Recent progress on precious metal single atom materials for water splitting catalysis

Lei Zhou1,2 | Shi-Yu Lu1,2 | Shaojun Guo1,2

1 BIC-ESAT, College of Engineering, Peking University, Beijing, P. R. China
2 School of Materials Science and Engineering, Peking University, Beijing, P. R. China

Correspondence
Shaojun Guo, BIC-ESAT, College of Engineering, Peking University, Beijing 100871, P. R. China.
Email: guosj@pku.edu.cn

Funding information
National Science Fund for Distinguished Young Scholars, Grant/Award Number: 52025133; Tencent Foundation through the XPLORER PRIZE, China Postdoctoral Science Foundation, Grant/Award Numbers: 2019M650337, 2020M70021; Beijing Natural Science Foundation, Grant/Award Number: JQ18005; National Key Research and Development Program of China, Grant/Award Number: 2017YFA0206701; Fund of the State Key Laboratory of Solidification Processing in NWPU, Grant/Award Number: SKLSP202004

Abstract
Electrochemical water splitting for hydrogen production has sparked intensive interests because it provides a new approach for sustainable energy resources and the avoidance of environmental problems. The precious metal-based single atomic catalysts (PMSACs) have been widely employed in water splitting catalysis by virtue of their maximum atom utilization and unique electronic structure, which can reduce metal amounts and remain high catalytic performance simultaneously. In this review, we will summarize recent research efforts toward developing SACs based on precious metals with excellent performance for electrochemical water splitting catalysis. First, the synthesis strategies for PMSACs will be classified and introduced including high-temperature pyrolysis, electrochemical method, photochemical reduction, wet chemistry method, etc. Then, a short description of characterization techniques for SACs will be given, which mainly involves the aberration-corrected scanning-transmission electron microscopy (AC-STEM) and X-ray absorption spectroscopy (XAS). In particular, the relationship between the electronic structure of the precious metal atomic sites and performance for water splitting will be discussed according to the theoretical and experimental results. Finally, a brief perspective will be provided to highlight the challenges and opportunities for the development of novel PMSACs suitable for electrochemical water splitting applications.

KEYWORDS
precious metals, single atom catalysts, water splitting

1 | INTRODUCTION

The exhaustion of fossil fuels on earth and the inevitable environmental problems caused by their combustion have driven the scientists to search and develop the clean and substitutable energy sources. Hydrogen has been regarded as one of the most promising energy carriers due to its high energy density, clean combustion production (only water), and easy preparation from water.1–4 Among several hydrogen synthesis strategies, electrochemical water splitting is an appealing route owing to the utilization of the electric energy derived from renewable and intermittent energy source (wind and solar),5–10 which conquers the present energy and environmental predicament triggered by fossil fuels. The water splitting process is composed of anodic oxygen evolution reaction (OER) and cathodic hydrogen
For nanoparticle catalysts, their intrinsic activity is determined by the exposed corners/edges, defects, and the interfaces between the two phases or heterojunctions. Along with the downsizing of the catalysts, the catalytic activity and selectivity can be extremely enhanced due to the increased exposed active sites and altered electronic structure. However, owing to the increasing surface energy with the decreasing of particle size, the single atoms are prone to aggregate into clusters and particles. Hence, the isolated atoms have to be anchored onto the appropriate supports to construct the stable configurations with atomic distribution. The supports should possess the large surface area and plentiful defects or heteroatoms to decorate the single atoms to the great extent. Besides, the supports of SACs employed for electrochemical applications are required to possess the good conductivity to ensure the fast electrons transport during the catalytic process. When the active metal atoms are atomically dispersed on the supports, the catalysts will maximize the efficiency of atom utilization and reduce the cost in large-scale applications. Furthermore, the electronic structure of the active centers in SACs can be precisely tuned by the strong metal-support interactions (SMSIs), resulting in the enhanced intrinsic catalytic activity and selectivity toward the electrochemical reactions. In addition, the individual metal atoms under unsaturated coordination environment can serve as the unique catalytic active sites for the adsorption of reactants and intermediates, thus, reducing the free-energy barrier and altering the reaction pathway. Besides, the uniform and well-defined structure of metal active sites in SACs can provide a platform to study the structure–performance relationship, which shed a light on the thorough investigation on the electrocatalytic mechanism. Thanks to these advantages, various precious metal-based single atomic catalysts (PMSACs) are developed and extensively employed in electrochemical water splitting, which exhibit the excellent activities and stabilities. Compared with nonprecious metal-based single-atom catalysts, (Co-, Fe-, Ni-based SACs), the precious metal SACs usually display better electrochemical performance in water splitting catalysis due to their high intrinsic catalytic activity and high durability.

In this review, we focus on the synthesis strategy and characterization technique of single precious metal atomic catalysts, and highlight how these SACs tune the catalytic performance and also their catalytic mechanism toward electrocatalytic water splitting. We begin by describing the widely employed synthesis strategies of PMSACs including high-temperature pyrolysis, electrochemical method, photochemical reduction, wet chemistry method, etc. Then, we give a brief introduction of characterization techniques for PMSACs, which are indispensable to analyze the specific structure, dispersion state, and coordination environment around the single atomic sites in PMSACs.
Subsequently, we summarize the strategy and mechanism as an efficient design guidance for PMSACs with engineered or enhanced activity toward electrocatalytic water splitting. Finally, a short discussion on the current challenges and future perspectives toward rapidly developed PMSACs for water splitting applications are proposed.

2 | SYNTHESIS STRATEGY

Developing the suitable synthesis strategies is important for fabricating the uniform and well-defined SACs due to their easily aggregation caused by high surface energy. Extensive approaches have been developed to synthesize the high-quality PMSACs through the bottom-up and top-down methods. In this regard, several main strategies for synthesizing SACs have been summarized, including high-temperature pyrolysis, electrochemical and photochemical reduction, and wet chemistry method, etc.

2.1 | High-temperature pyrolysis

High-temperature pyrolysis strategy is a widely adopted approach to synthesize atomically dispersed catalysts, which can be acquired through the thermal decomposition of certain precursors at appropriate temperatures under inert or corrosive atmosphere (such as Ar, N$_2$, NH$_3$, and PH$_3$). The precursors involved metal-organic frameworks (MOFs), polymers, graphene, carbon nanotube, metal-macromolecular complexes, and transition metal compounds. Basically, these precursors possess the porous framework structure and large surface area to encapsulate/anchor the suitable metal cations to obtain the grafted site-isolated catalyst. In addition, abundant heteroatoms (e.g., N, S, and O) with lone pairs of electron in these substrates can serve as the active coordinating sites to anchor individual metal atoms. The single atom materials obtained through the pyrolysis strategy usually exhibit superior stability and relative high-loading amount. Moreover, it has been experimentally validated that carbon materials are promising substrates to stabilize the single atom due to their abundant defects and heteroatoms as the efficient anchoring sites. Extensive efforts have been devoted to search the precursors and develop approaches to obtain the high-quality SACs. The high-temperature pyrolysis for SACs synthesis is mainly divided into two strategies: bottom-up and top-down methods.

The bottom-up method for pyrolysis is incorporating the target single atoms into the precursors through doping, adsorbing, or substituting. The graphene, carbon nanotube, and some polymers can serve as the precursors for single atoms synthesis. The target metal atoms can be dragged and stabilized onto the graphene and carbon nanotube surfaces via the electrostatic interaction with functional groups and the strong coordinated interaction with defects. In order to improve the loading amount of single atoms, heteroatoms (N, S, and O) are incorporated to serve as the active sites to anchor the target metals. Mixing with nitrogen-containing precursors and pyrolysis in NH$_3$ atmosphere are the most adopted strategies to increase the N-species amount in graphene and other carbon materials. A Ru-N-C SAC dispersed on nitrogen-doped graphene was prepared by employing graphene oxide (GO) as the support precursor to stabilize Ru(NH$_3$)$_6$Cl$_3$ through electrostatic interaction between Ru species and oxygen-containing groups on the surface. Then, the Ru-GO precursor was pyrolyzed at various temperature with feeding Ar and NH$_3$ to construct the isolated Ru atoms uniformly dispersed on N-doped graphene.

