOFs under oxygen-containing flow generates corresponding metal oxides. Tao and co-workers constructed the regular rod-like CeO_2 photocatalysts with rich oxygen vacancies, high crystallinity and wide UV absorption range by calcination of Ce-MOF under 450 °C for 4 h [90]. The prepared samples showed 98% degradation rate for methyl orange (MO) within 36 min under ultraviolet light. Likely, a mixed-phase (anatase and rutile) TiO_2 photoanode with octahedral structure was fabricated by using MIL-125- NH_2 as a sacrificial template and annealing under air atmosphere for 4 h at 500 °C [30]. The obtained photoanode was employed for hydrogen generation and performed well after sensitization.

Aside from single metal oxides, construction of polymetallic oxides also can be achieved. Typically, Cheng and colleagues developed a simple two-step process to obtain porous CuFe oxide (CuFeO) through heating the Cu-Fe prussian blue analogs (PBAs) under 550 °C and keeping at the same temperature for 2 h in air [91]. The formed CuFeO as catalyst showed massive and accessible active sites because of its large surface and high porosity. The synergistic effect among Cu, Fe and photo-induced electrons indicated prominently enhancement of performance in the catalytic activation of H_2O_2 , facilitating the generation of $\cdot OH$ and $\cdot O_2^-$. Jiang et al. obtained MnO_x - CeO_2 through the impregnation approach and subsequently by calcination at 300 °C for 6 h in air [92]. Mn cations were infiltrated into Ce-BTC (BTC stands for benzene-1,3,5-tricarboxylate) in solution by adding $MnNO_3$ as Mn source. The load of 7% manganese oxide on CeO_2 supports greatly increased the active sites and promoted the catalytic activity. Notably, the metal node of MOF precursor exerts an impact on final production. In 2012, Das et al. indicated that metal atom with -0.27 V reduction potential or larger (e.g. Cu, Ni or Co) in MOFs, pure metal nanoparticles were fabricated by calcination in an inert (e.g. N_2 or Ar) gas, and the formed carbon in the reaction may give rise to the metal nanoparticles by the reduction of metal ions. On the contrary, the MOFs consisting of the metal atom with reduction potential lower than -0.27 V (e.g. Mn, Mg, Al, Cr or Zn) can form metal oxide nanoparticles by combining with oxygen presented in the organic linker of MOFs during thermal treatment, because these metal ions are incapable of reducing to a zero oxidation state to generate their respective metal nanoparticles (Fig. 2) [93].

In addition to metal oxides, diverse metal-based functional materials, such as sulfides [94–96], selenides [97,98], phosphides [99,100], carbides [101,102], and their nanocomposites, can be afforded by introducing additional precursor into MOF solution and then following heat treatment. For example, Yu et al. investigated an anisotropic chemical etching and ion exchange approach to convert Ni-Co PBA nanocube templates into NiS nanoframes with tailored size by reacting with Na_2S in solution [94]. The annealed NiS nanoframes showed enhanced characteristics in relevant fields due to their large specific surface area, three-dimensional (3D) open structure and superb architectural robustness. It was demonstrated that diverse reactivity between the edges and the plane surface of the bimetallic PBA precursor was crucial for the preparation of NiS nanoframes. As the anions exchange process between the Ni-Co PBA nanocubes and S^{2-} ions prolonged from 0.5 h to 6 h, the morphology of product transformed from nanocubes to nanoframes which involved the continuously changed edges and plane surface of precursors. Unfortunately, rigorous and complicated reaction control (e.g. reactant concentration and reaction rate/time/temperature) was required for high quality NiS production.

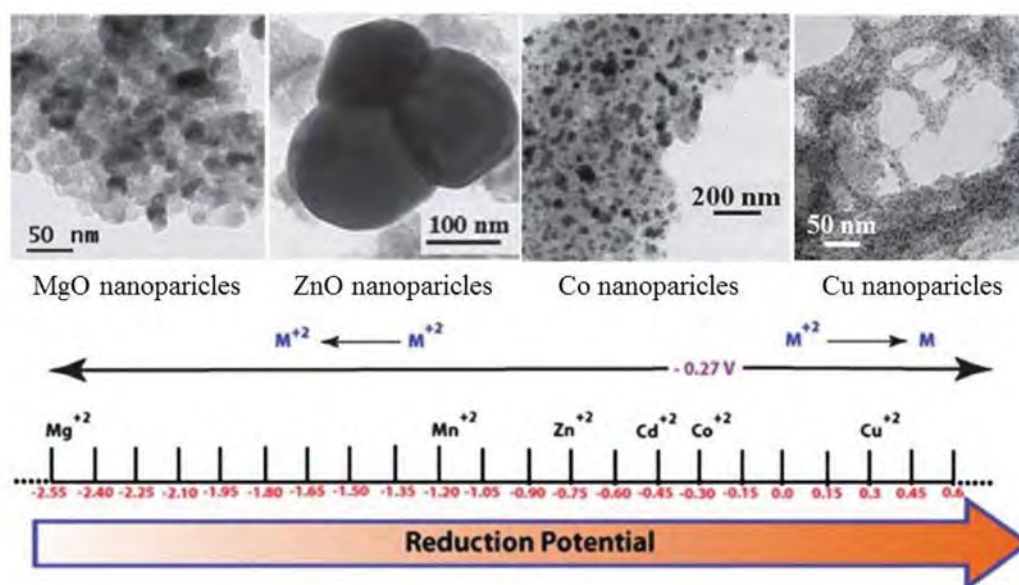


Fig. 2. The effect of reduction potential of metal atoms present in the MOFs on the formation of the metal/metal oxide nanoparticles. Metals having a reduction potential above -0.27 V undergo thermolysis in an N_2 atmosphere to give pure metal nanoparticles, whereas metals with reduction potential less than -0.27 V, even in an N_2 atmosphere, produces metal oxides only. Reproduced with permission from Ref. [93] Copyright 2012 The Royal Society of Chemistry.

Cho and colleagues demonstrated a solution infiltration approach to synthesize a series of CuS nanoparticles in/on a three-dimensional Cu-BTC with an ethyl alcohol solution of thioacetamide as the sulfide source under determined reaction time and temperature [95]. The amount of CuS generated in/on Cu-MOF can be modulated easily benefiting from such a construction route. Similarly, inserting desirable constituent into MOF cavity can prepare specific functional materials. Using MOFs-based compound (NENU-5) as precursor, relying on a copper-centered MOF (HKUST-1) precursor as a host and molybdenum-based polyoxometalates (Mo-based POMs) occupied the MOF channels, Wu and colleagues constructed mesoporous molybdenum carbide nanoparticles (MoC_x NPs) by thermal treatment under N_2 flow at $800^\circ C$ and subsequent Cu NPs etching with $FeCl_3$ solution (Fig. 3) [103]. The as-synthesized MoC_x nanomaterials with octahedral structure composed of ultrafine nanocrystallites with an unusual η - MoC phase embedded in an amorphous carbon matrix showed remarkable electrocatalytic activity.

However, considering the high cost of carbonization technology, a facile and low-cost ligand extraction process was proposed to prepare stable and porous inorganic materials with versatile functions. This appealing method focused on replacing organic ligands with inorganic component existing in the digestion solution or directly removing them from MOFs, which enabled the rapid and vast formation of nanomaterials without other fussy synthesis conditions [104]. The resultant inorganic materials can reserve highly porosity and large surface area and retain the morphology of the MOF precursors. For example, highly defective UiO-66-50Benz was used as precursor to fabricate porous oxide (ZrO_x), sulfide ($ZrSulf$) and phosphate ($ZrOxyPhos$) via a wet-treatment process in the presence of $NaOH$, $Na_2S \cdot 9H_2O$ and Na_3PO_4 , respectively [105]. During the ligand extraction process, the organic ligands were completely removed due to no other weight change except for residual solvent evaporation. The composition analysis demonstrated that nearly 4.2 wt% of S or 3.5 wt% of P was integrated into $ZrSulf$ or $ZrOxyPhos$. The obtained three materials inherited the original octahedral morphology but slightly smaller than that of parent MOFs because of the removal of the bridging organic linkers. Using different digest solutions and MOF precursors

may yield different metal compounds, suggesting the great promise of this ligand extraction strategy for the preparation of inorganic materials for wastewater treatment. Similarly, Peera et al. reported a simple, ecofriendly and low-cost mechanochemical coordination self-assembly strategy without solvent to prepare core-shell $Co@NC$ using $Zn_xCo_{1-x}(C_3H_4N_2)$ as precursor [106]. The resultant nanostructures were well-ordered and highly crystalline in nature and showed excellent catalytic activity.

3.1.2. MOF-derived carbons

In particular, porous carbonaceous nanostructures with tunable pore size, highly specific surface area, as well as facile heteroatom doping have been confirmed as promising materials for various applications, which can be produced through pyrolysis of MOFs in inactive gaseous and then by an acid-etching treatment (this process could be skipped if metal center could be *in situ* evaporation). Typically, Zn-centered frameworks are attracting ones and universally chosen as precursors/templates to construct porous carbons because of their simple operation to remove Zn. In detail, high-temperature calcination (greater than $900^\circ C$) enables metallic-Zn (boiling point: $907^\circ C$) to vaporize and is conducive to the formation of MOF-derived porous materials with numerous void spaces [107].

Accordingly, directly carbonizing MOFs without any auxiliary carbon source to obtain highly nanoporous carbons can be achieved due to the tremendous carbon content in MOFs. Carbonization of MOFs via single-step procedure greatly simplifies the preparation process. A novel type of hierarchically porous carbon (HPC) with nanostructure was exploited by direct thermolysis of MOF-5 at $950^\circ C$ (named HPC-950) [108]. Alternatively, MOF-5 calcined at $540^\circ C$ (named HPC-540) and subsequent elution step using HCl solution also implemented to yield carbon product. The results revealed that the pore volume and surface area of prepared carbon heated at $540^\circ C$ were $0.79\text{ cm}^3\text{ g}^{-1}$ and $1266\text{ m}^2\text{ g}^{-1}$, which were lower than those of HPC-950 ($0.94\text{ cm}^3\text{ g}^{-1}$ and $1512\text{ m}^2\text{ g}^{-1}$). Obviously, pore size distributions may rely on the temperature during carbonization and this phenomenon can be ascribed to the formation of more micro-, meso- and macropores at relatively high temperature, further leading to higher porosity.

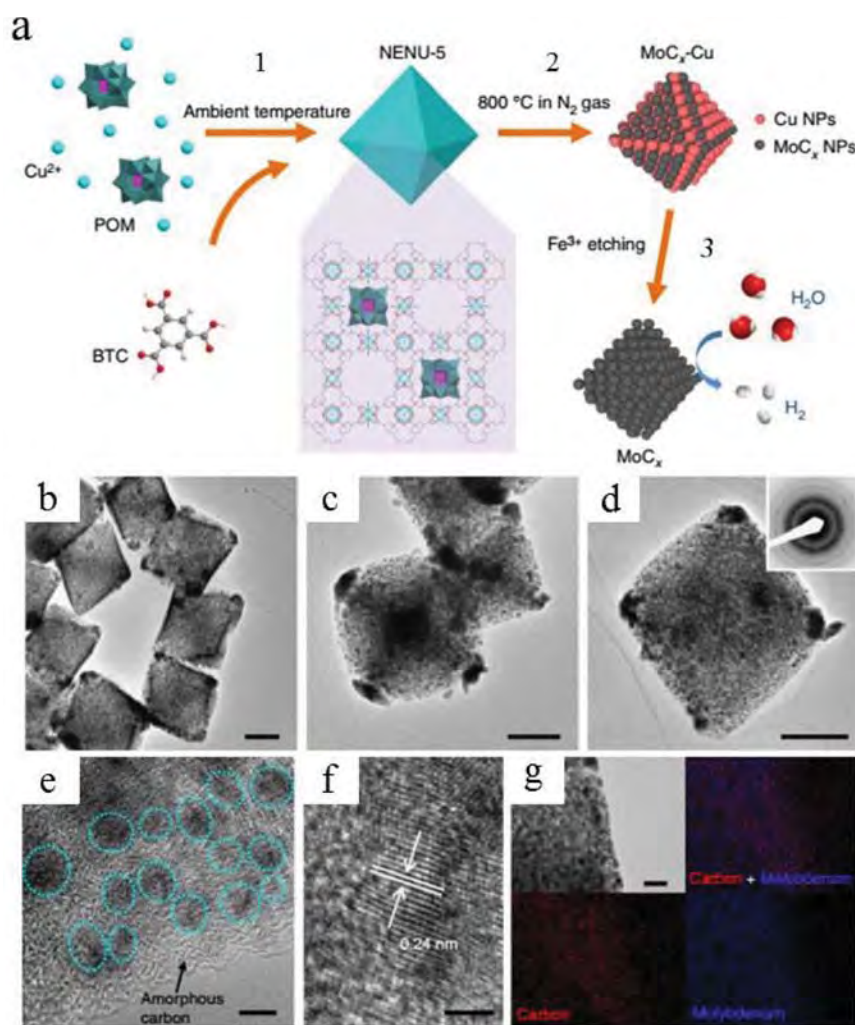


Fig. 3. (a) Schematic illustration of the synthesis procedure for porous MoC_x nano-octahedrons. (1) synthesis of NENU-5 nano-octahedrons with Mo-based POMs residing in the pores of HKUST-1 host. (2) formation of $\text{MoC}_x\text{-Cu}$ nano-octahedrons after annealing at 800°C . (3) removal of metallic Cu nanoparticles by Fe^{3+} etching to produce porous MoC_x nano-octahedrons. (b-d) TEM images of MoC_x nano-octahedrons (scale bar, 200 nm; inset in (c): SAED pattern). (e) magnified TEM image (scale bar, 5 nm), (f) HRTEM image (scale bar, 2 nm) and (g) elemental mapping (red: carbon; blue: molybdenum; scale bar, 50 nm) of porous MoC_x nano-octahedrons. Reproduced with permission from Ref. [103] Copyright 2015 Nature Publishing Group.

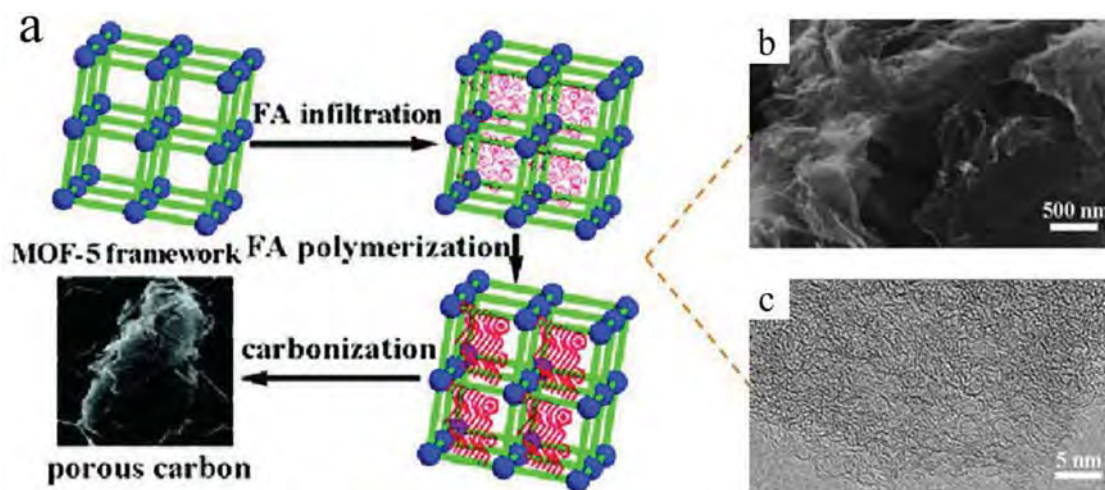


Fig. 4. (a) Schematic illustration of the synthesis procedure of NPC; (b) SEM and (c) HRTEM images of NPC. Reprinted with permission from Ref. [55] Copyright 2008 American Chemical Society.

The acquired HPC-950 possessed hierarchically porous architectures, high specific areas and partial graphitization, exhibiting excellent adsorption capacity (up to 310 mg g^{-1}) for *p*-nitrophenol.

However, the broad pore size distributions and larger cracks also simultaneously appear owing to the anisotropic shrinkage and lacking carbon sources of MOFs, which may impact their performance in various applications. Consequently, additional carbon source supplement plays a vital part in yielding carbon structure with appropriate pore size. Many organic compounds contained carbon have been utilized as secondary carbon sources for carbon materials generation, such as glucose [109], glycerol [110], phenolic resin [111], and typical FA [112].

In 2008, using MOF-5 as template, Liu and colleagues successfully synthesized porous carbon (NPC) [55]. In this process, FA was infiltrated into the cavities within the MOF-5 frameworks by a vapor phase method and then transformed to polymerized FA (PFA). Next, the PFA/MOF-5 composite was calcined in furnace filled with inert Ar gas under 1000°C (Fig. 4a). The resultant carbon materials showed sheet-like structure as revealed by scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) (Fig. 4b and c). The prepared NPC displayed a favorable Brunauer-Emmett-Teller (BET) surface area ($2872 \text{ m}^2 \text{ g}^{-1}$), closing to the theoretical surface area of a double-sided separated graphitic sheet ($2965 \text{ m}^2 \text{ g}^{-1}$), and excellent hydrogen uptake capacity (2.6 wt%) at 760 Torr, much higher than that of MOF-5 (1.3 wt%) at the same conditions. Considering that FA as the toxic, irritant and explosive reagent is extremely detrimental to the human health and environment, sucrose can alternatively serve as a green carbon source during MOF derivatives preparation. For instance, using IRMOF-3 (IR = isorecticular) as a template and sucrose as an additional carbon precursor, the functional NPC materials were synthesized by pyrolysis in a N_2 flow for 6 h under 900°C [113]. The generated ZnO species in the calcination process were removed after washing with HCl, affording the final NPC samples. It was demonstrated that sucrose as an external carbon precursor resulted in a beneficial influence to the high specific surface area ($3119 \text{ m}^2 \text{ g}^{-1}$) and high micropore volume ($1.93 \text{ cm}^3 \text{ g}^{-1}$) of NPC materials.

Owing to the N-moieties in organic ligands, N-containing carbons derived from MOFs are readily available. The doped N could break the inertness of sp^2 -hybridized carbon networks, regulate the electronic structures, and form more active sites [114]. Generally, directly doping heteroatoms in porous carbon materials in the synthesis is defined as *in situ* doping [115]. ZIFs, a class of N-enriched MOFs, comprise transition metal ions (e.g. Zn^{2+} and Co^{2+}) and imidazolate ligands, which can form 3D tetrahedral scaffolds like zeolite topologies. Other than those MOF analogues with carboxyl-ligands, many ZIFs not only show extraordinary chemical and thermal stability, but are rich in N source in imidazolate linkers. Therefore, ZIFs are usually selected as starting precursors to prepare N-doped carbons with superior performances. For instance, Li and colleagues obtained nanoporous carbon from ZIF-8 by one-step carbonization under N_2 atmosphere [116]. At different carbonization temperature, carbons converted from ZIF-8 possessed versatile adsorption capacity. In their work, the produced materials presented optimal adsorption capacity when carbonized at 700°C , because lower temperature caused the decrease of available pore and relatively higher temperature resulted in the destruction of structure. Compared with samples calcinated at other temperatures, large amounts of defects and more edge modification of N atoms were obtained in NPC-700, which might be responsible for its good adsorption ability.

3.1.3. MOF-derived metal/carbon hybrids

Apart from metal-containing materials and carbon products, their nanocomposites also can be fabricated by pyrolysis of MOFs

in an inert gas without acid leaching. The composites can combine the advantageous features of metallic component and carbon, inducing interfacial interactions and synergistic effects, thus further improving the performance in many applications. In reaction process, the metal compounds coated/supported by carbons could promote their stability, decreasing the metal leaching and ensuring the high recyclability. Furthermore, nanocomposites derived from MOFs afford a better distribution of metal-containing particles on the carbon matrix compared to conventional technology [117–119].

Metal compounds stabilized on carbons provide an extraordinary enhancement of overall properties. In Yang's research [120], ZnO nanoparticles with hierarchical coalescence were prepared under air atmosphere, while ZnO@C hybrid composites with large surface area were formed during heat treatment under a nitrogen condition, demonstrating calcination atmosphere played a pivotal part in generation of final products. Intriguingly, the resultant materials with unique features showed a different inclination for a particular application. The ZnO exhibited favorable photocatalytic degradation of target dye (almost 98% in 12 h) due to the low recombination rate of photogenerated hole-electron pairs, while ZnO@C displayed a much higher adsorption capacity (nearly 100% within 30 min) for organics ascribed to their high porosity and pore size.

Different from loaded metal compounds, isolated single metal atoms uniformly embedded in carbons can extremely promote the atomic utilization and further facilitate the reaction activity. Torad et al. reported a novel approach to construct magnetic Co nanoparticles with nanoporous carbon by one-step carbonization method of ZIF-67 [121]. The as-synthesized complex could be recovered and separated effectively from reaction system owing to their strong magnetism. The proposed strategy presented a powerful combination of metallic particles with magnetic response and catalytic activity as well as carbon materials with high porosity and surface area. The graphitic carbon presented good affinity to aromatic compounds, while the zeolite-like pore structure was adequate for adsorbing toxic metal ions. The high-weight Co nanoparticles located in the carbon matrix uniformly allowed it as an ideal adsorbent for water treatment. The Co/NPC-800 showed a remarkable methylene blue (MB) adsorption ability with the maximum adsorption amounts of 500 mg g^{-1} . Importantly, their method is quite facile and thus convenient for large-scale production.

3.2. Morphology control

Precisely controlling the morphology and structure in nanometer scale is a major motivation for developing MOF-derived functional materials and has been considered as another attracting route to enhance the performance of MOF-derived nanomaterials. MOFs with thermally stable can achieve morphology-preserved thermal transformation in pyrolysis process to obtain versatile structured hybrids [122,123]. The elaborate tuning of the morphology of MOF derivatives is essential to obtain a robust nanocomposite characterized by ultrahigh porosity, large surface area and more exposed active sites. With great progress developing, many methods such as the construction of hierarchically porous, hollow and/or core-shell nanostructure and 3D materials based on large substrate have been applied for regulating the morphology of MOF derivatives.

3.2.1. Hierarchical porous structure

Porous structure is a basic and common structure among derivatives of MOFs. Featuring high surface area, well-distributed pores and adjustable pore diameter, nanoporous materials exhibit great superiority in adsorption and catalysis. For example,

interconnected hierarchically N-doped porous carbon (IHNPC) with a reticular and typical microporous structures showed a larger pore volume ($0.68 \text{ cm}^3 \text{ g}^{-1}$) and higher surface area ($912.5 \text{ m}^2 \text{ g}^{-1}$) than precursors, making it beneficial for the 17β -estradiol capture (up to 455.95 mg g^{-1}) [124]. The huge specific surface area and abundant micro/mesopores in carbon materials enable the target molecules to have better chance to access to pores and penetrate into active sites of the carbon matrix, resulting in fast and high adsorption. Besides, Zhang et al. fabricated a morphology-retaining N-doped hierarchical porous carbon material (ZIFC@RUFC) with mesoporous shell and microporous core by a universal synthetic strategy [125]. The ZIFC@RUFC presented a huge surface area of $982 \text{ m}^2 \text{ g}^{-1}$ and total pore volume of $0.70 \text{ cm}^3 \text{ g}^{-1}$ in comparison of ZIFC ($713 \text{ m}^2 \text{ g}^{-1}$, $0.41 \text{ cm}^3 \text{ g}^{-1}$, respectively) and RUFC ($647 \text{ m}^2 \text{ g}^{-1}$, $0.38 \text{ cm}^3 \text{ g}^{-1}$, respectively) counterparts. Benefiting from highly developed microporosity in conjunction with ordered mesoporosity, the ZIFC@RUFC achieved greater promotion in CO_2 adsorption kinetics and amounts (3.37 mmol g^{-1}) than RUFC (3.10 mmol g^{-1}) and ZIFC (1.89 mmol g^{-1}).

