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REVIEW



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Recent advances and strategies in the stabilization of single-atom catalysts for electrochemical applications

Department of Mechanical and Materials Engineering, University of Western Ontario, London, Ontario, Canada

Correspondence

Xueliang Sun, Department of Mechanical and Materials Engineering, University of Western Ontario, 1151 Richmond Street, N6A 3K7 London, Ontario, Canada. Email: xsun@eng.uwo.ca

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Junjie Li | Lei Zhang | Kieran Doyle-Davis | Ruying Li | Xueliang Sun 💿

Abstract

Owing to the rapidly increasing consumption of fossil fuels, finding clean and reliable new energy sources is of the utmost importance. Thus, developing highly efficient and low-cost catalysts for electrochemical reactions in energy conversion devices is crucial. Single-atom catalysts (SACs) with maximum metal atom utilization efficiency and superior catalytic performance have attracted significant attention, especially for electrochemical reactions. However, because of the highly unsaturated coordination environment, the stability of SACs can be a challenge for practical applications. In this review, we will summarize the strategies to increase the stability of SACs and synthesizing stable SACs, as well as the application of SACs in electrochemical reactions. Finally, we offer a perspective on the development of advanced SACs through rational design and a deeper understanding of SACs with the help of in situ or operando techniques in electrochemical reactions.

KEYWORDS

electrochemical reaction, single-atom catalyst, stability

1 INTRODUCTION

Owing to the rapidly increasing consumption of fossil fuels and global warming, finding clean and reliable new energy sources is of the utmost importance. Using energy conversion devices to develop clean energy from sustainable and renewable energy sources is one promising alternative. Most of such devices operate using electrochemical redox reactions, for example, the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are involved in the water-splitting reaction.^{1,2} Oxygen reduction reaction (ORR) at the cathode and hydrocarbon (formic acid, methanol, and ethanol) conversion reactions are used in fuel cells and rechargeable metal-air batteries.^{1,3} Recently, electrochemical CO₂

reduction reaction (CO₂RR) and N₂ reduction reaction (N₂RR), which were used to synthesize hydrocarbon products and ammonia have seen significant development.^{4,5} Among these electrochemical reactions, Pt and other noble-metal-based catalysts have shown the best catalytic activities. However, for traditional electrocatalysts, the metal particles have a wide-sized distribution, but only the surface atoms of the metal particles participate in the reaction, thus a large proportion of the metal atoms remains inert and wasted. Therefore, an electrocatalyst with high atom utilization efficiency is in demand.

In this case, single-atom catalysts (SACs) seem to be the best scenario to solve this issue.⁶⁻⁹ SACs with atomically dispersed metal atoms on the support can reach the

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maximum metal atom utilization efficiency, as all the atoms can act as an active site. In addition, because of the unique electronic structure and highly unsaturated coordination of SACs, they showed improved catalytic activity and selectivity over that of nanoparticles (NPs)based catalysts in some reactions. Although the study of single-site catalysts is more prevalent in recent years, the discovery of SACs can date back to 1995. Maschmeyer et al support highly dispersed Ti species on mesoporous silica using a grafting method for the epoxidation of cyclohexene and cyclic alkenes. They found there were no obvious metal NPs, indicating that the Ti species may be dispersed at the atomic level.¹⁰ In 2003, Fu et al loaded Au NPs on CeO₂ and then etched the particles through NaCN, leaving the atoms and clusters of Au. In water-gas shift (WGS) conversion, they found that the catalysts and metal particle catalysts etched by NaCN were quite active, so they believed that the true reactive center consisted of single atoms and clusters of Au rather than NPs.¹¹ Similarly, in 2005, Zhang et al synthesized a very low loading Au/ZrO₂ catalyst (<0.1%) by an impregnation method. Interestingly, they found that highresolution transmission electron microscopy (TEM) cannot detect any Au NPs on this sample. In the selective hydrogenation of 1,3-butadiene, they found that the catalyst has good activity and high selectivity to olefins. Based on this result, they believe that the main active center in the selective hydrogenation of 1,3-butadiene is Au³⁺ ions.¹² Although these works suggest that the active center in the reactions may be single atoms, they are limited to characterization methods such as atomicresolution TEM to identify single atoms. Until 2011, Zhang and coworkers successfully synthesized a practical Pt_1/FeO_x SAC by a wet chemistry method with a Pt loading at 0.17%. Thanks to more advanced characterization techniques, the Pt_1/FeO_x was comprehensively investigated through atomic-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), X-ray absorption spectroscopy (XAS), and in situ CO chemisorption diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to confirm that Pt species were monoatomic without any obvious metal particles and cluster.¹³ From here, SACs have seen continuous growth and development across the field.

With a decrease in size from NPs to single atom, the atom utilization efficiency will improve, along with increasing surface-free energy, which leads to the migration of single atoms to form clusters or NPs.^{14,15} The aggregation of single atoms will decrease the active sites and could lead to deactivation in the worst case. Therefore, increasing the stability of SACs by some efficient strategies is important. Although there are many reviews

showing the promising application of SACs in electrocatalysis, rarely do they summarize the strategies to stabilize SACs and make adoption a realistic option. In this review, we will first briefly review the characterization tools for SACs. Second, we will systematically summarize some effective synthesis strategies to stabilize SACs. Then, we will present the application and development of SACs in some electrochemical reactions, including ORR, HER, formic acid oxidation reaction (FAOR), OER, CO₂RR, and N₂RR. In the end, the summary and perspective for single-atom catalysis will also be presented.

2 | CHARACTERIZATIONS OF SACS

Even before Zhang et al presented the concept of SACs, there were some works showing the possible discovery of SACs.¹⁰⁻¹² However, due to the limited characterization methods to understand the structure of catalysts at atomic level at the time, the development of SACs was hindered. Therefore, characterization tools that can directly observe or identify the structure of SACs are quite important. With the rapid development of catalytic characterization technologies, more comprehensive studies on SACs have become possible. Although there are many newly developed characterization tools for SACs such as scanning tunneling microscopy (STM),¹⁶ atom probe tomography (APT), and Mössbauer spectroscopy,¹⁷ they are limited to some specific application conditions, thus losing their general applicability. Therefore, in this review, we will summarize the three most widely used characterization tools for SACs (Figure 1).

2.1 | Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy

In aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF STEM), the contrast is proportional to the atomic number of the elements. Therefore, single atoms with heavier elements can be distinguished based on the different contrast of the single atoms and substrate. Up to now, successfully characterized SACs through AC-HAADF-STEM range from both noble (Pt, Ir, Au, Rh, Ru, Pd, etc) and non-noble (Fe, Co, Ni, Cu, Zn, etc) elements.^{13,18-30} For example, Pt single atoms on a FeO_x substrate can be clearly observed from AC-HAADF STEM due to its high atomic number difference. As shown in Figure 2A,B, the bright spots are the Pt single atoms on FeO_x support.³¹ Combining AC-STEM with electron energy loss