Furthermore, the MOFs with the highly regular pore sizes and well-defined coordination environment of atomically dispersed metal nodes are employed as precursors to anchor the targeted single atoms via pyrolysis strategy. In addition to metal-support interactions with coordination atoms (N, S, and O), the target single atoms can also be stabilized through trapped in abundant cavities in MOFs. After the pyrolysis process, the carbon supports derived from coordination molecular can provide the stable framework, and the coordination atoms can serve as active sites for anchoring active single atoms. In the meantime, the metal nodes ensure the target single atoms atomically dispersed at the carbon supports, avoiding their aggregation into clusters and particles at high temperature. The ZIF-8 with cavity diameter of 11.6 Å was the mostly employed precursor, which can serve as a host to accommodate various metal precursor guests with suitable diameters. Besides, the main metal element in ZIF-8 is Zn with boil point of 905°C, which can be removed during the pyrolysis process at high temperatures. A single Ru atomic catalyst was fabricated via the pyrolysis of in-situ encapsulated Ru(acac)$_3$ within the molecular cages of ZIF-8 precursor. The mononuclear Ru(acac)$_3$ was transformed into atomically dispersed Ru-C/N during the pyrolysis process and uniformly anchored on the surface of N-doped carbon framework. Furthermore, the prebleaching treatment in acid was involved to thoroughly remove the impurities in SACs. As displayed in Figure 1A, a Ru–N–C single-site dispersed at N-doped carbon supports was synthesized by pyrolysis Ru(acac)$_3$-ZIF-8 precursor at 950°C and prebleached in HNO$_3$ to remove unstable species subsequently. The resulted Ru single-site catalyst displayed pure coordination structure of RuN$_4$ with absorbed OH structure, in the absence of Ru–Ru or Ru–O coordination structures. Furthermore, the precious metal atoms can also be anchored by the strong interaction
between the metal atoms and the free-functional groups in MOFs (Figure 1B). The Ru$^{3+}$ was successfully stabilized via coordinating with free amine groups (−NH$_2$) at the skeleton of the UiO-66−NH$_2$ and transformed into Ru−N−C sites anchored on the carbon frameworks.58

The top-down method for SACs synthesis is to remove the excess atoms from nanoparticles or thermal emitting using bulk metal as a precursor. The pyrolysis process is usually supplemented with corrosive atmosphere, such as NH$_3$ and PH$_3$, facilitating the break of metallic bonds in particles or bulk metals. By utilizing such ingenious strategy, the precursors is more selectable, and the operation gets easier. Besides, the drawbacks of aggregation of precious metal species during the precursor synthetic processes can be efficiently avoided. A new PH$_3$-promoted strategy was proposed for the effective transformation of Pd particles at a low temperature (400°C) into stabilized P-coordinated single atoms on g-C$_3$N$_4$ nanosheets (PdP-SA/CN).67 The PdP-SA/CN catalyst was obtained through twice-phosphidated treatment of Pd/CN nanoparticle precursor via the strong Lewis acid–base interaction between PH$_3$ and the precious metal. Furthermore, the targeted single metal atoms can also be transformed from other bulk metals to the supports. In comparison to the PH$_3$ with high toxicity and flammability, the NH$_3$ has also been selected as the “carrier gas” to synthesize single atomic catalysts.
Figure 1C describes a simple approach to generate atomically dispersed Pt via a thermal emitting method using bulk Pt metal as a precursor. Under the high temperature, the in-situ produced NH\textsubscript{3} can coordinate with Pt via a strong coordinate interaction to form the volatile Pt(NH\textsubscript{3})\textsubscript{x}, which anchored onto the surface of defective graphene at downstream subsequently.

The high-temperature pyrolysis strategy is the most employed method for making the SAC, due to its good flexibility, vast selectable precursors, and high production. However, the homogeneity of coordination structure at single metal atom centers and the appearance of nanoparticles at high pyrolysis temperature need to be further specifically controlled.

### 2.2 Electrochemical strategy

The electrochemical deposition strategy is regarded as a simple and versatile approach to modify the surface characteristics or deposited the new composition onto the materials. Such strategy shows the advantages of facile preparation, easy control, and low energy consumption, which is friendly to environment. From the view of synthetic mechanism, there are two main electrochemical methods for SACs synthesis including conventional electrodeposition\textsuperscript{69–71} and potential cycling method.\textsuperscript{72–76}

With regards to the potential cycling method, the target metal atoms are usually as counter electrode, which can be dissolved from anode into electrolyte at high potentials and redeposited onto the substrates (working electrodes) during the cycling process. In such method, Pt foil or wire is the mostly employed counter electrode to deposit single atoms on materials. As shown in Figure 2A, a Pt single atom supported on CoP nanotube grown on Ni foam has been synthesized via a potential-cycling method.\textsuperscript{73} The Pt atoms were uniformly dispersed on the whole CoP nanotube with a relative high density (Figure 2B and C). Furthermore, the defects in support can provide more sites for anchoring single atoms, thus, improving the loading density and stability. As shown in Figure 2D, Pt single atoms were atomically anchored on Mxene utilizing Mo vacancies on the surfaces.\textsuperscript{72} During the electrochemical exfoliation process, the Mo vacancies are formed, and single Pt atoms are simultaneously immobilized and stabilized by the formation of covalent Pt–C bonds with the surrounding C atoms on the MXene.

As for the conventional electrodeposition, the target metal atoms are dispersed in electrolyte in advance and reduced onto the surface of substrates (working electrodes)
subsequently. Compared with potential cycling method, more species of precious metal can be incorporated into supports via conventional electrodeposition method. As displayed in Figure 3A and B, single Au atoms supported on NiFe-LDH nanoplates were first prepared utilizing HAuCl₄ as metal precursor. The Au atoms were uniformly dispersed on the surface of NiFe-LDH with atomic state instead of clusters or nanoparticles, indicating successfully preparation of single atomic Au-NiFe-LDH catalyst. Furthermore, this method can be extended to various precious metals and supports such as Ir, Ru, Rh, Pt, Pd, etc. and oxides, sulfides, selenides, carbon, etc., respectively. In addition, the SACs can be synthesized through cathodic and anodic deposition, which exhibit high activities toward HER and OER, respectively. Ir single atoms deposited on Co(OH)₂ nanosheets have been synthesized via the cathodic and anodically deposition process. For the cathodic deposition, IrCl₃⁺ cations were driven toward the cathode by the applied electric field, deposited on the supports and coordinated with three O atoms on Co(OH)₂. The Ir ions were reduced under the negative electronic field subsequently, giving rise to the oxidation state of Ir single atoms lower than +4 (Figure 3C). As for the anodic deposition, the Ir(OH)₆²⁻ anions acted as the depositing species, driven by the electric field toward the anode and oxidized, leading to the oxidation state of Ir single atoms higher than +4 (Figure 3D).