The pore characteristics (e.g. pore shape, pore size and porosity) of MOF derivatives is highly important for various applications. However, due to the lack of understanding of the MOF decomposition mechanism, the control of pore size is insufficient [126]. It is reported the structure and component of precursor have an effect on pore size [127]. Hussain et al. reported three different Zn-containing MOFs (i.e. MOF-5, ZIF-8 and MOF-74) derived porous ZnO/C nanocomposites by one-step carbonization [127]. The differences of the pore shape/size of these samples can be attributed to their diverse precursor frameworks. MOF-5 with an open pore structure consists of Zn_4O nodes and benzenedicarboxylate linkers. When pyrolysis at 800°C in water vapors saturated Ar flow, the organic linker decomposed and resulted in a little larger micro- and meso-pores. Likely, Zn-N_4 with tetrahedral structure in ZIF-8 framework are connected by methylimidazole rings forming spherical hexagonal architectures. Whereas, ZnN_4 -imidazole linked in spherical order causes more pore openings with a smaller pore size than that of MOF-5, leading to the higher micropore volume in $\text{ZnO/C}_{\text{ZIF-8}}$. Among these samples, $\text{ZnO/C}_{\text{MOF-5}}$ displayed the fast adsorption and photocatalytic MB dye degradation activity because of its larger pore diameters and the existence of micro/mesopores, allowing the MB molecules to permeate and access into the porous carbon.

In the research of Xu's group, the relationship between carbonization temperature and pore volume was studied by preparing NCo@CNT-NFT [128]. The pore volume of resultant samples was proportional to the abundant carbon nanotubes (CNTs), more CNTs in a unit mass afforded a higher pore volume. At 600°C , NCo@CNT-NF600 without formation of any CNTs can be obtained, which were contrary to 700 , 800 , 900 and 1000°C . Subsequently, the same group confirmed that the amounts of introduced guest iron ions exhibited a great influence on the porosity of the prepared samples, which possessed hierarchical porous superstructures (co-existence of meso- and micropores) [129]. With the increasing of Fe content, the pore volume decreases from 0.497 (Co@CC) to 0.350 (CoFe5@CC) and $0.301 \text{ cm}^3 \text{ g}^{-1}$ (CoFe10@CC) gradually, and then increased to $0.438 \text{ cm}^3 \text{ g}^{-1}$ (CoFe20@CC) with further increasing the iron amounts, due to the formation of the distinctive hydrangea-like superstructure. In the work reported by Shang et al., the hierarchically porous Co,N co-doped carbon nanoframework (Co,N-CNF)-derived from Zn/Co bimetallic ZIF precursor was synthesized by mesoporous silica (mSiO_2)-protected-calcination approach [130]. After remove the mSiO_2 outer shell with hydrofluoric acid (HF), the as-prepared Co,N-CNF presented obvious hierarchically porous structure, while the A-Co,N-CNF carbonized without mSiO_2 only exhibited mesopores.

3.2.2. Hollow structures

Complex hollow structures play a positive role in various applications because of their sizeable surface area, abundant active sites as well as more sufficiently accessible contact interfaces between reactants for fast mass transport [131,132]. Compared to the hard-template approaches with tedious procedures for construction of hollow structures, which involved in the preparation of starting template, the filling of organic precursor, pyrolytic treatment and removal of the template, MOF-templated approach greatly simplifies the fabrication steps and gives the obtained hollow structure with open pore channels [133]. Wei and co-workers proposed three pivotal factors for creation of hollow structures [134]: (i) an intensive interfacial interaction of core-shell; (ii) the clearly higher shrinkage degree of the inner core in comparison with the outer shell; (iii) the relatively loose core structures. Above-mentioned theories offer an explicit guide for the exploitation of MOF-derived nanostructures with hollow cavity.

Encouraged by the merits of MOF-derived hollow structures, numerous efforts have been dedicated to utilizing this unique architecture in catalysis. For example, the novel $\text{CoFe}_2\text{O}_4/\text{CuO}$ (sub)microcages derived from dual-MOF ($\text{Fe}^{\text{II}}\text{-Co}$ PBAs@HKUST-1) with core-shell structure were fabricated by thermal annealing in oxygen-containing atmosphere [135]. The obtained materials showed obvious core-shell hollow structure with a well-defined gap between the inside solid core and the outside shell as well as well-distributed Fe, Cu, Co and O elements. The high catalytic efficiency for the reduction of organic pollutants by NaBH_4 could ascribe to the unique yolk-shell hollow shape which offered hierarchical porosity structure and large surface area. Moreover, hollow semiconductor oxide nanomaterials are advantageous in gas sensing by accelerating the surface reaction and the diffusion of gas molecules. Song et al. prepared the NiFe_2O_4 microspindles with hollow structure by annealing Ni/Fe MOF in the air [136]. The as-synthesized NiFe_2O_4 consist of major nanosize particles and plentiful deep pores in the hollowed-out shells. Acting in synergistic action with the highly BET surface area, abundant oxygen species and unique hollow structure, the high-performance sensor behaved well towards acetone detection. This study provided a promising route to the efficient construction of gas sensors based of MOF-derived semiconductor oxide in future.

3.2.3. Core-shell structure

Core-shell structures have recently attracted intensive attention in view of their distinctive multilevel architecture and wide applications in many fields. Notably, the core-shell structures used for catalysts possess distinct superiorities as follows: (i) enhancement of the catalytic activity by the confinement effect; (ii) increase of the dispersibility by strong synergy within the inside core and the outside shell; (iii) the formed microenvironment in a void space between the shell and the core offers reaction driving force for degradation and adsorption; (iv) the active core within a hollow environment can improves the stability and extends service life while retains their all surface active sites [137,138]. In general, two common pathways have been used to construct MOF-derived core-shell buildings. One is the predesign of core-shell structures and then by a thermal treatment, including self-template method by creating MOF@MOF precursors, external-template method by creating template@MOF structures and introduction of guest nanoparticles; the other is the direct pyrolysis of pristine MOFs to their core-shell derivatives.

MOFs with a similar crystal/topological structure can be facilely fabricated into core-shell architecture. A novel ZnO@C-N-Co nanocomposites with core-shell structure were prepared by directly heating hollow bimetallic Zn/Co-ZIFs comprising a ZIF-8 as shell and some ZIF-67 nanoplates as core at 600°C for 2 h (Fig. 5) [139]. Intriguingly, ZnO nanoparticles derived from ZIF-8-

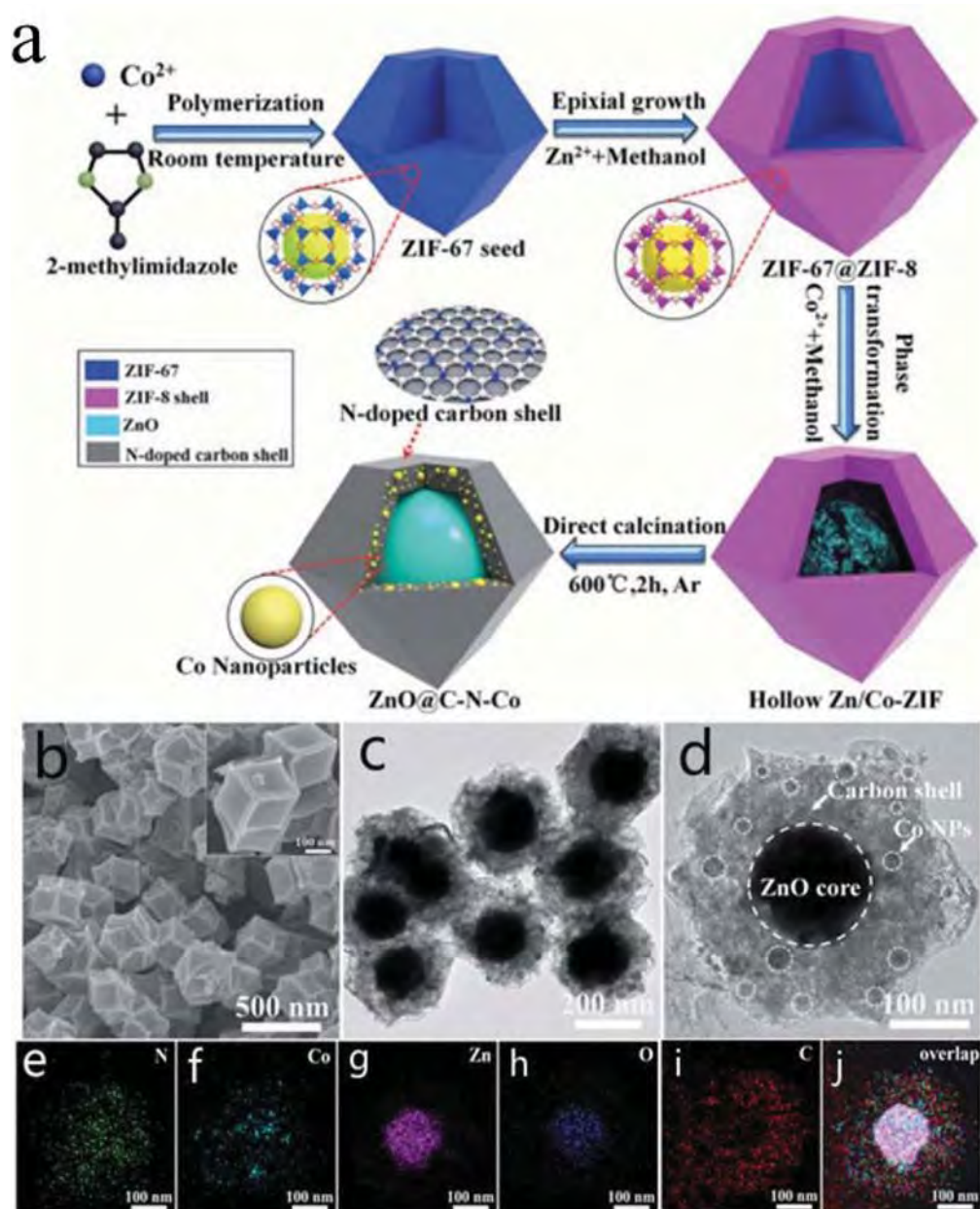


Fig. 5. (a) Schematic illustration of the preparation of core-shell ZnO@C-N-Co; (b) SEM image of the as-synthesized core-shell ZnO@C-N-Co (inset in (b): high magnification SEM image of ZnO@C-N-Co); (c) and (d) TEM images of ZnO@C-N-Co; (e–j) EDS mappings of the ZnO@C-N-Co. Reprinted with permission from Ref. [139] Copyright 2017 The Royal Society of Chemistry.

shell could agglomerate spontaneously and transfer to the hollow cavity internally. Whereas, the inside Co nanoparticles inversely moved to the organic ligand-derived outer N-C shell, leading to the final core-shell ZnO@C-N-Co. This unique nanostructure endowed the intermediate ZnO with good stability, high specific surface area, and effective electron-hole separation capacity. The prepared ZnO@C-N-Co exhibited a greatly enhanced photocatalytic activity (99.5%) than pure ZnO (60.2%) for MO due to the strong synergistic effect between the ZnO core and C-N-Co shell.

External templates such as SiO₂ and polymers are extensively applied for the creation of core-shell structure, in which MOF commonly served as inner core. Zhang et al. reported yolk-shell Co₃O₄/C@SiO₂ nanoreactors (YSCCs) for PMS activation (Fig. 6a–h) [140]. This hybrid with rational morphology and composition exhibited outstanding degradation effect of BPA compared to YSCCs (pyroly-

sis in air), Co₃O₄ and MOF-derived Co₃O₄/C NPs (Fig. 6i). It is noting that the superior catalytic activity of YSCCs can be attributed to their structure and composition optimization (Fig. 6j). Specifically, the confinement effect of yolk-shell nanoarchitecture and good dispersity of Co₃O₄ species improved the stability and catalytic performance; and the presence of graphitized carbon promoted the reaction kinetics because of the facilitation of electron transport from catalyst to oxidant.

Various porous core-shell morphologies of MOF-derived metal oxide semiconductors exert an important impact on the gas detection. Zhang and co-workers constructed four kinds of ZIF-67-templated porous hierarchical Co₃O₄ structures (i.e. nanoparticle Co₃O₄ (NP-Co₃O₄), porous core-shell Co₃O₄ (PCS-Co₃O₄), porous popcorn Co₃O₄ (PPC-Co₃O₄) and core-shell Co₃O₄ (CS-Co₃O₄)) (Fig. 7a–e) [141]. Benefiting from the elaborate architecture,

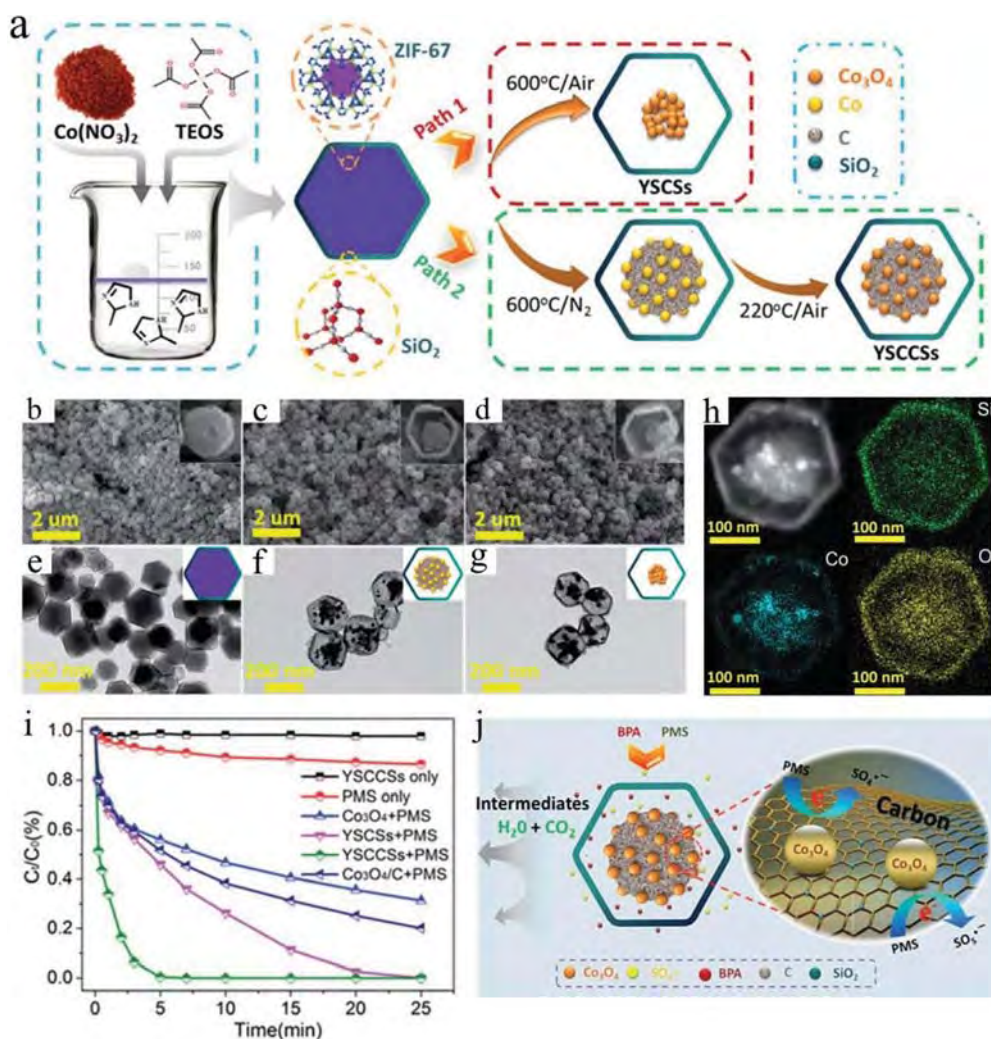


Fig. 6. (a) Illustration of the preparation process of the ZIF-67@SiO₂, YSCCs and YSCCs. (b–d) SEM images of ZIF-67@SiO₂, YSCCs and YSCCs (top-right inset: the enlarged SEM images of the broken structure); (e–g) TEM images of ZIF-67@SiO₂, YSCCs and YSCCs (top-right insets: the corresponding schematic diagram); (h) EDX line scan and elemental mapping in the yolk-shell structure; (i) BPA degradation efficiency in different reaction systems within 25 min; (reaction conditions: BPA = 20 mg L⁻¹, PMS = 0.1 g L⁻¹, catalyst = 0.1 g L⁻¹, and T = 298 K). (j) the possible synergistic mechanisms of BPA degradation in the YSCCs. Reprinted with permission from Ref. [140] Copyright 2018 The Royal Society of Chemistry.

ZIF-67-derived Co_3O_4 materials offered a sufficient exposed surface and active sites, which could be the reactive locations for the pre-adsorbed reducing analytes and O_2 . These obtained samples with mesoporous structure were beneficial to access and departure of target gas on the materials surface, further promoting a fast mass transfer. Among them, Co_3O_4 with core-shell structure showed the superior performance owing to its multilevel architecture, which could hold a stable structure as well as provide a large contact area between the target gas and surface regions of materials (Fig. 7f). In another study, $\text{NH}_2\text{-MIL}(\text{Fe})\text{-88B}$ -derived nano-ZVI@C-N was prepared through annealing the MOF precursor for 4 h under N_2 flow [142]. The presence of core-shell nano-ZVI and Fe_3O_4 NPs distributed along N-doped fusiform porous carbon rods ensured the conversion of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$, achieving 95% drug removal during 60 min in heterogeneous electro-Fenton process.

3.2.4. Three-dimensional monolithic materials

Despite the great success of powdery nanomaterials derived from MOFs, most of them undergo numerous drawbacks, such as weak durability, difficult separation from reaction system, and easy-clogging of the pipes, which largely thwart their practical demand. In view of the recycling problems in industrial operations,

MOF-derived functional materials integrated with 3D monolithic substrates or support have gained increasing attentions. Lin's group investigated a new concept to employ a self-assembly of melamine sponge and cobalt-centered ZIF-67 to yield a magnetic carbon sponge (MCS) by one-step carbonization (Fig. 8a) [143]. After calcination, the layer of melamine sponge coated with ZIF-67 converted into a layer of nanoscale cobalt/carbon hybrid immobilized on carbon sponge. Such carbon material with 3D monolithic structure showed not only nanosize porosity of carbonized ZIF-67 and macroporous carbon sponge but magnetic features of cobaltic components. The proposed synthetic strategy of 3D hierarchical carbon materials can be further explored by using versatile MOFs.

Su et al. reported a simple dipping-pyrolysis method to fabricate a unique 3D architecture photocatalytic microreactor, where the hollow ZnO nanocages derived from ZIF-8 were steadily and uniformly distributed in the overall surface of carbon sponge networks coated by rGO (Fig. 8b) [144]. The as-prepared porous ZnO based of carbon frameworks displayed superior adsorption and degradation performance for water pollutants. The rhodamine B (RhB) degradation efficiency was as high as 99% in 120 min and better than $\text{ZnO}_{\text{ZIF-8}}$ /carbon sponge without rGO (89%) and pristine carbon sponge (more than 20%). Owing to the good recyclability,

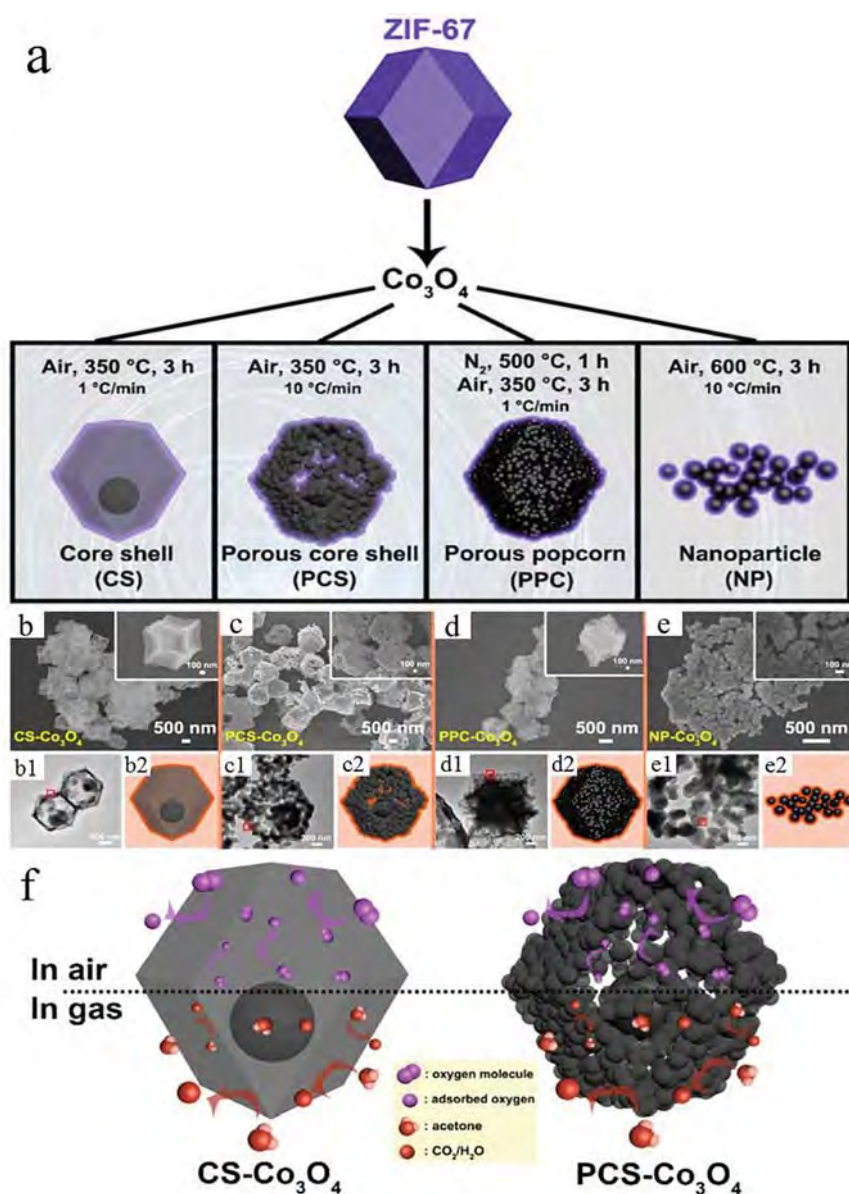


Fig. 7. (a) Schematic illustration of the formation of different Co_3O_4 structures. SEM images of the as-synthesized Co_3O_4 products derived from ZIF-67: (b) CS- Co_3O_4 , (c) PCS- Co_3O_4 , (d) PPC- Co_3O_4 , and (e) NP- Co_3O_4 ; (b1–e1) TEM image of various Co_3O_4 structures; (b2–e2) corresponding ideal geometrical models of individual Co_3O_4 structures; (f) schematic of sensing mechanism of Co_3O_4 samples. Reprinted with permission from Ref. [141] Copyright 2018 American Chemical Society.

robust structure and convenient maneuverability, the microreactors have great potential in sustainable environmental remediation towards industrial photocatalytic applications. In addition to carbon sponges/foams, cellulose aerogels, ceramics, ion-exchange resin and so on also can be developed as efficient anchor [145–147]. Such an elaborate design and novel strategy can be expanded to a wider series of 3D bulk supported with MOF-derived porous materials.

