Single-Atom Catalysts: Synthetic Strategies and Electrochemical Applications

Yuanjun Chen,1 Shufang Ji,1 Chen Chen,1 Qing Peng,1 Dingsheng Wang,1,* and Yadong Li1,*

The performance and the cost of electrocatalysts play the two most vital roles in the development and application of energy conversion technologies. Single-atom catalysts (SACs) are recently emerging as a new frontier in catalysis science. With maximum atom-utilization efficiency and unique properties, SACs exhibit great potential for enabling reasonable use of metal resources and achieving atomic economy. However, fabricating SACs and maintaining the metal centers as atomically dispersed sites under synthesis and catalysis conditions are challenging. Here, we highlight and summarize recent advances in wet-chemistry synthetic methods for SACs with special emphasis on how to achieve the stabilization of single metal atoms against migration and agglomeration. Moreover, we summarize and discuss the electrochemical applications of SACs with a focus on the oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), and CO2 reduction reaction (CO2RR). At last, the current issues and the prospects for the development of this field are discussed.

Introduction

Single-atom catalysts (SACs) with isolated metal atoms dispersed on solid supports have recently emerged as a new frontier in catalysis science and have attracted extensive research attention.1,2 Traditional heterogeneous catalysts usually contain a mixture of a broad size distribution of metal particles. Only a small fraction of metal particles with a suitable size distribution can serve as catalytic active species, whereas other-size particles are either inert or may trigger undesired side reactions.3,4 Such catalysts suffer from a low metal utilization efficiency and poor selectivity, which leads to a high metal consumption along with cumbersome and expensive product purification and waste disposal. Homogeneous catalysts with well-defined active sites and tunable coordination environments exhibit excellent activity and exclusive selectivity for a specific reaction. However, limitations such as poor stability and bad recyclability persist.

SACs inherit the merits of both heterogeneous and homogeneous catalysts and exhibit great potential to bridge the gap between heterogeneous and homogeneous catalysis.5–7 The development of SACs can enable the reasonable use of metal resources and facilitate atomic economy through recycling and maximum atom-utilization efficiency. The unique electronic structure and unsaturated coordination environments of the active centers in SACs have been proven to improve catalytic activity in a variety of reactions.8–12 The homogeneity in the active sites and geometric structure of SACs, which shows similarities to their homogeneous catalyst analogs, gives them great potential to enhance selectivity because of similar spatial and electronic interactions with substrates.13–16 Moreover, structural simplicity and homogeneity facilitate precise identification and characterization of

Context & Scale

The development of synthetic strategies plays a fundamental role in advancing catalysis science and practical application of single-atom catalysts (SACs). Owing to the high surface energy of single atoms, achieving the atomic dispersion of mononuclear metal precursors and stabilizing the as-formed single atoms against migration and agglomeration are key aspects in the synthesis of SACs. Several innovative synthetic strategies for SACs are summarized and highlighted through discussion of recent advances in the synthesis of SACs via wet-chemistry approaches.

Furthermore, the great potential of SACs in electrochemical applications, with special emphasis on key clean energy conversion reactions including the oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), and CO2 reduction reaction (CO2RR), are presented and discussed. Further research on single-atom catalysis should focus on understanding the structure-performance relationship and catalytic mechanism at the atomic scale by employing SACs as model systems with the aid of
active sites. This, in turn, facilitates a comprehensive understanding of the correlations between structure and catalytic performance and helps achieve rational catalyst design for targeted reactions at the atomic scale.6,17–20

The design concept of constructing isolated atoms as active species of heterogeneous catalysts can be traced back to the study by Thomas and co-workers in 1995.21 They reported a Ti single-site heterogeneous catalyst through grafting metallocene complexes onto mesoporous silica for the epoxidation of cyclic alkenes. In 2000, Heiz and co-workers used mass-selected soft-landing techniques to prepare size-selected Pd\(_n\) clusters (1 \(\leq\) n \(\leq\) 30) supported on thin MgO(100) and found that a single Pd atom is enough to catalyze acetylene cyclotrimerization for benzene.22 In 2003, Flytzani-Stephanopoulos and co-workers reported a cationic single-site Au catalyst for the water-gas shift reaction, which was synthesized by co-precipitation and then leaching Au particles by NaCN.23 In 2007, Lee and co-workers fabricated a single-site mesoporous Pd/Al\(_2\)O\(_3\) catalyst for selective aerobic oxidation of allylic alcohols by an impregnation method.24 In 2011, Zhang and co-workers employed a co-precipitation method to prepare single Pt atoms supported on iron oxide with high activity and stability for CO oxidation.6 However, owing to the high surface energy of isolated atoms, most available SACs must keep a low loading (usually near 0.1 wt %) to avoid aggregation, which limits the development of SACs. In 2016, Li and co-workers made a significant breakthrough to accomplish an order-of-magnitude improvement of the metal loading up to 4 wt %, which holds great promise for achieving the practical application of SACs.25 Moreover, they have developed a series of synthetic methods by making use of the features of metal-organic frameworks (MOFs),17,26–29 defective metal oxides,12,30–32 and polymers33–38 to achieve the versatile synthesis of various SACs, which offers a basis for single-atom catalysis science and industrial applications.

Advanced characterization techniques are very important for the development of single-atom catalysis, which offers strong data to confirm the electronic and structural properties of SACs. Sub-angstrom-resolution aberration-corrected scanning transmission electron microscopy (AC-STEM) can be used to directly observe the distribution of single atoms and even obtain the atomic structure of SACs.39 It is worth mentioning that the energy supplied by the electron beam may drive the dynamic hopping and migration of single atoms, resulting in inaccurate atomic characterization images. Therefore, when we perform AC-STEM analysis, we should ensure that test samples have great tolerance to the electron beam and take measures to mitigate the negative effect of electron beam. In addition, some foreign impurities may lead to deleterious effects on the quality of images. Warner and co-workers found that, compared with clean MoS\(_2\) surface, atomic structure and positions of Pt atoms change in contaminated carbon regions, because Pt atoms bond with the surrounding amorphous carbon, which destroys the intrinsic interactions between Pt atoms and MoS\(_2\).40 Therefore, the samples should be kept clean to eliminate impurity interference before testing. Synchrotron-radiated X-ray absorption fine structure (XAFS) measurement is a powerful tool for obtaining detailed information to determine the local atomic and electronic structure of SACs.41 The XAFS spectral region covering the energy from the absorption edge to 30–50 eV above the edge is generally called the X-ray absorption near-edge structure (XANES), which is sensitive to charge state and orbital occupancy of metal atoms. Extended X-ray absorption fine structure (EXAFS) spectroscopy represents the spectral region, extending the energy above the absorption edge range from 30–50 eV to 1,000 eV or more. The coordination number and distance between the center atoms and neighboring atoms can be extracted via Fourier transform (FT) analysis.
of EXAFS spectroscopy. Wavelet transform is a perfect supplement for FT, which can discriminate the backscattering atoms even when they overlap substantially in $R$ space and provide a powerful resolution in both $k$ and $R$ spaces. In addition, advanced computational methods such as density functional theory (DFT) calculations can be performed to confirm the most stable configuration of SACs and provide important information on atomic structure. Fourier transform infrared (FTIR) spectroscopy of a CO probe molecule can offer additional information to demonstrate the structure and dispersion of active centers.

