Review

Metal-Organic-Framework-Based Single-Atom Catalysts for Energy Applications

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Metal-organic frameworks (MOFs) have demonstrated their great potential for creating single-atom catalysts (SACs) in the last 2 years. In this review, we provide a sketch about the critical roles of SACs and some key issues that have to be contended while considering their energy applications. The great opportunities provided by MOFs for the further development of SACs are discussed in the sections that follow. Furthermore, we summarize the reported approaches and illustrate the potential strategies for the construction of MOF-based SACs by taking advantage of the structural features of MOFs. The accessible characterization techniques for SACs are briefly assessed. In addition, a series of representative reports on the successful fabrication of MOF-based SACs for energy-related applications (mainly photocatalysis and electrocatalysis) are overviewed. Finally, some foresighted ideas and predictions on the future directions of MOF-based SACs are pointed out.

INTRODUCTION

Catalytic processes are of vital importance for energy storage and conversion. In these processes, efficient catalysts play a central role. Given that only the coordinatively unsaturated atoms on (or close to) the surface of catalysts can participate in the catalytic process, downsizing the metal catalysts has been recognized to be an effective way to boost the catalytic performance.[1,2] Although great progress on nanomaterials has been made in the last two decades, metal atoms are still not fully utilized at their limits, and there is still "plenty of room at the bottom."[1]

Single-atom catalysts (SACs), with their catalytic sites dispersed at the atomic level, have very recently emerged as a new research frontier in catalysis.[1–9] Realizing the maximum utilization of active metal sites, SACs usually exhibit ultrahigh activity and even selectivity toward diverse reactions, comparable to their homogeneous counterparts. On the other hand, in comparison with homogeneous metal complexes, SACs present heterogeneous characteristics such as easy separation, excellent reusability, and high stability.[1–8] Therefore, SACs can serve as an idea bridge that fills the gap between homogeneous and heterogeneous catalysts (Figure 1). Because of their unique features, SACs exhibit excellent performance in energy-related catalysis, such as photocatalysis and electrocatalysis.[2,6,8] However, with the dispersion of catalysts at the atomic level, the surface free energy will increase sharply and result in the tendency of aggregation.[1,6,8] Although tremendous efforts have been devoted to bypass this, SACs still suffer from low metal loadings (usually <1 wt %) and are prone to aggregate, partially as a result of the low surface area of support and the lack of strong interaction between metal atoms and substrates, which hampers the further development and practical application of SACs

The Bigger Picture

To address energy and resource crises, the development of efficient catalysts is necessary. Single-atom catalysts (SACs), with maximized utilization of metal atoms, offer a great opportunity for energy-related catalysis. However, a rational and general construction strategy for SACs is lacking. Metal-organic frameworks (MOFs), featuring well-defined and tailored structures and high surface area, have been recognized as very promising candidates for producing SACs. MOF-based SACs are able to integrate the strengths of both SACs and MOFs and present impressive properties in energy-related catalysis.

In addition to the reported fabrication strategies, characterizations, and energy-related applications of MOF-based SACs, this review points out potential construction avenues and applications based on in-depth structural understanding of MOFs. More efforts should be made for their general and precise synthesis and characterization, as well as for understanding their structure-property relationship.
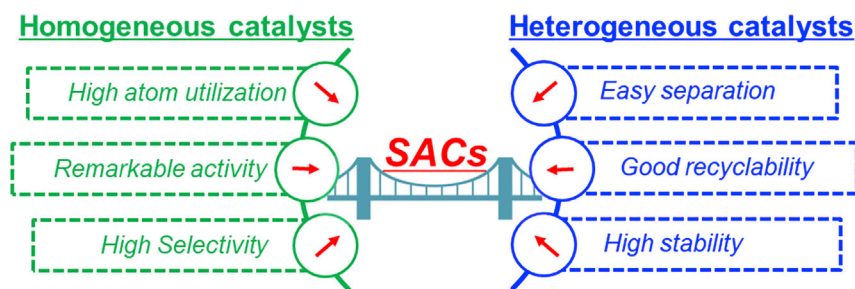
Figure 1. Relationship among SACs, Homogeneous Catalysts, and Heterogeneous Catalysts

(Figure 2).[1,6] Thus, the rational design and construction of proper substrates with high surface area and strong coordination ability are of critical importance for the anchoring of high-content SACs to ensure their stability during preparation and subsequent reactions.[1,6]

Metal-organic frameworks (MOFs), as a relatively new type of porous solid materials, have been sufficiently demonstrated to be promising in catalysis because of their ultrahigh surface area, well-defined structure, accurate designability, and flexible tailorability, all of which perfectly cater to the substrate requirement for stabilizing SACs.[10–14] Thus, they can be expected to be one of the most promising candidates to load single atoms (Figure 2). It has been widely reported that MOFs serve as supports for the construction of single-site catalysts; in sharp contrast, examples of MOF-supported SACs that have been reported so far are very limited.[15,16] On the other hand, MOF-derived materials, with (partially) inherited characteristics of MOFs, might also serve as ideal candidates for the preparation of SACs. Liu et al. first reported the thermal conversion of MOFs to porous carbon and metal oxides in inert and oxygen atmospheres, respectively.[17,18] Subsequently, Jiang et al. first pyrolyzed ZIF-8, a "star" MOF, to give highly porous carbon with very high surface area.[19] Since then, a variety of strategies have been explosively developed for the preparation of MOF-derived materials by thermal and chemical conversion.[20,21] The metal ions and clusters periodically distributed in MOFs can be converted, via high-temperature pyrolysis, to metal (oxide) nanoparticles well dispersed in the resultant composites.[20,21] With particular interactions between metal and S/N/O atoms that are usually involved in MOFs, it is highly feasible to afford SACs in MOF-derived materials by pyrolysis, i.e., MOF-derived SACs.[20–23]

Although the reports on MOF-based SACs are very limited,[24–30] they have indicated great advantages for SACs fabrication based on MOFs and demonstrated tremendous potential toward energy-related applications, opening a new chapter between MOFs and SACs. This timely review aims to provide deep insight into the construction and energy-related applications of MOF-based SACs and in turn promote the further development of this emerging research topic. Because the study of MOF-based SACs is still in its infancy, this review will propose novel strategies for the anchoring of single metal atoms onto MOFs and their derivatives. Moreover, structural characterizations and identification of MOF-based SACs and their energy-related catalysis are presented. Finally, the future outlook and our viewpoint on this exciting research topic are also discussed.