To sum up, versatile morphologies and structures of MOF-derived nanomaterials affect their properties seriously and hence lead to different removal efficiency for organic contaminants. Rational regulation of the morphology and structure endow these derivatives with highly porosity, large surface area, abundant reaction locations and suitable pore sizes, which can enhance the adsorption capacity of functional materials and create the chances for targeted molecules to close to the active sites, further facilitating the catalytic efficiency. Therefore, more representative researches for deeply analyzing the relationship between the

structures and the physical and chemical features of MOF-derived nanoscale materials are highly desirable.

3.3. Pre-synthetic modulation

Owing to the unique structure of MOFs, various approaches to modulate the active metal nodes, active linkers and/or incorporate active guest into the pore channels of MOFs before calcination have been employed. In this section, several methods related to pre-synthetic modulation are proposed emphatically: (i) introduction of heteroatoms through external template; (ii) modification of MOFs with functional groups; (iii) addition of extra activating agent; (iv) MOFs loaded/coated with other materials; (v) encapsulation of guest into MOF cavities.

Notably, introduction of heteroatoms such as nitrogen (N), phosphorus (P), sulfur (S), oxygen (O) or boron (B) into carbon frameworks can effectively enhance their physico-chemical features [148–150]. Doping heteroatoms into carbon-based materials

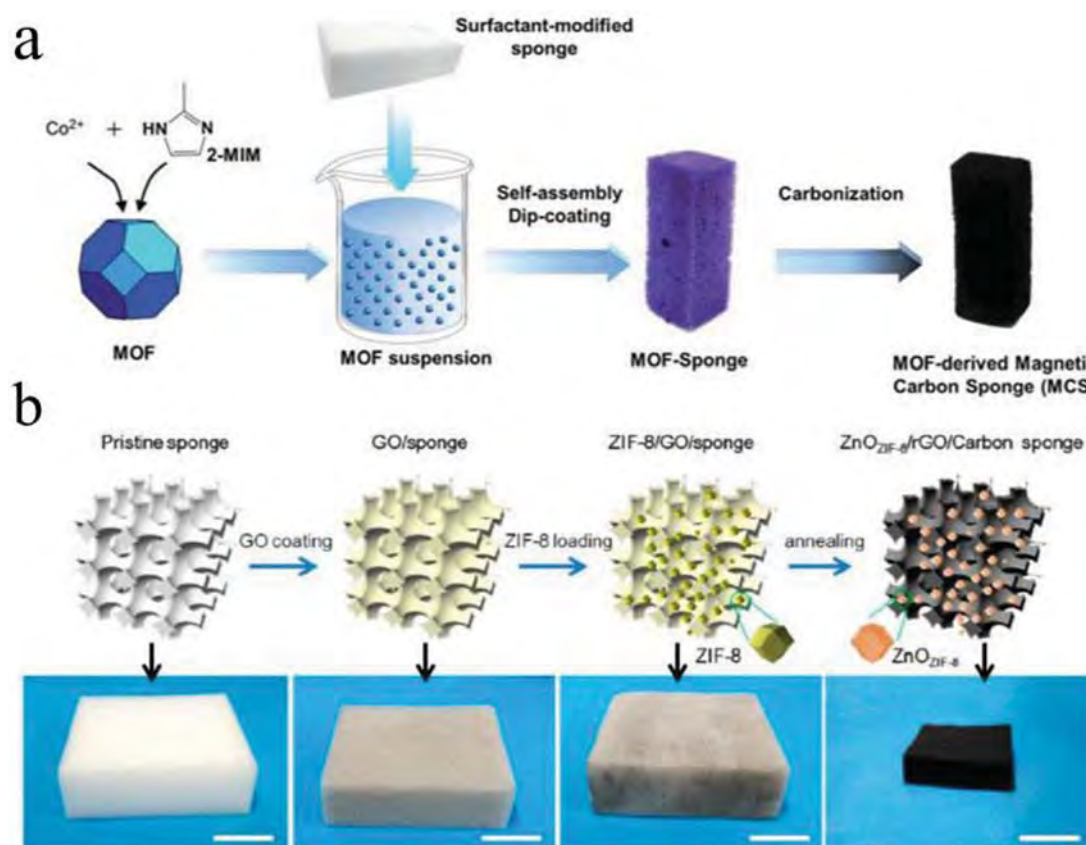


Fig. 8. (a) Preparation scheme of MCS. Reprinted with permission from Ref. [143] Copyright 2016 The Royal Society of Chemistry. (b) schematic illustration of the fabrication process. Reprinted with permission from Ref. [144] Copyright 2018 American Chemical Society.

derived from MOFs can (i) promote π -electron mobility through conjugation, (ii) offer more active sites for selective adsorption, and (iii) increase the defective edges and surface hydrophilicity [151–154]. These features highly promote the catalytic activity of carbon nanomaterials for refractory organic contaminants. For example, modified HKUST-1 with triphenylphosphine (TPP) was utilized for construction of carbon supported Cu_2O heterostructures doped with phosphorus [155]. Carbon materials doped with P can enhance the electrical conductivity, surface area, possible catalytic sites and mitigate the steric hindrance effects encountered in N-doped carbon materials [156]. This obtained carbon-based heterostructure showed superior photocatalytic activity for phenol decomposition, which was up to 99.8% within 90 min. The P-doping was advantageous in facilitating charge carrier separation and developed a synergistic effect with carbon/ Cu_2O towards promoting charge transport to the catalyst surface, thus resulting in the enhancement of photocatalytic degradation performance.

N-doped carbon nanomaterials have attracted extensive research. In addition to obtaining N-containing carbons by *in situ* doping, thermal treatment of MOF precursors with external N-source is another method to synthesize such materials, peculiarly those MOFs without any N-moieties in organic linker. In the research of Aijaz, highly N-decorated nanosized porous carbons were synthesized through using ionic liquids@MIL-100(Al) (IL@MIL-100(Al)) as the precursors, in which the IL (1-ethyl-3-methylimidazolium dicyanamide (EMIM-DCN)) was served as the external N source [157]. Particularly, ILs were impregnated into the as-prepared MIL-100(Al), and calcined at 800 °C for 7 h in argon flow. Then, the resultant samples were washed with HF to remove the Al_2O_3 species generated in carbonization, which

afforded the final carbon materials. The nanoporous carbons displayed large surface area ($2397 \text{ m}^2 \text{ g}^{-1}$) and high N amounts (14.8 wt%), where overall the N moieties came from the IL because the MOF precursor is free of N atoms, suggesting the achievement of efficient heteroatom doping from external template.

In reality, co-doped or tri-doped carbon materials may show good enhancement than monotonous N-doped carbon catalysts because of the possible synergy between multiple kinds of heteroatoms. Ma et al. successfully prepared N (8.09 at.%), P (0.69 at.%), and S (0.80 at.%) co-doped hollow carbon shells (NPSC-700) using poly (cyclotriphosphazene-co-4,4'-sulfonyldiphenol) and Co-centered MOF as precursors [158]. The NPSC-700 showed much better bisphenol A (BPA) degradation efficiency than N-doped CNTs, N-doped GO as well as N-doped mesoporous carbon, which suggested that N-doped carbons were far from enough to degrade model compounds, but introduction of P and S definitely broke the electroneutrality of sp^2 carbon and provided more charged sites for organics decomposition. The positive synergistic effect of N, P and S in carbon materials regulated the polarizability, the spin density and structural defects, facilitating the O–O cleavage of PMS and thus accelerating the formation of radicals. Likely, Jin et al. reported that Fe, N and S co-doped carbon matrix/carbon nanotube nanocomposites derived from ZIF-8 showed superior electrocatalytic activity in light of the synergy of carbon nanotubes and matrix, thiophene-S active sites and adequate iron nitrides [153].

The introduction of functional groups (e.g. CH_3 , NH_2 , NO_2 , OH, Cl and SH) into MOFs and subsequent pyrolysis has raised increasingly research interests, which could intensively improve their chemical durability and property. Particularly, amino groups as electron donor have been widely used due to their interactions with π^* -orbitals of the ligand benzene ring [159]. For example,

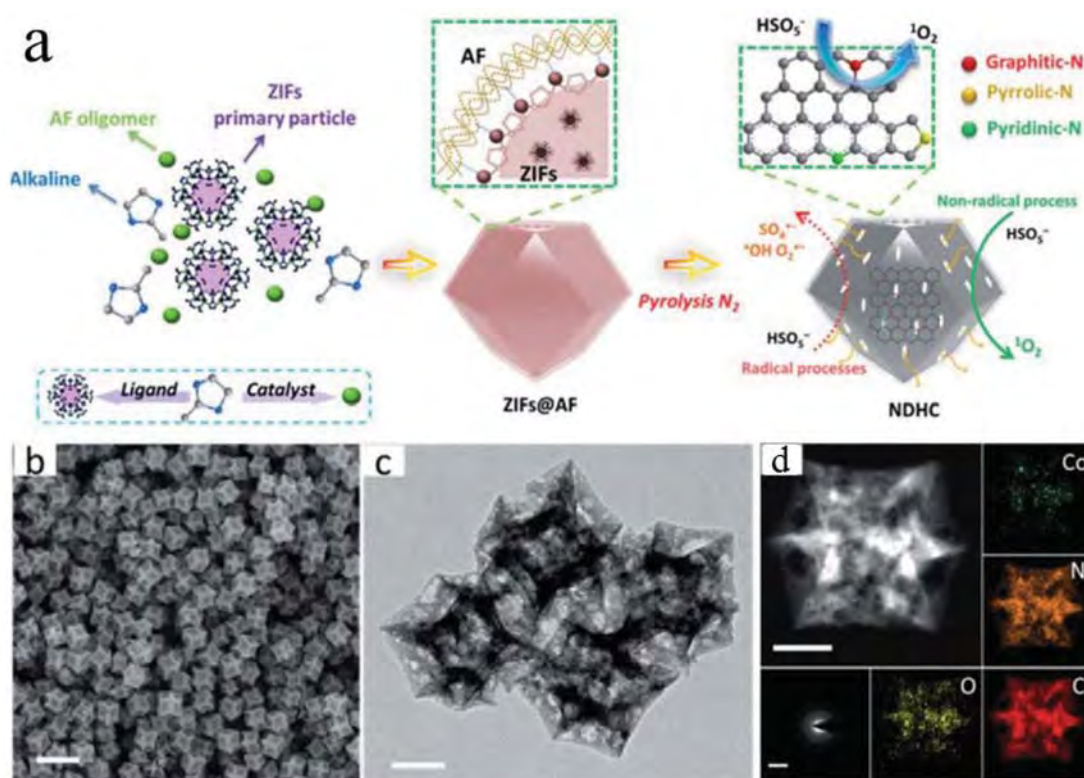


Fig. 9. (a) Illustration of the preparation process of NDHC; (b) SEM and (c) TEM images of NDHC-9; (d) the enlarged HAADF-STEM image, elemental maps. Reprinted with permission from Ref. [167] Copyright 2019 The Royal Society of Chemistry.

Liu et al. synthesized a NH_2 -functionalized carbon material using MOF-5 and tetraethylenepentamine (TEPA) by a fast approach in high temperature [160]. The introduction of amino groups could obviously promote the adsorption property of the products. 20% TEPA-C-MOF-5 showed the best capture amounts (550 mg g^{-1}) for U(VI), better than that of 10% TEPA-C-MOF-5 (342 mg g^{-1}) and raw MOF-5 (160 mg g^{-1}), which was because U(VI) could be coordinated with a large number of amino groups. In another case, single Ru sites derived from UiO-66- NH_2 was prepared by Li et al. for selective hydrogenation of the quinoline [161]. The amino group of UiO-66 ligands served as the Lewis base to stabilize RuCl_3 , allowing the confinement of the single Ru atom into the MOF channels.

A mild chemical activation with potassium hydroxide (KOH) was proved as another routine to improve the textural property of nanomaterials derived from MOFs [162–164]. Pyrolysis of MOFs along with KOH (as an activator) could greatly increase the surface area and porosity of as-synthesized carbon, broadening its various potential applications. For instance, MAF-6 (MAF = metal azolate framework, a kind of Zn-based MOF) was heated with KOH under a wide range of conditions to fabricate porous carbons [164]. The porosity of obtained carbons depended a lot on the concentration of incorporated KOH, while the pore size was controlled by the pyrolysis temperature. The KOH activator might generate K_2CO_3 and then dissociate into CO_2 , CO and K_2O to eliminate carbons [165], and this process primarily enhanced the present porosity instead of creating new larger pores. Benefiting from the presence of KOH, the defect phase and specific surface area (from 1484 to $3123 \text{ m}^2 \text{ g}^{-1}$) of resultant porous carbons both increased. The maximum adsorption capacities of CDM6-K1000 for ibuprofen and diclofenac sodium separately were 408 mg g^{-1} and 503 mg g^{-1} , much higher than those of commercial active carbon (AC) (168 mg g^{-1} and 79 mg g^{-1} , respectively).

The assembly of MOFs onto diverse substrates (e.g. graphene, CNTs and $\text{g-C}_3\text{N}_4$) has achieved extensive interests in many fields. Gong et al. synthesized a novel Zn-centered MOF-derived N doped carbon (ZIF-NC) loaded on $\text{g-C}_3\text{N}_4$ heterostructure by a two-step calcination approach [166]. The integration of ZIF-NC with $\text{g-C}_3\text{N}_4$ not only enhanced the light harvesting but also facilitated the activation of PMS to generate high active $\text{SO}_4^{\cdot-}$ radicals. Besides, the formation of junction between ZIF-NC and $\text{g-C}_3\text{N}_4$ could greatly accelerate charge transfer and shorten the charge transport distance, leading to acceleration of the photogenerated carrier separation. 0.5% ZIF-NC/ $\text{g-C}_3\text{N}_4$ with PMS exhibited the excellent photocatalytic performance with removal rate of 97% within 60 min irradiation, much higher than that of $\text{g-C}_3\text{N}_4$ and ZIF-NC counterparts. MOFs coated/doping with polymer exhibited outstanding electrocatalytic performance owing to the fabrication of hierarchically porous nanostructures and more exposure of active sites. Zhang et al. prepared N-doped hierarchical carbon (NDHC) catalyst by using ZIFs coated with phenolic resin (PR) as precursors (Fig. 9) [167]. The confinement effect of PR led to a NDHC catalyst with ample active N sites, well-distributed porous structure and high graphitization. The resultant NDHC-9 possessed a uniform dodecahedron (Fig. 9b), suggesting that the encapsulation of PR enabled the carbon framework more stable in pyrolysis. Besides, many macro- and meso-pores presented in the inner and outside of NDHC-9 (Fig. 9c), resulting in more exposed graphitic N active sites.

The nano-cavity of MOFs can afford good space to accommodate guest species to fabricate the guest@MOFs, which can be employed as platforms for host–guest chemistry researches and precursors for functional materials preparation. The rational encapsulation of guest species into the pore channels of MOFs can formulate versatile derivatives as required. A novel designed cage-containing MOF as a host and dicyandiamide (DCDA) and iron precursors as

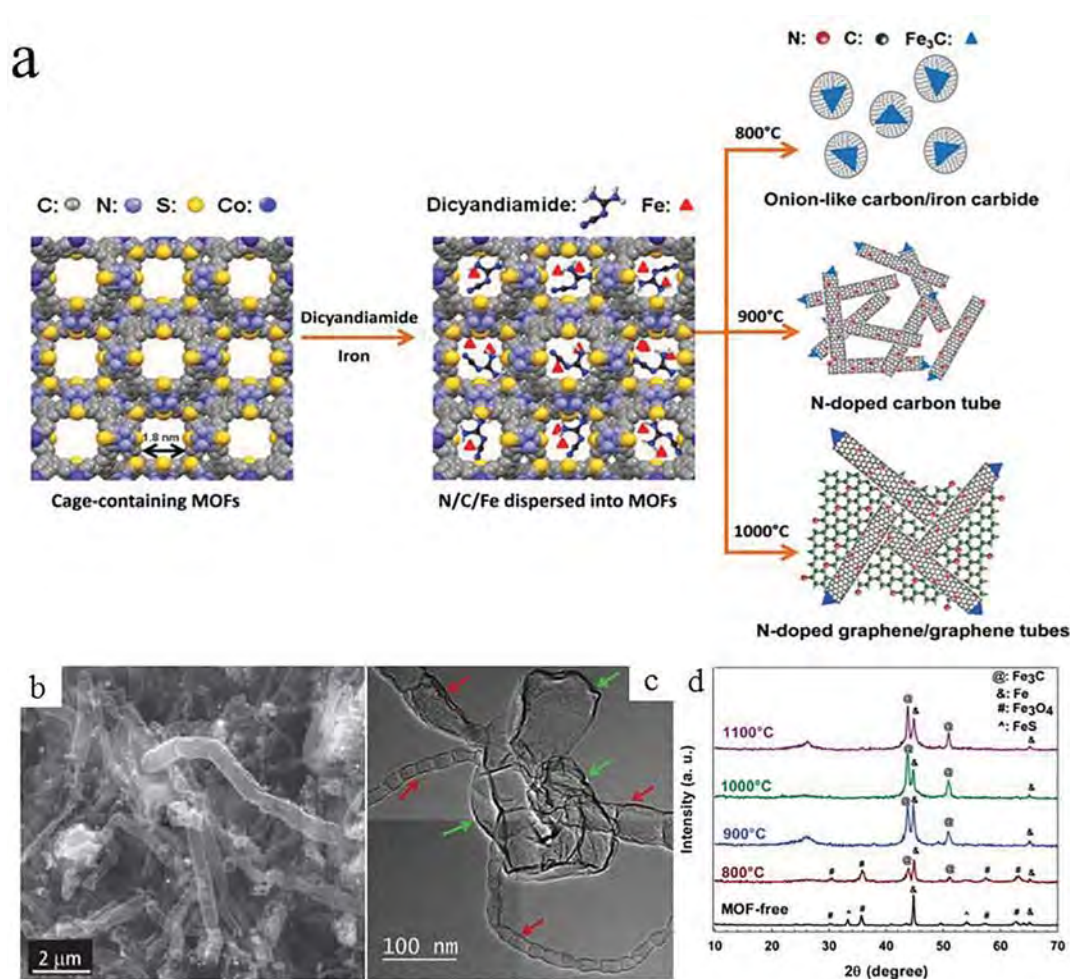


Fig. 10. (a) schematic illustration of formation of the carbon nanostructures found in the N-Fe-MOF catalysts synthesized at different heating temperatures; (b) SEM and (c) representative TEM images of the N-Fe-MOF catalyst prepared at 1000 °C with dominant graphene (green arrows) and graphenetube (red arrows) nanostructures; (d) X-Ray Diffraction (XRD) patterns of the MOF-free N-Fe and the N-Fe-MOF catalysts as a function of heating temperature. Reprinted with permission from Ref. [168] Copyright 2014 WILEY-VCH.

introduced guests was used for synthesizing N-Fe-MOF catalysts by a high-temperature route (Fig. 10a–c) [168]. In this study, the morphologies and properties of prepared samples greatly relied on the heating temperature. When heated at 800 °C, graphitized carbon structures together with Fe_3O_4 , residual Fe, and Fe_3C crystallites were yielded (Fig. 10d). As the temperature increased to 900 °C, carbon nanotube structures with visible metal particles at the end appeared due to the release of large amounts of carbon nitride gases (e.g. C_2N_2^+ , C_3N_2^+ , C_3N_3^+) generated from decomposed N-containing polymer evolved from DCDA. During treated at 1000 °C, the graphene/graphene tube-like nanocomposites became dominant because of the direct graphitization of DCDA and catalytic unzipping of *in situ* generated graphene tubes. However, further elevating the heating temperature to 1100 °C resulted in unevenness morphology along with numerous agglomerated particles.

Likely, in Pan's research, the active site K^+ was *in situ* introduced into the channels of bio-MOF-1 precursors through an ion-exchange strategy to prepare N-doped hierarchical porous carbons [169]. Bio-MOF-1 possesses a rigid anionic skeleton with Me_2NH_2^+ cations as counter ions in the pores, which could be easily exchanged with K^+ . During the carbonization process, the K^+ exchanged into the bio-MOF-1 scaffolds exerted an great influence in the porosity development, where carbon scaffold was removed by potassium carbonate, and then the formed K_2CO_3 decomposed into K_2O and CO_2 , which was closely related to the generation of

additional microporosity. The KBM-700 derived from K@bio-MOF-1 showed the highest pore volume ($0.55 \text{ cm}^3 \text{ g}^{-1}$) and specific surface area ($1129 \text{ m}^2 \text{ g}^{-1}$), nearly two-fold larger than that of the bio-MOF-1-derived BM-700 ($0.50 \text{ cm}^3 \text{ g}^{-1}$, $682 \text{ m}^2 \text{ g}^{-1}$, respectively). These results suggested the good distribution of K^+ in the bio-MOF-1 framework led to homogeneous and effective chemical activation without any additional activating agent.