2.3 | Photochemical reduction

Photochemical reduction is a common strategy for the synthesis of precious metal nanocrystals via utilizing light irradiation. The synthesis process includes nucleation and growth, finally transformation into metal nanocrystals. In order to generate the uniformly dispersed metal single atoms, the reaction rate of nucleation should be reduced as much as possible. An atomically dispersed Pt catalyst has been fabricated via the photochemical reduction of frozen chloroplatinic acid solution using ultraviolet (UV) light. Owing to the photochemical reduction at low temperature, the aggregation of atoms was prevented, and single atoms were successfully stabilized. Subsequently, the water was changed into the mixture of ethanol and water and photochemically reduced at ultralow-temperature (−60°C), which significantly improved the reaction kinetic barrier and suppressed the nucleation of metal atoms. Furthermore, the precious metal atoms could be also anchored on various solid supports. The Pd single atoms were anchored on the TiO₂ through in-situ photochemical reduction under frozen state. The irradiation excited TiO₂ to produce photogenerated electrons that subsequently promoted the reduction of PdCl₄²⁻ to form single Pd atoms anchored onto TiO₂, which exhibits excellent detection limit and selectivity in photocatalytic sensing for analyzing...
organophosphorus compounds. Besides, the atomically coordinated Pt–Co–Se moieties with highly asymmetrical electronic distribution could be synthesized via synergistically combining the defects (Se vacancies) anchoring and UV light photochemical reduction to stabilize the Pt single atoms onto the surface of CoSe$_2$. The resulted catalyst possesses relative high Pt loading amount and superior OER performance.

The photochemical reduction strategy is ecofriendly and low-energy consuming, which is also high efficient, easy operation, and rapid synthesis. Nevertheless, since the solvent is water, which is easily frozen at 0°C, this strategy is not suitable for the supports that are instable in aqueous. Furthermore, in order to generate the strong metal-support interaction, the supports are required to be photo-responded or with abundant defects or heteroatoms to efficiently anchor target single atoms. Besides, apart from Pt and Pd, some precious atoms are not sensitively responded to irradiation, thus, the reduction effect is not satisfied. Therefore, it is relative limited to choose the species of supports and single metal atoms.

### 2.4 Wet chemistry method

Owing to the potential in large-scale application, wet chemistry method has been widely employed in the synthesis of single atom materials. The wet chemistry method includes ion exchange, impregnation, coprecipitation, chemical reduction, etc. The ion-exchange approach based on the different migration rates of metal ions, which known as kirkendall effect, can be referred to synthesize the isolated metal atom catalysts with high loading amounts. As shown in Figure 4A and B, an atomically dispersed Pt site embedded in a hollow amorphous CuS$_x$ support (h-Pt$_1$-CuS$_x$) has been
ZHOU et al.

2.4 | Other synthesis strategies

Atomic layer deposition (ALD), also known as atomic layer epitaxy, is a gas-phase deposition strategy to deposit the thin films onto the substrate, in which metal precursors vapors are alternately pulsed into the reactant chamber and chemical adsorbed on the substrates. Moreover, the ALD approach can be applied to the synthesis of SACs and the amount of anchored single atoms can be controlled precisely by tuning the number of ALD cycles. Choosing the suitable precursors is vital importance to the deposited atoms owing to its essential chemical adsorption onto supports in ALD process. As displayed in Figure 5A, the isolated single platinum atoms and clusters supported on N-doped graphene nanosheets have been synthesized through an ALD method. The Pt precursor (MeCpPtMe3) first reacted with the N-dopant sites in the N-doped graphene, then completely oxidized to CO2 and H2O when exposed to O2, thus, creating a Pt containing monolayer. Notably, a new layer of adsorbed oxygen forms on the deposited Pt surface, which provides functional groups for the next ALD cycle process. Besides, laser ablation in liquid (LAL) technique is usually adopted to fabricate metastable nanostructures with unique properties due to its strong quenching effect. A single atom alloy (SAA) with Au atoms separately located on the Ru nanoparticles prepared by employing a nanosecond laser (pulse width of 7 ns) to irradiate the Ru target (Figure 5B), which leads to the vaporization of the solid target, thermal decomposition of HAuCl4, and formation of RuAu SAA during fast quenching subsequently. The ALD and LAL techniques can fastly synthesize the single precious metal atomic catalysts, which provide excellent model SACs for the exploration of metal-support interactions and structure-performance relationships. However, these techniques may not be suitable for commercial applications owing to their high cost and low yield.

3 | CHARACTERIZATION OF SACS

The characterization techniques play a significant role in understanding the atomic structure in-depth and developing the plenty of PMSACs with novel structures. With the development of advanced characterization techniques,
the fine structure of single metal sites at atomic level can be directly observed by using scanning transmission electron microscopy (STEM). The aberration-corrected STEM (AC-STEM) with the resolution down to subangstrom can clearly discern the single metal atoms in contrast to the supports with different brightness. Generally speaking, the distinct degree of atomic metal spots gets clearer along with the larger atomic number difference between the isolated atoms and supports. Besides, the electron energy loss spectroscopy (EELS) coupled with AC-STEM can be utilized to analyze the elemental compositions around the single atomic sites.

In contrast to electron microscopy that mainly focus on the isolated atoms in the local area of SACs, the synchrotron X-ray absorption spectroscopy (XAS) is generally employed to investigate the overall and average structure of single atom sites. The corresponding X-ray absorption fine-structure (XAFS) can reveal the detailed electronic structure and coordination environment at the isolated active sites, which is indispensable for confirming and analyzing the specific structure of SACs. The radial structure function (R space) obtained from the Fourier transformed extended X-ray absorption fine structure (FT-EXAFS) can visually distinguish the isolated atom sites from clusters and particles via detecting the backscattering paths according to the radial distance between the active metal centers and the coordinated atoms. As a result, the isolated atomic sites catalysts only display a single major peak, attributed to the coordination of metal–nonmetal atoms (N, C, O, B, P, etc.) and without the existence of metal–metal coordination assigning to clusters or particles (at ~ 2 Å) simultaneously. Furthermore, the coordination numbers, species, and distances of the atoms coordinated with single atom sites at short range can be simulated via the least-square curve fitting according to the experimental EXAFS data. Therefore, the combination of AC-STEM and XAS can be an effective strategy to investigate the fine structure information around isolated atoms, which has become the standard measurement for analyzing the atomically dispersion, coordination environment, and electronic structure of the SACs.

4 | PRECIOUS METAL SACS FOR WATER SPLITTING

Recently, extensive PMSACs have been employed for electrochemical water splitting reaction ($2H_2O \rightarrow 2H_2 + O_2$). As mentioned above, the SACs possess the maximum atom utilization, well-defined active sites and unique electronic structures, which can exhibit the enhanced intrinsic catalytic performance and provide an ideal model for the exploration of reaction mechanism.