DEFINITION OF MOF-BASED SACs

When it comes to SACs, it is useful to first define single-site heterogeneous catalysts (SSHCs): "the single site may consist of one or more atoms, but each site is structurally

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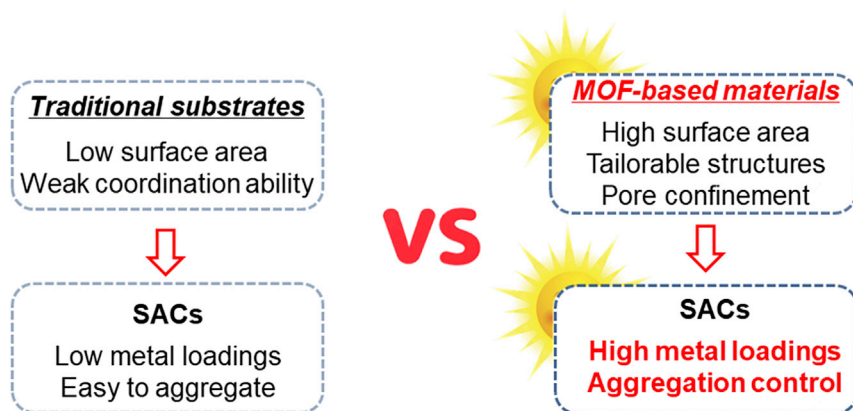
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Figure 2. Potential Advantages of MOFs over Traditional Substrates for the Fabrication of SACs

well-characterized, spatially isolated, and has the same energy of interaction between it and a reactant as every other single site, just as the single sites in homogeneous molecular catalysts are."[31,32] As indicated in the definition, single-site catalysts are composed of one or more atoms behaving the same way (each site has the same energy of interaction with the reactant as any other single site), and they are always structurally well defined. In SACs, however, the catalyst contains only isolated atoms, and the catalytic property of the individual active sites can be similar or different depending on the interaction between the single metal atom and its neighboring atoms.[1] There should be no spatial ordering or any other types of appreciable interactions among the isolated individual atoms. The active sites generally consist of the single metal atoms and the immediate neighboring atoms of the support surface or other functional species.[1] In general, the interaction between isolated metal atoms and the support in SACs strongly depends on the heterogeneous nature of the substrate surface structure rather than on the accurate and uniform coordination structure in single-site catalysts. On this basis, SACs are not a subclass of SSHCs because SAC active sites are not necessarily uniform because of the non-uniform nature of most solid supports, especially in practical industrial catalysts.

MOF-based SACs represent the SACs prepared from MOFs. They can be deemed as a subclass of the big family of SACs mentioned above, in which MOFs or MOF-derived materials (e.g., porous carbons and oxides) serve as the substrates for SACs. MOF-based SACs can be mainly classified into two types: MOF-supported SACs (with retained structure of MOFs) and MOF-derived SACs (mainly obtained by chemical and thermal conversion of MOFs).

SYNTHETIC PROTOCOLS AND IDENTIFICATION OF MOF-BASED SACs

In general, MOF-based SACs can be classified into two schemes. The first of these is the incorporation and stabilization of single metal atoms into MOFs directly, of which the original structure of MOFs would maintain to the maximum extent. The other is the derivation of MOFs via pyrolysis to construct MOF-derived SACs, endowing the resultant SACs with high stability. In addition to the summary of the reported synthetic approaches, some novel strategies that are theoretically feasible for the preparation of MOF-based SACs have also been put forward.

SACs Stabilized by MOFs
The metal stabilization effect in MOFs can be created with three possible opportunities: (1) functional organic linkers—supplying abundant coordination sites for the decoration
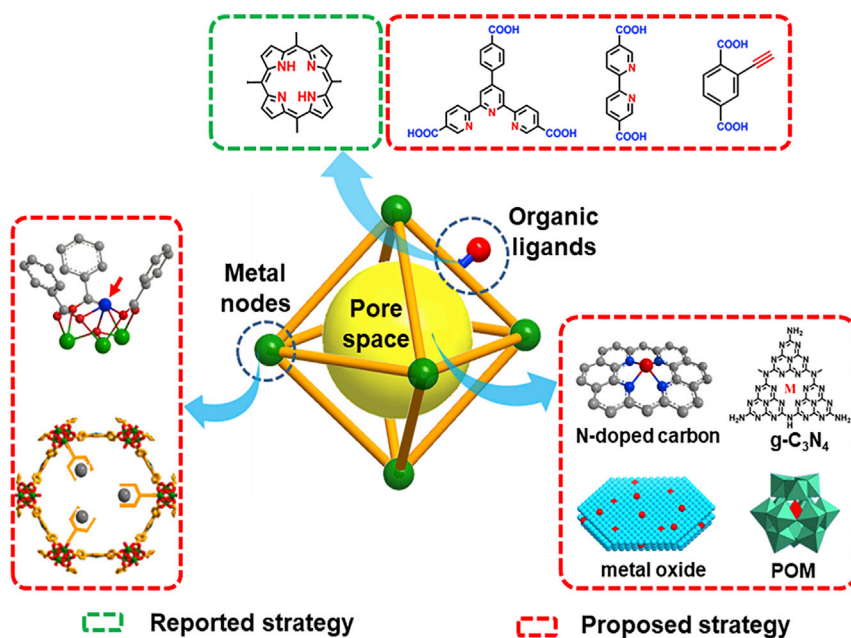
Figure 3. Various Construction Strategies for SACs Confined inside MOFs

of desired metal atoms; (2) coordinatively unsaturated metal clusters—providing coordination sites that can be furnished by other metal atoms; and (3) pore space—accommodating various guest species that can install metal atoms such as carbon-based materials, inorganic oxides, metal complexes, and polyoxometallates (POMs) (Figure 3). The great potential of the functionalization in organic linkers, metal nodes, and pore spaces makes MOFs an ideal platform for the fabrication of SACs. In this section, both reported methods and potentially feasible strategies are presented via the functionalization of organic linkers, metal nodes, or pore spaces of MOFs.

SACs Stabilized by Organic Linkers

SACs can be obtained with the assistance of the organic linkers which bear available coordination sites in MOFs. Most recently, Jiang and coworkers found that porphyrinic MOF was able to stabilize single Pt atoms through the four N atoms of porphyrin motifs (Figure 4A).[24] Similarly, single noble Pt and Ir atoms decorated on a porphyrinic MOF was also reported by Wang and coworkers.[25] Other nitrogen-containing ligands, such as bipyridine-, Salen-, and 1,10-phenanthroline-based linkers, might also offer empty coordination sites, just like porphyrin to a certain degree, for the immobilization of SACs. In addition to the coordination sites in pristine MOFs, the linkers can be grafted with chelating groups via post-synthetic strategies, which endows the organic linkers with a strong coordination ability—similar to the above N-rich ligands—to stabilize SACs.[33] In addition, the organic linkers bearing particular functional groups, such as alkyne group for Au[34] and sulfur-containing group for Pd,[35] are promising candidates for the preparation of SACs with these specific metal species. Until now, only porphyrin has been successfully applied to stabilize SACs in MOFs, and more linkers mentioned above should also be taken into consideration in future investigations.