These methods associated with the pre-synthetic modulation abovementioned are not completely independent. In some cases, they can be utilized simultaneously to dramatically enhance the performance of materials. For example, Koo and co-workers constructed Pd@ZnO- WO_3 nanofibers (NFs) by electrospinning and then by calcination in air for toluene sensing (Fig. 11), where ZIF-8-derived Pd-loaded ZnO nanocubes were functionalized on the inside and outside of the WO_3 NFs [170]. At first, Pd nanoparticles encapsulated in ZIF-8 cavities to construct metal@MOF templates, and then the as-prepared Pd@ZIF-8 particles were directly employed to decorate the ammonium metatungstate hydrate/polyvinylpyrrolidone composite nanofibers (AMH/PVP NFs). At last, the final product was acquired by calcination of Pd@ZIF-8/AMH/PVP composite NFs at 500 °C under air flow for 1 h. The well-distributed Pd and Zn in the Pd@ZnO- WO_3 NFs resulted in homogeneous sensitization both internal and external of the WO_3 matrix. Moreover, the formed mesopores within the WO_3 scaffold were on account of the burning-out of the organic ligands in MOFs. Multi-heterojunctions were created within the one

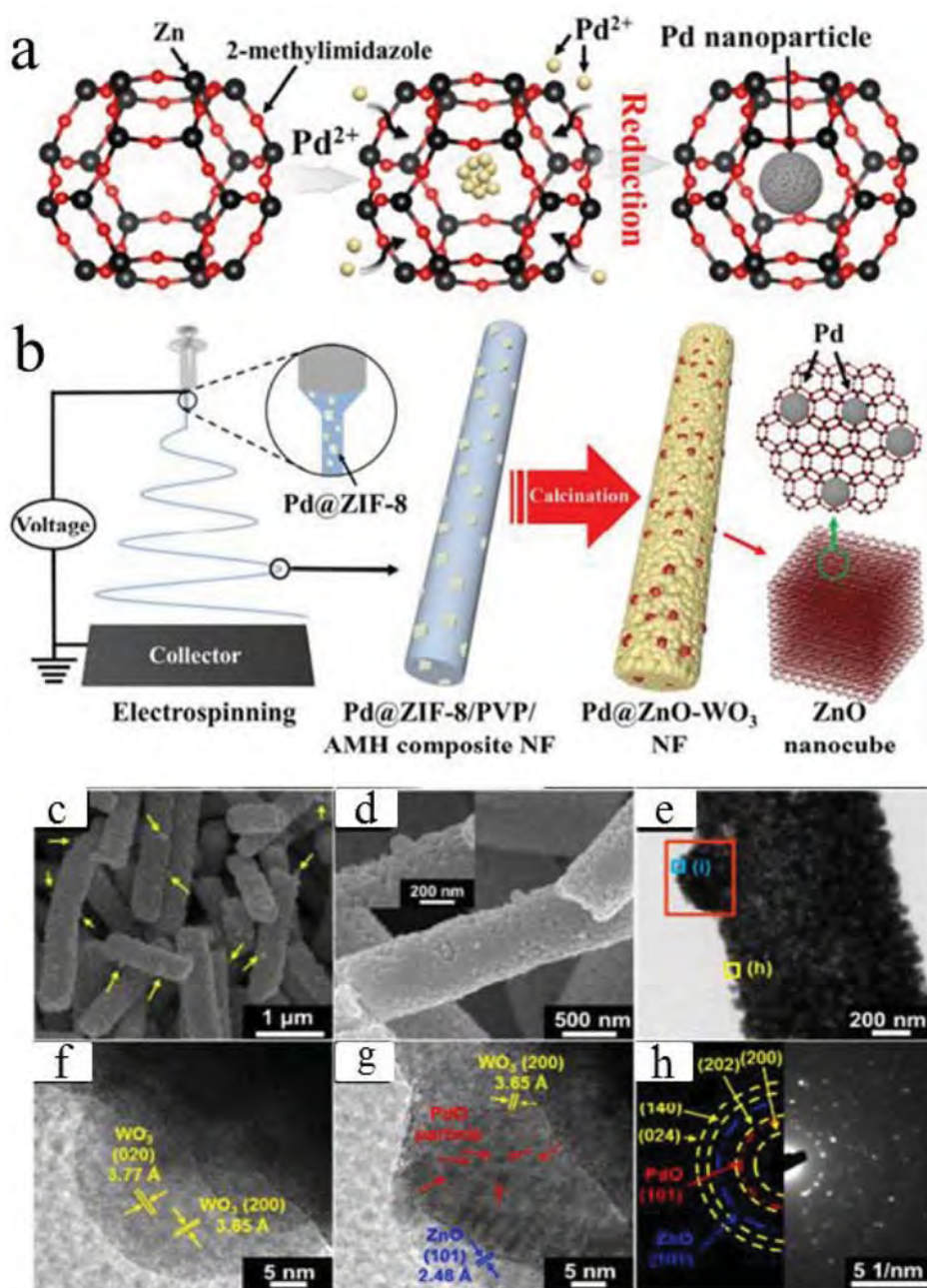


Fig. 11. Schematic illustration of (a) Pd NP encapsulation in the cavity of ZIF-8 and (b) synthetic process for the Pd@ZnO-WO₃ NFs; (c, d) SEM images of Pd@ZnO-WO₃ NFs (inset: magnified image of surface); (e) TEM image of Pd@ZnO-WO₃ NF; (f, g) HRTEM images of Pd@ZnO-WO₃ NF, and (h) SAED pattern of Pd@ZnO-WO₃ NFs. Reprinted with permission from Ref. [170] Copyright 2016 American Chemical Society.

dimensional composite NFs by the formation of ZnO-WO₃ and Pd-ZnO interfaces. Liu et al. fabricated a unique Fe@N-doped graphene-like carbon by using g-C₃N₄ and NH₂-MIL-53(Fe) as the precursors for 4-aminobenzoic acid ethyl ether and sulfamethoxazole (SMX) removal [171]. The g-C₃N₄ and NH₂ groups as N source not only endowed the obtained samples with the stability of framework morphology and phase composition but the remarkable improvement of PMS activation performance. Besides, the addition of g-C₃N₄ also increased the surface area.

3.4. Post-synthetic treatment

Post-synthetic treatment is a wonderful strategy to modify derivatives of MOFs with diverse functionalities, in which the

MOFs after pyrolysis could form favorable nanocomposites through integrating with other advance nanomaterials. Selecting different active atoms or compounds to combine with MOF-derived materials for on demand seems to be more conducive to the target reaction. Typically, hierarchical porous carbon nanoplates (HPCN) were prepared by a one-step calcination method of MOF-5, and then the obtained HPCN further encapsulated by active sulfur to prepare HPCN-S composite [172]. HPCN with outstanding conductivity, large surface area and well-distributed pore-size was proved to immobilize sulfur by capillary force of its pores and as an impressive candidate to improve the sulfur utilization. The HPCN-S composite with well-defined 3D porous plate nanostructure exhibited enhanced electrochemical performance and excellent cycling stability.

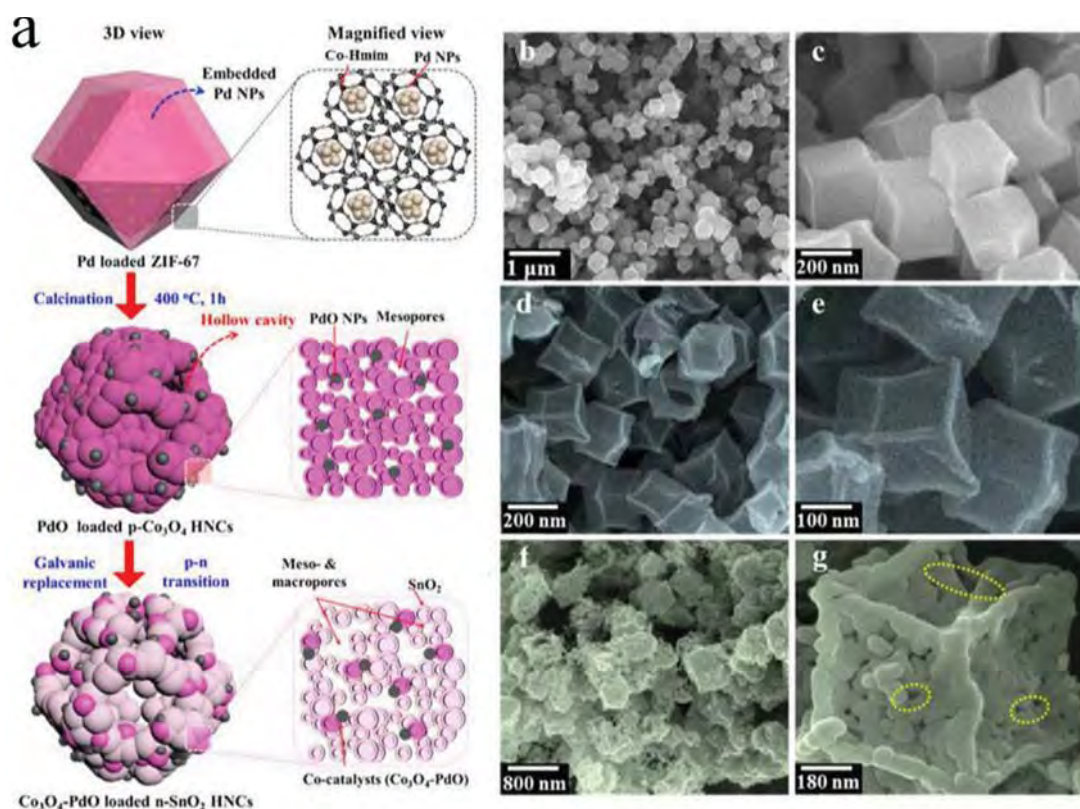


Fig. 12. Schematic illustration of synthetic process for the n-SnO₂ HNCs functionalized with Co₃O₄ and PdO. (b) SEM images of Pd NPs encapsulated ZIF-67. (c) magnified SEM images of Pd encapsulated ZIF-67. (d, e) SEM images of PdO loaded p-Co₃O₄ HNCs. (f, g) SEM images of Co₃O₄-PdO loaded n-SnO₂ HNCs. Reprinted with permission from Ref. [177] Copyright 2017 American Chemical Society.

More recently, hollow tubular-like carbon-coated metal sulfide (C-Cu_{2-x}S) by using a copper-based MOF as precursor was designed through sulfidation and calcination. Subsequently, C-Cu_{2-x}S mixed with graphitic carbon nitride (g-C₃N₄) upon heating to form a novel three-component heterojunction (C-Cu_{2-x}S@g-C₃N₄) [173]. As we know, g-C₃N₄ has the fast recombination rate of photogenerated electron-hole pairs and limited visible light adsorption [174–176]. Such features restrict its further development and wide application. The combination of Cu₂S and carbon layers with strong synergy showed satisfactory light-absorbing property and effective charge separation, facilitating the photocatalytic activity.

Jang et al. first introduced a method to prepare n-SnO₂ nanocubes (HNCs) with hollow polyhedron through combining MOF-templated route with galvanic replacement reaction (GRR) (Fig. 12) [177]. During this process, n-SnO₂ HNCs were yielded from p-n transition of ZIF-67-derived p-type Co₃O₄ (p-Co₃O₄) hollow cubes. In detail, Pd NPs were embedded in ZIF-67 network and then the formed MOF@Pd was calcined for 1 h under 400 °C to acquire PdO loaded Co₃O₄ HNCs. For the GRR procedure, Sn²⁺ ions were induced into the mesoporous of PdO loaded Co₃O₄ HNCs, where the Co₃O₄ surface was dissolved into solution and Sn²⁺ ions were transformed into SnO₂ by the precipitation, leading to the formation of Co₃O₄-PdO loaded n-SnO₂ HNCs. The successful functionalization of n-SnO₂ HNCs by co-catalysts (PdO NPs and discrete Co₃O₄ islands) showed enhanced acetone sensing compared with the general ZIF-67 templated p-Co₃O₄ hollow structures.

Obviously, many monomers or complexes can be utilized to form hybrids with MOF-derived produce in a variety of ways, such as impregnation of guest into framework cavity, load with support and so on. Integrating calcinated products with other substances

can improve their dispersity and stability as well as inhibit the leaching of toxic metal ions to some extent. Within such kind of composites, each component with special function possesses enhanced performance compared to individual counterparts, which can greatly improve the reaction activity. It is worthy of expecting that more functional nanomaterials can be synthesized and designed for on demand by using calcinated MOFs as one of the component units, which could afford great opportunity to construct fascinating hybrid structures with unique characteristics and ideal functions for environmental field. However, note that much more endeavor should be paid to simplify the post-methods procedures, minimize the damage to the structures of MOF derivatives, and adopt eco-friendly approaches.

4. Environmental applications of MOF-derived nanomaterials

With the rapid development of urbanization and industrialization, the earth is suffering unprecedented destruction. Global warming, resources depletion, and species loss are the grave warnings to mankind by our planet, which has become a high priority global concern. Protecting the environment has been regarded as an greatly urgent and important task for each of us. MOF-derived nanomaterials with numerous advantages have been applied in many areas successfully such as supercapacitor [178], lithium-ion battery [179], drug delivery [180], etc. Nowadays, these hybrids as excellent function materials show amazing potential in environment-related fields. The use of these materials for environmental remediation and contaminant detection is an exciting progress, as evidenced by a growing body of researches. In this section, MOF-derived nanomaterials for wastewater treatment, air purification, and target pollutant sensing are discussed emphatically.

Table 1
Summary of MOF-derived nanomaterials for adsorption.

MOF precursors	MOF-derived nanomaterials	Adsorption capacity	Reusability	Remarks	Ref.
MOF-5	HPC-950	310 mg g ⁻¹ for <i>p</i> -nitrophenol	The adsorbed amount of <i>p</i> -nitrophenol diminished slightly from 310 to 260 mg g ⁻¹ after five cycles.	The distinctive characteristics with hierarchical pores and partially graphitization enhanced the adsorption ability.	[108]
MOF-5	ZnO@C	Nearly 100% adsorption for RhB	Almost 80% after seven cycles, while nearly 20% in eighth cycle.	The high adsorption was attributed to the π - π interactions.	[120]
ZIF-8	IHNPC	455.95 mg g ⁻¹ for 17 β -estradiol	The adsorption capacity decreased only about 12% after the 5th cycle.	The high adsorption was attributed to the hierarchical porous structures, ample vacant sites and low internal diffusion resistance for adsorption.	[124]
MAF-6	CDM6-K1000	408 mg g ⁻¹ for ibuprofen and 503 mg g ⁻¹ for diclofenac sodium	There was negligible decrease after five cycles for ibuprofen adsorption.	The main adsorption mechanism for ibuprofen was the van der Waals interaction.	[164]
Bio-MOF-1	BMDC-12 h	552 mg g ⁻¹ for ATNL and 540 mg g ⁻¹ for CLFA	The ATNL removal did not decrease appreciably after four cycles.	The main adsorption mechanism for ATNL was electrostatic interaction and for CLFA was H-bonding.	[190]
ZIF-8	MDC-1000	435 mg g ⁻¹ for SMX	The adsorption capacity slightly decreased after four cycles.	The main adsorption mechanism was H-bonding.	[191]
ZIF-8	Carbon-ZD	1148.2 mg g ⁻¹ for MB	The MB degradation rate still reached 99% after five cycles.	The high adsorption was endorsed by cooperative effects of the large BET surface area, well-distributed pore widths and N-doping.	[192]
MIL-53	Porous P-Al ₂ O ₃	316.87 mg g ⁻¹ for U(VI) and 223.37 mg g ⁻¹ for Eu(III)	–	The higher adsorption capacity for U(VI) and Eu(III) were attributed to the existence of many hydroxy groups.	[193]
UiO-66	ZrSulf	824 mg g ⁻¹ for Hg(II)	The adsorption amounts had no obvious change after five runs.	The main adsorption mechanisms were ion exchange (at pH < 3.0), coordination of Hg(II) with sulfur-containing groups (at 3.0 < pH < 9.0), and precipitation (at pH greater than 9.0).	[105]
Ni-MOF	NiOx/ Ni@C400	454.94 mg g ⁻¹ for As(V)	The adsorption capacity decreased from 115 to 80 mg g ⁻¹ after five cycles.	The main adsorption mechanisms were electrostatic interaction and surface complexation (As-O bond).	[194]
MIL-53(Fe)	Carbon- α Fe/ Fe ₃ C 910	511.06 mg g ⁻¹ for TC	The adsorption capacity slightly decreased after five cycles.	The main adsorption mechanisms were pore filling effect and electrostatic adsorption.	[195]

4.1. MOF-derived nanomaterials for wastewater treatment

4.1.1. Adsorption

Enormous efforts have been devoted to removing environmental pollutants from water, and various technologies used for controlling wastewater pollution have emerged, such as chemical oxidation, coagulation-flocculation, membrane technology, and adsorption [181–183]. Among them, adsorption method is a priority option owing to a comprehensive consideration of operational feasibility, cost rationalization, procedures simplification, and removal efficiency. MOF-derived nanomaterials as a new type adsorbent are advantageous in this process. Furthermore, scalable fabrication provides more possibilities for the industrial-level production. Some representative MOF-derived adsorbents and their corresponding performance are listed in Table 1.

Noticeably, understanding the adsorption mechanism is important not only for knowing the basics of adsorption but also for improvement of the adsorption technology and further development for commercialization. For physical adsorption, van der Waals interaction usually regarded as primary mechanism when there are no specific adsorption sites to form any chemical interaction between adsorbate and adsorbent [184]. In general, the porosity and surface area of the adsorbents commonly affect the adsorption capacity by van der Waals interaction. With respect to chemical adsorption, the effect of solution pH on the adsorption is often employed to comprehend the probable adsorption mechanisms, as pH has a profound influence on the status of adsorbent and adsorbate [185]. Electrostatic interaction has been frequently utilized to elucidate the adsorption of organics/aromatics from water, which is greatly related to the dissociation constants of adsorbate and the zero-potential point of adsorbent [186]. The presence of various functional groups on adsorbent or adsorbate is very important for H-bonding. The direction of the H-bond

(H-donor and H-acceptor) can be determined via investigating the effect of solution pH on the adsorption. Typically, the H atoms in the ample acidic groups especially carboxylic and phenolic groups on adsorbent can serve as H-donors to promote the targets adsorption through H-bonding with the O-atoms or N-atoms [187]. π - π interaction as another vital mechanism for adsorption occurs between the aromatic ring of aromatic compounds and the graphitic layer of carbons [188]. Hydrophobic interaction should be considered when adsorbent and adsorbate both are hydrophobic. Besides, the surface complexation is significant for the adsorption process of metal ions, during which the presence of numerous functional groups in adsorbent can effectively bind with metal cations to form surface complexes [189]. Actually, these interactions usually take place synergistically. In short, exploring the adsorption mechanism is essential to improve the adsorptive performance.

Carbonaceous nanomaterials derived from MOFs are widely used as adsorbents because of their high porosity, adjustable pore volume, large surface area, uniformed pore size distribution and heteroatomic doping. For example, a highly porous carbon derived from bio-MOF-1 was applied in the adsorptive process for removing four pharmaceuticals and pharmaceutical and personal care products (PPCPs) [190]. The maximum adsorption ability for acidic clofibric acid (CLFA; 540 mg g⁻¹) and basic atenolol (ATNL; 552 mg g⁻¹) over BMDC-12 h were almost 2 and 10 times those of the commercial AC, making it superior to most reported adsorbents. ATNL adsorption can be explained by electrostatic interaction, and CLAF adsorption is dominated by H-bonding, in which CLAF and porous carbon serve as H-acceptor and H-donor, respectively. Similarly, ZIF-8-derived carbonaceous materials (MDC-1000) reported by Ahmed et al. exhibited incredible BET surface area (1964 m² g⁻¹) and pore volume (1.32 cm³ g⁻¹), which were much better than that of parent MOF and AC [191]. The maximum

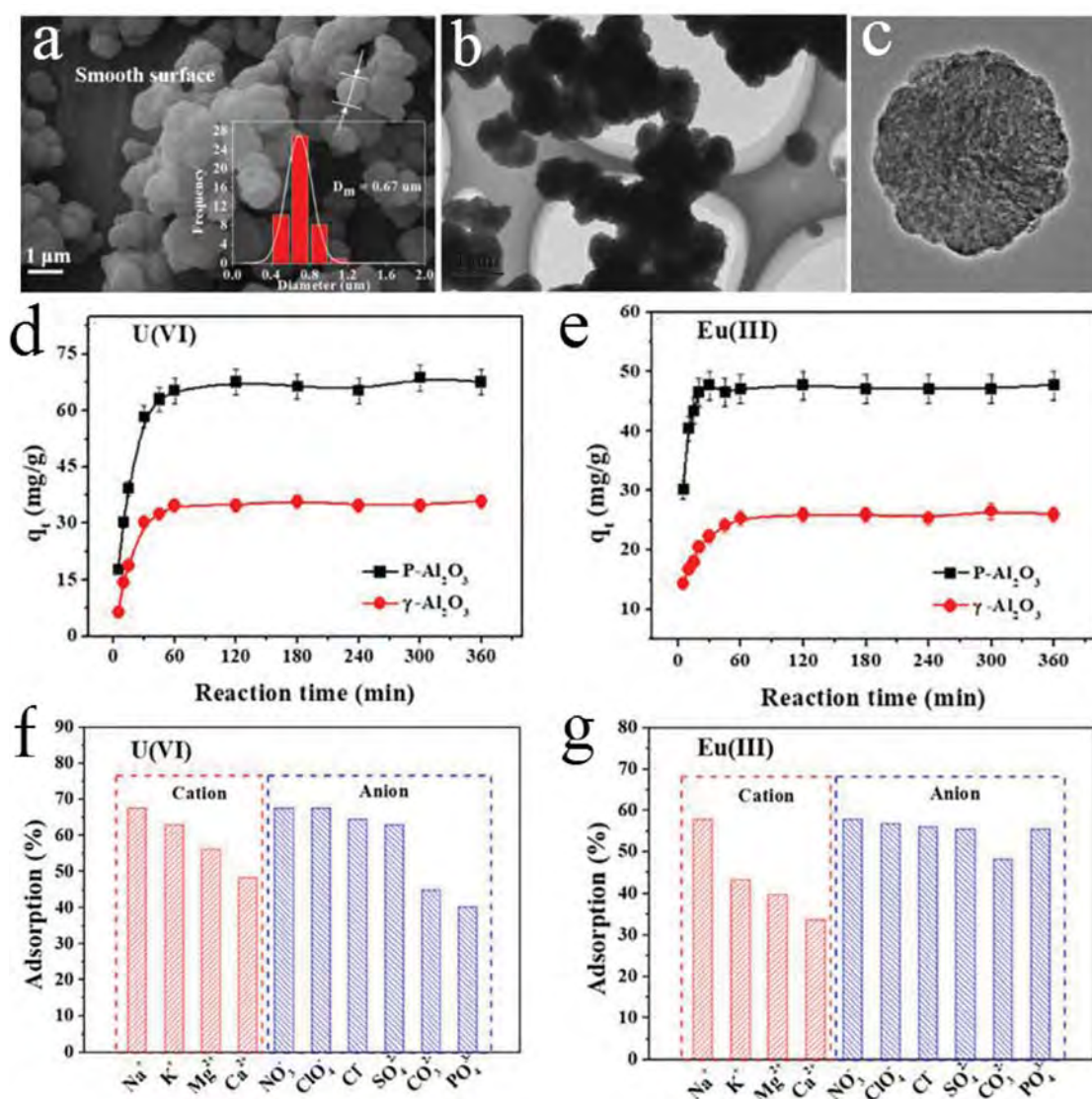


Fig. 13. (a) SEM images of P-Al₂O₃ (inset: the corresponding particle size distributions); (b) low magnification and (c) high magnification TEM images of P-Al₂O₃; adsorption kinetic curves of (d) U(VI) and (e) Eu(III) on γ -Al₂O₃ and P-Al₂O₃; effect of different cations and anions on the adsorption of (f) U(VI) and (g) Eu(III). (reaction conditions: T = 298 K; m/V = 0.1 g·L⁻¹; I = 0.01 M NaNO₃; pH = 5.0 for U(VI) and pH = 6.0 for Eu(III); C[U(VI)]_{initial} = 10.0 mg·L⁻¹; and C[Eu(III)]_{initial} = 10.0 mg·L⁻¹; the ionic strength is 0.01 M). Reprinted with permission from Ref. [193] Copyright 2018 Elsevier.

adsorption capacities of MDC-1000 for SMX were 435 mg g⁻¹, almost 20-fold higher than that of original MOF and 4-fold higher than that of AC. H-bonding can be adopted to reveal the adsorption mechanism based on the effect of the solution pH and the zeta potential of MDC.

In addition, pyrolysis of MOFs with additional carbon sources can extremely enhance the adsorption ability due to the increased specific surface area and optimal porous structure. As a typical example, Xu et al. synthesized three MOF-derived N-doped porous carbons for MB adsorption by carbonized ZIF-8 (carbon-Z), ZIF/sucrose (carbon-ZS) and ZIF/dicyandiamide (carbon-ZD), respectively [192]. Carbon-ZD not only possessed an incredible BET specific surface area of 1796.5 m² g⁻¹ but also a micro/mesoporous structures, while other two materials only contained the microporous. In this process, micropore was advantageous for MB molecules adsorption and mesopore was conducive to MB diffusion and adsorption. Owing to high electronegativity of nitrogen, the N-doped carbon-ZD enabled the surface charge of carbon matrix redistributed, which extremely promoted the surface affinity for MB pollutant.