FIGURE 1 Stabilization strategies for SACs and their applications in electrocatalysis. CO_2RR , CO_2 reduction reaction; FAOR, formic acid oxidation reaction; HER, hydrogen evolution reaction; N₂RR, N₂ reduction reaction; OER, oxygen evolution reaction; ORR, oxygen reduction reaction; SAC, single-atom catalyst

spectroscopy (EELS), the composition of single atoms can also be ascertained. Chung et al³² directly observed the coexistence of Fe and N atoms with the help of EELS, indicating Fe–N coordination in Fe SAC, as shown in Figure 2C,D. Besides EELS, energy-dispersive X-ray spectroscopy (EDX)-mapping coupled with AC-STEM is also very helpful to provide the dispersion of single atoms on the substrate. Chen et al synthesized Fe single atoms on a metal–organic framework (MOF) @polymer composite-derived N, P, and S co-doped hollow carbon. The element maps from the HAADF-STEM showed uniform distribution of Fe, C, N, S, and P, demonstrating the highly dispersed Fe single atoms (Figure 2E,F).³³

2.2 | CO chemisorption DRIFTS

Using CO as a probe molecular, DRIFTS shows its advantages to distinguish single atoms from NPs. Depending on the sites of the CO molecular adsorption, different C=O vibration bonds will be displayed. Based on this, the single atoms should only exhibit a CO linear adsorption while the large NPs should have both CO linear and bridge adsorption. Because of the low-coordinated single atoms, which are always high positively charged, the wavelength of CO linear adsorption on single atoms

shows a blue shift compared with the CO linear adsorption on NPs.³⁴⁻³⁷ Compared with the AC-HAADF STEM, which focuses on a limited local area, DRIFTS results can reflect the dispersion of single atoms at macroscopic scale, which can be more convenient and convincing.

Pei et al showed various Cu-alloyed Pd single atoms on SiO₂ with different Pd loadings. In the in situ Fourier transform infrared (FTIR) measurement, they found without the Cu, there was only one CO adsorption band at 1870 cm⁻¹, which can be ascribed to CO adsorption on the threefold Pd hollow sites, indicating the formation of big Pd NPs. However, for all the Cu-alloved Pd SACs, only one band at 2133 cm^{-1} can be found, which is the CO adsorption on Pd single atoms (Figure 3A).³⁸ Qiao et al showed that in the Pt_1/FeO_x catalyst, only the linear absorption peak (2080 cm⁻¹) of CO adsorbed to the Pt single atoms exists (Figure 3B). On the $Pt-NPs/FeO_x$, a linear absorption peak of CO on the NPs (2030 cm^{-1}) and a bridge absorption peak (1860 cm^{-1}) were observed (Figure 3C).¹³ Ding et al found that the CO linear adsorption peak wavenumbers on Pt NPs gradually decreased with the introduction of O2 under various temperatures. However, the CO linear adsorption peak on Pt single atoms, which was at higher wavenumbers (generally higher than 2100 cm^{-1}) remained constant under O₂ atmosphere (Figure 3D-F). These results



FIGURE 2 A and B, HAADF-STEM images Pt_1/FeO_x -C800. Scale bars = 2 nm for A and B. Reproduced with permission: Copyright 2019, Nature Publishing Group.³¹ C, HAADF-STEM image of individual Fe atoms (labeled 1, 2, and 3). D, EEL spectra of the N K-edge (N_K) and Fe L-edge (Fe_L) acquired from (C). Reproduced with permission: Copyright 2017, American Association for the Advancement of Science.³² E, HAADF STEM image of Fe-SAs/NPS-HC catalyst. Scale bar = 1 nm. F, HAADF-STEM image and corresponding element maps (Fe: yellow; C: blue; N: cyar; S: orange; P: green). Scale bar = 100 nm. Reproduced with permission: Copyright 2015, Nature Publishing Group.³³ EEL, electron energy loss; HAADF-STEM, high-angle annular dark-field scanning transmission electron microscopy; NPS-HC, nitrogen, phosphorus, and sulfur co-doped hollow carbon polyhedron; SA, single atomic site



FIGURE 3 A, FTIR spectra of CO adsorption over the (a) Cu/SiO₂, (b) CuPd_{0.006}/SiO₂, (c) CuPd_{0.025}/SiO₂, and (d) Pd_{0.006}/SiO₂ catalysts. Reproduced with permission: Copyright 2017, American Chemical Society.³⁸ B and C, In situ FTIR spectra of CO adsorption for Pt₁ and clusters catalysts. Reproduced with permission: Copyright 2011, Nature Publishing Group.¹³ D to F, Time-dependent IR spectra of CO adsorbed on 2.6 wt% Pt/HZSM-5, Pt/SiO₂, Pt/Al₂O₃, Pt/TiO₂, and Pt/ZrO₂ upon O₂ exposure. Reproduced with permission: Copyright 2015, American Association for the Advancement of Science.³⁷ FTIR, Fourier transform infrared; IR, infrared

demonstrated that only the Pt NPs are active for CO oxidation and WGS at low temperature, while the single atoms are inert due to the strongly adsorbed CO molecules.37

However, the CO chemisorption DRIFTS can only be applied to noble-metal-based SACs, as the non-noble metal has a very weak interaction with CO. It is also not applicable for carbon-based materials due to the strong light adsorption.

2.3 X-ray absorption spectroscopy

In comparison with AC-HAADF STEM, which can only give the information about local area of SACs and CO chemisorption DRIFTS, which can only apply for noblemetal-based SACs, synchrotron-based XAS shows its general applicability for all types of SACs.³⁹⁻⁴¹ It not only offers information on the electronic state but also the coordination environment of the probe atom, thus becoming one of the most widely used characterization techniques for SACs. In principle, when the X-rays are absorbed by the probed atom, the inner-shell electrons will be activated to higher unoccupied orbitals or continuum level. Depending on the energy range for the X-ray absorption coefficient vs the X-ray energy, it can be divided into two parts: the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) (Figure 4A). XANES can give the electronic structure of the probed atom, while the EXAFS provides the neighboring atom coordination information of the central atom.⁴²

Because of its high sensitivity to the electronic properties of the probe atom, XANES is used to determine the valence state of SACs. Shen et al synthesized atomically dispersed Pt single atoms on amorphous CuS_x for the selective reduction of O_2 to H₂O₂. From the XANES results, they found that the whiteline intensity of $h-Pt_1-CuS_x$ is between that of Pt foil, $Pt(acac)_2$, and PtO_2 , which indicated that the Pt single atom are slightly positively charged (Figure 4B). Based on the whiteline intensity, they found that the valence state of Pt single atoms is around +0.75, which is lower than the reported Pt SACs after a semiquantitative analysis (Figure 4C).⁴³ Cao et al performed operando XAS on Co₁/PCN (phosphorized carbon nitride) SAC in alkali-based HER. They observed that when changing the ex situ sample to the open-circuit condition, the absorption edge shifted 0.5 eV higher, indicating the increasing Co oxidation state. Based on the XANES results, the valence state of the Co single atoms at ex situ and open-circuit potentials are close to the CoO and Co_3O_4 . By applying higher overpotentials,