SACs Stabilized by Metal Nodes

The metal clusters in many MOFs usually possess abundant coordinatively unsaturated metal sites, which can be readily functionalized with additional metal ions, by different recently developed methodologies (Figure 4B).[13,16,36] The additional
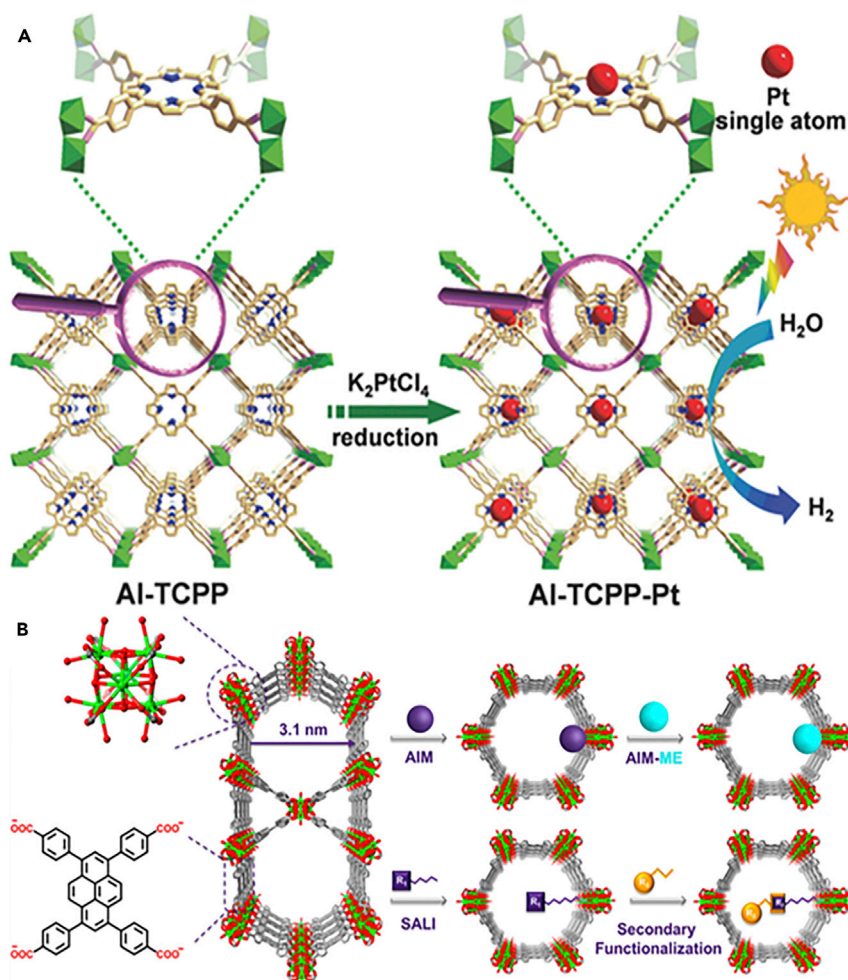
Figure 4. Examples of the Construction of SACs Stabilized by MOFs

(A) Schematic illustration for the synthesis of Al-TCPP-Pt. Reproduced with permission from Fang et al.[24] Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

(B) Schematic showing the possible synthetic strategy of SACs in MOFs by postsynthetic tuning of metal clusters. Reproduced with permission from Islamoglu et al.[16] Copyright 2017 American Chemical Society.

metal ions, which bind to the original metal clusters with low coordination numbers, might be readily reduced to SACs. Specifically, it has been reported that the atomic layer deposition (ALD) technique can be employed to construct various single-site catalysts on metal clusters.[16] Given that the ALD technique can be used to create SACs on various substrates, we believe that MOF-based SACs might also be achieved by ALD in a similar way.[37] Moreover, the ligands rich in coordination site can even be modified onto the metal nodes, which further create additional binding sites for additional single metal ions to give single-site catalysts.[38] Once these materials are further reduced, they might finally be converted to SACs.

SACs Stabilized in Pore Space

MOFs can accommodate many kinds of guest species into their pore space, offering great potentials to bind single metal atoms, thus further enriching the variety of MOF-based SACs. To endow the pore space with abundant interaction sites for SACs, some reported SAC supports (such as N-doped carbon,[39] g-C_3N_4,[40] metal

oxides,[41] and POMs[42]) in sizes smaller than MOF pore space can be incorporated into MOFs. This would cause the SACs to be confined in the MOFs. In addition, single-atom alloys (SAAs)—as another existence form of SACs—in which single metal atoms sit atop a metal support, can also serve as promising guests accommodated in the pore space of MOFs.[43] The well-defined pore structure of MOFs is beneficial for the isolation of guest species, such as SACs and fine metal clusters and nanoparticles, which integrates the merits of both the guest species and the MOFs to enable a synergistically enhanced catalysis.[44]

MOF-Derived SACs

In addition to the direct immobilization of SACs into MOFs, MOF-based materials can also be converted to SACs via a simple heat treatment. The resultant SACs usually exhibit a higher stability than single atoms immobilized in MOFs and can be applied to reactions under complex conditions, greatly extending the catalytic application. Because of these advantages, MOF-derived SACs have received significant attention in the last 2 years. However, a significant challenge lies in the tendency of the aggregation of metal atoms to give metal particles during the high-temperature pyrolysis. Through the predesign of atomically dispersed metal sites that are spatially separated with a certain distance in MOFs, the immigration of metal atoms should be effectively inhibited to give SACs after pyrolysis. In most cases, abundant nitrogen atoms are involved in MOFs constructed from N-rich ligands. Upon high-temperature pyrolysis, the organic part in the MOF can be converted to N-doped carbon materials, which possess particular advantages to anchor and stabilize single metal atoms by virtue of the metal-N interactions. The MOF-derived SACs can inherit the high surface area and porosity of MOFs to a large extent, which then contributes to the sufficient exposure of active sites and efficient mass transport, making them very promising in catalysis.

Currently, MOF-derived SACs are limited mostly to N-doped carbon-based materials. In 2015, Zitolo et al. demonstrated the feasibility for the preparation of MOF-derived SACs, and they investigated the structure of Fe-centered moieties in detail by Mössbauer spectra and X-ray absorption near-edge spectroscopy (XANES) spectra.[45] Since then, various strategies, such as mixed-metal and micropore confinement, have been developed. In addition, very recently, the mixed-ligand strategy has also been successfully implemented for the construction of MOF-derived SACs by our group (Figure 5).[30]

Mixed-Metal Strategy

By introducing two kinds of metal ions into the synthesis system, mixed-metal MOFs can be obtained if these metals can give isostructural MOFs.[26,46] Because MOF are hugely flexible, it becomes possible to introduce two or more kinds of metal ions and realize their homogeneous dispersion in the metal nodes of MOFs. Such a mixed-metal strategy has been successfully applied to the construction of MOF-derived SACs, currently focusing on the ZIF-derived SACs.[26,29] In this strategy, the second metal (such as Zn) is introduced to replace a certain proportion of targeted metal atoms (Fe, Co, Ni, etc.) in metal clusters and serve as a "fence" to expand the adjacent distances of targeted metal atoms. Followed by a pyrolysis process, the agglomeration of targeted metal atoms can be inhibited due to the long distance between them, thus making it possible for SACs to be created (Figure 6A).

Micropore Confinement Strategy

Because of to the well-defined porous structure of MOFs, pore confinement has been adopted to introduce functional guests in the creation of SACs. MOFs can encage and isolate mononuclear metal complexes that are encapsulated inside the pores.
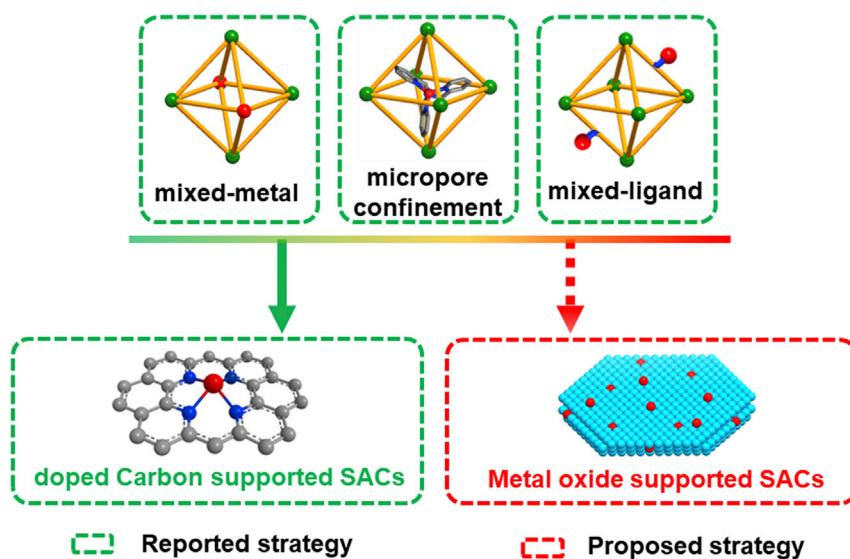
Figure 5. Construction Strategies for MOF-Derived SACs