As a result, carbon-ZD showed the best adsorption capacity of as high as 1148.2 mg g⁻¹, by comparison of carbon-Z (505.3 mg g⁻¹) and carbon-ZS (791.3 mg g⁻¹).

In contrast to carbons, the examples of pure metal compounds as adsorbents came from MOFs were relatively less owing to their limitations such as inevitable aggregation and low activity after reuse. A novel porous Al₂O₃ microsphere (P-Al₂O₃ MSs) was applied to immobilize radionuclides (U(VI) and Eu(III)) from wastewater, which showed ultrafast and high adsorption in this process and performed much better than the commercial γ -Al₂O₃ nanomaterials [193]. As shown in Fig. 13a–c, P-Al₂O₃ displayed a smooth surface and the hierarchical structures with high surface homogeneity. The optimal adsorption capacity of P-Al₂O₃ MSs reached 316.87 mg g⁻¹ and 223.37 mg g⁻¹ for U(VI) and Eu(III) within 25 min, respectively (Fig. 13d and e). The rapidly adsorption could be benefited from the porous characteristics of P-Al₂O₃ and thus resulted in the easy collision between binding sites with target ions. The coexisting cation ions exhibited an obvious decrease to Eu(III)/ U(VI) adsorption capacity, while a slight influence

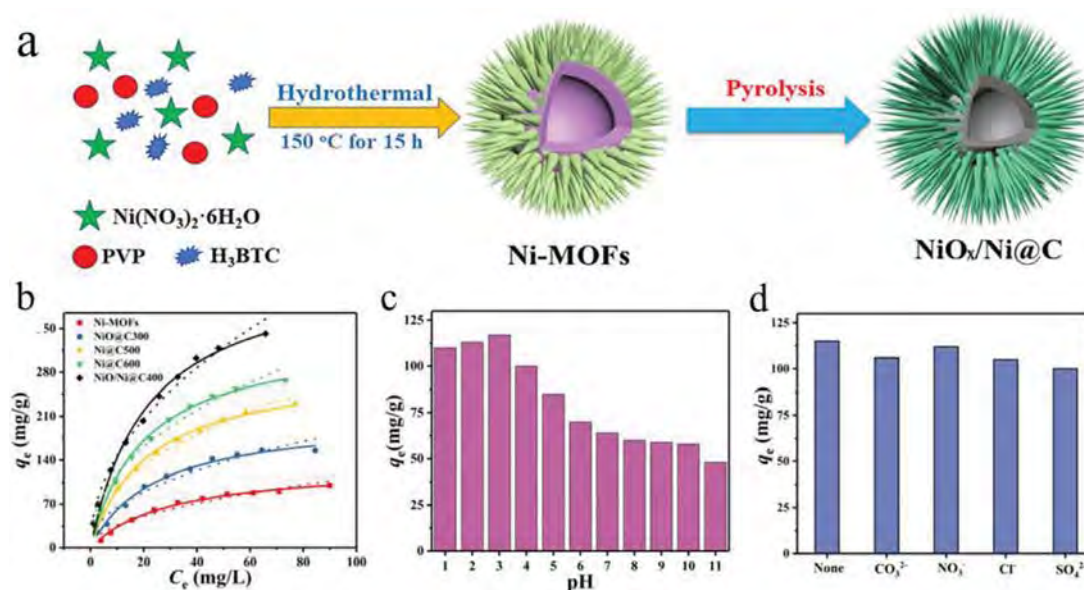


Fig. 14. (a) Schematic illustration of the synthesis of Ni-MOFs and NiO_x/Ni@C; (b) adsorption isotherms of Ni-MOFs, NiO/C300, NiO/Ni@C400, Ni/C500 and Ni/C600 for As(V) removal; (c) pH effect on As(V) adsorption; (d) coexisting anion effects on As(V) adsorption (reaction conditions: pH = 3.0 ± 0.1, m/V = 0.15 g L⁻¹, C[As(V)] = 20 mg L⁻¹, anions concentration = 0.5 g L⁻¹, T = 298 K). Reprinted with permission from Ref. [194] Copyright 2019 Elsevier.

indicated by anions ions except CO_3^{2-} and PO_4^{3-} , which could generate complexes with UO_2^{2+} and Eu^{3+} in many water body (Fig. 13f and g). The numerous hydroxy groups were found to play a vital role for the capture of radionuclides to P-Al₂O₃ because these functional groups were capable of binding target ions and forming surface complexes. Li et al. reported porous ZrSulf for the adsorptive removal of Hg(II) and its uptake capacity reached 824 mg g⁻¹, because of the accessibility of sulfur-based functionality and the formation of covalent bond with sulfur-based functionality combined with Na by ion exchange, making it superior to majority of other reported porous adsorbents [105].

Combined solid particles with carbon materials can attain the enhanced advantages than individuals and effectively overcome the aggregation of nanoparticles. Lv et al. reported a hollow sphere NiO_x/Ni@C400 composite with chestnut shell-like structure by Ni-MOF-template method (Fig. 14a), which showed excellent adsorption amount to As(V) (454.94 mg g⁻¹), higher than that of parent Ni-MOF (133.93 mg g⁻¹) and other obtained samples at different pyrolysis temperature (Fig. 14b) [194]. The favorable adsorption ability could be attributed to the high specific surface area as well as the abundant oxygen-containing functional groups of resulting adsorbents. Two aspects involved in surface complexation (As-O bond) and electrostatic interaction were confirmed as the main adsorption mechanism. The as-synthesized samples not only exhibited a good applicability in a wide pH range from 1 to 10 and hardly were affected when coexisting with other anions (Fig. 14c and d), but also a good separating ability due to the high magnetization intensity. Furthermore, Xiong et al. prepared magnetic carbon- $\alpha\text{Fe}/\text{Fe}_3\text{C}$ 910 and used it for tetracycline (TC) adsorption [195]. The obtained samples showed increased BET surface area (171.715 m² g⁻¹), pore volume (0.312 cm³ g⁻¹) and mesoporous volume (0.260 cm³ g⁻¹) than original Zn-MIL-53(Fe) (46.990 m² g⁻¹, 0.105 cm³ g⁻¹ and 0.086 cm³ g⁻¹, respectively). These improved physical properties provided more active adsorption sites and weakened the steric hindrance effect, thus facilitating the adsorption process. Pore filling effect controlled the physical adsorption due to the homogeneous pore size distribution, while electrostatic interaction induced by the change of pH value played a dominant part in chemical adsorption.

A number of adsorption mechanisms such as acid-base, electrostatic, hydrophobic, H-bonding and π - π interaction can be adopted to explain the uptake process where H-bond interaction is suggested as the primary reason for the high adsorption [196–198]. Based on the above discussion, those derivatives with unique structures require special attention. Besides, the adsorptive efficiency was mainly dependence on the heteroatom doping (e.g. N and/or O species) and the surface properties (e.g. BET area, pore volume and porosity) of adsorbents on the basis of large studies [199,200], which may be regulated by adding external template or activating agent. However, the effect of heteroatoms was not distinctly verified, more deep studies are need for the understand of adsorption mechanism. Large surface area and pore volume can facilitate material transfer and provide more exposure of active adsorption sites, thus enhancing the capture capacity. The pore size has an important effect on adsorption ability, which partly depends on the species of target pollutants. For example, micropore is beneficial to the MB adsorption, while mesopore is advantageous to TC capture [195,201]. However, the control method of pore size is still unclear. Notably, the micropore-dominated porous structure has an intrinsic drawback of limited diffusion [202]. In short, developing nanomaterials with admirable functionalities using MOFs as precursors could provide an effective pathway to increase their adsorption competitiveness in both academic research and industrial application.

4.1.2. Catalytic degradation

Recently, MOF-derived nanomaterials have been employed as great catalysts towards versatile catalytic process for contaminants elimination. The large surface area of MOF derivatives provides more exposure possibilities of active sites. The tunable pore size and retained morphology contribute to optimize the catalytic performance. Such advantages of MOF-derived hybrids can promote the catalytic efficiency dramatically and make them as highly attractive candidates for environmental catalytic reactions. In general, photocatalysis, Fenton-like catalysis and PS/PMS activation are studied extensively, thus the following description mainly develop around these catalytic processes. Table 2 summarizes some representative works in catalysis.

Table 2
Summary of MOF-derived nanomaterials for catalysis.

MOF precursors	MOF-derived nanomaterials	Application	Performance	Reusability	Ref.
ZIF-8	C-doped ZnO	Photocatalytic degradation for MB	Almost complete removal for MB within 90 min	There was no obvious deactivation after five degradation cycles.	[209]
MIL53/ MIL125	ZnO nanosheets	Photocatalytic degradation for MO	98.15% degradation by MIL53-ZnO ⁴⁰⁰ and 96.89% degradation by MIL125-ZnO ⁴⁰⁰ for MO in 60 min	There was no significant changes of all samples in the photocatalytic activity after five cycles.	[210]
Co/Fe-MOF	CoP/Fe ₂ P@mC	Photocatalytic degradation for RhB	97% degradation efficiency for RhB in 150 min	94% RhB was photodegraded after five cycle.	[211]
MIL-68(In)	ClInS-2	Photocatalytic degradation for TC	Almost 100% degradation for TC within 120 min	Less degradation efficiency decrease was observed after three cycles.	[213]
MIL-101(Fe)	Fe ₃ O ₄ /C	Fenton-like degradation for MB	Almost 100% degradation for MB within 60 min	97% removal efficiency was achieved for MB after ten cycles.	[221]
[Cu/Fe]-BTC	CuFe ₂ O ₄ /Cu@C	Fenton-like degradation for MB	Almost 100% degradation for MB within 15 min	Original activity was retained after ten cycles.	[223]
PB	Fe ₂ O ₃ @SnO ₂	Photo-Fenton degradation for RhB	99.7% degradation efficiency for RhB in 60 min	No obvious loss of RhB degradation was presented in three runs.	[224]
MIL-100(Fe)	CMIL-100@PCM	Electro-Fenton degradation for napropamide	82.3% degradation efficiency for napropamide in 60 min	A slight decrease of the napropamide degradation efficiency was observed after three cycles.	[225]
Fe _y Co _{1-y} -Co PBA	Fe _{0.8} Co _{0.2} O ₄	PMS degradation for BPA	95% BPA degradation efficiency within 60 min	Slight loss of the catalytic activity was observed in four cycles.	[232]
PB	Co ₃ O ₄ @Fe ₂ O ₃	PMS degradation for NOR	Almost 100% degradation for NOR within 45 min	There was no significant deterioration in the four cycles.	[233]
ZIF-67	CoN/N-C@SiO ₂	PMS degradation for TC	95% TC degradation efficiency within 30 min	The degradation efficiency of TC was reduced to 80% in 72 min.	[235]
MIL-100(Fe)	Nitrogen-doped graphene	PMS degradation for phenol	Almost 100% phenol removal within 30 min	Nearly 100% and 61% phenol removals were reached within 120 and 180 min in the second and third cycles.	[237]
Zn/Co-ZIF	NDHC	PMS degradation for BPA	98% of BPA removal efficiency in 5 min	Only 35% of BPA can be degraded in the second run.	[167]

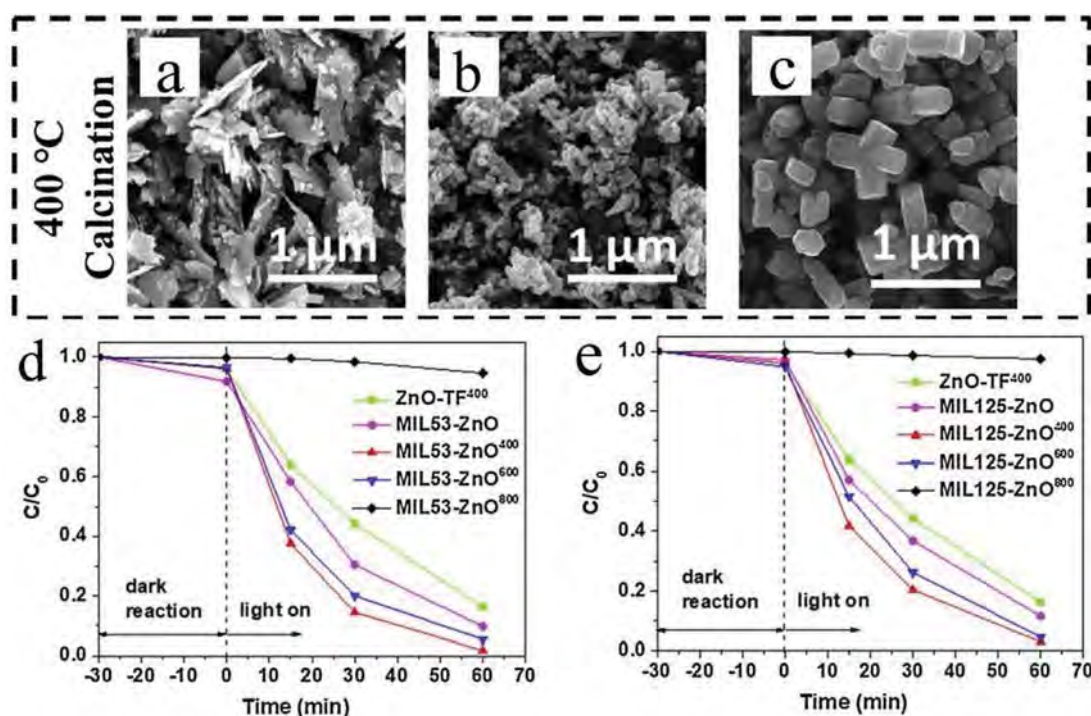


Fig. 15. SEM images of (a) MIL125-ZnO⁴⁰⁰, (b) MIL53-ZnO⁴⁰⁰ and (c) ZnO-TF⁴⁰⁰; photocatalytic degradation curves of MO on ZnO using (d) MIL-53(Al) and (e) MIL-125(Ti). Reprinted with permission from Ref. [210] Copyright 2019 Elsevier.

In recent years, MOF-derived nanocomposites as emerging heterogeneous catalysts show promising performance in photocatalysis. These hybrids possess great competitive strength no matter in composition or structure compare to traditional photocatalysts. Specifically, MOF with diverse metal center can be

directly converted into semiconductors such as metal oxide and metal sulfides. In addition, the doped heteroatom of derivatives can be obtained from organic linkers with no need for extra additions. With respect to their structure, ultrahigh porosity and distinctive monophony accelerate the contact between reactant and

charge carriers, thereby effectively restricting the recombination of photoinduced electron-hole pairs. Under UV/visible light irradiation, excitons e^-_{CB}/h^+_{VB} are formed by the absorbed photons in conduction band (CB) and valence band (VB) of photocatalysts respectively. In the case of thermodynamics, the photo-generated electrons could effectively reduce oxygen molecules into $\cdot O_2^-$ and the holes left in VB can react with H_2O or OH^- to generate $\cdot OH$. On the other hand, the holes, with strong oxidative capacity, can directly induced the photo-oxidation of target contaminants [203]. These highly active species play an important role in the photocatalytic degradation process. A large number of researches have proved that improving the optical and electronic characteristics of photocatalysts such as enhancing the light harvest ability, prolonging the lifetime of the separated e^-/h^+ pairs, and facilitating the transfer of charge carriers are of great significance for the photocatalytic process [204–207].

ZnO particles or clusters are suggested as the suitable photocatalysts due to their high electron mobility and thermal stability [208]. Considering that, Liang et al. synthesized carbon and nitrogen co-doped ZnO from ZIF-8 for MB degradation under solar-simulated light [209]. The obtained sample achieved almost complete removal of target pollutant within 90 min, better than commercial ZnO. The optimization could be attributed to their well-crystalline and proper contents of carbon/nitrogen dopants. Besides, the oxygen vacancy also played a positive role in the photooxidation process *via* inhibiting the recombination of electrons and holes. Xiao et al. used Zn-free MOF like MIL-53(Al) or MIL-125(Ti) to prepare ZnO nanosheets for MO photodegradation [210]. After calcination at 400 °C, MIL125-ZnO⁴⁰⁰ exhibited a nanoplate or flaky structure with a little amount of ultrafine nanosheets. Differently, MIL53-ZnO⁴⁰⁰ showed the same shape but with much more ultrafine nanosheets (Fig. 15a and b). While ZnO-TF⁴⁰⁰ (prepared without addition of any MOFs) presented the six square prism morphology (Fig. 15c). These Zn-free MOF not only served as a sacrificial template but also as a provider of doping metal atom. The resultant ZnO showed low content of Al or Ti < 2%, and their properties were significantly different depending on the type of MOF precursor, which affected the morphology, the specific surface area, the pore characteristics and the oxygen defects of as prepared ZnO. The MIL53-ZnO⁴⁰⁰ and MIL125-ZnO⁴⁰⁰ showed a better photocatalytic activity with removal rate of 98.15% and 96.89% than ZnO-TF⁴⁰⁰ (83.10%) prepared without MOF as well as a higher rate constant within 60 min irradiation (Fig. 15d and e). Such a method opens a new route of broad scope for the synthesis of metal oxides by MOF-template.

Based on the better properties of multiple components heterojunction materials, a visible-light-active CoP/Fe₂P@mC was prepared and utilized for RhB degradation [211]. The nanocomposite with suitable bandgap structure showed enhanced visible light harvesting ability. In this process, the CoP/Fe₂P@mC catalyst displayed 97% degradation efficiency for dye molecular, much higher than that of Co/Fe-MOF (9%), CoO_x/FeO_x@mC (4%), CoP@mC (49%), and Fe₂P@mC (17%) nanocomposites. CoP/Fe₂P@mC with the highest photodegradation ability exerted powerful synergistic effect for RhB destruction through combining the rapid electron transfer of CoP@mC, effective electron-hole separation of Fe₂P@mC, and the excellent adsorption ability of mesoporous carbon. Moreover, the TOC removal rate of RhB achieved around 67.4% by CoP/Fe₂P@mC. The catalyst dosages increased from 50 mg L⁻¹ to 200 mg L⁻¹ not only can promote the degradation rate, but also increase the reactive sites and photocurrent responses [212]. Likely, a novel tube 0.3%-MWCNT@MIL-68(In)-derived ClnS-2 achieved the highest photocatalytic activity (100%) for TC degradation driven by visible light within 120 min, much higher than that of the pure hollow In₂S₃ derived from MOF (61.7%) and conventional In₂S₃ bulk (47.1%), demonstrating the dramatic enhancement of photodegra-

degradation kinetics by introduction of MWCNT [213]. MWCNTs as electron acceptor and In₂S₃ hollow tube as active center could promote the separation of electron-hole pairs and shorten the transfer distance of charge carriers, respectively, which resulted in the boosted degradation efficiency of TC under visible light.

To sum up, research on photocatalytic degradation of organic pollutants is springing up obviously owing to the rapid development of nanomaterials. MOF-derived nanomaterials play a vital role in the fabrication of photocatalysts because of their devisable architectures and remarkable semiconductor behavior. Combination of the MOF derivatives with other materials such as metal nanoparticles, plasmonic metals, and carbons to construct heterojunction is a pivotal way to exert their synergy and further promote the photocatalytic activity. Additionally, morphology control and heteroatomic doping also provide impressive approaches to develop the highly efficient photocatalysts for environmental remediation [214,215]. Although tremendous outstanding explorations have been devoted to achieving the high efficiency and satisfied reusability of photocatalysts from MOFs, there still have lots of room for improvement in practical application. Hence, more systematic and comprehensive researches for developing industrial-level MOF-derived photocatalysts are urgently needed.

Recent years, Fenton-like catalysis as an advance oxidation technology for degradation of recalcitrant organic contaminants in wastewater has been a topic of much interest. In Fenton-like process, the *in situ* produced hydroxyl radicals are the highly active species and main oxidation agent for the degradation of organic pollutants. Generally, metal ions at low valence states can activate H₂O₂ decomposition to produce $\cdot OH$ radicals for continuous decomposition of targets, and then the high valence metal ions are reduced by H₂O₂ to achieve the redox cycle, which guarantees the catalytic reactions work consecutively. Besides, the presence of secondary metals in catalysts may provoke the rapid transformation of two metallic redox pairs in conjunction with the catalytic decomposition of the H₂O₂, thereby facilitating the efficiency of the electrolytic system [216]. Upon the introduction of light radiation, the photo-excited e^- can not only react with H₂O₂ to generate $\cdot OH$ but also accelerate the recycling of metal species. In the electro-Fenton system, the active $\cdot OH$ radicals can be yielded through reaction between cathodically produced H₂O₂ and metal ions on the catalyst surface [217]. Such a reaction of *in situ* generated H₂O₂ can enhance the efficiency of the subsequent oxidation process and lower the costs of H₂O₂ consumption as well. MOF-derived nanomaterials with permanent porosity, large surface area, tailored texture and well-designed structure possess enormous potential in this research field, which open up infinite opportunities for the rapid progress of heterogeneous catalysts for Fenton-like systems.

Among the various kinds of reported derivatives from MOFs, transition metal-based catalysts (e.g. Fe, Co, and Cu) show great potential in heterogeneous Fenton-like system [218–220]. For example, Li et al. constructed porous Fe₃O₄/C octahedral with magnetism by a two-step calcination of MIL-101 (Fe) for MB removal (Fig. 16a) [221]. The MB degradation efficiency reached 100% in 60 min in the present of Fe₃O₄/C and H₂O₂, whereas, only 67% degradation efficiency was reached during 120 min by the singular Fe₃O₄ NPs prepared from precipitation, indicating a synergistic effect between Fe₃O₄ and graphitic carbon layer (Fig. 16b and c). The mesoporous structure of Fe₃O₄/C provided abundant active sites and porous channels for full contact in both catalyst and MB molecule, leading to the improved Fenton-like catalytic behavior. Firstly, the graphitic carbon layer and porous structure adsorbed organic contaminants to the catalysts surface through π - π stacking interactions. Then the absorbed pollutant were diffused on the Fe₃O₄ surface by mesoporous channels and induced Fenton-like system with Fe³⁺/Fe²⁺. Besides, the good recyclability

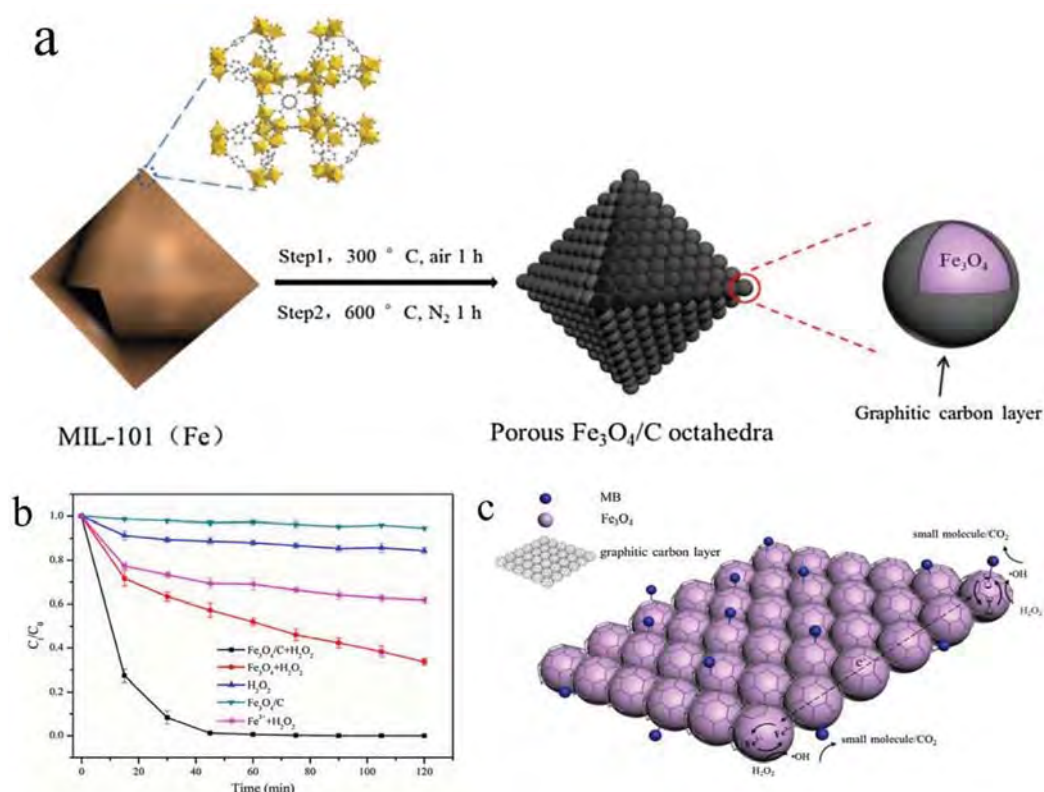


Fig. 16. (a) schematic illustration of the preparation process of MOF-derived magnetic porous Fe₃O₄/carbon octahedral; (b) MB removal efficiency under different conditions. (reaction conditions: [MB]₀ = 10 mg L⁻¹, [catalyst] = 0.5 g L⁻¹, [H₂O₂] = 90 mM L⁻¹, pH = 3 and 30 °C). (c) proposed mechanism for the heterogeneous Fenton-like reaction of the magnetic porous Fe₃O₄/carbon octahedra. Reprinted with permission from Ref. [221] Copyright 2017 Elsevier.

and stability of Fe₃O₄/C could be ascribed to the protection of the graphitic carbon layer.