4.1 | HER

Hydrogen evolution is the core reaction for hydrogen production via an electrochemical water splitting strategy. The HER is a two-electron transfer process, which can conduct in a wide pH, including acid ($H_2SO_4$), neutral (PBS), and alkaline (KOH) electrolytes. As mentioned in Introduction, the mechanism of HER involves two pathways: Volmer–Heyrovsky and Volmer–Tafel processes. The HER catalysis mainly consists of the suitable adsorption of proton or $H_2O$ molecular, rapid combination of
protons and the fast electron transportation accessing to the active sites during reaction process, which are the major aspects to improve the HER performance. As for PMSACs, the studies that have reported are primarily concentrated on Pt single atoms anchored on various conductive supports.68,72–75,94,98–107

For Pt-based SACs in HER, the single atomic Pt sites are widely considered as the real active centers. Besides, the reaction mechanism of Pt-based SACs in HER process is largely depended on the species of supports and preparation approaches. The Pt SACs synthesized by electrochemical potential cycling method usually exhibit relative low Tafel slope, which follows Volmer–Tafel process. For example, a 3D nanoporous Co$_{0.85}$Se loaded single Pt atoms catalyst, obtained by electrochemical method, shows an overpotential of 55 mV at 10 mA/cm$^2$ and a Tafel slope of 35 mV/dec (Figure 7A and B).74 In order to increase the loading density of single atoms, the electrodes with larger specific surface areas have been employed as supports to anchor the target precious metal atoms. A Pt single atom anchored CoP nanotube binder-free electrode was fabricated by potential-cycling method displays overpotential of 24 mA/cm$^2$ and a Tafel slope of 30 mV/dec.73 The resulted Volmer–Tafel mechanism of such Pt-SACs can be inferred that the supports could be activated during the fabrication process, thus, increasing the efficient expose of active sites, resulting in fast combination of adsorbed H on the surfaces. Besides, the adopted single atoms decorated on the 3D binder-free supports could enhance the electron transportation, leading to the improved reaction dynamics. The Volmer–Heyrovsky process was also discovered in Pt-based SACs toward HER, in which supports were usually with relative poor HER performance. As shown in Figure 7D and E, a Pt single atom decorated on graphdiyne through a wet chemical method displayed a current density of 23.64 A/mg at −0.1 V and a Tafel slope of 46.6 mV/dec, superior to the commercial Pt/C.103

Besides, a novel hydrogen-spillover effect mechanism was put forward over single atom Pt/m-WO$_{3-x}$ catalyst.105 In single atom Pt/m-WO$_{3-x}$, the maximized interfaces between Pt and tungsten oxide reduces the hydrogen diffusion length, thus, resulting in the faster kinetics of the hydrogen insertion/extraction and the enhanced hydrogen spillover effect (Figure 8A). The accelerated hydrogen insertion/extraction can induce the rapid re-exposure of the Pt surface and permit adsorption of another H$^+$, thus, speeding up HER process. In general, compared with particle and bulk counterparts, the Pt-based SACs display the unique electronic structure, derived from the support-metal strong interactions. The PDOSs of the 5d orbitals of Pt demonstrate a high electron densities near the Fermi level, which can facilitate H$^+$ absorption and improve the conductivity compared with pure supports (Figure 8B).
Furthermore, the Gibbs free energy of the intermediate state ($\Delta G_{\text{H}}$) of Pt-based single atom electrocatalysts is more close to zero, which means higher intrinsic HER activity compared with bulk Pt counterparts (Figure 8C and D). The unique electronic structure and high atomic utilization of Pt single atoms result in the excellent specific massive activity of Pt-based SACs.

Apart from Pt-based SACs, Ru- and Rh-based precious SACs were also developed for electrocatalytic hydrogen production.108–113 A Ru decorated MoS$_2$ SAC was synthesized and applied in alkaline HER.111 The incorporation of Ru atoms into MoS$_2$ resulted in the phase transformation from 2H to 1T and the generation of S vacancies, which reduced the energy barriers of the Volmer step and the adsorption/desorption of H* and enhanced the electroconductivity simultaneously. Besides, a N, S-coordinated Ru single atom dispersed on Mxene displayed an overpotential of 76 mV at 10 mA/cm$^2$ and a Tafel slope of 90 mV/dec.109 In addition, Rh atoms were also atomically confined into MoS$_2$, which showed excellent activity toward HER in 0.5 M H$_2$SO$_4$.113 The Rh atoms replaced the Mo atoms, and were dispersed in the lattice with distance. The HER activity of in-plane S sites adjacent to the Rh atoms could be modulated by changing the distance of the confined Rh atoms, resulting in activation of the catalytically inert plane in MoS$_2$, thus, improving the HER performance. Some SAA catalysts were also adopted for HER.97 A novel RuAu SAA was adopted as the electrocatalyst for alkaline HER. The RuAu SAA exhibited a low overpotential of 24 mV at 10 mA/cm$^2$ and a low Tafel slope of 37 mV/dec.

### 4.2 OER

The water oxidation is the key reaction for reducing the overpotential and energy consuming in electrochemical water splitting for hydrogen production, owing to the sluggish kinetics mainly caused by the four-electron transfer during OER. As a result, the electrocatalysts with excellent activity and stability are urgent demanded to overcome such problem. In order to efficiently improve the intrinsic catalytic activity of OER, the electronic structure of active centers has been specifically tailored through the interactions between single precious metal atoms and supports.69,83,85,89,114–117 There are two strategies to enhance the OER performance of SACs: incorporating new active sites and enhancing the activity of original active sites.

When anchored on the supports with OER activity, the newly incorporated single atoms can also be the new active centers. As shown in Figure 9A and B, a single atom dispersed Ru-N-C electrocatalyst was applied in acid OER, which exhibited a low overpotential of 267 mV at 10 mA/cm$^2$ and a high TOF of 13 392 O$_2$/h at overpotential of 300 mV.114 Due to the basically negligible OER activity of (heteroatoms doped), carbon supports in metal-N-C based SACs, the active centers for water oxidation were generally considered as the isolated metal atoms. Furthermore, the materials with good OER activity were employed as supports to anchor single precious metal atoms to enhance the OER performance of PMSACs. As displayed in Figure 9C, a CoFe-LDH supported Ru SAC was synthesized, and displayed a low overpotential of 198 mV at 10 mA/cm$^2$.85
enhanced performance was attributed to the strong synergistic electron coupling between single atomic Ru and LDHs substance. An Ir decorated NiO nanosheet electrode with high loading amount (18 wt% Ir) was fabricated, and showed a low overpotential of 215 mV at 10 mA/cm² for alkaline OER. The enhanced performance can be attributed to the high loading density and newly Ir-O bonds aroused by atomically dispersed Ir.

Some precious metal atoms were atomically introduced into the supports with superior OER activity itself, such as NiFe-LDH, which can enhance the OER activity via tailoring the electronic structure of original active sites. As shown in Figure 9D, Au single atoms supported on NiFe-LDHelectrode showed a low overpotential of 280 mV at 10 mA/cm² for alkaline OER. The incorporation of Au atoms could induce the net Au-to-LDH charge redistribution, which transferred to surrounding O, Ni, and Fe atoms. The tailored electronic structure could facilitate the adsorption of OH⁻ and modify the adsorption energies of O* and OOH* intermediates, resulting in the enhanced OER performance. In addition, the OER activity of PMSACs could be enhanced through both two strategies. An electrocatalyst with Ir single atoms anchored on Co nanosheets displayed a low overpotential of 267 mV at 10 mA/cm² in 1 M KOH. The Ir–Co dinuclear sites was considered as the active centers, in which hydroxyl group tends to adsorb on Co sites and dissociates into adsorbed O*, then further transfer to Ir–O* via a Co–O–Ir intermediate subsequently.

The stability of the PMSACs can be greatly enhanced via engineering the electronic structure by the single atomic metal-support interactions. RuO₂ is considered as the most promising catalyst for the commercial OER applications. However, the poor stability during OER caused by the dissociation of high oxidation stated Ru⁶⁺ into electrolyte is required to be solved. A Pt–Cu alloy decorated with Ru single atoms electrocatalyst demonstrated the enhancement of stability via the compressive strain of the Pt skin. The Pt–Cu alloys could act as an electron reservoir to donate electrons towards reaction intermediates, thus, suppress the overoxidation and dissolution of Ru single atoms. The Ru atoms could be also stabilized by nonmetallic elements in hydroxides, which were anchored on CoFe-LDH through the metal-support interactions. The oxidation state of Ru in Ru/CoFe-LDHs was lower than +4 during the OER process, thus, resisting the Ru dissociation and, thus, improving the stability.