Upon pyrolysis, the aggregation of metal atoms between nearby metal complexes is expected to be prevented, leading to atomic metal dispersion in MOF-derived materials.[27] It is worth noting that there are some prerequisites for this strategy: (1) the guests should be well encaged with particular sizes between pore diameter and pore opening, (2) mononuclear metal complexes as guests would be favorable to the aggregation control of SACs, and (3) the removal or escape of metal species in MOF skeletons after pyrolysis should be taken into account. Therefore, only special guest-MOF composites are suitable to produce SACs through this synthetic approach. For example, Fe(acac)$_3$ molecules have been successfully trapped in the cage of ZIF-8 to afford single-atom Fe catalytst upon further conversion (Figure 6B).[27]

Mixed-Ligand Strategy

Incorporation of single metal sites onto organic linkers, such as porphyrin-based ligands, in MOFs has been widely reported to afford atomically dispersed metal cations. In a manner similar to the mixed-metal strategy referred above, the mixed metal-free and metalated ligands can also be employed to construct MOFs without disturbing the topology and crystallinity of their original framework. Because of the periodic and tailorable MOF structures, it is convenient to modulate the distance between adjacent metalated ligands by simply changing the ratio of the mixed ligands. When the distance reaches a critical value, the formation of metal clusters and nanoparticles can be effectively inhibited during pyrolysis and the SACs can be successfully achieved. Taking this into account, we have successfully prepared single-atom Fe catalysts from a mixed-ligand porphyrinic MOF, clearly demonstrating the feasibility of the mixed-ligand strategy (Figure 6C).[30]

Other Strategies

Not limited to the predesign of MOFs, other unconventional strategies, while rarely reported, may also be able to afford SACs. One important finding is that, starting from a MOF-derived Ni-based catalyst, the electrochemical activation process is an effective way to transform the catalyst to isolated nickel atoms on the carbon support (Figure 6D).[47] It is a pity that the universality of this novel method has not been proved yet. In addition, using ZIF-8 derived N-doped carbon as the anchoring substrate, an unexpected phenomenon that noble metal nanoparticles (Pd-, Pt-, and
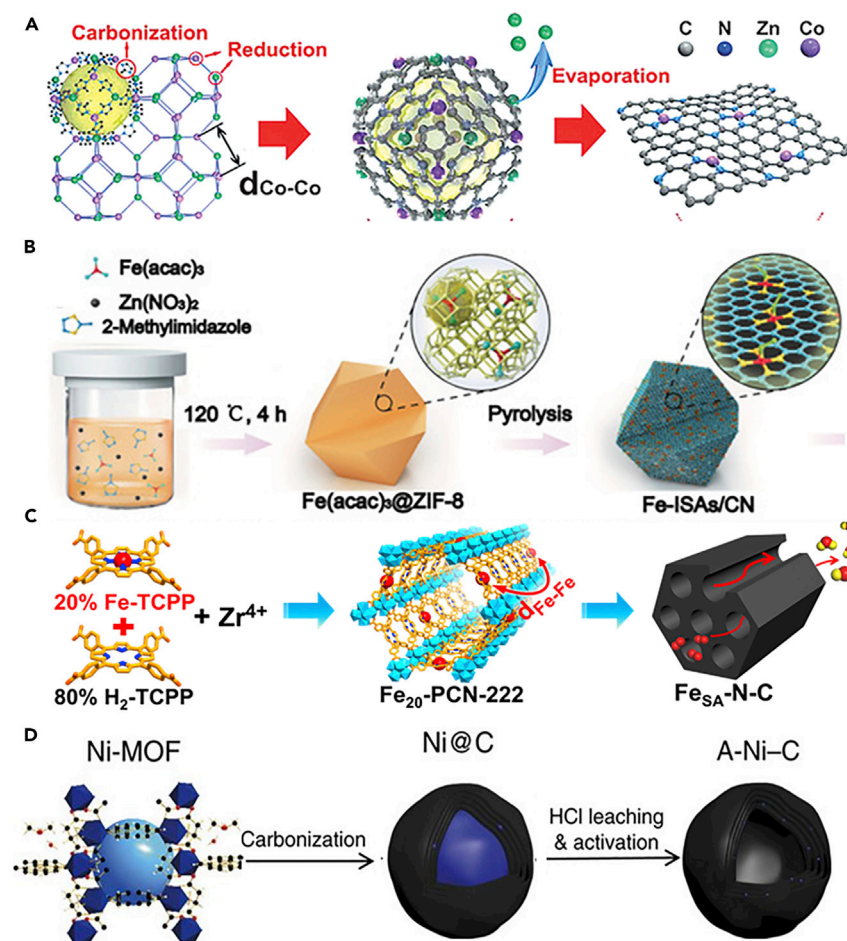
Figure 6. Examples of the Construction of MOF-Derived SACs

(A) Schematic illustration of the formation of Co SAs/N-C via a mixed-metal strategy. Adapted with permission from Yin et al.[26] Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

(B) Schematic illustration for the formation of Fe-ISAs/CN via micropore confinement strategy. Adapted with permission from Chen et al.[27] Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA.

(C) The rational fabrication of Fe$_{SA}$-N-C via a mixed-ligand strategy. Adapted with permission from Jiao et al.[30] Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

(D) Synthesis of single-atom Ni-C catalysts by electrochemical activation process. Adapted with permission from Fan et al.[47] Copyright 2016 Springer Nature.

Au-NPs) can be transformed to thermally stable single atoms (Pd-, Pt-, and Au-SAs) has also been reported by Li and coworkers. This established a convenient top-down route to obtain SACs from nanoparticles.[48]

Although various strategies toward MOF-derived SACs have been developed in a rapid pace, most of them focused on ZIF-based materials.[26,27] In most cases, the high-temperature pyrolysis of other MOF precursors usually leads to aggregated metal nanoparticles rather than SACs. The choice of proper MOFs and fine control over the preparation conditions are always required for generating SACs. The percentage of metal ions, nitrogen content of MOFs, pyrolysis temperature, and pyrolysis atmosphere all have subtle influence on the successful formation of SACs.[26,27,30,45] To realize the single-atom dispersion of targeted metals, the modulation on concentration of metal atoms, high nitrogen content, low pyrolysis temperature, and proper pyrolysis atmosphere (NH$_3$ is usually more helpful) should all be taken into consideration.

Presently, almost all reports on MOF-derived SACs are limited to N-doped carbon-based materials. Other heteroatom-doped carbon materials, such as sulfur-doped carbons, have also been proved to be effective for anchoring single atoms. These should be considered in the future designing of MOF-based SACs. In addition to carbon-based SACs, other important materials that are widely reported in other systems—such as metal-oxide-supported SACs—have never been achieved in MOF-derived materials. This is definitely a large blank in this research field.[1,3] Its successful realization would open up a wider world for the MOF-derived SACs.