Furthermore, the introduction of other metals into Fe-containing MOF-derived materials could induce the generation of more free radicals through a powerful synergistic effect, further accelerating the catalytic degradation of organic pollutants in water body [20,222,223]. For instance, Bao et al. prepared a novel CuFe₂O₄/Cu@C catalyst consisting of CuFe₂O₄ (64.84%), Cu (3.80%), and C (31.36%) to degrade MB [223]. The removal efficiency of MB reached 100% within 15 min when CuFe₂O₄/Cu@C as a catalyst, owing to the formation of more hydroxyl radicals, while only 56% was attained by Fe₃O₄@C. These phenomena suggested the effective synergy of Cu⁰ in the generation of hydroxyl radicals, which resulted in excellent MB degradation. Similarly, He et al. reported hollow Fe-Pd@C nanomaterials with core-shell structure for strengthened Fenton catalysis, which achieved rapid (within 10 min) and effective degradation of phenol (95% mineralization rate) [20]. Low contents of Pd NPs in Fe-Pd@C (mass ratio of the original material: Fe/Pd = 100:1) promoted the fast redox cycle of Fe³⁺/Fe²⁺, hence enhancing the catalytic activity and pH endurance of the nanomaterials.

The integration of external energy also can improve the catalytic activity of MOF-derived heterogeneous catalysts in Fenton-like process for wastewater treatment. Using Prussian blue (PB) nanocubes as precursors, Wang and co-workers constructed SnO₂-encapsulated α-Fe₂O₃ (Fe₂O₃@SnO₂) nanocubes as photo-Fenton catalysts for RhB removal [224]. The resulting samples displayed excellent degradation efficiency (up to 99.7%) in 60 min, much better than that of commercial Fe₃O₄ and α-Fe₂O₃ (both lower than 30%). This was mainly ascribed to the indirect contribution of SnO₂ shells to the simultaneous optimization on

microstructure and crystalline phase of Fe₂O₃. Nearly complete removal was attained after 30 min in the presence of catalyst, H₂O₂ and visible light simultaneously, illuminating the synergy between individual in heterogeneous catalytic photo-Fenton reaction was responsible for the effective degradation of target pollutants. Besides, the radical-based oxidation process was inferred as the dominant route for RhB degradation where ·OH worked as the main reactive species.

Liu et al. reported CMOF@PCM electro-Fenton catalysts from three pyrolyzed Fe-MOFs (MIL-88(Fe), MIL-101(Fe) and MIL-100(Fe)) for the degradation of napropamide at neutral pH in aqueous solution [225]. In this electro-Fenton reaction system, the relative removal efficiency of napropamide decreased by the order of CMIL-100@PCM (82.3%) > CMIL-88@PCM (64.1%) > CMIL-101@PCM (60.56%). The best catalytic ability with degradation efficiency of 97% within 60 min was observed when using CMIL-100@PCM25 as catalyst. Low leaching concentration of reactive Fe (approximately 6.5 ppb) from CMIL-100@PCM exhibited the excellent durability of this system. Besides, the pores with narrow distribution in CMOF@PCMs resulted in an easy accessibility to the active Fe²⁺/Fe³⁺ catalytic centers. The optimization of the availability of Fe²⁺ sites by porous CMOFs allowed to induce the initial oxidation of Fe²⁺ to Fe³⁺ and ·OH in the presence of H₂O₂.

Importantly, however, in spite of several classes of MOF-derived nanomaterials are able to degrade organic contaminants effectively in Fenton-like system, while research in this area is still at an early stage, more derivatives or their composites with great potential should be investigated. The combination of photo- or electro-energies with pyrolytic MOFs to catalyzed Fenton-like process is currently a vibrant research area for this technology [226]. Up till now, iron leaching cannot be avoided completely even

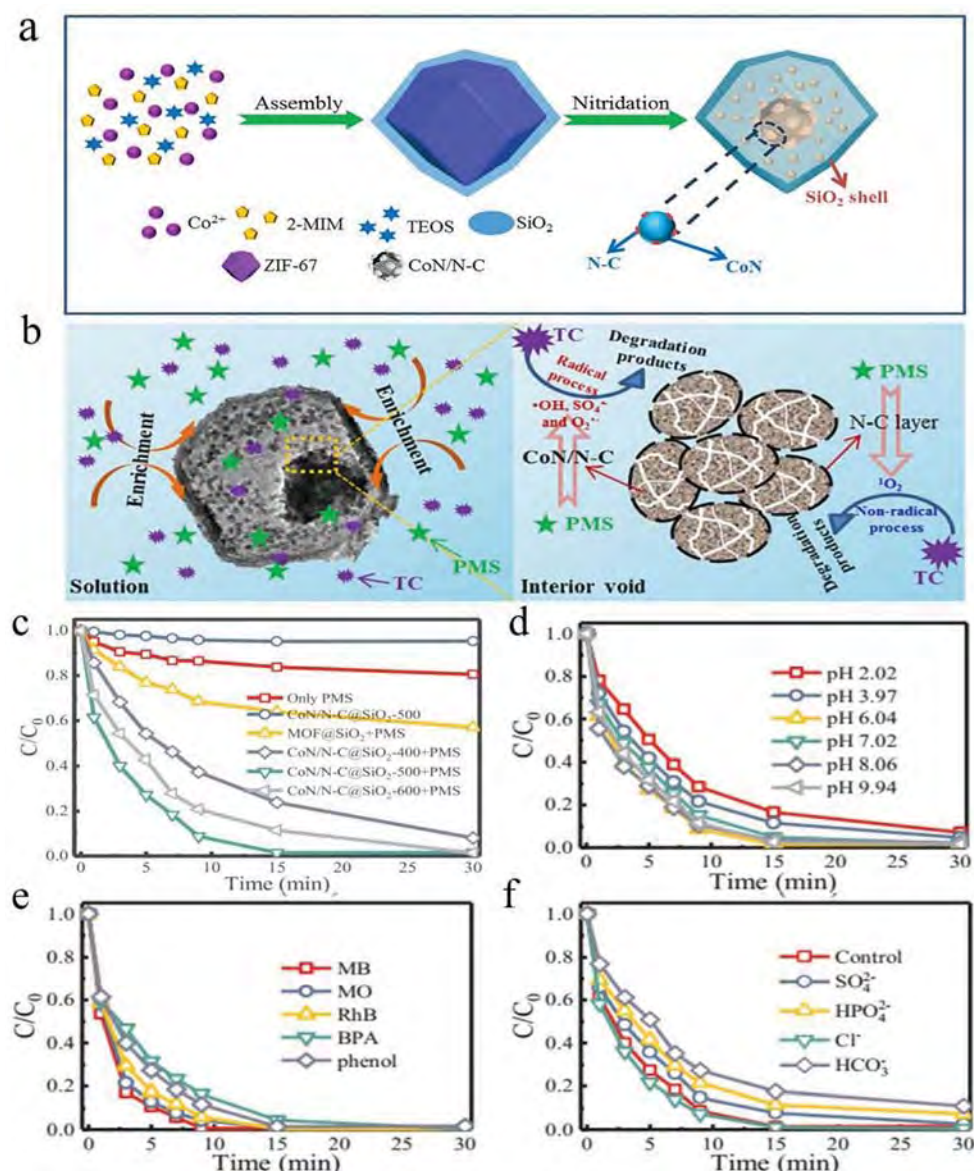


Fig. 17. (a) Schematic illustration of the fabrication procedure of the yolk-shell CoN/N-C@SiO₂ nanoreactor; (b) mechanisms for TC degradation by CoN/N-C@SiO₂-500 + PMS systems; the effect of (c) different catalysts and (d) initial pH value on TC degradation; (e) degradation of other organics in CoN/N-C@SiO₂-500 + PMS systems; (f) the effect of foreign ions on TC degradation. Reprinted with permission from Ref. [235] Copyright 2020 Elsevier.

though enormous attempts have been devoted. Moreover, the continuous loss during supernatant discharge and the limited working pH range hinder their practical use. Thus, a large amount of improvements are required for their flexibility with real wastewater.

Recently, employing catalysts to activate PS/PMS have been frequently studied to treat wastewater pollution due to their strong oxidizing ability and high selectivity. MOF-derived nanocomposites with favorable structural and compositional properties as emerging catalysts are intensively used in this process. The possible mechanisms responsible for PS/PMS activation towards the removal of organic contaminants in MOF-derived nanomaterials are involved in radicals and non-radical pathway. As for metal oxides, the catalytic degradation is dominated by radicals (commonly as SO₄^{•-} and [•]OH). In this oxidation process, the breakage of the peroxide bond (–O–O–) of PS/PMS can be induced to generate SO₄^{•-}, which can degrade and partly decompose the pollutant molecules into CO₂ and H₂O, and the residual transform into small molecule intermediates [227]. With respect to metal/carbon hybrids and car-

bon materials, non-radicals (mainly as ¹O₂ and electron-transfer) catalytic process could be induced to activate PS/PMS and further degrade organic pollutants. Graphitic N atoms in carbons can trigger electron transfer from carbon atoms to neighboring graphitic nitrogen by breaking the chemical inertness of the sp²-hybridized carbon configuration, thus producing positively charged active sites [228]. The efficiency of non-radical oxidation process is primarily dependent on the conductivity, graphitic degree and N-doping of carbonaceous catalysts. However, non-radical pathway has not revealed completely and more deep researches are required to make it clear.

Transition metal catalysts particularly the multiple metal oxides with versatile advantages such as being highly redox active in catalytic process, ferromagnetic and multifunctional (e.g. antibacterial, etc.) are regarded as the dominant and superb catalysts for promoting PS/PMS activation [229–231]. For instance, Li and colleagues reported hollow porous Fe_xCo_{3–x}O₄ nanocages through pyrolyzing the pre-designed precursors of Fe_yCo_{1–y}-Co PBAs nanospheres for BPA removal with PMS activation [232]. In

their work, the Fe doping amount was demonstrated significantly influence the final morphology of $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$. The particle size increased to 160 nm from about 80 nm and the shape gradually became more uniform as the increase of Fe amount. $\text{Fe}_{0.8}\text{Co}_{2.2}\text{O}_4$ showed the most uniform nanocages, which achieved 95% BPA degradation efficiency during 60 min when the simultaneous presence of $\text{Fe}_{0.8}\text{Co}_{2.2}\text{O}_4$ nanocages and PMS. The B-site Co^{II} on the surface of catalyst was confirmed as the primary factor for the superior activity. Similarly, a magnetic core-shell $\text{Co}_3\text{O}_4@\text{Fe}_2\text{O}_3$ almost removed 100% norfloxacin (NOR) within 45 min, while Fe_2O_3 /PMS system could not degrade NOR effectively and Co_3O_4 /PMS system only showed a moderate performance for NOR elimination [233].

In addition, transition-metal nitrogen carbon materials are attractive alternatives because of their high efficiency and lower adsorption energy [234]. For instance, Zhang et al. constructed yolk-shell structured $\text{CoN}/\text{N}-\text{C}@\text{SiO}_2$ as nanoreactor with dual active sites through nitridation of parent $\text{ZIF-67}@\text{SiO}_2$ for TC degradation (Fig. 17a) [235]. The *in-situ* formed N-doped carbon layer not only acted as catalytic sites but promoted electron transfer. Benefiting from the structural and composition modulation (Fig. 17b), the $\text{CoN}/\text{N}-\text{C}@\text{SiO}_2$ nanoreactor degraded about 95% TC in 30 min within a broad pH working range (Fig. 17c and d). Specifically, the microenvironment in the yolk-shell structure and the hydrophilic SiO_2 shell improved the catalytic stability and offered driving force to promote reaction rate; dual active sites referred to the CoN core and N-doped carbon layer performed the synergic action of non-radicals and radicals during PMS activation. The $\text{CoN}/\text{N}-\text{C}@\text{SiO}_2$ -500 exhibited excellent removal performance towards various organic pollutants and a slight decrease in the presence of four anions (Fig. 17e and f), suggesting the great potential in practical use. Liu et al. synthesized nitrogen-doped porous Co@C nanoboxes ($\text{Co}@\text{NC}$) from ZIF-67 for p-chloroaniline (PCA) degradation with PS activation [236]. A complete removal of high concentration PCA within 2 min was achieved, which could be explained by the formation of radical species (mainly sulfate radicals and hydroxyl radicals) and non-radical species. Notably, the porous and hollow carbon nanobox architecture offered large surface areas, benefiting the target molecule adsorption and further oxidation. Unfortunately, the cobalt leaching was inevitable even though the prepared materials implemented etching treatment to remove away excess metallic cobalt.

To avoid secondary pollution for environment, metal-free catalysts are required to eliminate the organic contaminants. Nitrogen-doped graphene derived from MOF acted as a PMS facilitator and displayed almost 100% phenol removal within 30 min [237]. The high specific surface area, pore volume, nitrogen atoms doping as well as the structure of graphene all can account for the fascinating degradation efficiency of target pollutant. During the process of PMS activation, singlet oxygen exerted a dominant impact on the removal process. In addition, the pH effect on phenol decomposition also investigated and the results indicated the degradation efficiency was better in alkaline conditions, which could promote the $\text{SO}_5^{\cdot-}$ generation and further produce more singlet oxygen. In Zhang's work, N-doped hierarchical carbon catalysts showed 98% of BPA removal efficiency in 5 min, which surpassed many other PMS activators [167]. In this process, a singlet oxygen-dominated non-radical mechanism was proposed.

MOF-derived carbonaceous materials are superior catalysts for wastewater treatment under PMS/PS presence in which radical and non-radical pathway both play a significant role in destructing environmental pollutants. Most of these derivatives show an incredible improvement in performances than pristine MOFs owing to their expanded surface areas, ultrahigh porosity and heteroatom introduction. Among them, metal/carbon hybrids and carbon materials seem to have better stability and more eco-friendly.

Undesirably, the formed $\text{ClO}_3^-/\text{BrO}_3^-$ and halogenated disinfection byproducts in catalytic process are potentially toxic as well as excess SO_4^{2-} and residual PMS in water have an adverse effect on environment [238–240], more simple and efficient methods should be used for overcoming these obstacles.

For wastewater treatment, just like the discussed-above, MOF-derived nanomaterials can not only serve as selective adsorbents of contaminants but also act as platforms for environmental pollutants degradation through catalytic processes. In most cases, both characters of MOFs can synergistically function in the degradation. Specifically, MOF derivatives could adsorb large amount of target molecules in solution owing to their high surface area and suitable pore sizes, enabling these adsorbed contaminants with better access to the surface sites on catalysts [88,141]. The close distances between targets and catalytic sites improve the utilization efficiency of active species. Besides, the increased local concentration of pollutant molecules facilitates the catalytic activity as well [138]. Characterized by the excellent degradation efficiency, favorable mineralization rate and good stability, MOF-derived nanostructured catalysts show promising potential in this area. Well-designed structure such as hierarchical porous and hollow core-shell are advantageous to the facilitated mass/electron transport and highly exposed active sites. In order to avoid secondary pollution and control cost, the selection of the compositions of MOF precursors needs to be more judicious. In general, environmentally friendly metal nodes and relatively simple organic ligands are more popular. Notably, a large number of researches at present have been concentrated on the removal of dyes, BPA and phenols, while the studies concerned with other emerging contaminants such as PPCPs, pesticides and perfluorinated compounds are rare. In spite of some favorable achievements have been realized for the elimination of organic contaminants by using MOF-derived materials as heterogeneous catalysts, issues related to the large-scale preparation and efficient recycling impose restrictions on their industrial applications. To overcome these challenges still has a long way to go. How to successfully apply the outcomes of the laboratory to the commercial field is the key question for researchers to ponder in the future work.

4.2. MOF-derived nanomaterials for air purification

4.2.1. CO_2 capture and separation

Enormous carbon dioxide emission produced by anthropogenic activities especially fossil fuel combustion poses a severe threat to the natural environment. The resulting greenhouse effect leads to climate change and environmental deterioration, further exerting a negative influence on animal survival and human health. In order to alleviate the ever-increasingly serious damage, developing technology to adsorption CO_2 effectively is receiving growing concern around the world. MOF-derived nanoporous materials as sorbents provide an advisable choice for CO_2 capture, as already proved by many publications [241–243]. Notably, physisorption occurs mainly in the pore channels and surface of adsorbents, where ultrahigh porosity and large surface area of adsorbents are beneficial to improve the CO_2 uptake capacity [242]. Microporous structure plays an important role in CO_2 adsorption at ambient pressure, but mesopore and macropore structure have a less enhancement effect for it. Besides, heteroatoms doping into carbon framework such as O-doped and N-doped has a prominent impact on CO_2 uptake ability [244,245]. For the pyrrole and amine group-functionalized adsorbents, CO_2 molecules can interact with the N and H atoms on the surface through Lewis acid-base and H-bond [246]. Specifically, upon adsorption, CO_2 as acidic gas locates in close proximity to basic N active site in pyridine group owing to Lewis acid-base interaction where the lone pair electron of N atom provides the electronic change for the carbon atom in CO_2 as well

as the steric hindrance effect within CO₂ and functional group [247]; the H atom in hydroxyl group react with the O atom in CO₂ cause the H-bond interaction.

Recently, nanoporous carbons (MUCT) were synthesized from MOF-5 and urea [248]. The optimal sample MUC900 indicated the best CO₂ uptake ability of 3.71 mmol g⁻¹ at 273 K (1 atm). The CO₂ capture was improved thanks to the high nitrogen amounts, microporous surface area, and C–OH groups of porous carbons. The interaction of CO₂ with functional groups was facilitated by the hydroxyls through electrostatic potentials as well as hydrogen-bonding interactions, hence contributing to the increasing CO₂ capture of MUCT samples. Later on, MOF-5-derived carbon materials achieved CO₂ uptake capacity of 2.43 mmol g⁻¹ at 298 K and 1 bar [249]. The calculated total pore volume, micropore volume as well as BET surface area of the prepared porous structure were equal to 1.84 cm³ g⁻¹, 0.59 cm³ g⁻¹ and 1884 m² g⁻¹, respectively, higher than those of pristine MOF-5 (0.33 cm³ g⁻¹, 0.24 cm³ g⁻¹ and 477 m² g⁻¹, respectively). The CO₂ uptake decreased persistently with the increasing temperature (from 298 K to 373 K). Conversely, the increasing pressure value (from 0 up to 40 bar) resulted in higher CO₂ capture. In Zou's work, the high CO₂ adsorption capacity (4.76 mmol g⁻¹ at 273 K) of the ZIF-68-derived N-doped carbons was influenced by the surface area as well as governed by the local structure and doped N-species [163].

It is worth noting that high selective CO₂ adsorption from mixed gases and high CO₂ capture ability at low pressure are of great practical significance for industrial-level application. Early on, the 24 h@500 °C derived from ZIF-8 displayed favorable CO₂ adsorption of 1.79 mmol g⁻¹ at 1 bar and 25 °C, more than twice of initial ZIF-8 (0.7 mmol g⁻¹) [250]. Benefitting from the interaction of the lone-pair electrons on nitrogen, the basic N-containing functional groups exhibited high affinity towards acidic CO₂, which could account for the improved CO₂ capture [251,252]. Importantly, the 24 h@500 °C exhibited a significantly enhanced CO₂ selectively over N₂, two-fold higher than that of the original ZIF-8. Pan et al. developed the KBM-700 with large nitrogen amount (10.16%) and pore volume with microsize (73%) by calcination of K⁺@bio-MOF-1, which displayed enhanced performance in CO₂ capture (4.75 mmol g⁻¹) at 1 bar and 298 K than the BM-700 (3.52 mmol g⁻¹) without K⁺ introduction, where the N functional groups and microporosity played a dominant part [169]. The BM-T presented a large number of mesopores, while the dominance of micropores indicated in the KBM-T. The CO₂ over N₂ selectivity of KBM-700 was much higher than that of BM-700, such a great improvement could contribute to the well-designed micropore structure as well as the narrow distribution of pore size owing to K⁺ activation.

Wang and colleagues synthesized oxygen-doped nanoporous carbonaceous material by thermal treatment of pristine MIL-100Al, MIL-100Al/F127 composite, and MIL-100Al/KOH mixture, namely AAC-1, AAC-2 and AAC-3, respectively [253]. The obtained AAC-2 W (washing with HCl) showed the highest CO₂ adsorption even at different temperatures, which was 4.8 mmol g⁻¹ at 298 K and 6.5 mmol g⁻¹ at 273 K. The incredible CO₂ uptake ability could be put down to the well-defined porous structure and adequate oxygen incorporation. The ultrahigh porosity offered sufficient space to take in gas molecules and the surface polarity and basicity afforded by abundant functional groups strengthened the bonding force with acidic CO₂. Importantly, the high CO₂ adsorption amounts of 1.72 and 1.74 mmol g⁻¹ at 298 K and 0.2 bar was also observed when AAC-1 W and AAC-2 W as sorbents, suggesting a desirable performance even under low CO₂ partial pressure environment. Benefitting from the higher quadrupole moment and polarizability, the highest CO₂/N₂ selectivity was attained by AAC-1 at 298 K and 1 bar, as well as the highest CO₂/CH₄ selectivity was achieved by AAC-2 in the same circumstances. The great dis-

tingtion of CO₂ capture over CH₄ and N₂ capture capacity demonstrated the good binary separation selectively of these derivatives, in favor of a real application for flue gas and natural gas separation.

MOFs with permanent porosity have been broadly employed in CO₂ uptake while the reports related to their derivatives are relatively limited. The highest CO₂ capture capacity of 4.8 mmol g⁻¹ at 298 K 1 bar was achieved by Wang's group, comparable with the 4.75 mmol g⁻¹ at the same conditions in Pan's work, suggesting the good contribution of additional activating agents for enhanced performance. Owing to the predominant role of micropore in CO₂ adsorption, many attempts to construct the microporous structure and modulate micropore volume should be made. Remarkably, improving the selectivity of CO₂ capture in binary even polynary gas system as well as enhancing the adsorption ability at low pressure are important for practical applications.