FIGURE 4 A, Illustration of XANES and EXAFS. Reproduced with permission: Copyright 2017, AMSI press.⁴² B, Pt L₃-edge XANES spectra and (C) corresponding linear fitting curve of $h-Pt_1-CuS_r$ and reference materials. Reproduced with permission: Copyright 2019, Elsevier.⁴³ D, Operando XANES spectra recorded at the Co K-edge of Co₁/PCN, at different applied voltages during electrocatalytic hydrogen evolution reaction, and the XANES data of the reference standards of CoO, Co₃O₄, and CoOOH. Inset, magnified pre-edge XANES region. E, Normalized difference spectra for Co K-edge XANES. F, The fitted average oxidation states of Co from XANES spectra. Reproduced with permission: Copyright 2019, Nature Publishing Group.²³ G, Comparison between the K-edge XANES experimental spectrum of Co_{0.5} (black hollow circles) and the theoretical spectrum calculated with the depicted structures (solid red lines). Reproduced with permission: Copyright 2017, Nature Publishing Group.⁴⁴ EXAFS, extended X-ray absorption fine structure; PCN, phosphorized carbon nitride; XANES, X-ray absorption near-edge structure

a higher energy shift in absorption edges were also observed (Figure 4D). The fitted average oxidation states from the Co K-edge XANES for the Co single atoms was +2.02, while the Co average valence state increased from +2.02 to +2.40 with the change in overpotentials (Figure 4E,F).²³ In addition to the analysis of valence state of probe atoms, XANES can also be used to identify the geometrical arrangement of atoms around the central atom. For example, Zitolo et al prepared a pyrolyzed Co-N-C SACs. They used their XANES analysis to determine the structure and electronic state of the three porphyrinic Co moieties (Figure 4G).⁴⁴

EXAFS, normally beginning in the energy range much higher (~50 eV) than the absorption edge, can give information on the local structure of the probe atom, including the coordination number and the bonding distance. In most of the reported references, metal foils and corresponding metal oxide are used as the reference samples.^{7,45} In SACs, the lack of metal-metal coordination became the fingerprint feature to distinguish single atoms from NPs. Li et al synthesized Pt single atoms on four different substrates (Co₃O₄, CeO₂, ZrO₂, and graphene). All of them showed a Pt-O coordination at 1.6 Å with a coordination number of 5.7, 4.9, 4.8, and 4.0, respectively. None of them showed any Pt-Pt coordination, indicating the absence of Pt NPs. Pt₁/Co₃O₄ showed a second shell peak at 2.56 Å, which can be attributed the Pt-Co coordination after EXAFS curve-fitting (Figure 5A). The Pt-Co coordination indicated the strong interaction between Pt single atoms and Co₃O₄ substrate.³⁴ Liu et al reported a Pd₁/TiO₂ SAC through a photochemical strategy for the hydrogenation of C=C bonds. In the Pd K-edge EXAFS results, only the Pd-O coordination peak can be found on Pd₁/TiO₂, but without showing any obvious



FIGURE 5 A, k^2 -weighted Fourier transform spectra of Pt_1/Co_3O_4 , Pt_1/CeO_2 , Pt_1/ZrO_2 , and Pt_1 /graphene SACs as well as the Pt foil and PtO₂ reference at the Pt L₃-edge. Reproduced with permission: Copyright 2019, American Chemical Society.³⁴ B, EXAFS spectra of Pd_1/TiO_2 and bulk palladium foil at the Pd K-edge. Reproduced with permission: Copyright 2016, American Association for the Advancement of Science.⁴⁶ C, EXAFS spectra of Fe SAC and reference samples. Reproduced with permission: Copyright 2019, Nature Publishing Group.⁴⁷ D, EXAFS at Co K-edge of isolated single atomic sites anchored on hollow N-doped carbon spheres (ISAS-Co/HNCS), CoO, Co_3O_4 , and Co foil. Reproduced with permission: Copyright 2017, American Chemical Society.⁴⁸ EXAFS, extended X-ray absorption fine structure; SAC, single-atom catalyst

metal-metal coordination between 2 and 3 Å (Figure 5B), which indicated the highly dispersed Pd₁ atoms on TiO₂.⁴⁶ Zhao et al developed a general method to produce M-NC SACs at scale, using the cascade anchoring strategy. In the Fe K-edge EXAFS, they found the Fe-NC SAC showed no Fe-Fe coordination peak, but a very strong peak at 1.5 Å. Based on the Fe-Pc reference, this peak can be ascribed to the Fe–N shell around the Fe single atoms (Figure 5C).⁴⁷ Han et al prepared Co single atoms on hollow N-doped carbon spheres for the ORR. From the Fourier-transformed k³-weighted EXAFS, the ISAS-Co/HNCS only showed one peak at 1.32 Å, which can be the Co-N-C coordination in the first shell (Fgure 5D). The absence of Co-Co coordination at 2.17 Å demonstrated the singly dispersed Co atoms. Further EXAFS curve fitting indicated the Co1 atom bonded with four N atoms.48

3 | SYNTHETIC STRATEGIES TOWARD THE STABILITY OF SACs

In the last few years, because of the increased atom utilization efficiency and unique catalytic activity, SACs have become one of the hottest research areas. Because of the highly unsaturated coordination environment, the mobility of single atoms on the surface of the support was strongly enhanced. During the catalysis process, when the reactant is adsorbed on the single atoms, the interaction between the single atoms and the substrate will decrease, leading to the migration of single atoms on the support. As such, the stability of SACs can become even worse in some rigorous reaction conditions, such as high temperature and high pressure. For example, Bayram et al⁴⁹ found the Ir₁ atoms gradually aggregated to clusters in the presence of cyclohexene and H₂ reactants under cyclohexane solvent. Similar aggregation can also be found on Pt₁/CeO₂ SAC, in which some Pt clusters can be found after three cycles of propane dehydrogenation.¹⁵ As a result, finding a suitable and effective method to stabilize single atoms is an urgent requirement for the widespread adoption of SACs. Aiming to solve this issue, several synthesis strategies have been introduced to improve the stability of SACs.^{7-9,50}

3.1 | Spatial confinement

Due to the fact that the single atoms tend to form the big clusters or NPs because of the enhanced mobility on the surface of substrate, the possibility to "meet" other atom increases, forming larger-sized species. Based on this, researchers designed several methods to synthesize the catalysts with special structures that confine the single atoms in a limited space, which dramatically decrease the space for single atoms to move. This method is generally referred to as spatial confinement.

One such method was to artificially or naturally create a nano-cage structure to increase the stability of SACs. Liu and coworkers combined the organometallic chemisorption and atomic layer deposition (ALD) method to stabilize Pt SACs. First, they used a grafting method to make the (PhPCP)Pt-OH chemisorbed on the Al_2O_3 , and then coated a metal oxide, such as TiO_2 , ZnO, and Al₂O₃ through ALD. Due to the ligand effect, the coated oxide will only be deposited around the Pt singleatom species instead of reacting with them. After several cycles of layer by layer deposition, the oxide become oxide nano-cages that capture the Pt single atoms. After that, thermal treatment will be conducted to remove the Pt ligand (Figure 6A). Without the nano-cage protection, the size of the Pt was calculated as 3.8 ± 2.8 nm, while the Pt sizes of the Al₂O₃-, TiO₂-, and ZnO-coated samples decreased to 1.7 ± 1.4 , 0.6 ± 0.3 , and 1.4 ± 1.1 nm, respectively (Figure 6B). They further used the CO DRIFTS analysis to confirm the dispersion of the Pt species with different coatings. DRIFTS results showed that the oxidecoated samples have a reduced CO linear adsorption peak intensity on NPs compared with the pristine sample. Combined with STEM and DRIFTS results, they demonstrated that this oxide nano-cage structure can help obtain more Pt single atoms.⁵¹

Apart from the artificially created nano-cage, some materials offer a naturally formed cavity that can be a good support to stabilize single atoms. For example, carbonitride (C_3N_4) , which has N-coordinating "six-fold cavities" has shown promise. Vilé and coworkers were the first to use C_3N_4 as a substrate for SACs.