Moreover, the PMSACs have been developed as bifunctional electrocatalysts toward both OER and HER. According to the reported studies, Ir-based SACs are the promising candidate for bifunctional water splitting in both acid and alkaline medium. Ir single atoms were
dispersed on the N-doped carbon and Co particles via the pyrolysis of Ir-ZIF-67 precursor, which only requires an applied potential of 1.603 V to achieve 10 mA/cm² in 1.0 M KOH electrolyte. When the structured materials were employed as supports, the water splitting activity of PMSACs could be greatly enhanced. The Ir single atoms were decorated on Co₀.₈Fe₀.₂Se₂ nanosheets grown on Ni foam utilizing electrochemical deposition, which only needs a voltage of 1.39 V to get 10 mA/cm² in alkaline electrolyte.

### 5 SUMMARY AND PERSPECTIVE

Electrocatalytic water splitting is demonstrated as an efficient approach for generating hydrogen with the reduced environmental pollution problems and high energy conversion efficiency. The development of highly efficient OER/HER catalysts holds the key to the practical application of electrochemical water splitting. Precious metal catalysts downsizing to single atomic states can not only greatly improve the atomic utilization, but also enhance the intrinsic catalytic activity owing to the strong interactions between single metal atoms and supports. Extensive strategies have been developed to synthesize the high quality PMSACs, including widely employed high-temperature pyrolysis, electrochemical method, wet chemistry method, photochemical method, and other novel approaches. The specific structure and dispersion state of the single atomic sites in PMSACs can be distinctly observed by AC-STEM result at the atomic level analysis. Furthermore, the XAFS is usually employed to exclude the existence of clusters or particles and confirm the specific coordination state around the single atomic sites. Consequently, the PMSACs display excellent activity and stability toward both OER and HER in water splitting under various pH solutions, which are attributed to the engineering of electronic structure at active centers via incorporation of single atoms.

Despite extensive efforts have been devoted to develop the PMSACs with high performance for water splitting, several problems are still required to be resolved and further improved.

1. In order to get a high specific massive/areal activity to provide abundant active centers for electrocatalysis, the loading densities of efficient exposed single atom sites in SACs need to be further increased. The increased accessible single atomic sites can meet the requirements for combination of adsorbed H to produce H₂ molecule at high H coverage, thus, facilitating the HER process. Up to now, the loading amounts of precious metal in SACs are relative low (mostly <10 wt%), which remains a large space for further improvement. Besides, choosing the appropriate supports with high specific surface area and anchoring sites (defects, heteroatoms, dangling bonds, etc.) is also crucial for improving the single atomic density in SACs.

2. The structural investigation of active sites at atomic level is significantly important for understanding the reactive mechanism and structure-activity relationship. Up to now, the most efficient characterization techniques are performed by AC-STEM and EXAFS measurements. Besides, the computational theoretic calculations and operando characterizations are employed to provide several basis information for the structural and energetic changes at some specific points along the electrocatalytic process. Nevertheless, it is still difficult to in-situ detect the detailed structural evolution at single atomic sites and the variation of adsorbed intermediates from steric and electronic side during the electrochemical water splitting. Therefore, new characterization techniques are highly demanded to give a straightforward and exhaustive results for the real-time variation of the single atomic sites during catalytic process, which can provide instructive suggestions for deducting the reactive mechanism and revealing structure-activity relationship of PMSACs toward electrochemical water splitting.

3. The PMSACs are highly attractive for industrial electrochemical hydrogen production owing to their inherent activity advantage. However, the major challenge lies in the unsatisfying stability of PMSACs, especially at high single atomic metal loading density. The time scale for stability of catalysts in industrial applications is usually months or even years, much longer than that in laboratories researches. Hence, how to keep the active sites maintain the original structures and avoid the aggregation or leaching of metal atoms during the electrocatalytic water splitting process plays a crucial role in developing the efficient and stable PMSACs subsequently. If this problem is well solved, the PMSACs will become a vigorous candidate in industrial electrochemical water splitting technology for large-scale hydrogen production applications.

### ACKNOWLEDGMENTS

This work was financially supported by the National Science Fund for Distinguished Young Scholars (No. 52025133), Tencent Foundation through the XPLORER PRIZE, China Postdoctoral Science Foundation (Nos. 2019M650337, 2020M670021), Beijing Natural Science Foundation (JQ18005), National Key Research and Development Program of China (2017YFA0206701), and the Fund of the State Key Laboratory of Solidification Processing in NWPU (Grant No. SKLSP202004).
CONFLICT OF INTEREST
The authors declare no conflict of interest.