Structural uniformity should be defined as one of the essential properties of SACs, and it is the basis for suggesting that SACs have great potential to connect heterogeneous and homogeneous catalysis and serve as ideal model systems to investigate the structure-performance relationship. FTIR spectroscopy of CO probe molecule is an effective tool to assess the degree of uniformity of SACs. Gates and co-workers used full width at half-maximum values of metal carbonyl infrared spectra to guide the synthesis for uniformity of SACs and revealed that the degree of the uniformity can be controlled by the optimization of the synthesis temperature, the zeolite Si/Al ratio, and the degree of metal oxide crystallinity. In addition, they found that isolated Ir atoms are predominantly located at sites with three O atoms at low loading; however, isolated Ir atoms increasingly populate the sites of edges and corners as the loading increases because not enough sites with three O atoms serve as anchoring sites to incorporate with Ir atoms, leading to structural nonuniformity of SACs. Christopher and co-workers reported that Coulombic attraction between the surface oxygen anion of TiO$_2$ support and the cationic [(NH$_3$)$_4$Pt]$^{2+}$ precursor can be enhanced by tuning the solution pH, which facilitates the formation of isolated Pt atoms at the same adsorption sites on the TiO$_2$ support. Obviously, careful control of synthetic conditions plays a critical role in the synthesis of uniform SACs. Li and co-workers have proposed several original strategies to achieve the structural uniformity of SACs. They exploited materials with uniform morphology and definite defect structure as supports or constructed the same anchoring sites on supports to ensure the same interaction between metal atoms and supports for homogeneous single-atom active sites. Moreover, they employed MOFs with fine-tunable and uniform pore structure as supports to encapsulate or anchor metal precursors to achieve their homogeneous atomic dispersion, followed by thermodynamic control with high-temperature thermal treatment to form a thermodynamically stable single-atom configuration.

With the increasing depletion of resources and environmental concerns, sustainable and fossil-free electrochemical energy conversion has attracted extensive attention, which has been regarded as a promising pathway to produce clean energy and value-added chemicals. Many advanced clean energy technologies, such as fuel cells, metal-air batteries, water splitting, and CO$_2$ reduction for fuel production have been exploited based on key electrochemical transformations of small molecules (e.g., oxygen, water, and carbon dioxide). The prosperous implementation of these clean energy technologies is significantly affected by the cost and catalytic performance of electrocatalysts. Employing single-atom materials as electrocatalysts is a promising approach to reduce catalyst cost and enhance catalytic performance for electrocatalysis. The maximum atom-utilization efficiency of SACs makes them exhibit excellent performance at a low consumption, which is beneficial for the decrease of catalyst cost. It is well accepted that increasing the number of active sites and enhancing the intrinsic activity of each active site are two aspects for boosting the activity of electrocatalysts. SACs with fully exposed active atoms can effectively increase the number of active sites.
low-coordination environment and charge-transfer effect of SACs via enhanced metal-support interaction has been proven to enhance the intrinsic activity of active sites. The simultaneous improvement of these two aspects endows SACs’ great potential to enhance electrocatalytic activity. The homogeneous structure enables the enhancement of selectivity of SACs due to similar spatial and electronic interaction with reactive species.

In this review, we highlight recent advances in wet-chemistry synthetic strategies for SACs and discuss how to accomplish the atomic dispersion of metal precursors and stabilize the as-formed single atoms against migration and agglomeration, which are key to achieving synthesis of SACs. Furthermore, we summarize the great potential for the application of SACs in key clean energy conversion reactions including the oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), and CO₂ reduction reaction (CO₂RR). The introduction of electrochemical applications of SACs focuses on the origin of the excellent electrocatalytic performance of SACs by correlating with the unique electronic and structural properties of SACs. In the end, the major issues and prospects for the synthesis and application of SACs are presented, and the challenges and opportunities for further research on single-atom catalysis are proposed.

**Wet-Chemistry Synthetic Methods for SACs**

Exploration and development of synthetic methodologies for SACs has become one of the most important research focuses. However, owing to high surface energy, isolated single atoms easily migrate and aggregate into particles. Therefore, fabricating SACs and maintaining atomic dispersion of metal species under realistic synthesis and reaction conditions are challenging. Mass-selected soft loading and atomic layer loading are two effective approaches to fabricate SACs; however, high-cost equipment and low yield limit large-scale production. Another, more desirable approach, from a practical viewpoint, is to develop wet-chemistry synthetic methods for SACs due to easy operation and feasibility of large-scale manufacturing. In the wet-chemistry synthetic approach, mononuclear metal species usually are selected as the precursor; therefore, taking synthetic strategies to achieve atomically dispersed separation and isolation of precursor and preventing the as-formed single atoms from migration and agglomeration are vital for the synthesis of SACs.