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They successfully supported 0.5 wt% Pd single atoms on mpg-C₃N₄, which was confirmed by HAADF-STEM (Figure 6C), XAS, and X-ray photoelectron spectroscopy (XPS) (Figure 6D,E). Density functional theory (DFT) was used to study the nature of the Pd single atoms and they found the Pd single atoms can be electrostatically stabilized by the N species from the support. The sixfold N cavity will trap the Pd single atoms through the strong interaction between N atoms and Pd atom. Hence, the stability of Pd single atoms is improved. Hydrogenation of 1-hexyne was used as a probe reaction to investigate the benefit of this [Pd]mpg-C₃N₄. Under 363 K and 2 bar, the [Pd]mpg- C_3N_4 showed nearly 100% selectivity to 1-hexene. At 343 K and 5 bar, it also displayed a much higher activity and high selectivity to olefin (90%) than the Lindlar catalyst even with a high Pd content (5 wt%). In the stability test, the $[Pd]mpg-C_3N_4$ exhibited no decrease in both the activity and selectivity, indicating that the metal loss and single-atom aggregation were not obvious. DFT revealed that the optimized activation of H₂ and adsorption of alkyne on Pd single sites lead to its high catalytic activity and selectivity.⁵² Following this study, C₃N₄ was reported to have the ability to stabilize other single atoms.⁵⁵⁻⁵⁷ Similar as the C_3N_4 , zeolite with high surface area and porous structure also showed great potential to stabilize the single atoms.^{53,54,58} For instance, Liu et al developed a general way to synthesize different types of SACs, including Pt, Pd, Ru, Rh, Co, Ni, and Cu single atoms in Y zeolite. The metal-ethylenediamine complex was confined into the β -cages of Y zeolite during the thermal treatment (Figure 6F). As a result, the single atoms can be stabilized in the skeletal O atoms in the Y zeolite (Figure 6G,H).⁵³ Kistler et al reported that a [Pt (NH_4) ²⁺ complex can be confined in a KLTL zeolite in its pores (Figure 6I-M). Then, the sample will be oxidized at 633 K to achieve the Pt SAC. IR and XAS results demonstrated the excellent stability of Pt SAC, as the isolated Pt single atoms still remained after the CO oxidation reaction.54

3.2 | Neighbor site modification

Due to the highly unsaturated coordination environment, the neighbor atoms near the single atoms will largely affect their electronic property and local structure. Therefore, modification on the proximity sites of single atoms may increase both the catalytic activity and stability.

Due to the requirement of conductivity, carbon-based materials were the first choice, especially for the applications of fuel cells,⁵⁹ but the metal atoms always have a very weak interaction with the carbon substrate, which



FIGURE 6 A, Overall schematic for proposed single Pt atom synthetic methodology combining surface organometallic chemisorption and ALD approaches. B, (^{Ph}PCP)Pt-Al₂O₃-400 cal, 20Al-(^{Ph}PCP)Pt-Al₂O₃-400 cal, 40Ti-(^{Ph}PCP)Pt-Al₂O₃-400 cal, and 20Zn-(^{Ph}PCP)Pt-Al₂O₃-400 cal. Reproduced with permission: Copyright 2017, American Chemical Society.⁵¹ C, Structure and HAADF-STEM image of [Pd]mpg-C₃N₄. D, k²-weighted Fourier transform EXAFS (not phase-corrected), and (E) Pd_{3d} core level XPS of the catalysts. Reproduced with permission: Copyright 2014, Wiley.⁵² F, Schematic illustration of the in situ separation and confinement of a platinum precursor in a β-cage. Followed by thermal treatment. G, Elements mapping, and (H) AC-HAADF-STEM image of Pt-ISAS@NaY. Reproduced with permission: Copyright 2019, American Chemical Society.⁵³ I to M, HAADF-STEM images of site-isolated Pt atoms in KLTL zeolite. Reproduced with permission: Copyright 2014, Wiley.⁵⁴ AC-HAADF-STEM, aberrationcorrected high-angle annular dark-field scanning transmission electron microscopy; ALD, atomic layer deposition; EXAFS, extended X-ray absorption fine structure; ISAS, isolated single atomic sites; Mpg, mesoporous polymeric graphitic; XPS, X-ray photoelectron spectroscopy



FIGURE 7 A, Schematic illustration of the Pt deposition mechanism on N-doped graphene. B and C, HAADF-STEM images of Pt single-atom sample. Scale bars, 10 nm (B); 5 nm (C). Reproduced with permission: Copyright 2016, Nature Publishing Group.⁶⁰ D, Fourier transforms results of k³-weighted Pt L3-edge. E, Proposed atomistic structure of the Pt/HSC. Reproduced with permission: Copyright 2016, Nature Publishing Group.⁶¹ HAADF-STEM images and particle size distributions of (F) 1Pt-SiO₂ and (G) 1Pt-3Na-SiO₂ washed samples. Reproduced with permission: Copyright 2010, American Association for the Advancement of Science.⁶² H to J, HAADF-STEM images of the Na-containing Pt catalysts. Reproduced with permission: Copyright 2015, American Chemical Society.⁶³ HAADF-STEM, high-angle annular dark-field scanning transmission electron microscopy; HSC, high S content

makes it even more challenging to stabilize single atoms on carbon. In the reported reference, increasing the surface area and introducing the stable anchor sites are the design principles for supporting single atoms. Doping other elements on the neighboring sites of single atoms can be an effective way to increase the stability of SACs. Nitrogen-doped materials were found to be one of the most widely used substrate to stabilize single atoms.

Cheng et al demonstrated that Pt single atoms can be achieved on N-doped graphene using ALD (Figure 7A-C). This SAC showed remarkable stability in the HER with no catalytic activity decrease even after 1000 cycles of stability testing. From the Bader charge analysis, a 0.25e charge transfer from the Pt atom to the N-doped graphene only occurred on the Pt single atoms, and no charge transfer between the Pt atom and the pristine

graphene was observed. These results strongly indicated that a very strong interaction between Pt single atoms and the N atoms occurs, which can be attributed to be the main reason for achieving this highly stable SACs.⁶⁰ Choi et al reported a sulfur-doped zeolite-templated carbon, which has 17 wt% S, can stabilize 5 wt% Pt single atoms. From the XANES results, the Pt/HSC showed the highest whiteline intensity and E_0 , indicating the highly oxidized Pt species on higher support S content. EXAFS analysis further confirmed that the Pt single atom was bonded with four S atoms, which led to the high loading and dispersion of Pt single atoms (Figure 7D,E).⁶¹

Apart from N and S atoms doping, alkali ions are also proved to stabilize single atoms. Flytzani Stephanopoulos and coworkers demonstrated the Na⁺ and K⁺ ions were important to stabilize different types of SACs.62,63 Zhai et al found that the alkali ions strongly suppresses the growth of Pt NPs. On the Na-modified silica, Pt clusters and single atoms were stable even after calcination in air at 400°C, which showed much smaller Pt particle size than the pristine sample (Figure 7F,G). The theoretical calculation indicated that Pt-alkali- $O_{y}(OH)_{y}$ species is the active site for the WGS reaction.⁶² Later on, they extend this synthesis strategy to TiO₂, L-zeolites, and MCM-41. In the sample preparation, they made the atomic ratio of Na/Pt as 10:1 from the Pt(NH₃)₄(NO₃)₂ and NaOH precursors using a solid-state impregnation method. On a different substrate with the same Pt loading (0.5 wt%) they showed similar atomic level dispersion (Figure 7H-J). They believed that the Pt single atoms were stabilized by solidum through -O ligand, which was quite active and stable in WGS reaction. This study provides a general method to prepare stable SACs.63

3.3 | Strong metal-support interactions

According to Ostwald ripening, single atoms and NPs tend to aggregate to larger size under high-temperature catalysis because of the dramatically increased high surface-free energy. The size change will lead to the decrease in number of active surface atoms and catalytic deactivation. Recently, researchers found that some supports showed a very strong interaction with the metal species, which can suppress the metal migration and trap the single atoms under high-temperature conditions.