4.2.2. VOCs degradation

VOCs, as a typical pollutant in atmospheric environment, are defined as organic compounds that begin to boil at below or equal to 250 °C [254,255]. VOCs have a wide range of types, including acetone, acetic acid, toluene and benzene. These varieties of VOCs mainly emitted from industrial processes and human activities cause severe harm to human health and the ecological environment because of their toxicity and environmental persistence [256–258]. Moreover, VOCs are the primary precursors of secondary aerosols and photochemical smog, which have adversity effects on human survival and sustainable development [259,260]. Inspired by rigorous regulations of air pollution control, many techniques have been applied for the abatement of VOCs, such as plasma process, adsorption, catalytic combustion and photocatalysis [261–263]. MOF-derived metal oxides or their hybrids (e.g. Mn-based, Ce-based, Cr-based, Ti-based, etc.) are deemed to be the potential catalysts for VOCs elimination due to their superiorities.

Recently, Chen et al. reported a series of three-dimensional penetrating mesoporous Pt@M–Cr₂O₃ for toluene combustion [263]. Particularly, the unique structure of three-dimensional penetrating mesoporous channels is useful for facilitating the contact possibility of toluene molecules with active sites, thereby showing higher reactivity in catalysis of toluene oxidation [264,265]. In comparison with M–Cr₂O₃ derived from MIL-101–Cr, the catalytic activity of Pt@M–Cr₂O₃ was improved remarkably after Pt loading, indicating the promotion of Pt NPs in catalytic activity. The 0.82Pt@M–Cr₂O₃ catalyst (Pt = 0.824 wt%) showed the best degradation performance for toluene combustion at 145 °C. It is worth pointing out that the synergic effect among more lattice defects, smaller-size and well-dispersed Pt nanoparticles, high ratio of Pt⁰/Pt²⁺, large surface area and distinct architecture of 0.82Pt@M–Cr₂O₃ contributed to the strongest catalytic ability to toluene oxidation. The combustion of toluene by 0.82Pt@M–Cr₂O₃ was achieved through fast transformation to aldehydic and subsequently benzoate and form CO₂ and H₂O at final.

Supported noble metal catalysts display outstanding catalytic oxidation activities for VOCs at low temperatures [266,267]. However, expensive price and low reserve impede their further development in practice. Therefore, exploiting transition metal oxides catalysts derived from MOFs with low cost and high performance are attracted more attention [268–270]. For instance, Sun and co-workers prepared MnO_x–CeO₂–MOF through heating Ce/Mn–MOF-74 and used it for toluene oxidation [271]. The obtained catalysts showed the T₅₀ and T₉₀ (corresponding to the toluene conversion of 50% and 90%, respectively) of 210 and 220 °C as well as the apparent activation energy of 82.9 kJ mol⁻¹. These parameters were lower than those of MnO_x–MOF, MnO_x–CeO₂–CP and MnO_x–D, which were prepared by directly pyrolysis of MOF-74

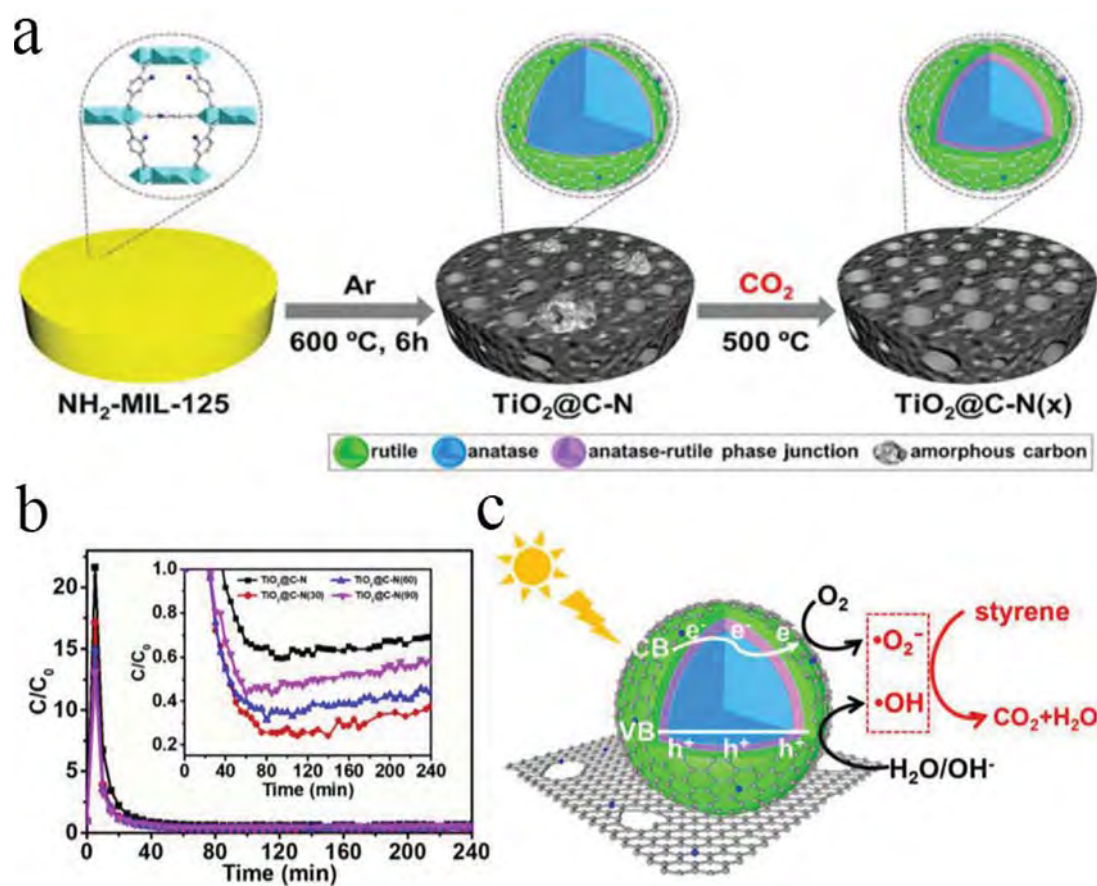


Fig. 18. (a) Illustration of the preparation strategy of $\text{TiO}_2@\text{C-N}(x)$ nanocomposites. (b) evolution of styrene during the photocatalytic oxidation reaction by $\text{TiO}_2@\text{C-N}$ and $\text{TiO}_2@\text{C-N}(x)$ composites. (c) possible reaction mechanism for the photocatalytic oxidation of styrene over $\text{TiO}_2@\text{C-N}(x)$ nanocomposites. Reprinted with permission from Ref. [81] Copyright 2019 Elsevier.

without Ce, co-precipitation and thermal decomposition of MnOOH , respectively. The introduction of Ce into MnO_x framework was conducive to the enhancement of catalytic performance in toluene degradation owing to the rich oxygen vacancies, large surface area, good oxygen mobility, excellent low-temperature reducibility and considerable Mn^{4+} contents in surface, which exerted an important effect on catalytic process.

Non-thermal plasma (NTP) technology has great potential to remove diluted VOCs whereas it possess some shortcomings including low CO_2 selectivity and formation of unwanted by-products. Combining the advantages of NTP and heterogeneous catalysis can overcome these limitations and efficiency enhance the VOC removal. Feng's group developed a novel method for toluene removal by MOF-derived porous tri-metallic oxide catalyst (MnCoNiO_x , MCNO) combined with NTP technology [272]. MCNO composite showed much higher BET surface area ($59.82 \text{ m}^2 \text{ g}^{-1}$) and total pore volume ($0.350 \text{ m}^3 \text{ g}^{-1}$) than NiO_x ($11.24 \text{ m}^2 \text{ g}^{-1}$, $0.046 \text{ m}^3 \text{ g}^{-1}$), CoO_x ($4.98 \text{ m}^2 \text{ g}^{-1}$, $0.090 \text{ m}^3 \text{ g}^{-1}$) and MnO_x ($7.69 \text{ m}^2 \text{ g}^{-1}$, $0.110 \text{ m}^3 \text{ g}^{-1}$). As expected, the toluene degradation efficiency achieved 75.7% by NTP-MCNO, better than that of NTP alone (42.9%), NTP- MnO_x (59.3%), NTP- CoO_x (70.9%) and NTP- NiO_x (65.0%). The highest degradation efficiency attained by MCNO catalyst was 99.72% with the specific input energy of 444 J L^{-1} . The as-synthesized samples and NTP performed well in synergy and thus resulted in good catalytic activity of toluene elimination. Furthermore, semiconductor photocatalytic oxidation is a promising approach to degrade VOCs into innocuous CO_2 and H_2O . In recent, $\text{TiO}_2@\text{C-N}(30)$ photocatalysts derived from $\text{NH}_2\text{-MIL-125}$ showed the best mineralization efficiency of 51.9% and removal rate of

62.4% for styrene under visible light irradiation within 240 min (Fig. 18a and b) [81]. In this reaction system, $\text{TiO}_2@\text{C-N}(x)$ formed $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals with powerful oxidation capacity owing to the generated anatase-rutile phase junction and the effective interface interaction between the N-doped mesoporous carbon shell and TiO_2 core, which endowed it with superior photocatalytic activity and remarkable mineralization efficiency for photocatalytic degradation of styrene (Fig. 18c).

4.2.3. Radionuclide adsorption and separation

The continuous growth of human population and the rapid development of industrialization have intensified the demand for energy. For the past few years, the massive consumption of non-renewable fossil-fuel resources such as petroleum products (4%), natural gas (22%) and coal/peat (41%) and the limited contribution from renewable energy sources (3.5%) such as wind, solar and hydro pose a pressing task for mankind about the exploitation of new primary energy sources [273,274]. Actually, nuclear power as a cheap and feasible alternative has been utilized in electricity production [275]; however, radioactive gaseous pollutant (e.g. Kr, and Xe) are inevitable products in this process. These hazardous gases are generated from the pre-treatment/shipping procedures of high- or low-level waste and cause damage to living things [276]. Although cryogenic distillation has been used to concentrate Xe and Kr from air, its high energy consumption and high cost are undesirable. Alternatively, MOF-derived porous nanomaterials with more economical and energy-efficient have great potential for the adsorption separation of Xe and Kr at low pressure and room temperature.

For example, Zhong et al. employed ZIF-8/xylitol as precursors to synthesize carbon-ZX and further studied Xe capture and separation [277]. Xe adsorption ability of carbon-ZX reached up to 4.42 mmol g^{-1} at 298 K and 1 bar, which was significant promotion compared to carbon-Z (directly carbonization of ZIF-8 without xylitol) of 3.17 mmol g^{-1} and parent ZIF-8 of 1.21 mmol g^{-1} . Moreover, carbon-ZX displayed the best selectivity for both Xe/N_2 and Kr/CO_2 gas mixtures in comparison of carbon-Z and original ZIF-8. The asymmetrical charge distribution on the N-doped porous carbon framework and removal of excluded effects from hydrogen atoms on aromatic rings were beneficial for the enhancement of affinity both in resultant material and Xe molecular as well as the electrostatic attraction between the surface charges and polarizable Xe molecules, which give rise to the outstanding performance of carbon-ZX.

Later on, Gong's group reported on a series of nanoporous carbons using ZIF-11 and FA as precursors for Xe/Kr separation at dilute conditions [278]. It is noting that the Xe capture capacity of these prepared materials and commercial AC are greatly relevant to their micropore size which is $<1 \text{ nm}$. The Z11CBF-1000-2 showed much higher BET surface area ($1020 \text{ m}^2 \text{ g}^{-1}$) and micropore volume (pore diameter $<1 \text{ nm}$, $0.316 \text{ cm}^3 \text{ g}^{-1}$) than other resulting samples and AC. The Xe uptake of Z11CBF-1000-2 was 4.87 mmol g^{-1} at 298 K and 1 bar, which was not only better than that of parent ZIF-11 (1.22 mmol g^{-1}), but also CC3 (2.32 mmol g^{-1}) [279], Ni-MOF-74 (4.16 mmol g^{-1}) [280], carbon-ZX (4.42 mmol g^{-1}) [277] and Ag@MOF-74-Ni (4.81 mmol g^{-1}) [281] in other reported studies. The excellent performance could be attributed to their microporous structure with narrow pore-size distribution ($5\text{--}8 \text{ \AA}$) that proper for Xe capture. Such a candidate may provide an outstanding choice for adsorption and separate Xe in used nuclear-fuel reprocessing facilities and motivate further work in this area.

Currently, the research associated with this area is relatively narrow but the great potential of MOF-derived nanomaterials for radionuclide adsorption and separation can be gained from above efficient results. The surface properties like BET surface area, pore volume and porosity play an important effect on the adsorption and separation of radionuclide, which could be regulated by adding second carbon source. Moreover, tuning the pore width to adapt to the gas molecule is also important for the improvement of the capture ability and selectivity.

4.3. MOF-derived nanomaterials for target-specific sensing

4.3.1. Gaseous pollutants sensing

As is well-known that long-run exposure to gaseous pollutants, such as VOCs, H_2S , formaldehyde, NO_x , etc., can induce many diseases to humans, further causing damage to health and even death. For example, excess dispersion of *n*-butanol in air may lead to dizziness, headache, somnolence and dermatitis [282]. Acetone released into environment may cause skin and eye irritation, narcosis and nausea [283]. In addition, H_2S gas with more than 100 ppm may impact human's nervous system while above 250 ppm can directly lead to death as well as NO_2 gas in 60 min period beyond 106 ppb may result in serious health problems [284–286]. From the perspective of environmental protection and public health, it is imperative to exploit gas sensors with satisfactory capabilities for the determination of these harmful gases, especially detecting sub-ppm level from industrial emission sources and/or low concentration at workplace and residential conditions. Sensing materials are the critical portion for gas sensor, which intensively affect the sensing performance in practice. As far as we know, the gas-sensing mechanism of metal oxides-based sensors is based on the varying resistance resulted from the reaction of target gas with sensing material surface. When sensors

are exposed to air, the oxygen molecules are chemisorbed on the surface of the metal oxides. These O_2 can capture free electrons from CB of semiconductors, resulting in the generation of negatively charged oxygen species (O_2^- , O^- , and O_2^{2-}). Consequently, an electron depletion layer with high resistance will be produced on the surface of metal oxides. Once reductive gas molecules are introduced, the pre-adsorbed oxygen species could react with targeted gases, and then the captured electrons will be released to the metal oxide semiconductors, finally decreasing the resistance of the sensors. MOF-derived materials with porous structures offer excellent flexibility in the aspect of selectivity and sensitivity. Gas sensors based on MOF-derived metal oxide semiconductors are promising materials in gas detection in light of their diverse morphologies, high response as well as easy integration.

A mass of the gas sensors based on MOF-derived nanomaterials perform well in VOCs detection [287–289]. For instance, Li et al. constructed the hierarchical hollow ZnO nanocages by direct pyrolysis of MOF-5 (Fig. 19a–c), which showed ppb level sensitivity with 15.3 ppm^{-1} to 50 ppb acetone at 300°C , and sub-ppm level sensitivity with 2.3 ppm^{-1} to 0.1 ppm benzene at 400°C , better than singular ZnO nanoparticles (1.5 ppm^{-1} and 0.9 ppm^{-1} respectively) [290]. The unique architectures with interpenetrated ZnO NPs within porous shells presented a relative lower potential barrier than agglomeration singular ZnO NPs and afforded large number of channels with mesoporous and macroporous for promoting the diffusion and surface reaction of targeted gases (Fig. 19d and e). Moreover, the distinct hierarchical structure with highly BET surface area and sufficient exposed reaction locations provided more surface oxygen vacancies, thus gaining the significantly enhanced sensing performance. Afterwards, this group reported another study, where core-shell Au@ZnO nanoparticles derived from Au@MOF-5 performed good gas-sensing response and selectivity towards acetone with sub-ppm concentration range at 300°C operation temperature (Fig. 19f–i) [291]. The sensitivity value of Au@ZnO (3.42 ppm^{-1}) was 11-fold higher than that of the singular ZnO nanoparticles (0.313 ppm^{-1}) towards 1 ppm acetone at 300°C . Besides, Au@ZnO sensor exhibited better selectivity towards acetone than other interference gases at 300°C . The enhanced gas-sensing properties were mainly dependent on the electronic and chemical sensitization of Au NPs because of the formation of Schottky junction within Au-ZnO core-shell architectures (Fig. 19j and k). Both of above cases illuminated the importance of architecture-property relationships in gas sensing materials.

The single-phase binary metal oxides provide more options to tune the chemical composition [292–294]. As an example, Cui et al. synthesized a series of mesoporous In/Ga oxides (IGOs) with hexagonal morphology by calcinating In/Ga-centered MIL-68 for ethanol sensing [293]. Among them, the response value of IGO (In/Ga molar ratio = 3:2) and IGO(In/Ga molar ratio = 1:1) to 300 ppm ethanol reached up to 81 and 101, respectively, which was higher than that of In_2O_3 at the value of 11. In addition, the IGO(3:2) and IGO(1:1) displayed a detection limit of 2 ppm and exhibited more than 2.6 times higher response to ethanol than other gases (CH_3COCH_3 , CH_3CHO , CH_3OH , CH_4 , CO , NO_2 and H_2) at 300 ppm. The excellent gas-sensing performance could be ascribed to their comparatively large specific surface area and high oxygen vacancy concentration. Similarly, porous NiFe_2O_4 crystalline nanocubes derived from PBA showed a response value of 1.9 and a detection limit of 0.52 ppm to acetone gas at a low working temperature of 160°C [294].

As for H_2S gas sensor, Co_3O_4 -1 derived from ZIF-67 showed superior performance for H_2S sensing at operating temperature of 241°C and the detection limit was measured as $1 \mu\text{g L}^{-1}$ (signal/noise (S/N) = 3) [295]. Meanwhile, seventeen interferences except carbon disulfide showed no effect on the detection of H_2S

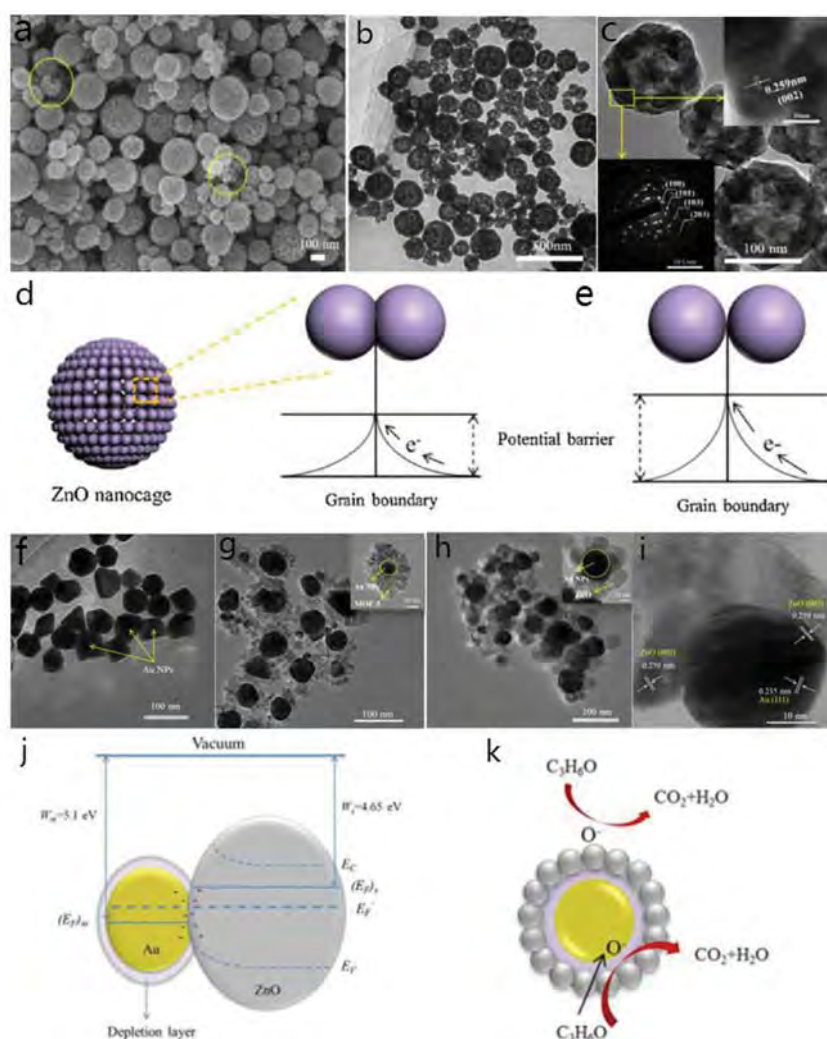


Fig. 19. (a) SEM and (b) TEM images of the as-synthesized hierarchical hollow ZnO nanocages; (c) HRTEM image of ZnO nanocages obtained at 450 °C (insets: lattice distance and SAED pattern); Schematic comparison of potential barrier between (d) melt ZnO nanoparticles within shells of hierarchical hollow ZnO nanocages and (e) singular ZnO nanoparticles. Reprinted with permission from Ref. [290] Copyright 2016 Elsevier. TEM images of (f) Au NPs; (g) Au@MOF-5 precursors; (h) Core-shell Au@ZnO nanoparticles; (i) HRTEM image of Au@ZnO nanoparticles; (j) energy band diagram of core-shell Au@ZnO nanoparticle. (k) redox process between acetone molecule and active oxygen species. Reprinted with permission from Ref. [291] Copyright 2016 Elsevier.

even if their concentration was almost 12 times higher than H_2S gas. It is worth mentioning that the active Co^{3+} cations and large specific surface area could account for the high catalytic performance of Co_3O_4 -1. Such a remarkable sensing material may offer a promising alternative in routine analysis. In addition, PB nanocubes derived hollow Fe_2O_3 nanoboxes with hierarchically porous structure displayed a high response (resistance ratio) of 1.23 to 0.25 ppm at 200 °C [296]. The obtained sensing materials with fully reversible response to 5 ppm of H_2S at a low working temperature of 50 °C illustrated its potential for operating at near room temperature, which was conducive to environment monitoring indoor and outdoor.

For gaseous formaldehyde sensing, Co_3O_4 -350 derived from Co_5 -based MOF showed an operating temperature of 170 °C, a limit of detection of 10 ppm and long-run stability of one month, making it superior to most reported Co_3O_4 materials for the formaldehyde detection and even a majority of Co_3O_4 -based composites [297]. The extremely effective properties could ascribed to its unique pore structure, larger surface area and hierarchical structure. With respect to NO_2 detection, MIL-68-derived $\text{In}_2\text{O}_3/\text{MoS}_2$ nanocomposite was successfully constructed by layer-by-layer self-assembly method [298]. As shown in

Fig. 20a–d, the MoS_2 particles were loaded on the surface of In_2O_3 hollow microtubes and both of them had good contact with each other. The $\text{In}_2\text{O}_3/\text{MoS}_2$ composites exhibited superior response value towards 100 ppm NO_2 than that of individual In_2O_3 sensor and displayed much higher selectivity to NO_2 than six other interfering gases ($\text{C}_2\text{H}_6\text{O}$, CH_2O , NH_3 , $\text{C}_3\text{H}_6\text{O}$, C_6H_6 and H_2S , 10 ppm) as well as outstanding long-run stability of one month. Moreover, the sensor may need humidity compensation under the circumstance of different relative humidity because its response value dropped with the ambient humidity increasing. The significantly improved NO_2 sensing behavior were endorsed by the formation of n-n heterojunction at interface between In_2O_3 hollow microtubes and MoS_2 NPs and the distinct structure (Fig. 20e and f).