**Defect Engineering Strategy**

To restrict the migration of metal atoms on supports, controlled construction of defects on supports is an effective approach. The existence of defects can alter the surrounding electronic structure and coordination environment, leading to the appearance of vacancies and unsaturated coordination sites. These defects on supports can serve as “traps” to capture metal precursors and anchor metal atoms during post-treatment. As a class of typical defects, cation vacancies have been recently exploited for synthesizing SACs. The synthesis of Pt SACs with a high Pt loading, up to 2.3 wt %, was achieved by employing defect-rich nickel hydroxide (Ni(OH)ₓ) nanoboards with abundant Ni²⁺ vacancies as support. For comparison, Pt nanoparticles (NPs) were formed by using the perfect Ni(OH)₂ as support even with the lower Pt loading of 0.9 wt %. X-ray absorption spectrometry analyses and DFT calculations reveal that high metal loading and excellent stability of single Pt atoms are ascribed to the stabilization effect of Ni vacancies as anchoring sites via an enhanced charged-transfer mechanism (Figures 1A and 1B). Much effort has been devoted to constructing surface oxygen vacancies in metal oxide as “traps” to prevent the leaching and aggregation of isolated metal atoms.
a defective TiO2 nanosheet with oxygen vacancies was prepared as support. The oxygen vacancies not only accommodate and stabilize isolated Au atoms, but also promote the formation of a unique Ti-Au-Ti structure (Figure 1C).30

The enhanced interaction between metal atoms and the coordinatively unsaturated sites is usually detected, which is beneficial for stabilization of single atoms. It is proved that employing the coordinatively unsaturated pentacoordinate Al\(^{3+}\) (Al\(^{3+penta}\)) centers in alumina as anchoring sites can achieve atomic dispersion of metal species.63,64 The amorphous alumina with 29% coordinatively unsaturated Al\(^{3+penta}\) was prepared and used as support to accomplish atomic dispersion of Ru species.64 Sulfur vacancies frequently exist in layered transition metal...
dichalcogenides such as MoS$_2$ and WS$_2$. The important role of sulfur vacancies in the formation of isolated metal atoms against sintering has been revealed.\textsuperscript{9,40} Tsang and co-workers synthesized single MoS$_2$ molecular layers with rich sulfur vacancies on the basal plane through Li intercalation and chemical exfoliation.\textsuperscript{9} These S-deficient MoS$_2$ layers can trap and bind thiourea-based Co species with high affinities via refilling of the S vacancies to obtain isolated Co atoms dispersed on MoS$_2$ monolayers (Figure 1D). Experiments and DFT calculations reveal unexpected activity and excellent stability as well as the lack of sulfur loss are attributed to strong covalent attachment of Co atoms to monolayer MoS$_2$ and the presence of Co-S-Mo interfacial sites, which are formed with the help of S vacancies. C vacancies often appear in carbon-based materials, which can serve as anchoring sites to bind single metal atoms via electron transfer between metal atoms and carbon atoms.\textsuperscript{65,66} Chisholm and co-workers reported a catalytically active Nb catalyst with isolated Nb atoms in onion-like carbon shells.\textsuperscript{65} Theoretical calculations demonstrated that the tri-vacancy sites in the carbon layer are the most energetically favorable for anchoring Nb atoms. The enhanced electronic conductivity and chemical stability is attributed to the redistribution of d-band electrons of Nb atoms owing to incorporation with carbon atoms. Chen and co-workers also revealed that great stabilization of single Ni atoms in acidic solutions is ascribed to the charge transfer between Ni atoms and surrounding C atoms.\textsuperscript{66} Step edges are one of the most ubiquitous surface defects on solid supports. Rational design and utilization of step edges can improve metal dispersion.\textsuperscript{42,43} Fabris and co-workers reported that Pt segregation at monolayer-high ceria step edges contributes to the stabilization of single Pt$^{2+}$ ions in planar PtO$_4$ moieties (Figure 1E).\textsuperscript{61}

When we apply the defect engineering strategy to synthesize SACs, we should first optimize the construction conditions of defect engineering to ensure the formation of uniform defective centers as anchoring sites to homogeneously stabilize single atoms. In addition, the type of defects should be clearly characterized, which is beneficial for selecting suitable metal species as precursors and taking measures to avoid the disappearance and transformation of defects during the post-treatment process.

Compared with the common synthetic process of SACs, the defect engineering strategy takes advantage of defects to trap metal precursors and stabilize isolated metal atoms against sintering via an enhanced charge-transfer mechanism between single atoms and defective sites. Defect engineering strategy can tune the metal loading content of SACs by controlling the concentration of defects. The presence of defects on supports is beneficial for the formation of unique atomic structure to enhance catalytic performance. Moreover, defects can tailor the optical and electronic properties of supports, which facilitates the synergetic catalysis with SACs and expands the application of SACs in photocatalysis and electrocatalysis.

**Spatial Confinement Strategy**

Spatially confining single metal atoms into molecular-scale cages to prevent migration has been developed as an effective approach. Typically, this spatial confinement strategy includes two steps: (1) achieving high spatial distribution and atomic dispersion of metal species by separating and encapsulating suitable mononuclear metal precursors with the aid of porous materials such as zeolites, MOFs, and covalent-organic frameworks (COFs); (2) following by post-treatment for removing ligands of precursors and forming single metal atoms stabilized by the skeletons of supports.
Utilizing zeolites as hosts, mononuclear organometallic complexes with labile ligands are generally selected as precursors, which are easily converted to cationic complexes in solution. These metal precursors can be confined by regular three-dimensional molecular-scale pores of the zeolites and occupy the location of the cationic sites (such as $\text{H}^+$, $\text{Na}^+$, $\text{K}^+$) in the zeolite frameworks via ion exchange, followed by post-treatment to yield grafted site-isolated catalysts stabilized by neighboring oxygen centers within the zeolite frameworks. The $[\text{Pt}(\text{NH}_3)_4]^{2+}$ complex entered the pores of zeolite KLTL and preferentially underwent ion exchange with $\text{K}^+$ ions to be anchored by oxygen atoms from the zeolite frameworks (Figures 2A and 2B). Then, a well-defined single-site Pt catalyst was obtained by oxidation treatment. Another approach is to in situ encapsulate metal precursors into zeolite frameworks during the self-assembly crystallization process. The interaction between the metal precursors and incipient aluminosilicate building blocks is important in this method, so that the cationic metal complexes are favorable, owing to the anionic nature of the aluminosilicate building blocks. Corma and co-workers demonstrated the generation of a zeolite-confined single Pt atoms and clusters catalyst, which was accomplished by entrapping Pt complex into the lamellar zeolitic precursor during the swelling process, followed by calcination to remove the surfactant molecules.