Identification of SACs

The microstructures of MOF-based SACs are closely related to their properties. Therefore, it is necessary to determine their structures to better understand the catalytic properties of MOF-based SACs. Until now, various techniques—including aberration-corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), X-ray absorption fine structure (XAFS) measurement, infrared (IR), and nuclear magnetic resonance (NMR) spectroscopy techniques—have been developed to investigate the detailed microstructure of SACs. Given that a single technique usually cannot give comprehensive information, the complementary results are adopted through the use of different tools to better identify the SACs and understand their comprehensive properties.

Aberration-Corrected HAADF-STEM

The advent of aberration-corrected HAADF-STEM makes it possible to identify the active sites at the atomic level. The isolated single metal atoms can be well identified from the bright spots in the image of aberration-corrected HAADF-STEM because of the different Z value of single metal atoms compared with the atoms of the supports. This is one of the most powerful techniques to confirm the existence of single metal atoms without any metal clusters or nanoparticles (NPs) and determine the spatial distribution of the single metal atoms intuitively (Figures 7A and 7B).

XAFS Measurement

XAFS measurement is of great importance not only in the demonstration of atomic dispersion of metal atoms but also in the more detailed information of the oxidation states, coordination numbers, and coordination configurations of SACs, which is the most powerful technique to get insight into the structural information of SACs. The X-ray absorption spectrum can be divided into X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. XANES can mainly reflect the valence state and some structure information of the absorbing atom. EXAFS is strongly sensitive to the coordination environment of the absorbing atom. The absence of metal-metal bonds with the same metals in EXAFS spectra is an important implication for the successful construction of SACs. Taking the Fe_{SA}-N-C as an example, the energy absorption threshold of Fe_{SA}-N-C in XANES spectra locates between Fe foil and Fe_2O_3, implying the positively charged $Fe^{\delta+}$ Fe_{SA}-N-C (Figure 7C).[30] EXAFS spectrum of Fe_{SA}-N-C presents only a main peak attributed to the Fe-N scattering path, and no Fe-Fe bond signal at ~2.13 Å can be detected, manifesting the evolution of single-atom Fe sites in Fe_{SA}-N-C (Figure 7D).

IR Spectroscopy

It has been found that the adsorbed molecules on various active sites always present different vibrational frequencies and intensities. With the help of IR spectroscopy, it is able to deduce the dispersion state of metal atoms by monitoring the adsorption behavior of the probe molecules, such as carbon monoxide (CO).[24,50] For example, from the diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy
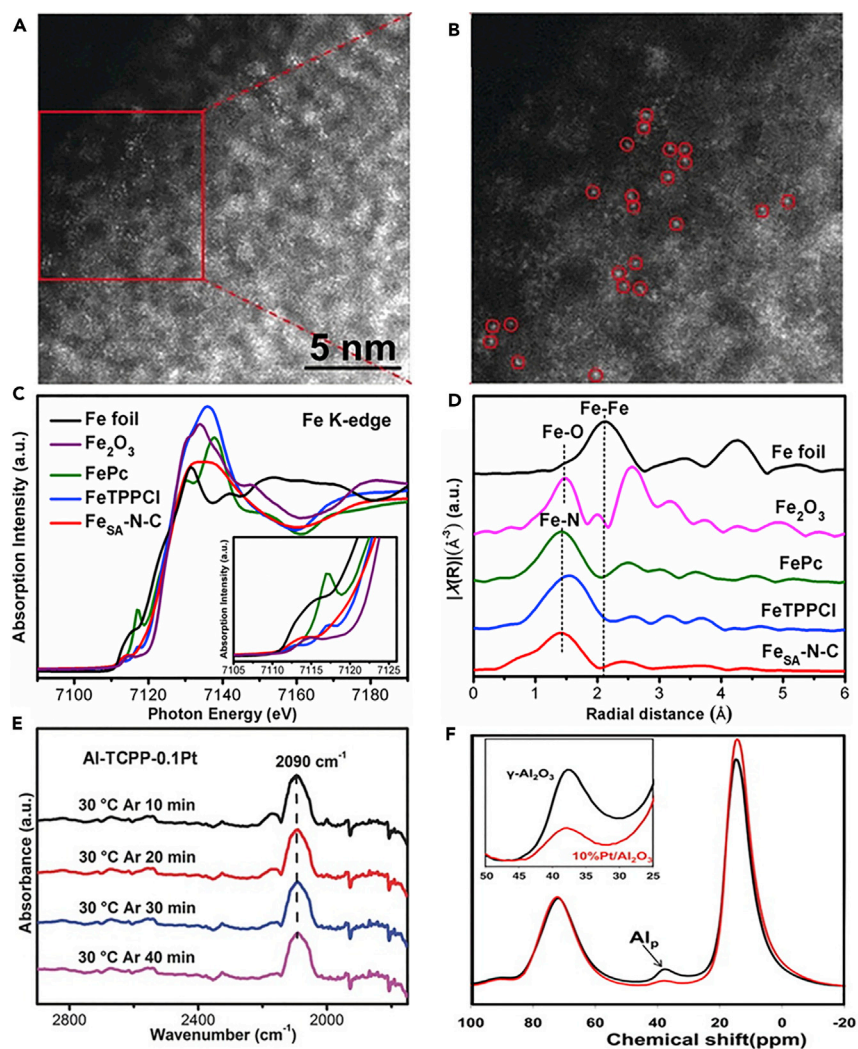
Figure 7. Various Techniques for the Identification of SACs

(A and B) Aberration-corrected HAADF-STEM image (A) and enlarged image of HNTM-Ir/Pt (B). Single Ir and Pt atoms are indicated by red circles. Adapted with permission from He et al.[25] Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

(C and D) Fe K-edge XANES (C) and EXAFS spectra of Fe_{SA}-N-C (D). Adapted with permission from Jiao et al.[30] Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

(E) DRIFT spectra of carbon monoxide adsorbed on Al-TCPP-0.1Pt after being purged with Ar gas for different time lengths. Reproduced with permission from Fang et al.[24] Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

(F) The ^{27}Al MAS-NMR spectra of γ-Al_2O_3 (black) and 10 wt % Pt/γ-Al_2O_3 (red). Adapted with permission from Kwak et al.[49] Copyright 2009 AAAS.

performed on Al-TCPP-0.1Pt, upon purging with Ar to remove any loosely adsorbed carbon monoxide, only a peak centered at 2,090 cm^{-1} can be observed, which is assignable to carbon monoxide chemisorbed on single Pt atoms (Figure 7E).[24]

NMR Spectroscopy

Solid-state magic-angle spinning NMR can provide information about the nature of the metal species and the binding ligands. This technology has been used to analyze single-atom Pt and Au catalysts.[49,51] For example, high-resolution ^{27}Al solid-state MAS-NMR spectra have been successfully applied to investigate the anchoring sites

of Pt on Al_2O_3, in which the coordinatively unsaturated penta-coordinated Al^{3+} were identified to anchor single-Pt atoms on the γ-Al_2O_3 surface through oxygen bridges (Figure 7F).[49]

MOF-BASED SACs FOR ENERGY-RELATED PHOTOCATALYSIS

With conjugated organic linkers, the MOFs are responsive toward UV and even the broad range of visible light, making them suitable photosensitizers. The high porosity of MOFs might shorten the transport distance of charge carriers to the pore surface, which can effectively suppress the volume recombination of electron-hole (e-h) pairs that is common in traditional semiconductors, making MOFs promising photocatalysts.[52,53] Meanwhile, the introduction of additional electron acceptors can further improve the charge separation and photocatalytic efficiency. The SACs stabilized by MOFs will behave as extremely dispersed co-catalysts (active centers), which improves the charge separation and then significantly promotes the photocatalytic process. Particularly, the strong interaction and close contact between SACs and MOFs would greatly facilitate the charge transfer. By the rational integration of the respective functionalities between MOFs and SACs, the SAC/MOF composites exhibit great potential toward photocatalysis.