Using bulk metal or NPs to achieve single atoms is one of the most widely used SACs preparation method through thermal treatment. Jones et al demonstrated that the Pt_1/CeO_2 can be obtained from the thermal treatment because of the atomic migration trapping. They found that the CeO_2 with various shapes with different exposed surface facets showed different ability to trap the Pt single atoms (Figure 8A). When they mixed the Pt/aluminum with differently shaped CeO₂, which can suppress the sintering, the mobile Pt atoms can be trapped by CeO_2 during heating at very high temperature (800°C) in air. They further confirmed that the CeO₂ in rods or polyhedral structure are more efficient than cubic CeO₂ for trapping the mobile Pt atoms from HAADF-STEM results (Figure 8B,C).⁶⁴ Lang et al reported that a thermally stable Pt SACs can be achieved from NPs through a strong covalent meta-support interaction (CMSI) after high-temperature calcination. They first supported Pt NPs with 2 to 3 nm diameters on Fe₂O₃ support and then calcinated in air at 800°C for 5 hours. After that, the Pt NPs were disappeared and a high density of Pt single atoms formed, which were confirmed by the HAADF-STEM and XAS results. However, if the Pt-NPs/Fe₂O₃ was calcinated in Ar, the Pt particles would become larger, indicating that the oxidizing atmosphere is quite important (Figure 8D). The in situ STEM results indicated that the reducible iron oxide substrate is critical for the formation of Pt single atoms (Figure 8E-G). This method provides a new way to synthesize Pt SACs by simply introducing the iron oxide.³¹ Yao et al reported a high-temperature shockwave to achieve the thermally stable single atoms. They first loaded H₂PtCl₆ precursor on the defective CO₂-activated carbon nanofiber and then used an electrical Joule heating process for shockwave heating, in which the temperature can reach as high as 1500 K at 55 milliseconds for one pulse (Figure 8H). Based on the HAADF-STEM and EXAFS results, after one pulse, Pt clusters and single atoms were found to coexist on the substrate. However, after 10 shock pulses, high-density Pt single atoms can be achieved (Figure 7I,J), which was also confirmed by the EXAFS (Figure 8K). Theoretical calculation results indicated the thermodynamically favorable metal-defect bonds were formed under high temperature. They also believe the off-state also played a key factor to make the substrate exhibit an overall stability. More important, they found that this high-temperature shockwave strategy can also be a general method for the synthesis of different types of SACs, such as Pt, Ru, and Co single atoms.⁶⁵

Recently, MOFs-derived SACs attracted great attention as the SACs were achieved under pyrolysis, thus leading to thermally stable SACs. Among the reported reference, there are lots of synthetic methods for SACs from MOFs, including direct pyrolysis from MOFs with stabilizing the single atoms in the framework, pyrolysis of MOFs with spatial-confined metal molecules, and also using a mixed method with pyrolysis and acid washing. The strongly coordinated N–M bond from the pyrolysis process from MOFs provide SACs with increased stability. Very recently, Wei et al⁶⁶ reported that the SACs





FIGURE 8 A, Illustration the sintering of Pt NPs, showing how ceria can trap the mobile Pt to suppress sintering. Representative HAADF-STEM images of 1 wt% Pt/CeO₂-rod (B) and 1 wt% Pt/CeO₂-polyhedra (C) after aging at 800°C for 10 hours in flowing air. Reproduced with permission: Copyright 2016, American Association for the Advancement of Science.⁶⁴ D, Illustration of thermally induced Pt NPs restructuring. E to G, Sequential HAADF-STEM images from the same area showing the dissociation of small particles during in situ calcination: 5 nm scale bars. Reproduced with permission: Copyright 2019, Nature Publishing Group.³¹ H, The schematic diagram shows the HT-SA synthesis and dispersion process. Typical HAADF images of Pt HT-SAs after one (I) and ten (J) cycles of the thermal shock (0.01 µmol/cm²). K, EXAFS profiles (without phase correction) for Pt HT-SAs on CA-CNFs after one and ten cycles of the thermal shock treatment. Reproduced with permission: Copyright 2019, Nature Publishing Group.⁶⁵ EXAFS, extended X-ray absorption fine structure; HAADF-STEM, high-angle annular dark-field scanning transmission electron microscopy; HT-SA, high-temperature-synthesized single atoms; NP, nanoparticle

can also be achieved with the pyrolysis of MOFs from metal NPs. They first mixed with Pt-NPs, $Zn(NO)_3$, and 2-methylimidazole to make a Pt-NPs@ZIF-8 composites. Then the sample was thermally treated under inert atmosphere at 900°C for 3 hours. After that the Pd NPs disappeared but highly dispersed Pd single atoms were

observed under HAADF-STEM. To understand the mechanism for the NPs converted to single atoms, in situ ETEM was performed on the Pd NPs from 100 to 1000°C under Ar atmosphere. When the temperature increased from room temperature to 900°C, the size of Pd NPs increased but the amount of Pd NPs decreased, indicating

the competitive formation of Pd single atoms and larger Pd NPs. However, the Pd NPs disappeared under 1000°C after 162 seconds (Figure 9A-C). DFT results indicated that the conversion of NPs to single atoms were driven by the more thermodynamically stable Pd-N₄ sites during thermal treatment process. They also demonstrated that this strategy can also be applied to synthesize Pt and Au SACs.⁶⁶

3.4 | Electronic metal-support interactions

Due to the highly uncoordinated environment of SACs, increasing the metal-support interactions is one of the

most promising ways to improve the stability of SACs. However, the single atom is bonded with the substrate, which will induce an electronic perturbation to the central atom. This kind of electronic metal-support interactions (EMSI) will help to modulate the electronic properties of single atoms through charge transfer, which can increase both the catalytic activity and stability of SACs.

Tang and coworkers supported Ag NPs on hollandite manganese oxide (HMO) nanorods, and then were thermally treated to form the Ag_{AOR} -HMO through anti-Ostwald ripening. According to the TEM results, they found that the silver atoms were in the porous space of the HMO on the (001) facets, in which the Ag single atoms anchored at the fourfold hollow sites of