Employing uniform and interconnected pores of MOFs as cages to achieve spatial separation and confinement of metal species has been developed to fabricate SACs. As illustrated in Figure 2C, by using molecular-scale cavities of ZIF-8 as hosts, one iron(III) acetylacetonate molecule ($\text{Fe}($acac$)_3$) can be separated and encapsulated by one cavity and not be released, since the molecular diameter of $\text{Fe}($acac$)_3$ ($d_m = \text{ca. 9.7 Å}$) is in between the diameters of the ZIF-8 pores ($d_p = 3.4 \text{ Å}$) and the cage diameter ($d_c = 11.6 \text{ Å}$). After pyrolysis, single Fe atoms stabilized by surrounding nitrogen species were formed. Apart from spatial confinement of tailorable pores, versatile and functional organic linkers of MOFs can serve as anchoring sites to stabilize single metal atoms. With the assistance of uncoordinated amine groups that located in the terephthalic acid as linkers, Ru ions were coordinated and confined in the skeletons of UiO-66-NH$_2$, which effectively inhibits the migration of Ru species (Figure 2D). Followed by thermal treatment, single-atom Ru catalyst was obtained. COFs are composed of light elements (e.g., B, C, N, O) via covalent bonds and can provide a desirable micro-environment for incorporating alien metal species into well-ordered porous structures. For example, uniform single Mo sites were confined by the robust coordination between molybdenyl acetylacetonate ($\text{MoO}_2($acac$)_2$) and benzoyl salicylal hydrazone ligands in a COF. Abundant and designable MOFs and COFs exhibit great potential to provide a broad field for creative and versatile methods for the synthesis of SACs.

Selecting suitable mononuclear metal precursors based on the molecular size and charge state is of great significance in the synthesis of SACs via spatial confinement strategy. Also, employing materials with uniform pores and regular structures as supports plays an important role in ensuring the uniformity of spatial confinement of metal species. In order to stabilize as-formed single metal atoms during the post-treatment process, some effective measures should be taken, such as selecting suitable supports to utilize their skeletons as anchoring sites or constructing abundant nitrogen species as anchoring sites through high-temperature carbonization of MOFs.

During the synthesis process via the spatial confinement strategy, the tendency for migration and agglomeration of metal species is restricted, and as-formed single
metal atoms are in situ anchored by the skeletons of supports. Therefore, SACs can be fabricated in harsher conditions compared to conventional synthetic methods. Moreover, confining single metal atoms to functionalized supports can integrate their respective advantages, which shows great promise for synergistically promoting catalysis and expanding the application of SACs. For example, constructing composite catalysts with single metal atoms confined in zeolites can combine the high activity of atomic sites and shape-selective effect of zeolites to enhance highly efficient and selective catalysis.
Coordination Design Strategy

Rationally designing coordination sites as “paws” to adsorb and bind metal precursors or metal atoms against migration and agglomeration has been developed to synthesize SACs. Based on the strong interaction between metal species and coordinating atoms with lone pairs of electrons such as N, O, and S, constructing supports with these coordinating atoms as anchoring sites allows the synthesis of SACs.34,76,77 As illustrated in Figure 3A, N sites of 5, 10, 15, and 20-tetra(4-(imidazole-1-yl)phenyl)porphyrindine (TIPP) ligands were designed to catch and separate cobalt (II) ions.34 Followed by pyrolysis, single Co atoms were anchored by surrounding N atoms. In addition, graphitic carbon nitrides (C3N4) possess a unique tri-s-triazine structure with the characteristic N/C-coordinating holes, which can provide abundant N coordination sites for the stabilization of various SACs, such as Au,82 Pt,83 and Pd.34 The supports’ own coordination features can be exploited to synthesize SACs.6,25,78,85 As shown in Figure 3B, Zn2+ ions were introduced to partly occupy coordination sites of Co, which accomplishes the systematical atomic distribution of Co nodes.25 After pyrolysis, Co nodes were in situ reduced to form stable single Co atoms stabilized by N species. Yan and co-workers employed four-coordinate oxygen holes on phosphomolybdic acid (H3PMo12O40, PMA) to stabilize single Pt atoms (Figure 3C).78 To achieve high loading content of SACs, one promising approach is to choose supports with a high specific surface area and functionalized ligands. Ethylene glycol (EG) not only protects and modifies the surface of ultrathin TiO2(B) nanosheet support but also adsorbs and binds PdCl4−2 for the formation of an atomically dispersed Pd catalyst under UV irradiation.6 Recently, nitrogen-doped carbon materials derived from polymers with N functional groups have been presented as supports to fabricate SACs.33,36–38 Li and co-workers developed a novel polymer encapsulation strategy to fabricate various SACs supported on nitrogen-doped porous carbon by pyrolysis of metal-complex-encapsulated polydopamine nanospheres.36 Nitrogen-doped graphene possesses a large specific surface area and abundant N species as anchoring sites, which has been regarded as an excellent substrate for SACs.56,79 Bao and co-workers synthesized atomically dispersed Cu(I)-N active sites with high density in a nitrogen-doped graphene matrix by pyrolysis of copper phthalocyanine and dicyandiamide.79 Obvious bright dots were observed in atomic-resolution scanning tunneling microscopy (STM) images (Figure 3D), which demonstrates that Cu atoms were atomically dispersed and that their surrounding C and N atoms are electronically rich. The atomic structure of this catalyst with atomically dispersed Cu-N2 center embedded in the graphene lattice was further revealed by the STM simulation (Figure 3E). Liu and co-workers reported single-atom Ni catalyst with high density and low valent metal centers anchored on nitrogen-doped graphene, which was prepared by pyrolysis of a mixture of amino acids, melamine, and nickel acetate.56 In addition, it is effective to introduce nitrogen or sulfur dopants as coordination sites into the substrates for capturing and anchoring isolated metal atoms against migration and aggregation.13,80,81 Tour and co-workers used this design concept to fabricate a single-atom Co catalyst by introducing nitrogen species into graphene oxide to anchor single Co atoms.80 As revealed by the AC-STEM image in Figure 3F, several bright dots corresponding to Co atoms are atomically dispersed in the nitrogen-doped graphene matrix. Huang and co-workers reported a general approach for synthesizing a series of atomically dispersed transition metals (e.g., Fe, Co, or Ni) in a nitrogen-doped graphene matrix with a definitive MN4C4 moiety.51 Nitrogen-doped graphene was prepared by embedding an exogenous nitrogen source from an ammonia atmosphere into the graphene lattices at a 900°C annealing process, which provides abundant N sites to stabilize single metal atoms (Figure 3G). Similarly, abundant doping S atoms were introduced into zeolite-templated carbon and served as anchoring sites to stabilize isolated Pt atoms.13
When fabricating SACs via the coordination design strategy, uniform coordination sites on the supports should first be controlled to incorporate single metal atoms for the formation of homogeneous active centers. And selecting suitable mononuclear metal precursors based on the strong interaction with coordination sites is