Photocatalytic Hydrogen Production

Being integrated with MOFs behaving as the photosensitizer and stabilizer, the SACs, serving as electron acceptors and highly active centers, will significantly boost the photocatalytic reduction reactions, such as proton reduction. Very recently, Jiang's group successfully stabilized single Pt atoms into a MOF (Figure 8A). They deliberately selected a porphyrinic MOF and stabilized the single Pt atoms (0.07 wt %) on the basis of the Pt-porphyrinic N interaction. The XANES spectrum shows that oxidation state of Pt in the single-atom Pt catalysts (named Al-TCPP-0.1Pt) is +δ (δ is close to zero). Thanks to the wide spectral response of the porphyrinic MOF, the great electron trap of Pt, and the efficient electron transfer channel between the MOF and single-atom Pt, efficient photocatalytic hydrogen production, with a turnover frequency (TOF) 30 times higher than that of Pt nanoparticle/MOF composites, has been achieved under visible light irradiation.[24] In contrast, Al-TCPP-0.1Pt(II) without hydrogen reduction displays negligible hydrogen production, indicating that the reduction of Pt^{2+} to $Pt^{\delta+}$ and/or the formation of single Pt atoms are crucial to catalytic activity. Ultrafast transient absorption spectroscopy and density functional theory (DFT) calculations also give experimental and theoretical evidences to support the excellent activity of Al-TCPP-0.1Pt. Right after, Wang and coworkers reported a porphyrinic MOF decorated with two kinds of single noble metal atoms (Pt and Ir). With the high-mass loadings of Ir and Pt at 1.05% and 2.54%, respectively, the resultant material shows excellent catalytic performance for visible-light photocatalytic hydrogen production (Figure 8B).[25]

Photocatalytic Oxygen Evolution, CO_2 Reduction, and Organic Reactions

Since this is the burgeoning stage of this topic, only a few MOF-based SACs have been prepared for hydrogen production, in which the MOF and SACs mainly act as photosensitizer and cocatalyst, respectively. Other important photocatalytic reactions, such as oxygen evolution, CO_2 reduction, and organic reactions, have not been investigated yet. In fact, MOFs can not only serve as photosensitizer and/or cocatalyst (depending on the demand of targeted reactions) but also realize the enrichment of substrate molecules, such as CO_2, boosting their catalytic conversion. Therefore, MOF-based SACs have a great potential for their future development
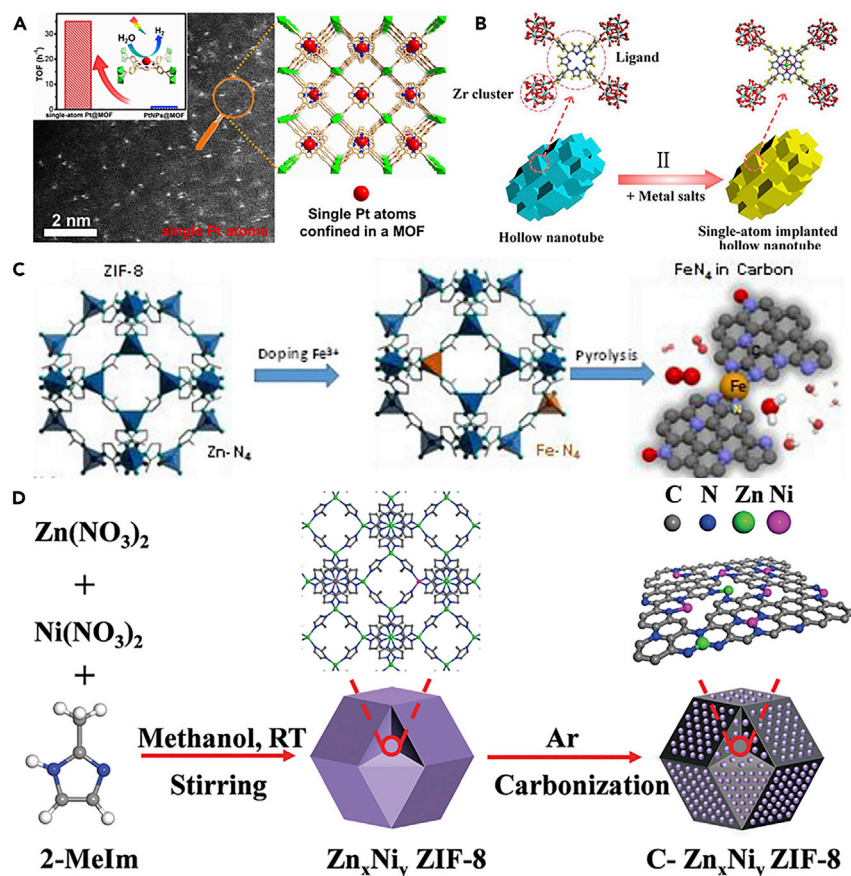
Figure 8. Schematic Illustrations of the Construction of MOF-Based SACs for Energy-Related Applications

(A) Schematic illustration of Al-TCPP-Pt SACs for efficient photocatalytic hydrogen production. Adapted with permission from Fang et al.[24] Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

(B) The formation of a single-atom immobilized hollow nanotube MOF. Adapted with permission from He et al.[25] Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

(C) The formation of Fe-doped ZIF-derived catalysts via mixed-metal strategy. Reproduced with permission from Zhang et al.[54] Copyright 2017 American Chemical Society.

(D) The formation of Fe-ISAs/CN via micropore confinement strategy. Reproduced with permission from Jiang et al.[55] Copyright 2018 American Chemical Society.

toward photocatalysis. Given the related photocatalytic mechanism, we believe that the above redox reactions are feasible and should be anticipated for MOF-based SACs.

MOF-BASED SACs FOR ENERGY-RELATED ELECTROCATALYSIS

Although MOFs for electrocatalysis are mostly restricted by their poor conductivity and weak stability under acidic and alkaline conditions, they are ideal precursors and templates to afford diversified nanostructured electrocatalysts with high conductivity and stability.[44] The MOF-derived materials can inherit the advantageous characteristics of pristine MOFs to a certain degree, including high surface area, tunable porosity, and so on. In addition, various metal sites can be uniformly introduced into MOFs. Moreover, the abundant heteroatoms in the ligands of MOFs can immobilize metal atoms and inhibit their migration under pyrolysis. As a result, the MOF-derived catalysts not only overcome the limitation of pristine MOFs but also extend

the application of MOF-based materials in catalysis. Because of these advantages, MOF-derived SACs, as special MOF derivatives, have increasingly received attention toward energy-related electrocatalysis in the last 2 years.

Oxygen Reduction Reaction

Fuel cell has been regarded as a promising choice for the green energy conversion process. However, the sluggish kinetics of oxygen reduction reaction (ORR) are still the bottleneck in fuel cells, causing efficient ORR catalysts to be highly required. The pyrolysis of MOFs has been proven to be an effective approach to the precise fabrication of efficient ORR catalysts. Among transition-metal-involved carbon-based systems, Co–N–C and Fe–N–C are important representatives because of their high performance and excellent stability toward ORR.