FIGURE 9 A, Frames of Pd-NPs@ZIF-8 pyrolyzed in situ with ETEM under an Ar atmosphere, scale bars are 50 nm. B, Average diameter and number of particles as a function of heating temperatures. C, Average diameter and number of particles versus pyrolyzing time at 1000°C. D, Calculated energies along the stretching pathway of the Pd atom from the Pd₁₀ cluster to Pd-N₄ defect by CI-NEB, and the corresponding initial and final configurations. Reproduced with permission: Copyright 2018, Nature Publishing Group.⁶⁶ CI-NEB, climbing image-nudged elastic band; ETEM, environmental transmission electron microscopy; ZIF, zeolitic imidazolate frameworks

oxygen (Figure 10A-F). XAS and theoretical calculation indicated that higher depletion of 4d electronic state from EMSI on Ag single atoms lead to the higher activation ability of O₂, which resulted in a high catalytic activity of oxidation of formaldehyde.⁶⁷ Li et al synthesized Pt single atoms on four different substrate, which were graphene, CeO₂, ZrO₂, and Co₃O₄ to investigate the EMSI. From the XANES results, the four Pt SACs showed different Pt 5d electronic states. Pt₁/Co₃O₄ showed the highest whiteline intensity, indicating a higher valence state of Pt₁ atoms on Co_3O_4 than other supports (Figure 10G). The high valence state of Pt1 atoms on Co3O4 was also confirmed by CO DRIFTS (Figure 10H) and XPS (Figure 10I), indicating the EMSI between Pt single atoms and Co₃O₄. In the dehydrogenation of ammonia borane, the $Pt_1/$ Co₃O₄ showed up to 68 times higher catalytic activity than other Pt SACs. It also exhibited an excellent stability without showing any obvious deactivation after 15 recycling tests, while others deactivated seriously only after five cycles (Figure 10J). DFT results indicated that the EMSI modulated the unoccupied state of Pt 5d orbitals of ARBON ENERGY-WILEY

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 Pt_1/Co_3O_4 , which lead to an optimization of AB adsorption and H_2 desorption, thus leading to high catalytic activity and stability.³⁴

4 | THE APPLICATIONS OF SACS IN ELECTROCHEMICAL REACTIONS

Because of the unique properties of SACs, they showed outstanding catalytic performance in electrochemical reactions.^{7,9,68} In the following section, we will highlight some examples, which demonstrated the promising applications of SACs as electrocatalysts (Tables 1 and 2).

4.1 | Oxygen reduction reaction

ORR is one of the most important reactions at the cathode for many electrochemical energy conversion devices.



FIGURE 10 High-resolution HAADF-STEM images and EDX line scans along the yellow lines of Ag_{AOR} -HMO (A, C, and E) and Ag_{IMP} -HMO (B, D, and F). Corresponding models of the CAS on the (001) planes (E and F). Scale bars: 1 nm (A and B), 2 nm (C and D), and 40 nm (E and F). Reproduced with permission: Copyright 2014, Wiley.⁶⁷ G, XANES spectra of Pt₁/Co₃O₄, Pt₁/CeO₂, Pt₁/ZrO₂, and Pt₁/graphene SACs as well as the Pt foil and PtO₂ reference at the Pt L₃-edge. H, DRIFTS of CO chemisorption on Pt₁/Co₃O₄, Pt₁/CeO₂, and Pt₁/ZrO₂ at the saturation coverage. I, XPS spectra of Pt₁/Co₃O₄, Pt₁/ZrO₂, Pt₁/ZrO₂, Pt₁/ZrO₂, Pt₁/ZrO₂, and Pt₁/ZrO₂, and Pt₁/graphene, and PtO₂ in the Pt 4f region. J, Recyclability test on various Pt₁ single-atom catalysts. Reproduced with permission: Copyright 2019, American Chemical Society.³⁴ CAS, catalytically active sites; DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy; EDX, energy-dispersive X-ray; HAADF-STEM, high-angle annular dark-field scanning transmission electron microscopy; HMO, hollandite manganese oxide; XANES, X-ray absorption near-edge structure; XPS, X-ray photoemission

The ORR can occur at acidic and alkaline solution. However, the main disadvantage for alkaline fuel cells is their high sensitivity to the CO_2 , which can poison the electrolyte and further lead to the deactivation of catalysts. Therefore, in this review, we will only focus on the ORR under acidic electrolyte. Depending on the dissociation the O-O bond of O₂, the ORR can be divided into two parts, the two electron (2e⁻) and four (4e⁻) paths.^{103,104} When the O₂ adsorbs on the surface through a side-on adsorption model on Pt NPs, the O-O bond weakens, thus producing H₂O through the 4e⁻ path. Of note, the reaction path will also change by the geometry effect as well. In another path, when O₂ adsorbs through an end-on adsorption model, H₂O₂ will be the product. In the selective reduction of O₂ through the 2e⁻ path, hydrogen peroxide will be produced.¹⁰⁵ If the O–O bond can be broken through catalysis, O₂ will be directly reduced to H₂O, which is highly desired for both metal-air batteries and fuel cells. It worth noting the 4e⁻ path is the most preferred one due to its high-energy efficiency.^{106,107}

Direct 4e⁻ pathway:

Pt₁-N/BP

$$O_2 + 4H^+ + 4e^- \to H_2O.$$
 (1)

Electrolyte

0.1M HClO₄

 $E_{1/2}$

0.76

References

69

Metal loading

0.4 wt%

fuel cells is

 $O_2^* \rightarrow O^* + O^*,$

$$O^* + H^+ + e^- \to OH^*,$$
 (3)

$$OH^* + H^+ + e^- \to H_2O^*.$$
 (4)

 $2e^{-} + 2e^{-}$ pathways:

Associative pathway:

$$O_2 + 2H^+ + 2e^- \to H_2O_2,$$
 (5)

$$H_2O_2 + 2e^- + 2H^+ \to 2H_2O.$$
 (6)

In the practical applications of catalysis toward ORR, Pt-based catalysts are still the most widely used, especially in fuel cells due to their superior catalytic performance.^{103,106-108} In most of the cathode catalysts for fuel cells, Pt NPs are loaded on carbon-based materials, which always show very weak interaction between Pt NPs and the carbon support.¹⁰⁸ Therefore, the aggregation and detachment of Pt NPs occur, especially under low pH value, high overpotential, and highly oxidizing atmosphere in ORR. Hence, lots of efforts have been devoted to

TABLE 1Summary of reported SACsalong with the corresponding material,metal loading, and their performance forORR under acidic electrolyte

Pt ₁ @Fe-N-C	2.1 wt%	0.1M HClO ₄	0.75	70
Ru-N/G-750	1.7 wt%	0.1M HClO ₄	0.75	19
Pt _{1.1} /BP _{defect}	1.1 wt%	0.1M HClO ₄	0.85	71
Ir-SAC	0.2 wt%	0.1M HClO ₄	0.86	72
(CM + PANI)-Fe-C	0.3 at%	$0.5M H_2SO_4$	0.80	32
Fe-ZIF _{50 nm}	0.45 at%	$0.5M H_2SO_4$	0.85	73
Fe-SCN	0.2 at%	$0.5M H_2SO_4$	0.77	74
CNT@Fe-N-PC	0.3 at%	0.1M HClO ₄	0.82	75
SA-Fe/NG	0.6 at%	$0.5M H_2SO_4$	0.80	76
FeSA-G	7.7 ± 1.3 wt%	0.1M HClO ₄	0.80	77
ISAS-Co/HNCS	2.2 wt%	$0.5M H_2SO_4$	0.77	48
CoNC700	0.73 at%	$0.1M \text{ HClO}_4$	0.73	78
Co-N-C	6.2 wt%	$0.5M H_2SO_4$	0.84	79
Cu-SAs/N-C	0.54 wt%	0.1M HClO ₄	0.75	29
20Mn-NC-second	3.03 wt%	$0.5M H_2SO_4$	0.80	80
Zn–N–C	5.64 wt%	0.1M HClO ₄	0.75	81
Cr/N/C-950	1.9 wt%	0.1M HClO ₄	0.76	82

Note: The half-wave potential $(E_{1/2})$ are reported vs RHE.

Abbreviations: HNCS, hollow N-doped carbon spheres; ISAS, isolated single atomic sites; ORR, oxygen reduction reaction; RHE, reversible hydrogen electrode; SAC, single-atom catalyst.