ORCID
Shaojun Guo https://orcid.org/0000-0003-4427-6837

REFERENCES
1. Seh ZW, Kibsgaard J, Dickens CF, et al. Combining theory and experiment in electrocatalysis: insights into materials design. Science. 2017;355:1-12.
2. Setzler BP, Zhuang Z, Wittkopf JA, et al. Activity targets for nanostructured platinum-group-metal-free catalysts in hydroxide exchanged membrane fuel cells. Nat Nanotechnol. 2016;11:1020-1025.
3. Wang L, Zeng Z, Gao W, et al. Tunable intrinsic strain in two-dimensional transition metal electrocatalysts. Science. 2019;363:870-874.
4. Shen G, Liu J, Wu HB, et al. Multi-functional anodes boost the transient power and durability of proton exchange membrane fuel cells. Nat Commun. 2020;11:1191.
5. Lin L, Zhou W, Gao R, et al. Low-temperature hydrogen production from water and methanol using Pt/alpha-MoC catalysts. Nature. 2017;544:80-83.
6. Feng JX, Tong SY, Tong YX, et al. Pt-like hydrogen evolution electrocatalysis on PANI/CoP hybrid nanowires by weakening the shackles of hydrogen ions on the surfaces of catalysts. J Am Chem Soc. 2018;140:5118-5126.
7. Yu X, Yu ZY, Zhang XL, et al. Superaerophobic” nickel phosphide nanoarray catalyst for efficient hydrogen evolution at ultrahigh current densities. J Am Chem Soc. 2019;141:7537-7543.
8. Li Y, Sun Y, Qin Y, et al. Recent advances on water-splitting electrocatalysis mediated by noble-metal-based nanostructured materials. Adv Energy Mater. 2020;10:1903120.
9. Stamenkovic VR, Strmcnik D, Lopes PP, et al. Energy and fuels from electrochemical interfaces. Nat Mater. 2016;16:57-69.
10. Zhao D, Zhuang Z, Cao X, et al. Atomic site electrocatalysts for water splitting, oxygen reduction and selective oxidation. Chem Soc Rev. 2020;49:2215-2264.
11. Feng J, Lv F, Zhang W, et al. Iridium-based multimetallic porous hollow nanocrystals for efficient overall-water-splitting catalysis. Adv Mater. 2017;29:1703798.
12. Lv F, Feng J, Wang K, et al. Iridium-tungsten alloy nanodendrites as pH-universal water-splitting electrocatalysts. ACS Cent Sci. 2018;4:1244-1252.
13. Wang P, Jiang K, Wang G, et al. Phase and interface engineering of platinum-nickel nanowires for efficient electrochemical hydrogen evolution. Angew Chem Int Ed. 2016;55:12859-12863.
14. Yao Q, Huang B, Zhang N, et al. Channel-rich RuCu nanosheets for pH-universal overall water splitting electrocatalysis. Angew Chem Int Ed. 2019;58:13983-13988.
15. Salomón FG, Albiter L, Alia SM, et al. Self-supported hydrous iridium-nickel oxide two-dimensional nanoframes for high activity oxygen evolution electrocatalysts. ACS Catal. 2018;8:10498-10520.
16. Yang K, Xu P, Lin Z, et al. Ultrasmall Ru/Cu-doped RuO2 complex embedded in amorphous carbon skeleton as highly active bifunctional electrocatalysts for overall water splitting. Small. 2018;14:e1803009.
17. Sun H, Yang JM, Li JG, et al. Synergistic coupling of NiTe nanoarrays with RuO2 and NiFe-LDH layers for high-efficiency electrochemical-/photovoltage-driven overall water splitting. Appl Catal B-Environ. 2020;272:119888.
18. Yang Y, Luo M, Xing Y, et al. A universal strategy for intimately coupled carbon nanosheets/MoM nanocrystals (M = P, S, C and O) hierarchical hollow nanospheres for hydrogen evolution catalysis and sodium-ion storage. Adv Mater. 2018;30:e1706085.
19. Liu J, Xu H, Yan J, et al. Efficient photocatalytic hydrogen evolution mediated by defect-rich IT-PtS2 atomic layer nanosheet modified morphosporous graphic carbon nitride. J Mater Chem A. 2019;7:18906-18914.
20. Chia X, Adriano A, Lazar P, et al. Layered platinum dichalcogenides (PtS2, PtSe2, and PtTe2) electrocatalysis: monotonic dependence on the chalcogen size. Adv Funct Mater. 2016;26:4306-4318.
21. Wang K, Huang B, Lin F, et al. Wrinkled Rh2P nanosheets as superior pH-universal electrocatalysts for hydrogen evolution catalysis. Adv Energy Mater. 2018;8:1801891.
22. Zhou L, Jiang S, Liu Y, et al. Ultrathin CoNiP@layered double hydroxides core-shell nanosheets arrays for largely enhanced overall water splitting. ACS Appl Energy Mater. 2018;1:623-631.
23. Zhou L, Shao M, Li J, et al. Two-dimensional ultrathin arrays of CoP: electronic modulation toward high performance overall water splitting. Nano Energy. 2017;41:583-590.
24. Duan H, Li D, Tang Y, et al. High-performance Rh2P electrocatalyst for efficient water splitting. J Am Chem Soc. 2017;139:5494-5502.
25. Yin J, Li Y, Lv F, et al. NiO/CoN porous nanowires as efficient bifunctional catalysts for Zn-air batteries. ACS Nano. 2017;11:2275-2283.
26. Lai J, Huang B, Cao Y, et al. Strongly coupled nickel-cobalt nitrides/carbon hybrid nanocages with Pt-like activity for hydrogen evolution catalysis. Adv Mater. 2019;31:e1805541.
27. Li Y, Wei X, Chen L, et al. Nickel-molybdenum nitride nanoplate electrocatalysts for concurrent electrolytic hydrogen and formate productions. Nat Commun. 2019;10:5335.
28. Suen NT, Hung SF, Quan Q, et al. Electrocatalysis for the oxygen evolution reaction: recent development and future perspectives. Chem Soc Rev. 2017;46:337-365.
29. McCreery CC, Jung S, Ferrer IM, et al. Benchmarking hydrogen evolving reaction and oxygen evolving reaction electrocatalysts for solar water splitting devices. J Am Chem Soc. 2015;137:4347-4357.
30. Sun Y, Huang B, Li Y, et al. Trifunctional fishbone-like PtCo/Ir enables high-performance zinc-air batteries to drive the water-splitting catalysis. Chem Mater. 2019;31:8136-8144.
31. Lv F, Zhang W, Yang W, et al. Ir-based alloy nanoflowers with optimized hydrogen binding energy as bifunctional electrocatalysts for overall water splitting. Small Methods. 2019;4:1900129.
32. Li Z, Niu W, Yang Z, et al. Stabilizing atomic Pt with trapped interstitial F in alloyed PtCo nanosheets for high-performance zinc-air batteries. Energy Environ Sci. 2020;13:884-895.
33. Kim J, Kim H, Lee WJ, et al. Theoretical and experimental understanding of hydrogen evolution reaction kinetics in alkaline electrolytes with Pt-based core-shell nanocrystals. J Am Chem Soc. 2019;141:18256-18263.
34. Du R, Wang J, Wang Y, et al. Unveiling reductant chemistry in fabricating noble metal aerogels for superior oxygen evolution and ethanol oxidation. Nat Commun. 2020;11:1590.

35. Kobayashi S, Tryk DA, Uchida H, et al. Enhancement of hydrogen evolution activity on Pt-skinnedPt3Co [(111), (100), and (110)] single crystal electrodes. Electrochem Commun. 2020;110:106615.

36. Kristoffersen HH, Vegge T, Hansen HA, et al. OH formation and H2 adsorption at the liquid water-Pt(111) interface. Chem Sci. 2018;9:6912-6921.

37. Zhao Z, Liu H, Gao W, et al. Surface-engineered PtNiO nanotexture with record-high performance for electrocatalytic hydrogen evolution reaction. J Am Chem Soc. 2018;140:9046-9050.

38. Zheng X, Cui P, Qian Y, et al. Multifunctional active-center-transferable platinum/lithium cobalt oxide heterostructured electrocatalysts towards superior water splitting. Angew Chem Int Ed. 2020;59:14533-14540.

39. Wang P, Shao Q, Guo J, et al. Promoting alkaline hydrogen evolution catalysis on P-decorated, Ni-segregated Pt-NiP nanowires via a synergetic cascade route. Chem Mater. 2020;32:3144-3149.

40. Panda C, Menezes PW, Yao S, et al. Boosting electrocatalytic hydrogen evolution activity with a NiPt3@NiS heteronanotexture evolved from a molecular nickel-platinum precursor. J Am Chem Soc. 2019;141:13306-13310.

41. Wang P, Zhang X, Zhang J, et al. Precise tuning in platinum-nickel/nickel sulfide interface nanowires for synergistic hydrogen evolution catalysis. Nat Chem. 2017;9:14580.

42. Sun Y, Li Y, Qin Y, et al. Interfacial engineering in PtNiCo/NiCoS nanowires for enhanced electrocatalysis and electroanalysis. Chem Eur J. 2020;26:4032-4038.

43. Lao M, Rui K, Zhao G, et al. Platinum/nickel bicarbonate heterostructures towards accelerated hydrogen evolution under alkaline conditions. Angew Chem Int Ed. 2019;58:5432-5437.

44. Zhang BW, Wang YX, Chou SL, et al. Fabrication of superior single-atom catalysts toward diverse electrochemical reactions. Small Methods. 2019;3:1800497.

45. Zhang H, Liu G, Shi L, et al. Single-atom catalysts: emerging multifunctional materials in heterogeneous catalysis. Adv Energy Mater. 2018;8:1701343.

46. Han A, Wang B, Kumar A, et al. Recent advances for MOF-derived carbon-supported single-atom catalysts. Small Methods. 2019;3:1800471.

47. Alarawi A, Ramalingam V, He JH, et al. Recent advances in emerging single atom confined two-dimensional materials for water splitting applications. Mater Today Energy. 2019;11:1-23.

48. Peng Y, Lu B, Chen S, et al. Carbon-supported single atom catalysts for electrochemical energy conversion and storage. Adv Mater. 2018;30:e1801995.

49. Wang Q, Lei Y, Wang D, et al. Defect engineering in earth-abundant electrocatalysts for CO2 and N2 reduction. Energy Environ Sci. 2019;12:1730-1750.

50. Yang XF, Wang AQ, Qiao BT, et al. Single-atom catalysts: a new frontier in heterogeneous catalysis. Acc Chem Res. 2013;46:1740-1748.