Via a mixed-metal strategy, the Zn/Co bimetallic MOF with a homogeneous distribution of Zn and Co was systematically designed and synthesized from the methanol solution of Zn^{2+}, Co^{2+}, and 2-methylimidazole by one-pot reaction. The Zn^{2+} in Zn/Co bimetallic MOF can serve as a "fence" to expand the adjacent distances of Co atoms. After pyrolysis, Co can be reduced along with the carbonization of the organic linker and Zn can be evaporated away at high temperatures. Under a proper molar ratio of Zn/Co, single-Co-atom-implanted N-doped porous carbon with high Co loading (over 4 wt %) can be successfully obtained, presenting a higher half-wave potential (0.881 V) than the state-of-the-art Pt (0.811 V) (Figure 6A).[26] Wu and coworkers also reported an Fe-based SAC with Fe loadings of 0.5 at % from Fe-doped ZIFs, also demonstrating much higher activities than Pt/C (Figure 8C).[54] Utilizing a similar mixed-metal strategy, Ye et al. also reported 2D mesoporous carbon doped with highly exposed single-atom Fe sites, which showed much higher ORR activities than Pt/C and those derived from 3D ZIF-7.[56] In addition, Fe(acac)$_3$ molecule was trapped in the cage of ZIF-8 via micropore confinement strategy. Upon pyrolysis, a single-atom Fe catalyst with Fe content up to 2.16 wt % was synthesized, exhibiting unexpectedly higher ORR performance than commercial Pt/C in 0.1 M KOH (Figure 6B).[27]

Not limited to the mixed-metal and micropore confinement strategy, very recently our group first put forward a mixed-ligand strategy to produce single-atom Fe catalyst based on porphyrinic MOFs with Fe content of 1.76 wt % (Figure 6C).[30] When served for ORR, the single-atom Fe catalyst demonstrated superior ORR performance in both alkaline and acidic media when compared to most reported non-noble metal catalysts and even the commercial Pt/C.

CO$_2$ Reduction Reaction

Converting CO_2 into value-added products, such as CO, HCHO, CH_3OH, C_2H_4, and other C–C coupling products, offers an attractive route toward mitigating global warming and simultaneously realizing energy storage. This provides great opportunities to MOF-based SACs. Double solvents approach (DSA), an effective method for the preparation of ultrafine nanoparticles inside MOFs,[57] can also be employed for the preparation of MOF-derived SACs. Via DSA, single-atom Ni catalyst with 1.53 wt % Ni loading derived from MOFs was prepared to present high selectivity (over 71.9%) and excellent TOF (5,273 h^{-1}) for CO_2 reduction to carbon monoxide.[58] Using mixed-metal strategy, single-atom Ni catalysts were also reported by Bao and coworkers, realizing high CO faradaic efficiencies of 92.0%–98.0% over a wide potential range of −0.53 to −1.03 V versus RHE (Figure 8D).[55] A series of single-atom Co catalysts with different nitrogen coordination numbers were obtained using a mixed-metal strategy under different pyrolysis conditions. The best single-atom

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Co catalyst with a metal loading of 0.25 wt %, in which each Co site is coordinated with two nitrogen atoms, gives a faradic efficiency up to 94% for CO_2 formation.[28] A similar mixed-metal strategy has also been employed to create single-atom Fe (0.1 at %) electrocatalysts for efficient CO_2 reduction with a high carbon monoxide faradic efficiency up to 93%.[29] The currently reported SACs based on M–N–C materials mostly produce carbon monoxide with high selectivity, while it is difficult to use them to achieve C–C coupling. The most likely explanation we proposed is that the isolated metal atoms in M–N–C materials are difficult to realize C–C coupling and stabilize C_2 intermediates. However, it could be realized in single-atom alloys (SAAs), as we think they would be favorable to the stabilization of the C_2 intermediates by the synergistic effect between single metal atoms and the supported metal NPs, which can facilitate the C–C coupling in SAAs.

In addition to MOF-derived SACs, other carbon-based SACs have also been reported for electrocatalytic CO_2 reduction.[9,59] The crystalline structures make MOFs much easier to achieve the rational design and controllable synthesis, which is of great significance for the preparation of highly-loaded SACs.[26] On the basis of MOFs, it is convenient to afford highly porous structure of SACs. In comparison, the conductivity of MOF-derived carbons is usually inferior to that of many other conductive substrates, especially graphene and carbon nanotube.[13,59] Delightedly, the successful combination of MOFs and these conductive substrates has been proved as an effective way to improve the conductivity of MOF-derived materials, supplying an effective way to improve the electrochemical performances of MOF-derived SACs.[13]

Water Splitting, Nitrogen Fixation, and Other Reactions

At this stage, MOF-derived SACs are mainly applied to the above ORR and CO_2 reduction. Other important electrocatalytic reactions, such as water splitting (hydrogen and oxygen evolution) and other related reactions have rarely been investigated over MOF-based SACs yet, while some of these reactions have been realized in other SACs systems.[37,39,60] Water splitting is an alternative way to produce hydrogen via the conversion of solar energy into chemical fuels. Traditionally, Pt is the state-of-the-art catalyst for hydrogen evolution. To reduce the use of precious metals, single-atom Pt on N-doped carbon has been developed which presents a much higher activity than Pt particle.[37] Taking advantage of strong coordination between W atoms and the free amine groups (–NH_2) in UiO-66-NH_2, a single-W-atom catalyst supported on MOF-derived N-doped carbon (W-SAC) was reported, presenting high activity and excellent stability for HER.[61] From a Ni-based MOF, Yao and coworkers obtained a single-atom Ni catalyst by electrochemical activation of Ni-MOF derived materials. When being investigated for hydrogen evolution, the single-atom Ni catalyst exhibits extreme low overpotential and impressive durability.[47] One of the significant advantage of SACs is the well-defined active sites, which could benefit the precise understanding of the catalytic reaction pathway. Based on a general approach to a series of monodispersed atomic transition metals (Fe, Co, Ni, et al.) embedded in nitrogen-doped graphene, Huang and coworkers successfully identified single-atom Ni catalyst (Ni-NHGF) to be a highly active and stable OER catalyst.[39] In addition, nitrogen reduction, another new research topic in electrocatalysis, can also be efficiently promoted by SACs, although the related investigation was just started. By the pyrolysis of Ru(acac)$_3$@ZIF-8 composite, single-atom Ru catalyst was first reported for nitrogen reduction very recently, achieving a faradic efficiency of 29.6% for NH_3 production with a yield up to 120.9 µg $mg_{cat.}^{-1}$ h^{-1}, which is one order of magnitude higher than the highest value ever reported.[62] The

attempt to apply MOF-based SACs toward these reactions would throw open a large space for energy applications.

CONCLUSIONS AND PERSPECTIVES

MOF-based SACs, which integrate the merits of both MOFs and SACs, present impressive physicochemical properties and a huge potential toward energy applications. Although the study of MOF-based SACs is in its primary stage, it has demonstrated very attractive and promising prospects, which deserves much more efforts. More energy-related applications, such as hydrocarbon oxidation, CO_2 hydrogenation, and dehydrogenation of formic acid,[63,64] which have been successfully catalyzed by other single atom systems, should also be realized by MOF-based SACs.