(2)

TABLE 2Summary of reported SACsalong with the corresponding material,metal loading, η_{10} , and Tafel slope for HERand OER

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Catalysts	Metal loading	Electrolyte	η ₁₀ (mV)	Tafel slope (mV/dec)	References
PtSA-NT-NF	1.76 wt%	pH 7.2 (PBS)	24	30	83
Pt ₁ /MC	2.6 wt%	$0.5M H_2SO_4$	30	26	84
Pt ₁ @Fe-N-C	2.1 wt%	$0.5M~\mathrm{H_2SO_4}$	60	42	70
Pt SASs/AG	0.44 wt%	$0.5M H_2SO_4$	12	29.33	85
Pt SAs/DG	2.1 wt%	$0.5M H_2SO_4$	23	25	86
Pt ₁ /OLC	0.27 wt%	$0.5M H_2SO_4$	38	36	87
Pt ₁ /hNCNC	2.92 wt%	$0.5M H_2SO_4$	15	24	45
Pt-MoS ₂	1.7 wt%	$0.1M~{\rm H_2SO_4}$	130	96	88
ALD50Pt/NGNs	2.1 wt%	$0.5M \ H_2SO_4$	55	31	60
RuSAs@PN	0.33 wt%	$0.5M~{\rm H_2SO_4}$	24	38	89
Co-NG	0.57 at%	$0.5M H_2SO_4$	147	82	90
Co ₁ /PCN	0.2 wt%	$0.5M H_2SO_4$	151		23
		1М КОН	89	52	
Co-SAS/HOPNC	0.49 wt%	$0.5M~{\rm H_2SO_4}$	137	52	91
aNi@G5775	1.24 wt%	$0.5M~{\rm H_2SO_4}$	70	31	92
Ni/GD	0.278 wt%	$0.5M H_2SO_4$	66	37.8	93
np-Ni/graphene	4-8 at%	$0.5M~{\rm H_2SO_4}$	180	45	94
Fe-N ₄ SAs/NPC	1.96 wt%	1M KOH	202	123	95
Fe/GD	0.68 wt%	$0.5M H_2SO_4$	66	37.8	93
Pt ₁ @Fe-N-C	2.1 wt%	0.1M KOH	310	62	70
Fe-N ₄ SAs/NPC	1.96 wt%	1М КОН	43	95	96
Ni-NGHF	0.05 at%	1М КОН	331	63	97
Co-NGHF			402	80	
Fe-NGHF			488	164	
^s Au/NiFe LDH	0.4 wt%	1М КОН	237	36	98
Ru ₁ -Pt ₃ Cu	Ru: 8.2 at%, Pt: 68.7 at%	0.1M HClO ₄	220		99
Ru/CoFe-LDHs	0.45 wt%	1М КОН	198	39	100
Ru–N–C	1.0 wt%	$0.5M H_2SO_4$	267	52.6	101
Co-C ₃ N ₄ /CNT	0.2 at%	1M KOH	380	68.4	102

Abbreviations: HER, hydrogen evolution reaction; OER, oxygen evolution reaction; PBS, phosphatebuffered saline; PCN, phosphorized carbon nitride; SAC, single-atom catalyst.

increasing the low stability and keep the competitive stability of Pt-based catalysts. Pt SACs are one of the best candidates to solve both the activity and stability issues due to their high atomic utilization efficiency and enhanced metal-support interactions.⁵⁰ However, the conclusion on Pt SACs still could not reach an agreement: Can Pt single atoms catalyze O_2 into $4e^-$ path or not in ORR? According to Siahrostami et al's work,¹⁰⁹ at least two

continuing active sites are required to break the O–O bond of O₂. Therefore, the Pt SACs should exhibit high selectivity for the reduction of O₂ to H_2O_2 .^{110,111} Choi et al successfully supported Pt single atoms on sulfur-doped zeolite-templated carbon (Pt/HSC). The Pt SAC showed up to 96% selectivity of H_2O_2 , which was much higher than the 4e⁻ path in the electrochemical ORR (Figure 11A,B).⁶¹ Yang et al synthesized Pt single atoms and Pt NPs on TiN

NPs, which showed very different behaviors in ORR. The 0.35 wt% Pt/TiN exhibited the selectively of H_2O_2 as high as 65%, while the 2.0 wt% Pt/TiN can only achieve 20% to 30% H_2O_2 . For the Pt NPs on TiN, the achieved H_2O_2 was less than 5% (Figure 11C-E). They attributed the high selectivity of H_2O_2 on 0.35% Pt/TiN to the low proportion of Pt ensembles, as the mostly Pt single sites cannot break

the O–O bond.¹¹² In their following work, they further demonstrated the support effect in selective ORR on Pt single atoms.¹¹³ They supported Pt₁ atoms on TiC and TiN, which were measured in ORR for comparison. The achieved disc and ring currents indicated that the Pt₁/TiN showed higher H₂O₂ selectivity than Pt₁/TiC (Figure 11F). At 0.2 V (vs reversible hydrogen electrode [RHE]), the



FIGURE 11 A, ORR activities of the prepared catalysts measured in an O_2 -saturated 0.1M HClO₄ electrolyte. B, H_2O_2 production selectivity estimated by RRDE experiments (Pt ring potential: $1.2 V_{RHE}$). Reproduced with permission: Copyright 2016, Nature Publishing Group.⁶¹ C, Ring currents concurrently obtained during the ORR with a potential maintained at 1.2 V for various samples. D, ORR polarization curves in O_2 -saturated 0.1M HClO₄ and (E) H_2O_2 selectivity calculated from the ORR and H_2O_2 oxidation current. Reproduced with permission: Copyright 2016, Wiley.¹¹² F, Ring, disk currents, and the H_2O_2 selectivity measured concurrently during ORR with a potential held at 1.2 V of single-atom Pt in O_2 -saturated 0.1M HClO₄ solution with a scan rate of 0.01 V/s. G, Free-energy diagrams at 0.2 V for the ORR on Pt/TiC (100) and Pt/TiN (100). Reproduced with permission: Copyright 2017, American Chemical Society.¹¹³ ORR, oxygen reduction reaction; RHE, reversible hydrogen electrode; RRDE, rotating ring-disk electrode

current density and H₂O₂ selectivity of Pt₁/TiC were -0.96 mA/cm^2 and 68%, while Pt₁/TiN achieved that of -0.34 mA/cm^2 and 53.1%. Their DFT results indicated that the adsorption energies of oxygen species are different on Pt₁/TiN and Pt₁/TiC. The more well-preserved O-O bond on Pt₁/TiC lead to its high selectivity to H₂O₂ (Figure 11G). However, some reported work also showed that the Pt SACs showed potential application for 4e⁻ ORR. Liu et al achieved Pt single atoms on black porous carbon, which showed higher performance and stability in both acid- and alkali-based ORR through the 4e⁻ path (Figure 12A-D). Their DFT results indicated the single Pt atom on single pyridinic nitrogen atom is the active center for its high performance (Figure 12E).⁶⁹ In their following work, they anchored Pt₁ atoms on a defective carbon support, which showed a good ORR performance (Figure 12F) and power density of 520 mW/cm^2 at 80° C in the acidic H_2/O_2 single cell (Figure 12G). The DFT results indicated that the Pt single atom bonded with four carbon

atoms are the active center for the main catalytic activity in $4e^{-}$ path ORR (Figure 12H,I).⁷¹