51. Zhou P, Chao Y, Lv F, et al. Designing noble metal single-atom-loaded two-dimension photocatalyst for N2 and CO2 reduction via anion vacancy engineering. Sci Bull. 2020;65:720-725.

52. Chen Y, Ji S, Chen C, et al. Single-atom catalysts: synthetic strategies and electrochemical applications. Joule. 2018;2:1242-1264.

53. Zhou P, Hou X, Chao Y, et al. Synergetic interaction between neighboring platinum and ruthenium monomers boosts CO oxidation. Chem Sci. 2019;10:5898-5905.

54. Xiao M, Chen Y, Zhu J, et al. Climbing the apex of the ORR volcano plot via binuclear site construction: electronic and geometric engineering. J Am Chem Soc. 2019;141:17763-17770.

55. Ji S, Chen Y, Zhao S, et al. Atomically dispersed ruthenium species inside metal-organic frameworks: combining the high activity of atomic sites and the molecular sieving effect of MOFs. Angew Chem Int Ed. 2019;58:4271-4275.

56. Xiao M, Gao L, Wang Y, et al. Engineering energy level of metal center: Ru single-atom site for efficient and durable oxygen reduction catalysis. J Am Chem Soc. 2019;141:19800-19806.

57. Xiao M, Zhu J, Li G, et al. A single-atom iridium heterogeneous catalyst in oxygen reduction reaction. Angew Chem Int Ed. 2019;58:9640-9645.

58. Wang X, Chen W, Zhang L, et al. Uncoordinated amine groups of metal-organic frameworks to anchor single Ru sites as chemoselective catalysts toward the hydrogenation of quinoline. J Am Chem Soc. 2017;139:9419-9422.

59. Tao H, Choi C, Ding LX, et al. Nitrogen fixation by Ru single-atom electrocatalytic reduction. Chem. 2019;5:204-214.

60. He T, Chen S, Ni B, et al. Zirconium-porphyrin-based metal-organic framework hollow nanotubes for immobilization of noble-metal single atoms. Angew Chem Int Ed. 2018;57:3493-3498.

61. Liu J, Jiao M, Mei B, et al. Carbon-supported divacancy-anchored platinum single-atom electrocatalysts with super-high Pt utilization for the oxygen reduction reaction. Angew Chem Int Ed. 2019;58:1163-1167.

62. Feng Q, Zhao S, Xu Q, et al. Mesoporous nitrogen-doped carbon-nanosphere-supported isolated single-atom Pd catalyst for highly efficient semihydrogenation of acetylene. Adv Mater. 2019;31:e1900509.

63. Zhang C, Sha J, Fei H, et al. Single-atom ruthenium catalytic sites on nitrogen-doped graphene for oxygen reduction reaction in acidic medium. ACS Nano. 2017;11:6930-6941.

64. Lu B, Guo L, Wu F, et al. Ruthenium atomically dispersed in carbon outperforms platinum toward hydrogen evolution in alkaline media. Nat Commun. 2019;10:631.

65. He X, He Q, Deng Y, et al. A versatile route to fabricate single atom catalysts with high chemoselectivity and regioselectivity in hydrogenation. Nat Commun. 2019;10:3663.

66. Zhou S, Shang L, Zhao Y, et al. Pd single-atom catalysts on nitrogen-doped graphene for the highly selective photothermal hydrogenation of acetylene to ethylene. Adv Mater. 2019;31:e1900509.

67. Zhou P, Li N, Chao Y, et al. Thermolysis of noble metal nanoparticles into electron-rich phosphorus-coordinated noble metal single atoms at low temperature. Angew Chem Int Ed. 2019;58:14184-14188.

68. Qu Y, Chen B, Li Z, et al. Thermal emitting strategy to synthesize atomically dispersed Pt metal sites from bulk Pt metal. J Am Chem Soc. 2019;141:4505-4509.
ZHOU et al.

69. Zhang J, Liu J, Xi L, et al. Single-atom Au/NiFe layered double hydroxide electrocatalyst: probing the origin of activity for oxygen evolution reaction. J Am Chem Soc. 2018;140:3876-3879.

70. Zhou M, Dick JE, Bard AJ, et al. Electrodeposition of isolated platinum atoms and clusters on bismuth-characterization and electrocatalysis. J Am Chem Soc. 2017;139:17677-17682.

71. Zhang Z, Feng C, Liu C, et al. Electrochemical deposition as a universal route for fabricating single-atom catalysts. Nat Commun. 2020;11:1215.

72. Zhang J, Zhao Y, Guo X, et al. Single platinum atoms immobilized on an MXene as an efficient catalyst for the hydrogen evolution reaction. Nat Catal. 2018;1:985-992.

73. Zhang L, Han L, Liu H, et al. Potential-cycling synthesis of single platinum atoms for efficient hydrogen evolution in neutral media. Angew Chem Int Ed. 2017;56:13694-13698.

74. Jiang K, Liu B, Luo M, et al. Single platinum atoms embedded in nanoporous cobalt selenide as electrocatalyst for accelerating hydrogen evolution reaction. Nat Commun. 2019;10:1743.

75. Tavakkoli M, Holmberg N, Kronberg R, et al. Electrochemical activation of single-walled carbon nanotubes with pseudo-atomic-scale platinum for the hydrogen evolution reaction. ACS Catal. 2017;7:3121-3130.

76. Zhang L, Jia Y, Liu H, et al. Charge polarization from atomic metals on adjacent graphitic layers for enhancing the hydrogen evolution reaction. Angew Chem Int Ed. 2019;58:9404-9408.

77. Zhang Y, Yan J, Ren X, et al. 2D WS2 nanosheet supported Pt nanoparticles for enhanced hydrogen evolution reaction. Int J Hydrog Energy. 2017;42:5472-5477.

78. Zhou M, Li M, Hou C, et al. Pt nanocrystallines/TiO2 with thickness-controlled carbon layers: preparation and activities in CO oxidation. Chin Chem Lett. 2018;29:787-790.

79. Liu P, Zhao Y, Qin RX, et al. Photochemical route for synthesizing atomically dispersed palladium catalysts. Science. 2016;352:797-801.

80. Wei H, Huang K, Wang D, et al. Iced photochemical reduction to synthesize atomically dispersed metals by suppressing nanocrystal growth. Nat Commun. 2017;8:1490.

81. Wei H, Wu H, Huang K, et al. Ultralow-temperature photochemical synthesis of atomically dispersed Pt catalysts for the hydrogen evolution reaction. Chem Sci. 2019;10:2830-2836.

82. Ge X, Zhou P, Zhang Q, et al. Palladium single atoms on TiO2 as a photocatalytic sensing platform for analyzing the organophosphorus pesticide chlorpyrifos. Angew Chem Int Ed. 2020;59:232-236.

83. Zhuang L, Jia Y, Liu H, et al. Defect-induced Pt-Co-Se coordinated sites with highly asymmetrical electronic distribution for boosting oxygen-involved electrocatalysis. Adv Mater. 2019;31:e1805581.

84. Shen R, Chen W, Feng Q, et al. High-concentration single atomic Pt sites on hollow CuSe for selective O2 reduction to H2O2 in acid solution. Chem. 2019;5:2099-2110.

85. Li P, Wang M, Duan X, et al. Boosting oxygen evolution of single-atomic ruthenium through electronic coupling with cobalt-iron layered double hydroxides. Nat Commun. 2019;10:1711.

86. Mori K, Taga T, Yamashita H, et al. Isolated single-atomic Ru catalyst bound on a layered double hydroxide for hydrogenation of CO2 to formic acid. ACS Catal. 2017;7:3147-3151.