Figure 3. Coordination Design Strategy for the Synthesis of SACs
(A) Illustration of the synthesis of single Co atoms stabilized on hollow nitrogen-doped carbon. Reprinted from Han et al.,\textsuperscript{34} with permission. Copyright 2017, American Chemical Society.
(B) Formation process of single Co atoms with precise N-coordination. Reprinted from Yin et al.,\textsuperscript{25} with permission. Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
(C) The most stable structure of single-atom Pt on PMA, based on DFT calculations. Reprinted from Zhang et al.,\textsuperscript{78} with permission. Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
(D and E) Atomic-resolution scanning tunneling microscopy image (D) and the corresponding simulation image (E) of single Cu atoms embedded in nitrogen-doped graphene. Reprinted from Wu et al.,\textsuperscript{79} with permission. Copyright 2016, The Royal Society of Chemistry.
(F) AC-STEM image of single Co atoms stabilized on nitrogen-doped graphene. Reprinted from Fei et al.,\textsuperscript{80} with permission. Copyright 2015, Nature Publishing Group.
(G) Schematic illustration of atomically dispersed transition metal (e.g., Fe, Co, or Ni) catalysts. Reprinted from Fei et al.,\textsuperscript{81} with permission. Copyright 2018, Nature Publishing Group.
very important. Maintaining strong interaction between coordination atoms and single metal atoms during the whole synthesis process plays a vital role in fabricating SACs. It is worth noting that the capacity of coordination atoms to bind metal atoms can be affected by the synthesis conditions, such as solution pH and solvent type. Therefore, precise control of synthesis conditions is necessary for the successful synthesis of SACs.

The mononuclear metal precursors are adsorbed and bound by coordination sites via the coordination design strategy, which can effectively prevent their migration and agglomeration during the post-treatment process. As-formed single metal atoms exhibit higher stability via strong interactions with coordination atoms on supports compared to those SAC materials synthesized by traditional wet-chemistry methods. Moreover, the electronic structure of single-atom active centers can be tuned by the surrounding coordination atoms, leading to enhanced catalytic performance.

Other Synthetic Strategies
Other than the above-mentioned synthetic strategies, some ingenious methods have been developed for the synthesis of SACs. As illustrated in Figure 4A, an α-FeOOH nanorod was chosen as a template with coated polydopamine on the surface, followed by carbonizing the polydopamine-coated α-FeOOH nanorod composite and leaching unstable Fe species with hydrochloric acid, leading to the formation of single iron atoms anchored on the hollow nitrogen-doped carbon substrates. In this method, the α-FeOOH nanorod not only acts as a sacrificial template for obtaining a hollow structure with high surface area but also provides iron sources for production of atomically dispersed Fe species stabilized by nitrogen species. Similar sacrificial template approaches have been extended to other supports for preparing SACs. To restrict thermal motion of metal atoms, one direct method is to freeze a homogeneous solution of metal precursors. Wu and co-workers reported an iced-photochemical reduction strategy to synthesize atomically dispersed Pt catalysts. As shown in Figure 4B, an aqueous chloroplatinic acid (H₂PtCl₆) solution was frozen rapidly with liquid nitrogen. The Pt complex was atomically dispersed in ice, which was stabilized by water molecules through forming H-Pt-OH species to suppress decomposition. After reduction by ultraviolet irradiation, the frozen Pt species solution was mixed with various substrate dispersions. The final Pt SACs were obtained by centrifugation and drying. In addition, downsizing metal NPs to single atoms is achieved by the atom-trapping approach. Pt NPs supported on Al₂O₃ can convert to volatile PtO₂ and migrate into CeO₂ in air at 800°C (Figure 4C). During this process, single Pt atoms can be trapped and anchored by CeO₂ to form an atomically dispersed Pt₁/CeO₂ catalyst. Electrochemical corrosion is also employed to synthesize SACs. Yao and co-workers applied a direct constant potential to remove little Ni NPs in the graphene layers, resulting in the formation of isolated nickel atoms fixed by C species (Figure 4D).

Electrochemical Applications of SACs
Developing high-efficiency, durable, and economical electrocatalysts is of great importance for the development and commercial application of electrochemical energy conversion technologies. However, it remains a great challenge. Recently, many advanced single-atom electrocatalysts with excellent activity, selectivity, and stability have been reported. In the following section, we introduce and summarize the electrochemical application of SACs in key energy conversion reactions such as ORR, HER, and CO₂RR to demonstrate the great potential of SACs for achieving
highly efficient and selective electrochemical processes. Moreover, the relationship between the structure and performance of SACs together with the catalytic mechanism is discussed.

**Electrocatalytic ORR**

The ORR occurring at the cathode of electrochemical energy devices proceeds via either a two-electron (2e⁻) or four-electron (4e⁻) pathway. The selective 2e⁻ oxygen reduction pathway is a clean and energy-saving route to produce important fine chemical hydrogen peroxide compared to the energy-intensive anthraquinone process. The 4e⁻ pathway that reduces oxygen directly into water is highly preferred for fuel cells and metal-air batteries because of its higher energy-conversion efficiency.