Though several synthetic protocols, such as mixed-metal, mixed-ligand and micropore confinement strategies, have been developed to fabricate MOF-based SACs, they are mostly amenable to a specific system. Moreover, the metal loading amount of SACs is still low from the viewpoint of practical applications. The general synthesis of high-loading SACs based on MOFs in a simple and scalable way still remains an imposing challenge. This basic goal will directly determine the subsequent development of energy-related applications.

Meanwhile, some foreseeable challenges, including precise fabrication, complete characterization, performance evaluation, and mechanism exploration, need to be emphasized and addressed prior to the success.

Accurate Control over Coordination Environment and Number of SACs

The accurate control over coordination environment and number of single atoms is thought to be crucial toward catalysis while poses a great challenge (Figure 9A). The catalytically active site is composed of single metal atoms as well as its neighboring atoms, and both reactivity and selectivity rely on the accurate structure of the active sites. Therefore, the control and regulation of the coordination environment and number of single metal atoms will be of great significance for their further applications in catalysis and energy. The crystalline and tailorable structure of MOFs makes them ideal candidates to realize this goal.

Synergetic Catalysis between Single-Atom Metal Sites and MOFs (Derivatives)

The local environment of active sites plays a vital role in the modulation of catalytic properties. MOFs featuring abundant functionalities, such as uniform pore size, gas enrichment, and electronic state regulation, could endow SACs with improved performance (Figure 9B). The functional synergy between single metal atoms and MOFs would enable the resultant composite catalysts to have not only high activity but also multifunctionality. Actually, not limited to MOFs, MOF-derived doped carbon materials possibly exert their special functionality together with SACs to deliver synergistically enhanced catalytic performance toward energy-related applications.

The Development of More Powerful Characterization or Analytic Methods

Presently, the techniques used for the structural characterization of SACs such as aberration-corrected HAADF-STEM, IR spectroscopy, and XAS spectroscopy, are difficult to identify the accurate coordination environment of metal atoms. Although the single-atom feature of SACs can be recognized by means of these tools, it poses a challenge to distinguish the slight difference in the coordination environment, even with the powerful XAS technique. More powerful characteristic technologies or more advanced analytic methods, which can accurately identify the light atoms
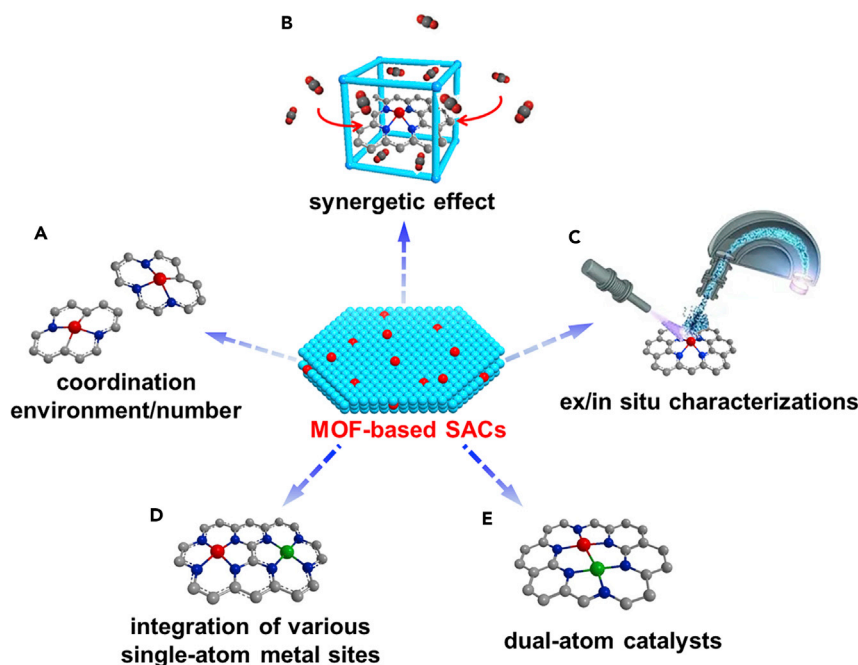
Figure 9. Foreseeable Trends in the Development of MOF-Based SACs
(A) Accurate control over coordination environment and number of SACs.
(B) Synergetic catalysis between single-atom metal sites and MOFs (derivatives).
(C) Development of more powerful characterization or analytic methods.
(D) Integration of various single-atom metal sites in a single MOF-based material.
(E) From SACs to dual-atom or multi-atom catalysts.

(such as C, H, O, and N) around the single atoms, are highly desired for the structural analysis of SACs for their exact structural information (Figure 9C). These would help us better understand the relationship between structure and properties, as well as the reaction mechanism of SACs.

Although SACs have been investigated for several years, little knowledge has been obtained about the intermediate process of their catalytic reaction. In many cases, only the fresh catalyst has been carefully characterized. It has been demonstrated that dynamic structural transformation of nanoparticulate metal catalysts is quite common in heterogeneous catalytic reactions. Taking this point into consideration, more time-resolved technologies, such as *in situ* XAS, XPS, IR, and Raman spectroscopy, should be adopted to trace the intermediate states and detect the evolution of SACs under reaction conditions. The information would be of great significance for a deep understanding of the catalytic mechanism of SACs and promote the development of efficient SACs for further applications.

Integration of Various Single-Atom Metal Sites in a Single MOF-Based Material

More than one kind of single-atom active sites stabilized to a single MOF-based material might be able to offer multi-functional catalysts and/or multi-active sites. Because of their particular structural advantages, MOFs are ideal precursors to incorporate (or pyrolyze to give) different types of single metal atoms. The intimate contact and synergistic effect among these single-atom metal sites will greatly improve energy conversion (especially photocatalytic applications), or be possibly applicable to cascade catalytic process (Figure 9D). For example, single-atom Fe and Co dual active sites on

nitrogen-doped carbon have been proved to possess better ORR performance than pure Fe–N–C or Co–N–C material by Zhang et al.[65] In addition, Fe, Mn–N/C with single-atom Fe and Mn dual active sites was also reported by Chen and coworkers and presented a much higher ORR performance than commercial Pt/C.[66]

From SACs to Dual-Atom or Multi-atom Catalysts

It needs to be emphasized that SACs would not be definitely superior to any other catalyst in all aspects. Especially, some catalytic processes require multi-metal active sites which a single metal atom might not be able to accomplish. The accurate design and fabrication of dual-atom and/or multi-atom catalysts would also be significant research targets in advanced catalysis for energy applications (Figure 9E).[67,68] MOFs with designable and tailorable structures make it possible to realize the accurate control over the atom species and the numbers of the catalytic sites. By means of well-designed synthetic strategies, advanced characterization technologies, and theoretical simulations, significant progress would be achieved, at a very quick pace, in understanding the fundamental properties of MOF-based SACs and achieving the ultimate goal of tuning the catalytic process at the atomic level. As a new research topic, the study of MOF-based SACs is becoming a new frontier and lies at the interface of chemistry, materials, catalysis, and energy. As a matter of fact, in addition to MOFs, COFs and other porous polymer materials, which feature very similar structural frameworks could also be served as promising platforms for the preparation of SACs, though they are rarely reported on.[69,70]

Currently, the limited reports we have read might be the tip of the iceberg with respect to the energy application potential of MOF-based SACs. We are confident that the future of this field is indeed very bright.

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AUTHOR CONTRIBUTIONS

H.-L.J. proposed the topic of the review. L.J. investigated the literature and wrote the manuscript. H.-L.J. and L.J. discussed and revised the manuscript.

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