87. Lin J, Wang A, Qiao B, et al. Remarkable performance of Ir1/FeO(x) single-atom catalyst in water gas shift reaction. J Am Chem Soc. 2013;135:15314-15317.

88. Sun X, Chen C, Liu S, et al. Aqueous CO2 reduction with high efficiency using alpha-Co(OH)2-hydrated atomic Ir electrocatalysts. Angew Chem Int Ed. 2019;58:4669-4673.

89. Babu DD, Huang Y, Anandhababu G, et al. Atomic iridium@cobalt nanosheets for dinuclear tandem water oxidation. J Mater Chem A. 2019;7:8376-8383.

90. Zuo Q, Liu T, Chen C, et al. Ultrathin metal-organic framework nanosheets with ultrahigh loading of single Pt atoms for efficient visible-light-driven photocatalytic H2 evolution. Angew Chem Int Ed. 2019;58:10198-10203.

91. Shao X, Yang X, Xu J, et al. Iridium single-atom catalyst performing a quasi-homogeneous hydrogenation transformation of CO2 to formate. Chem. 2019;5:693-705.

92. Lou Y, Zhang Y, Li X, et al. Pocketlike active site of Rh1/MoS2 single-atom catalyst for selective crotonaldehyde hydrogenation. J Am Chem Soc. 2019;141:19289-19295.

93. Zhao D, Chen Z, Yang W, et al. MXene (Ti3C2) vacancy-confined single-atom catalyst for efficient functionalization of CO2. J Am Chem Soc. 2019;141:4086-4093.

94. Cheng N, Stambula S, Wang D, et al. Platinum single-atom and cluster catalysis of the hydrogen evolution reaction. Nat Commun. 2016;7:13638.

95. Zhang L, Si R, Liu H, et al. Atomic layer deposited Pt-Ru dual-metal dimers and identifying their active sites for hydrogen evolution reaction. Nat Commun. 2019;10:4936.

96. Zhang L, Liu H, Liu S, et al. Pt/Pd Single-atom alloys as highly active electrochemical catalysts and the origin of enhanced activity. ACS Catal. 2019;9:9350-9358.

97. Chen CH, Wu D, Li Z, et al. Ruthenium-based single-atom alloy with high electrocatalytic activity for hydrogen evolution. Adv Energy Mater. 2019;9:1803913.

98. Zhang H, An P, Zhou W, et al. Dynamic traction of lattice-confined platinum atoms into mesoporous carbon matrix for hydrogen evolution reaction. Science. 2018;4:eaau6657.

99. Kwon HC, Kim M, Grote JP, et al. Carbon monoxide as a promoter of atomically dispersed platinum catalyst in electrochemical hydrogen evolution reaction. J Am Chem Soc. 2018;140:16198-16205.

100. Li T, Liu J, Song Y, et al. Photochemical solid-phase synthesis of platinum single atoms on nitrogen-doped carbon with high loading as bifunctional catalysts for hydrogen evolution and oxygen reduction reactions. ACS Catal. 2018;8:8450-8458.

101. Sahoo SK, Ye Y, Lee S, et al. Rational design of TiC-supported single-atom electrocatalysts for hydrogen evolution and selective oxygen reduction reactions. ACS Energy Lett. 2018;4:126-132.

102. Yan QQ, Wu DX, Chu SQ, et al. Reversing the charge transfer between Platinum and sulfur-doped carbon support for electrocatalytic hydrogen evolution. Nat Commun. 2019;10:4977.

103. Yin XP, Wang HJ, Tang SP, et al. Engineering the coordination environment of single-atom platinum anchored on graphdiyne for optimizing electrocatalytic hydrogen evolution. Angew Chem Int Ed. 2018;7:9382-9386.

104. Liu D, Li X, Chen S, et al. Atomically dispersed platinum supported on curved carbon supports for efficient electrocatalytic hydrogen evolution. Nat Energy. 2019;4:512-518.
105. Park J, Lee S, Kim HE, et al. Investigation of the support effect in atomically dispersed Pt on WO$_3$-x for utilization of Pt in the hydrogen evolution reaction. *Angew Chem Int Ed*. 2019;58:16038-16042.

106. Ye S, Luo F, Zhang Q, et al. Highly stable single Pt atomic sites anchored on aniline-stacked graphene for hydrogen evolution reaction. *Energy Environ Sci*. 2019;12:1000-1007.

107. Fang S, Zhu X, Liu X, et al. Uncovering near-free platinum single-atom dynamics during electrochemical hydrogen evolution reaction. *Nat Commun*. 2020;11:1029.

108. Yang J, Chen B, Liu X, et al. Efficient and robust hydrogen evolution: phosphorus nitride imide nanotubes as supports for anchoring single ruthenium sites. *Angew Chem Int Ed*. 2018;57:9495-9500.

109. Ramalingam V, Varadhan P, Fu HC, et al. Heteroatom-mediated interactions between Ruthenium single atoms and an MXene support for efficient hydrogen evolution. *Adv Mater*. 2019;31:e1903841.

110. Tiwari JN, Harzandi AM, Ha M, et al. High-performance hydrogen evolution by Ru single atoms and nitride-Ru nanoparticles implanted on N-doped graphitic sheet. *Adv Energy Mater*. 2019;9:e1900931.

111. Zhang J, Xu X, Yang L, et al. Single-atom Ru doping induced phase transition of MoS$_2$ and S vacancy for hydrogen evolution reaction. *Small Methods*. 2019;3:e1900653.

112. He Q, Tian D, Jiang H, et al. Achieving efficient alkaline hydrogen evolution reaction over a Ni$_5$P$_4$ catalyst incorporating single-atomic Ru sites. *Adv Mater*. 2020;32:e2006972.

113. Meng X, Ma C, Jiang L, et al. Distance synergy of MoS$_2$-confined Rhodium atoms for highly efficient hydrogen evolution. *Angew Chem Int Ed*. 2020;59:10502-10507.

114. Cao L, Luo Q, Chen J, et al. Dynamic oxygen adsorption on single-atomic ruthenium catalyst with high performance for acidic oxygen evolution reaction. *Nat Commun*. 2019;10:4849.

115. Yao Y, Hu S, Chen W, et al. Engineering the electronic structure of single atom Ru sites via compressive strain boosts acidic water oxidation electrocatalysis. *Nat Catal*. 2019;2:304-313.

116. Luo X, Wei X, Zhong H, et al. Single-atom Ir-anchored 3D amorphous NiFe nanowire@nanosheets for boosted oxygen evolution reaction. *ACS Appl Mater Interfaces*. 2020;12:3539-3546.

117. Wang Q, Huang X, Zhao ZL, et al. Ultrahigh-loading of Ir single atoms on NiO matrix to dramatically enhance oxygen evolution reaction. *J Am Chem Soc*. 2020;142:7425-7433.

118. Lai WH, Zhang LF, Hua WB, et al. General pi-electron-assisted strategy for Ir, Pt, Ru, Pd, Fe, Ni single-atomic electrocatalysts with bifunctional active sites for highly efficient water splitting. *Angew Chem Int Ed*. 2019;58:11868-11873.

119. Luo F, Hu H, Zhao X, et al. Robust and stable acidic overall water splitting on Ir single atoms. *Nano Lett*. 2020;20:2120-2128.

120. Zhou L, Zhou P, Zhang YL, et al. 3D star-like atypical hybrid MOF derived single-atom catalyst boosts oxygen reduction catalysis. *J Energy Chem*. 2021;55:355-360.

How to cite this article: Zhou L, Lu S-Y, Guo S. Recent progress on precious metal single atom materials for water splitting catalysis. *SusMat*. 2021;1:194–210. https://doi.org/10.1002/sus2.15