The selectivity toward H₂O₂ or H₂O depends on whether the O-O bond is preserved during the ORR process. Breaking of the O-O bond requires two continuing sites to
synergistically adsorb an O₂ molecule.⁹⁷ Therefore, Pt-based SACs with isolated atomic sites show great potential for achieving the selective production of H₂O₂. Choi and co-workers reported that isolated Pt atoms anchored by sulfur-doped zeolite-templated carbon (Pt/HSC) predominantly undergo a 2e⁻/C₀ pathway for the electrochemical synthesis of H₂O₂ with high selectivity, up to 96%, rather than the conventional 4e⁻/C₀ pathway to produce H₂O₂ (Figure 5A and 5B).³ As shown in Figure 5C, Pt/HSC exhibited 97.5 μmol hr⁻¹ cm⁻² H₂O₂ production rate during the initial
1 hr in an electrochemical H₂-cell test, which confirms that the concept of selective 
H₂O₂ production in a fuel cell can be achieved by single-site electrocatalysis. Lee 
and co-workers prepared single Pt atoms and Pt NPs deposited on a TiN support 
and evaluated their behaviors on the electrochemical ORR. They found that the re-
action pathway of single-atom Pt/TiN was different from that of Pt NPs/TiN, owing 
to the absence of Pt ensembles. Single-atom Pt/TiN exhibited high selectivity to-
ward H₂O₂ with a record-value mass activity of 78 A/g at an overpotential of 
0.05 V. Furthermore, they demonstrated the support effect in single-atom Pt cata-
lysts for production of H₂O₂. They reported that a simple change of support 
from TiN to TiC can enhance catalytic activity, selectivity, and stability of Pt SACs. 
DFT calculations revealed that this disparity of properties was attributed to the dif-
fences in adsorption energies of oxygen species on TiC and TiN. It is expected that 
future optimization of coordination environment of single-atom Pt active sites and 
careful selection of the supports would enable a more selective and effective process 
for production of H₂O₂.

The high cost and scarcity of precious metal Pt and sluggish kinetics of the electro-
chemical cathode ORR are two major bottlenecks for the development of fuel cells 
and metal-air batteries. Therefore, developing high-efficiency and durable 
non-noble metal catalysts as alternatives to Pt-based materials to catalyze the ORR 
is highly desirable. Transition metal-nitrogen coordination sites supported on carbon 
matrix (M-Nₓ/C, M = Fe, Co, etc.) materials have been regarded as the most prom-
ising substitutes for Pt-based catalysts. Despite tremendous progress in M-Nₓ/C 
catalysts, their catalytic properties are still far from satisfactory. Downsizing the active 
species of M-Nₓ/C catalysts to single atoms can accomplish maximum atom-utiliza-
tion efficiency and fully expose the active sites, which is an effective approach for 
enhancing the intrinsic activity of catalysts. Moreover, structural uniformity of single-atom M-Nₓ/C catalysts makes them a model system to precisely control 
their coordination environments and geometric configurations at the atomic scale for 
optimization of catalytic properties and deeper understanding of the ORR mecha-
nism. Li and co-workers reported stable Co single atoms on nitrogen-doped 
porous carbon (Co SAs/N-C) with precise N-coordination. The dominant active 
centers for Co SAs/N-C formed at 800°C and 900°C can be defined as planar 
Co-N₄ and Co-N₂, respectively. The Co SAs/N-C with Co-N₂ center exhibited 
higher ORR activity than those of commercial Pt/C and Co SAs/N-C with Co-N₄ in 
an alkaline solution. DFT calculations demonstrated that Co-N₂ species had a stron-
ger interaction with peroxide than Co-N₄ species, which promoted the 4e⁻ ORR 
process for enhanced performance. Furthermore, they prepared a highly reactive 
single-atom Fe ISAs/CN catalyst with an Fe-N₄ active center (Figure 5D). The de-
signed experiments were carried out to reveal that maintaining Fe as isolated atoms 
and incorporating N was essential for excellent alkaline ORR performance. When Fe 
NPs were removed and isolated Fe atoms were exposed by acid leaching, enhanced 
activity was observed in view of more positive E₁/₂, which was ascribed to the expo-
sure of single-Fe atomic sites. When atomically dispersed Fe-N₄ sites were poisoned 
by SCN⁻, Fe ISAs/CN exhibited remarkably degraded ORR performance (Figure 5E). 
The performance of Fe ISAs/CN can be restored to the original level by removing 
SCN⁻ (Figure 5F). These results revealed that the active centers for the ORR on Fe 
ISAs/CN were isolated Fe-N₄ sites. DFT calculations further demonstrated that the 
outstanding activity of Fe ISAs/CN originated from the high efficiency of single-
atom Fe-N₄ sites in transporting electrons to the adsorbed OH species.

Compared with alkaline media, the ORR performance of M-Nₓ/C materials in acid 
media is less satisfactory for Pt substitution, owing to slower kinetics. Li and
co-workers reported a hollow N-doped carbon sphere with isolated Co atomic sites (ISAS-Co/HNCS).34 Aside from the excellent properties of atomically dispersed Co sites for ORR, the hollow substrate enhanced the transport of the ORR-relevant species. ISAS-Co/HNCS exhibited an excellent acid ORR activity whose $E_{1/2}$ approached that of the commercial Pt/C. Zelenay and co-workers reported an iron-nitrogen-carbon ((CM+PANI)-Fe-C) catalyst with atomically dispersed Fe-N$_4$ sites and hierarchial porosity.54 This catalyst exhibited an outstanding performance in both a rotating ring-disk electrode (RDE) test in 0.5 M H$_2$SO$_4$ and membrane electrode assembly (MEA) under realistic cathode operation in air conditions. They suggested that the catalytic active sites were carbon-embedded Fe-N$_4$ sites, which were directly visualized by AC-STEM measurement. Li and co-workers reported a unique atomically dispersed dual-metal site catalyst with porphyrin-like Fe-Co dual sites anchored on hollow nitrogen-doped carbon ((Fe,Co)/N-C).99 The performance of the (Fe,Co)/N-C catalyst in the RDE test under acidic conditions (Figure 5G) and a H$_2$/O$_2$ fuel cell test (Figure 5H), as well as H$_2$/air fuel cell operation (Figure 5I), all surpassed most reported Pt-free catalysts and approached that of commercial Pt/C. In addition to the outstanding activity, (Fe,Co)/N-C also had long-term stability and great tolerance to CO and methanol. Furthermore, DFT calculations revealed that great ORR activity and high selectivity for a 4e$^-$ ORR pathway was attributed to the unique Fe-Co dual-sites structure, which can reduce the energy barrier of O-O bond cleavage.