At present, most studies about gaseous environmental pollutants focus on the VOCs detection, especially acetone. Other harmful gases such as H_2S , HCHO and NO_x need to be given more attention in the future. Hierarchical and hollow porous structure and formed heterojunction are beneficial to the diffusion and surface reaction of targeted gases. The highly specific surface area and sufficient active sites also can afford the enhanced sensing performance. Generally speaking, gaseous pollutants usually exist in the

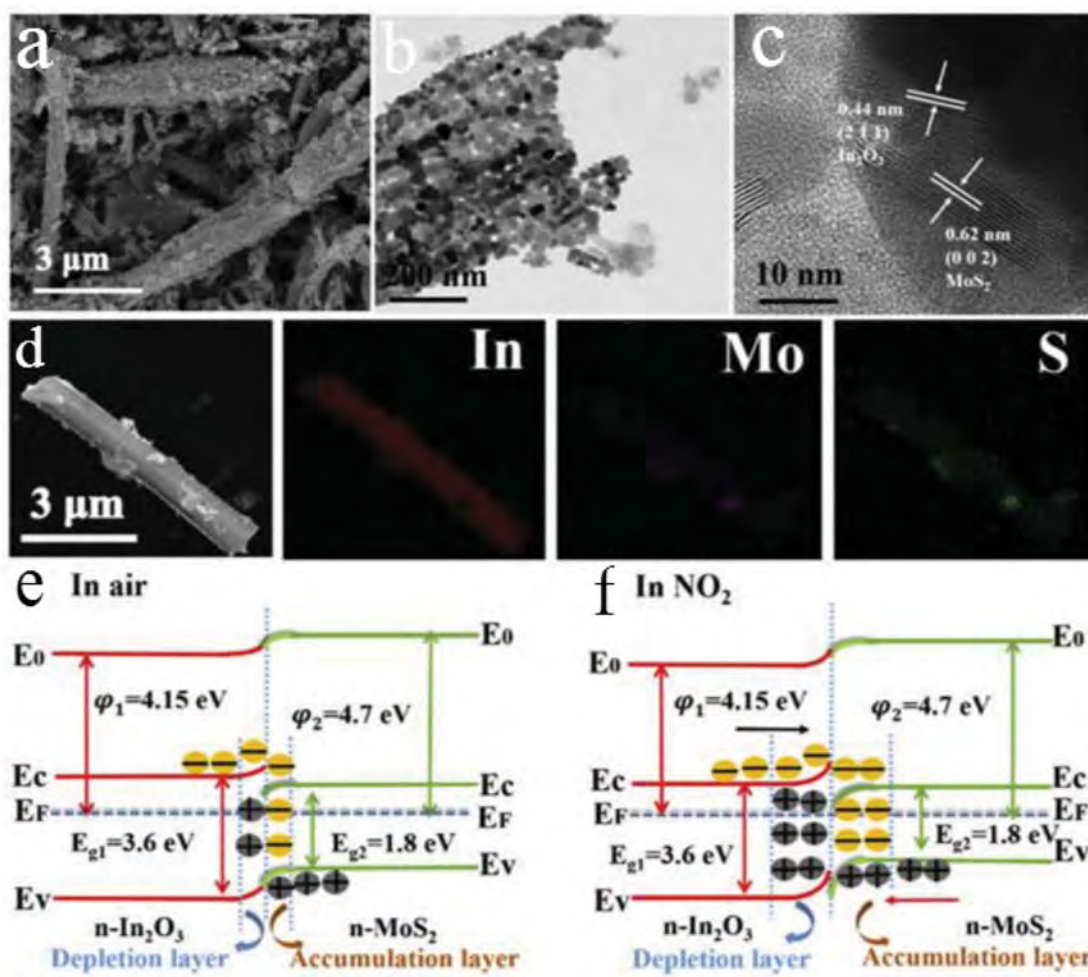


Fig. 20. (a) SEM and (b) TEM images of $\text{In}_2\text{O}_3/\text{MoS}_2$; (c) HRTEM micrograph of $\text{In}_2\text{O}_3/\text{MoS}_2$; (d) EDX mapping analysis of $\text{In}_2\text{O}_3/\text{MoS}_2$; Energy band structure diagram of $\text{In}_2\text{O}_3/\text{MoS}_2$ heterojunction in air (e) and in NO_2 (f). Reprinted with permission from Ref. [298] Copyright 2019 Elsevier.

environment at low concentration, especially sub-ppm level in residential or working place. Therefore, it is valuable and challenging to develop excellent sensing materials for the trace amounts of hazardous gases detection. MOF derivatives show great potential in sensing materials because they have much advantageous in texture adjustment, morphology control, and component selection, which highly determine the detecting properties of gas sensors.

4.3.2. Organic pollutants sensing

Many harmful chemicals are released into natural waters including surface water, groundwater and seawater through industrial, agricultural, medical, domestic drainage and animal manure, which threaten the survival of marine plants and animals, and of course include human beings, thus working severe damage to the ecological environment. Some toxic pollutants, even at an extremely low concentration in ambient water, can cause irreversible harm to living things [299]. Currently, the accepted standard techniques, including capillary electrophoresis [300], chemiluminescence [301], liquid chromatography-mass spectrometry [302], and high performance liquid chromatography (HPLC) [303], commonly have the shortcomings of sophisticated instruments and cumbersome operations [304–306]. From this viewpoint, special attentions are given to the sensing platform on the basis of MOF-derived materials because of their numerous advantages.

A novel electrochemical sensing platform based on Mn-MOF-derived $\text{MnO}_2/\text{Mn}_3\text{O}_4$ and Ti_3C_2 MXene/Au NPs composites was reported for pesticide detection [307]. The 3D $\text{MnO}_2/\text{Mn}_3\text{O}_4$ hierarchical microcuboids combined with Ti_3C_2 MXene/Au NPs composite with high surface area, excellent electrochemical performance and good environmental biocompatibility yielded synergistic signal amplification effect. The reported sensor possessed a low detection limit of 1.34×10^{-13} M under the optimum conditions, along with a fine linearity of $R = 0.995$. Similarly, single hierarchical CuO material derived from Cu-BTC with high photocurrent conversion efficiency was employed to detect malathion by photoelectrochemical (PEC) method [308]. The constructed sensor in this work showed a detection limit of 8.6×10^{-11} mol L^{-1} within the linear range of 1.0×10^{-10} – 1.0×10^{-5} mol L^{-1} .

Aside from single metal oxides, metal oxide/porous carbon composites are used extensively owing to the combination of individual advantages. Wang et al. proposed electrochemical sensors comprising $\text{FeO}_x/\text{TiO}_2/\text{mC}_{700}$ NPs derived from bimetallic Fe/Ti-based MOFs for 4-nitrophenol (4-NP) detection [309]. Benefiting from the hierarchically micro/mesoporous structure and highly specific surface area of $158.2 \text{ m}^2 \text{ g}^{-1}$, the synthesized materials possessed rapid mass transport and plentiful available active sites. The combination of good catalytic activity of FeO_x and TiO_2 and excellent electronic conductivity of mesoporous carbon resulted in high detection ability. $\text{FeO}_x/\text{TiO}_2/\text{mC}_{700}/\text{GCE}$ sensor showed a low detection limit of $0.183 \text{ } \mu\text{M}$ ($S/N = 3$) towards 4-NP in a wide

concentration range of 5 to 310 μM , and exhibited outstanding selectivity for 100 μM 4-NP compared with other interferences. Feng et al. reported plasmon Au coupling with $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$ nanostructures (AuInCN) for TC detection by PEC aptasensor first time [310]. The as-prepared materials showed remarkable PEC performance due to the fast separation and transfer of electron-hole pairs by $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$ (InCN) heterojunction as well as the enhanced light harvest and photoelectron transfer by Au nanoparticles. In this study, the PEC aptasensor presented long-term stability, acceptable reproducibility, good selectivity and high recovery value in actual samples for TC detection and exhibited a detection limit of 3.3 pmol L^{-1} ($S/N = 3$) with a broad concentration range of 0.01 nmol L^{-1} –500 nmol L^{-1} . These favorable results clarified the AuInCN composite with good visible light PEC response give a novel platform for target-specific sensing in environment.

4.3.3. Heavy metal ions sensing

The continuous decrease of freshwater resulted by serious pollution from industrial wastewater has become a high priority global concern. In particular, heavy-metal contamination in water supply systems has been receiving growing attention. Generally, heavy metal ions such as Pb^{2+} , As^{2+} , Cd^{2+} and Hg^{2+} are known as the extremely harmful contaminants in the biosphere, and pose a detrimental risk to ecosystem even trace amounts due to their considerable toxicity, high stability and easy to accumulation through food chains [311–314]. In the past few decades, great attention has been paid to the detection of heavy metal ions in a variety of matrices and consequently, tremendous outstanding explorations have been developed to converting MOFs or their composites into sensing materials for metals detection by electrochemical method.

The first example of using MOF-derived sensing platform to determine heavy metal ions was reported by Xiao's group in 2014 [315]. Nafion-bismuth/nitrogen doped microporous carbon (NMC) composite with good reproducibility and stability was employed as electrode modifying material for simultaneous detection of trace Cd^{2+} and Pb^{2+} in aqueous solution. The highly specific surface area of 941 $\text{m}^2 \text{g}^{-1}$, large nitrogen amounts of 25.0 at.%, satisfied dispersibility and good electrical conductivity of NMC composite, as well as the synergy between Nafion and bismuth film were responsible for the enhanced signals in the simultaneous sensing of Cd(II) and Pb(II) . The detection limits of Cd(II) (1.5 $\mu\text{g L}^{-1}$, $S/N = 3$) and Pb(II) (0.05 $\mu\text{g L}^{-1}$, $S/N = 3$) were 2-fold and 200-fold lower than the allowed concentration in drinking water by the World Health Organization (WHO) [316], which afforded a promising prospective for the metals sensing platform in practice. Such a remarkable sensing material possibly paves an innovative pathway for the construction of the sensitive platform based on heteroatom-doped modified electrode for the trace detection of heavy metal ions.

Zhao et al. reported a well-design Ag/Au HPNSs@FO as electrochemical sensing system for As(III) detection, which showed excellent performance due to the combination of advantages of the plasmonic and ultramicroelectrode property [317]. The as-obtained Ag/Au HPNSs@FO presented uniformity and porous structure and the thin layers of Fe oxide (FO) showed crystallinity and nanoporosity (Fig. 21a–g). The porous FO was introduced by pyrolyzing MIL-100 grown on the Ag/Au porous nanoshells (Ag/Au HPNSs) and as assisted adsorbent contributed to the improvement of As(III) sensing. The detection limit was calculated to be 0.01 ppb, much lower than the guideline values of drinking water proposed by the WHO [316]. Besides, the Ag/Au HPNSs@FO displayed good long-term stability after 1000 cycles and high detection selectivity in the existence of various co-existing metal ions (Fig. 21h and i), demonstrating the potential application in practical

water system. Benefitting from the highly micro-reactive sites of the plasmonic Ag/Au HPNSs and good adsorption ability towards As(III) of Fe oxide, the ultra-sensitive detection of As(III) with extremely low concentrations (about 1 ppt and even lower concentrations) was achieved by Ag/Au HPNSs@FO system, which raised an effective approach to boost the commercialization for ultra-trace As(III) detection and the construction of As(III) sensing platform.

Notably, heavy metals could affect the catalytic activity of MOF-derived nanomaterials. Based on this unique property, many sensing platforms with high sensitivity and selectivity for the colorimetric detection of heavy metal ions are established. Taking HKUST-1-derived CuS particles (PCuS) as example, Xiong et al. reported a novel peroxidase-mimicking system for Hg^{2+} determination using a colorimetric method [318]. The as-synthesized PCuS had intrinsic peroxidase-like activity and can oxidize 3,3',5,5'-tetra methylbenzidine (TMB, a kind of chromogenic agent) in the presence of H_2O_2 . Upon the addition of Hg^{2+} , the catalytic activity of PCuS was greatly inhibited, which could ascribed to the formation of HgS in conjunction with the highly specific binding sites on the PCuS surface, causing the blocked active sites. This study could enlighten new thoughts and provide deeper understanding for heavy metal ions monitoring by using MOF-derived materials as peroxidase-mimicking detector. In the research of Wang's group, conversely, a trace amount of Cr(VI) dramatically accelerated the TMB oxidation without H_2O_2 because of Cr(VI)-boosted oxidation, leading to a color change of TMB in a very short time [319].

Emphasis in section 4 has been made on the environmental applications of MOF-derived nanomaterials. Among various reported technologies, adsorption and catalysis have been extensively studied and utilized for the removal of pollutants in aquatic solution. In the air purification, MOF-derived nanomaterials with the ultrahigh porosity and adjustable pore sizes show remarkable capture ability and high selectivity for CO_2 from flue gas and natural gas. Radionuclide (mainly Xe and Kr) adsorption and separation from gas mixtures are also covered in this section. Though rare articles have been issued to illustrate Xe/Kr separation using MOF-derived materials, the potential of these derivatives as adsorbents to separate noble gases (Xe and Kr) has been presented in the limited studies. As for targeted pollutants detection, MOF-derived hybrids can serve as sensing materials to construct sensing platform for the determination of gaseous pollutants, organic pollutants and heavy metal ions. The sensitivity, stability, reproducibility and selectivity of the prepared sensing materials have been discussed in detail. Moreover, the control of selectivity, which more relies on the properties of sensing materials, is still a main challenge in sensors. Therefore, more in-depth investigations are required to further optimize the sensing performance.

5. Summary and perspectives

Over the last few decades, the extremely rapid development of global economy is accompanied by unprecedented destruction of the environment. The search of advance materials with suitable properties has become a impressing method to mitigate the ever-increasing concerns related to the environment pollution. Recent research progress in MOFs has demonstrated they can function as ideal precursors or sacrificial templates for the preparation of various nanomaterials, including metal compounds (e.g. metal oxides/chalcogenides/phosphides/carbides and their composites), carbons with or without heteroatom doping (e.g. S, B, P, O and N), as well as metal/carbon composites. To date, MOF-derived hybrids with versatile compositions, morphologies and properties have been acquired successfully and subsequently utilized in wide fields. Particularly, nanostructured materials derived from MOFs

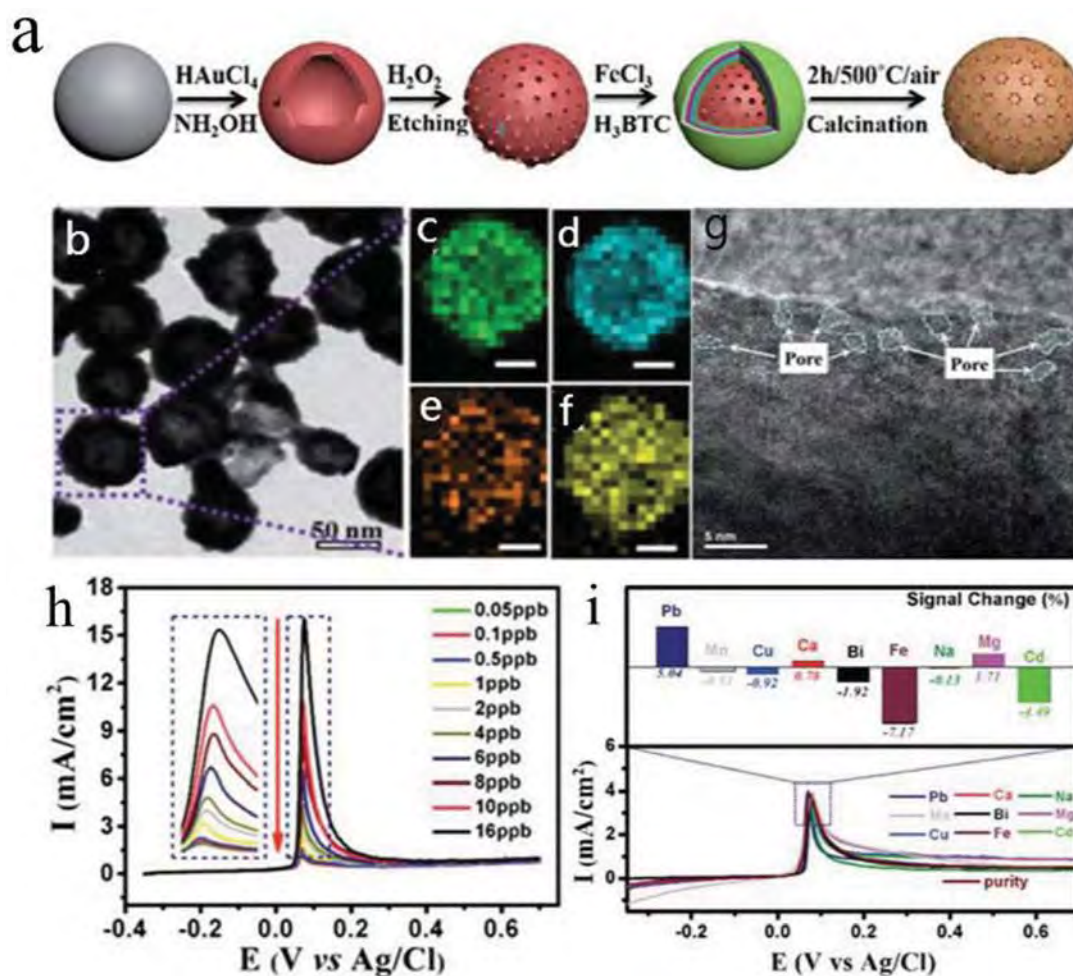


Fig. 21. (a) Schematic of the fabrication of the plasmonic Ag/Au HPNSs@FO. (b) typical TEM images of Ag/Au HPNSs@FO; (c–f) the corresponding EDS elemental mapping images of a fragment of the Ag/Au HPNSs@FO: (c) Au, (d) Ag, (e) Fe, and (f) O (scale bar in (c–f): 20 nm); (g) High-resolution TEM image of Ag/Au HPNSs@FO; (h) stripping voltammograms of the plasmonic Ag/Au HPNSs@FO electrode in 1 M HCl containing 2 ppb As(III) before (black) and after (red) 1000 cycles of accelerated stability test; (i) selectivity of the Ag/Au HPNSs@FO for As(III) in 1 M HCl containing 2 ppb As(III) in the presence of other metal ions; the concentration of each of the ions was 20 ppb. Reprinted with permission from Ref. [317] Copyright 2018 The Royal Society of Chemistry.

are impressive candidates for environmental cleaning and monitoring owing to their superiorities in synthesis and performance.

In the future, many issues still need to be investigated at the lab-scale, especially on the basis of obtaining a fundamental understanding of adsorption/catalytic/sensing mechanism and the relationship between structure of MOF derivatives and their performance, which could provide a guidance for the predesign and development of MOF-derived nanomaterials. Of course, to realizing environmental protection in real, further development should be made on MOF derivatives to meet their commercial demonstrations. Researchers must focus on the simplification of synthesis procedures and cost optimization while seeking routes to improving their stability, selectivity and reusability. Therefore, attention must be paid to the fabrication of MOF derivatives with unique properties to maximize their efficiencies and ensure their industrial applications under various harsh conditions.

Though amazing progress have been developed, advanced materials derived from MOFs are still in infancy and some challenges remain to be solved. Numerous efforts are needed to realize the practical usage of MOF-derived nanostructures. Here, we present several bottlenecks and perspectives for future work in this field.

(1) In view of environmental protection, MOF precursors with eco-friendly metal nodes are more worthy of consideration in future work. The pH endurance, recyclability and resistance to the concentrations of chemicals present in the contaminated environment of adsorbents/catalysts are required to further improvement by wide investigations. Additionally, the good separability of these materials are important, which can be achieved by applying affordable gravitational (centrifugal) or endowing them with magnetism. Adsorption ability is greatly related to the heteroatom doping (e.g. N and/or O species) and the surface properties (e.g. BET area, pore volume and porosity), while the contribution of heteroatoms was not distinctly demonstrated. Besides, N-doped carbons derived from MOFs have abundant adsorption sites whereas they are usually hydrophobic. Thus, such studies are impressive and important for enhancement of adsorption capacity. For catalysis, many researches currently have been concentrated on the removal of dyes, BPA and phenols. The studies concerned with other emerging contaminants such as PPCPs, pesticides and perfluorinated compounds are in urgent need. Moreover, researchers are supposed to identify precisely the specific active sites in

catalytic process especially those with well-dispersed active species, which can be achieved by some advance technologies such as density functional theory (DFT). As for air purification, the selective capture of target gas from mixed gas system are of great important, many attempts to prepare the MOF derivatives with well-designed structure and favorable surface properties should be made. In regard to sensing, most studies about gaseous environmental pollutants focus on the VOCs detection, especially acetone. Other harmful gases such as H₂S, HCHO and NO_x need to be given more attention in the future. Moreover, further development is necessary in the functional properties of MOF-derived nanomaterials to achieve the trace detection in water and air and important fundamental and mechanistic researches are imperative to fully explore their real potentials.

- (2) Most studies have the tendency to choose the widely used and common type of MOFs as precursors/sacrificial templates, such as ZIFs, MILs and PBAs. More alternative MOFs should be explored especially those with exclusively designed characteristics to gain the optimization in performance. Moreover, most of the reported investigations have focused on converting MOFs into carbonaceous materials, metal oxides and their composites, while reports on metal chalcogenides, metal phosphides and metal carbides are relatively rare due to the narrow understanding of their reaction mechanism.
- (3) Pyrolytic treatment is the most widely used method for the preparation of MOF derivatives, while the harsh synthesis conditions such as long reaction time and high temperature lead to the increased operational cost. In addition, high-temperature calcination in the synthesis may cause the destruction of inherited ordered structure and porous morphology, further weaken their reaction activity. Ligand extraction method and mechanochemical synthesis (solvent-free) seen to be better choices owing to the mild reaction conditions. However, only a few examples were reported, thus further investigation is needed. Taking production cost and benefit into consideration, operative, low cost but effective synthetic methods are eager to be introduced for the development of MOF-derived nanomaterials with enhanced performance.
- (4) The morphology and structure of MOF derivatives determine their performance in a specific domain to some extent, which are greatly related to the reaction conditions such as heating rate/time, pyrolysis temperature and gas atmosphere. However, the transformation process from MOFs to their derivatives is unclear owing to the limited knowledge of the evolution mechanism. More systematic researches are highly needed to realize the precise control of synthetic routes for the preparation of fine nanostructures. Emerging technologies such as X-ray absorption fine structure, X-ray absorption near edge structure and aberration-corrected high-angle annular dark-field imaging scanning transmission electron microscopy are helpful to understand these mechanisms.
- (5) To date, the long-term efficiencies of MOF derivatives in practice still leaves much to be desired, hampering their possible commercial applications. Hence, significant efforts are required to improve these functional materials for real environmental cleanup. Besides, the high price and low productivity of MOF precursors also hinder their large-scale preparation in industry. To bridge the gap between lab-scale and industrial production, the closer cooperation between scientists and factory's workers should be promoted.

In conclusion, MOF derivatives, without any doubt, have emerged as the exciting advance materials in environment-related fields, where opportunities and challenges coexist. With sustained efforts devoted to this topic, there is plenty of space to achieve the real industrial application of MOF-derived nanomaterials in the field of environmental remediation and monitoring.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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