**Electrocatalytic HER**

Hydrogen (H$_2$) is a clean and renewable fuel. Electrochemical splitting of water through the HER is a green and sustainable route to produce hydrogen.105 Active catalysts are urgently needed to reduce the overpotential for the improvement of HER efficiency. The hydrogen adsorption free energy ($\Delta G_{\text{H}}$) is a key parameter for estimating the rate of HER.106 $\Delta G_{\text{H}}$ close to zero is a necessary but insufficient condition for high-efficiency HER catalysts. A volcano relationship plot can be obtained by DFT based on the calculation of exchange-current densities against $\Delta G_{\text{H}}$ of catalysts.107 Pt locates very close to the top of the volcano plot and has an almost thermo-neutral $\Delta G_{\text{H}}$, which has been regarded as the best HER catalyst. However, the high cost and low abundance limit the commercial application of such Pt-based catalysts. To address this issue, one approach is to increase Pt atom-utilization efficiency to reduce Pt consumption. Another approach is to develop highly active and earth-abundant Pt-free catalysts as the alternatives to Pt.

Downsizing Pt NPs into single atoms is an effective strategy for maximizing metal utilization for cost-effective HER catalysts. Sun and co-workers employed the atomic layer deposition (ALD) technique to synthesize single Pt atoms and clusters supported on N-doped graphene nanosheets.108 A remarkable enhancement of HER activity by a factor of 37 compared to the commercial Pt/C was observed on this Pt SAC. DFT calculations demonstrated that the excellent HER performance was ascribed to partially unoccupied 5d orbital density of states (DOS) of single Pt atoms on N-doped graphene nanosheets. Luo and co-workers reported a potential-cycling method to prepare single Pt atoms on CoP-based nanotube arrays supported on a Ni foam (Pt SA-NT-NF) catalyst (Figure 6A).109 This catalyst exhibited lower overpotential and better stability compared to the Pt/C for the HER in neutral media (Figure 6B). This work offers a great reference for scalable synthesis of large-area and binder-free single-atom Pt electrodes for highly efficient HER catalysts. In addition to being active sites for the HER, single Pt atoms can trigger HER performance of inert catalysts. Bao and co-workers reported that the HER activity of an inert 2D MoS$_2$ surface can be triggered through single-atom Pt doping.110 AC-STEM and
XAFS analysis verified that single Pt atoms were introduced into the in-plane domain of MoS2 nanosheets via the substitution of Mo sites. This single-atom Pt-MoS2 catalyst achieved a significant improvement of HER activity and stability compared with pure 2D MoS2 (Figure 6C). DFT calculations revealed that the absorption behavior of H on the S sites can be tuned by neighboring single Pt atoms, leading to enhanced HER performance. Furthermore, the HER activity of a variety of single-metal-atom-doped MoS2 materials was investigated by DFT calculations. A volcano curve based on the relation of current density and ΔG_H was obtained (Figure 6D), which provides theoretical guidance to design other single-atom-doped MoS2 catalysts for HER.

Although much progress has been made in the development of Pt-free catalysts, their HER performance remains to be improved compared to Pt-based catalysts.
The low-coordination environment and unique electronic structure endow nonprecious-metal SACs with great potential to be alternatives to Pt. Tour and co-workers prepared a robust and highly active HER electrocatalyst comprising single Co atoms on N-doped graphene (Co-NG) (Figure 6E). They found that the excellent HER activity was attributed to a small amount of isolated Co atoms incorporating with N as active sites. The strong coordination between Co and N induced by high-temperature treatment contributed to great stability of the Co-NG catalyst. Chen and co-workers reported an efficient and stable HER catalyst with single Ni atoms anchored on three-dimensional nanoporous graphene. They demonstrated that the unusual catalytic activity and stability originated from a sp-d orbital charge transfer between Ni atoms and the surrounding C atoms. Yao and co-workers prepared a Ni-C-based catalyst (HCl-Ni@C) through carbonization of Ni-based MOF, followed by acid leaching. The electrochemical cyclic-potential activation of HCl-Ni@C was carried out until optimized and stable HER activity was achieved to obtain an activated catalyst (A-Ni-C). They discovered that isolated Ni species anchored on graphitized carbon were formed during the activation process, which contributed to the enhanced HER performance (Figure 6F). Mo-based materials such as MoS2, MoC, and MoN have attracted extensive research attention because of their great HER performance. Li and co-workers, for the first time, synthesized a single-atom Mo (Mo-SAs) catalyst with atomically dispersed Mo1N1C2 as active centers, which was confirmed by AC-STEM and XAFS analysis. Compared to Mo2C and MoN, this Mo-SAs catalyst exhibited greatly improved HER activity. DFT calculations demonstrated that the Mo-SAs catalyst possessed a lower absolute value of \( \Delta G \) than Mo2C and MoN. Further DOS calculations revealed that the DOS of Mo1N1C2 near the Fermi level was much higher than that of Mo2C and MoN, which was more beneficial for charge transfer during the HER process, owing to a higher carrier density.

**Electrocatalytic CO2RR**

Electrochemical reduction conversion of CO2 into value-added chemical fuel provides a promising approach for decreasing CO2 emissions and mitigating the energy crisis. However, the high overpotential of CO2RR for activation of the extremely inert C = O bond and the presence of the competitive side HER result in poor selectivity of product and low conversion efficiency, which are the main bottlenecks for the practical application of the electrocatalytic CO2RR. Therefore, developing highly effective and selective electrocatalysts to drive the CO2RR with a low potential and yield exclusive products is urgently needed but remains a great challenge. Single-atom materials with maximum atom efficiency and low-coordination metal centers have delivered excellent activity in a variety of reactions. Uniform active sites and geometric structure endow SACs with similar spatial and electronic interaction with substrates, which is beneficial for the enhancement of catalytic selectivity. Thus, SACs show great promise for achieving high efficiency and selectivity in the CO2RR process. Li and co-workers were the first to exploit SACs to catalyze the CO2RR. They prepared single Ni atoms anchored on N-doped porous carbon (Ni SAs/N-C) through a ZIF-assisted strategy. This Ni SAs/N-C catalyst exhibited excellent activity and selectivity for the CO2RR, achieving a high turnover frequency (TOF) of 5,273 hr\(^{-1}\) and a great Faradaic efficiency, over 71.9%, for CO production at an overpotential of 0.89 V (Figures 7A and 7B). Xie and co-workers reported atomically dispersed Ni-N4 sites synthesized by a topochemical transformation strategy. The exclusive Ni-N4 centers as active sites enhanced the efficiency and selectivity of the CO2RR with a high Faradaic efficiency, over 90%, for CO conversion in the potential range from –0.5 to –0.9 V, giving a maximum Faradaic efficiency of 99% at –0.81 V with a high current density of
28.6 mA cm$^{-2}$, Zhang and co-workers reported single-Ni atomic sites with high density and low valence on N-doped graphene for the efficient CO$_2$RR. Operando X-ray absorption and photoelectron spectroscopy analysis confirmed that the active centers for CO$_2$ molecular activation and electrochemical reduction were monovalent Ni(I) atomic sites with a d$^9$ electronic configuration. Benefiting from a unique electronic structure, this single-atom Ni catalyst exhibited high-efficiency CO$_2$RR activity with a remarkable TOF of 14,800 hr$^{-1}$ and a large specific current of 350 A g$_{\text{catalyst}}^{-1}$ at a low overpotential of 0.61 V for CO production with a high Faradaic efficiency of 97% (Figures 7C and 7D). In addition to the excellent activity and selectivity, this catalyst had long-term durability, which can maintain 98% of its initial
activity after 100 hr of continuous reaction test. Zhang and co-workers attributed the outstanding CO$_2$RR performance of this catalyst to the delocalization of the unpaired electron Ni 3d$_{x^2-y^2}$ orbital and spontaneous charge transfer from Ni(I) to C 2p orbital in CO$_2$ to yield CO$_2$$^\delta^-$ species, leading to the enhancement of the CO$_2$RR process by reducing the energy barrier.

Apart from atomically dispersed Ni species as active sites for the CO$_2$RR, single Co atomic sites have been reported to enhance the CO$_2$RR performance. Li and co-workers synthesized a series of single-atom Co catalysts with different nitrogen coordination numbers through regulation of the volatile CN fragment under different pyrolysis conditions. When evaluating their performance for the electrochemical reduction of CO$_2$, they found that compared to atomically dispersed Co with other N coordination numbers, single-Co atomic sites with two-coordinate N atoms exhibited better activity and selectivity with a current density of 18.1 mA cm$^{-2}$ and a CO Faradic efficiency of 94% at a low overpotential of 0.52 V, which achieved a record-value TOF of 18,200 hr$^{-1}$ for CO formation. This work demonstrates the crucial role of coordination regulation on active sites in triggering catalytic performance. Furthermore, Li and co-workers reported single Co atoms anchored on polymer-derived hollow N-doped porous carbon spheres for the CO$_2$RR. This single-atom Co catalyst achieved a 15.5-fold activity enhancement compared to cobalt phthalocyanine (CoPc) and showed outstanding selectivity with a high CO Faradic efficiency (> 90%) over the whole potential range from $-0.57$ V to $-0.88$ V (Figures 7E and 7F). No obvious decay in CO current density and CO Faradic efficiency was detected, indicating great stability. The electrochemical measurements and DFT calculations revealed that the designed single-atom Co-N$_5$ sites predominantly contributed to CO activation, the rapid formation of key intermediate COOH*, and the desorption of CO.

**Conclusions and Perspective**

The development of synthetic methodologies plays a fundamental role in advancing catalysis science and the practical application of SACs. In this review, recent advances in wet-chemistry methods have been summarized and classified. For successful fabrication of SACs, the following aspects need to be considered: (1) selecting suitable mononuclear metal complexes as precursors based on the features of the supports; (2) accomplishing atomically dispersed separation and isolation of these precursors and inhibiting their migration and agglomeration on the supports through effective approaches, for example, spatial confinement, trapping by defects, anchoring at coordination sites, and mitigating thermal motion of molecules; and (3) stabilizing single metal atoms on the supports through enhanced metal-support interactions or strong interactions between single atoms and surrounding coordination atoms.

We highlight the potential application of SACs in the field of electrocatalysis through the discussion of concrete examples. Currently, many advanced electrocatalysis systems significantly rely on the utilization of precious-metal electrocatalysts. Improving the utilization efficiency of metal atoms is a promising approach for reducing consumption of precious metals, which is of critical importance for reducing the catalyst cost and promoting sustainability. SACs represent the lowest size limit for achieving maximum atom utilization, which holds great promise for enabling reasonable use of metal resources and promoting the economic feasibility of electrocatalysis systems. The fully exposed active sites, unique electronic structure, and enhanced metal-supported interactions endow SACs with enhanced electrocatalytic performance. Moreover, structural simplicity and homogeneity of
SACs facilitate the precise structure identification of active sites, which provides a vast opportunity for investigating the electrochemical process and mechanism at the atomic scale through a combination of experiment and theory. The deep understanding of the correlation between structure and catalytic mechanism will shed light on the optimization and design of electrocatalysts for the high-efficiency electrochemical energy conversion process.

To meet the demand for fundamental research and practical applications of electrocatalysis and other catalysis, improving the loading content of SACs and achieving the large-scale and simple synthesis of SACs are currently two major challenges in the field of the synthesis of SACs. In addition, precisely controlling the coordination environment of metal atoms is highly desirable, which holds great promise for optimizing and improving the catalytic properties of SACs. Furthermore, we should focus on advancing the investigation of the structure-performance relationship and catalytic mechanism at the atomic scale by employing well-defined SACs as ideal model systems with the help of theoretical calculation and in situ characterization technologies, such as in situ electron microscopy and in situ X-ray absorption fine structure. If the above-mentioned achievements are attained, it is expected that we can design specific catalysts for the targeted reactions and achieve the atomic-economic green catalytic process.

ACKNOWLEDGMENTS

This work was supported by China Ministry of Science and Technology under Contract 2016YFA (0202801), the National Natural Science Foundation of China (21521091, 21390393, U1463202, 21471089, 21671117), and 111 Project (B16028).

AUTHOR CONTRIBUTIONS

Y.L. and D.W. supervised the preparation of this review article. Y.L., D.W., and Y.C. conceived the topic. Y.C. contributed to most of the writing, and S.J. contributed to some content and figures. C.C. and Q.P. revised the manuscript. Y.L., D.W., and Y.C. revised and finalized the manuscript. All authors approved the final version of the manuscript.

REFERENCES