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However, the low abundance and increasing high cost of Pt strongly limits their applications. In this case, PGM-free SACs such as Mn. Fe. and Co have seen extensive development. For instance, Li et al⁸⁰ prepared the Mn-ZIF-derived Mn₁-N₄ SAC through carbonization acid leaching and thermal treatment. After the second adsorption of MnN₄, the 20Mn-NC-second sample showed much improved catalytic activity than the pristine sample, with the half-wave potential to 0.8 V vs RHE, which is the best activity in all the PGM- and Fe-free catalysts (Figure 13A). It also exhibited good performance in both H₂/O₂ and H₂/air cell tests (Figure 13B). The 20Mn-NC-second also showed a very high selectivity to the 4e⁻ path, in which the yield proportion of H₂O₂ was less than 2%. The stability of 20Mn-NC-second was further measured from 0.6 to 1.0 V in O₂-saturated 0.5M H₂SO₄. After 30 000 cycles,



FIGURE 12 A, Polarization curves of BP, N/BP, Pt₁/BP, Pt₁-N/BP, and commercial Pt/C in O₂-saturated 0.1M HClO₄. B, The tolerance of Pt₁-N/BP to CO (saturated) and methanol (0.5M) in O₂-saturated 0.1M HClO₄. C, Long-term operation stability of Pt₁-N/BP in O₂-saturated 0.1M HClO₄. D, Polarization curves of BP, N/BP, Pt₁-BP, Pt₁-N/BP, and commercial Pt/C in O₂-saturated 0.1M KOH. E, Free-energy diagram for oxygen reduction reaction on the g-P-N₁-Pt₁ catalyst in acidic medium. Reproduced with permission: Copyright 2017, Nature Publishing Group.⁶⁹ F, RDE polarization curves of BP, Pt_{1.1}/BP, Pt_{1.1}/BP, Pt_{1.1}/BP_{defect} and the commercial Pt/C in O₂-saturated 0.1M HClO₄. G, Polarization and power density curves of an acidic H₂/O₂ fuel cell with Pt_{1.1}/BP_{defect} as the cathode. H, Optimized structures of different substrates and the corresponding Pt single atom. I, Free-energy diagram for complete O₂ reduction of various substrates in acidic media at 0.83 V. Reproduced with permission: Copyright 2019, Wiley.⁷¹ BP, black pearls; N/BP, nitrogen-doped black pearls; RDE, rotating disk electrode

the half-wave potential of 20Mn-NC-second only drops 17 mV while the Fe-N-C and 20Fe-NC-second samples lose 80 and 29 mV. The DFT results suggested that the MnN_4C_{12} active sites modulate the binding energy of O species, which lead to the easy cleavage of the O-O bond for the 4e⁻ pathway (Figure 13C). Xiao et al synthesized a Fe-N-C SAC through MOF-confined strategies. In ORR, the Fe-N-C SAC showed an onset potential at 0.92 V, which is competitive even to the catalytic activity of Pt/C in 0.1M HClO₄ (Figure 13D). The ⁵⁷Fe Mössbauer spectrum confirmed the high-spin Fe³⁺-N₄ moiety, while the in situ XANES on Fe K-edge demonstrated that the $Fe^{3+}-N_4$ will convert to $Fe^{2+}-N_4$ at low potential (Figure 13E,F). They suspected that the reduced Fe²⁺-N₄ moiety contributed to its high ORR performance.¹¹⁴ In Wang et al's work, N-coordinated Co SAC was derived from a Co-doped MOFs after a onestep thermal treatment. In the HAADF-STEM results, uniformly dispersed Co single atoms can be found. They also did EELS on the Co single atom, which showed both N and Co signal can be observed. This solid evidence confirms the formation of a CoN_x structure. XAS further confirmed the Co-N₄ structure. In the ORR under acidic media, the Co SAC achieved a half-wave potential at 0.8 V vs RHE (Figure 13G) along with good stability after 10 000 cycles durability test (Figure 13H). In the fuel cell test, the Co SAC showed an overpotential up to 0.95 V, which are comparable with even Fe-based catalysts (Figure 13I). The Co atomic catalysts showed competitive stability in PEMFC, which showed great potential to replace the Fe-based PGM-free catalysts, which have Fenton reagent issues in PEMFCs.¹¹⁵



FIGURE 13 A, Comparison of catalytic activity of Fe-, Co-, and Mn-NC catalysts. B, Fuel cell performance 20Mn-NC-second and 20Fe-NC-second catalysts in both H_2/O_2 and H_2/air conditions. C, Calculated free-energy evolution diagram for ORR through a 4e⁻ associative pathway on the MnN₄C₁₂ active site under electrode potential of U = 1.23 and 0.80 V. Reproduced with permission: Copyright 2018, Nature Publishing Group.⁸⁰ D, ORR polarization plots in O₂-saturated 0.1M HClO₄. E, In situ XANES and (F) concomitant first derivatives of Fe–N-C-950. Reproduced with permission: Copyright 2018, American Chemical Society.¹¹⁴ G, Steady-state ORR polarization plots for the best performing 20Co-NC-1100, state-of-the-art Fe–N–C (0.5M H₂SO₄), and Pt/C (0.1M HClO₄). H, Potential cycling (0.6-1.0 V) stability in O₂-saturated 0.5M H₂SO₄. I, H₂-air fuel cell polarization plot. Reproduced with permission: Copyright 2018, Wiley.¹¹⁵ ORR, oxygen reduction reaction; XANES, X-ray absorption near-edge structure

4.2 | Hydrogen evolution reactions

Hydrogen, a clean and renewable fuel, has been regarded as one of the most promising candidates as a future energy source. HER, as a half reaction of water splitting has attracted significant attention due to its green way to produce hydrogen. The target for HER is to develop highly efficient and stable catalysts at relatively low overpotential. As demonstrated by both experiment and theoretical calculation, the rate determined step is the adsorption of H*. When the adsorption free energy is close to zero, the high catalytic activity of catalysts would be achieved. Of note, when the HER occurs under alkaline-based electrolyte, the adsorption of OH⁻ may also affect the overall reaction. Up to now, Pt-based catalyst showed the best catalytic activity in HER. However, due to its high price and low abundance, their application is strongly limited. Based on this, decreasing the size of Pt NPs to single atoms and developing PGM-free SACs are used to address this issue.

Overall reaction (acidic electrolyte):

$$2H_{(aq)}^{+} + 2e^{-} \rightarrow H_{2(g)}.$$
 (7)

Volmer step:

$$\mathrm{H}^{+} + \mathrm{e}^{-} \to \mathrm{H}_{\mathrm{ads}}.$$
 (8)

Tafel step:

$$2H_{ads} \rightarrow H_2.$$
 (9)

Overall reaction (alkaline electrolyte):

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-.$$
 (10)

Heyrovsky step:

$$2H_2O + H_{ads} + e^- \rightarrow H_{2(g)} + OH^-.$$
 (11)

Volmer step:

$$H_2O + e^- \to H_{ads} + OH^-.$$
(12)

Tafel step:

$$2H_{ads} \rightarrow H_2.$$
 (13)

Unlike ORR, the selectivity is not obvious in HER. Decreasing the size of Pt from NPs to single atoms will increase the atom utilization efficiency as every single Pt atom will be an active site. Cheng and coworkers prepared Pt single atoms on N-doped graphene using ALD 507

for HER. The ALD50Pt/NGNs SAC showed excellent catalytic activity in HER, exhibiting a current density as high as 16 mA/cm^2 at 0.05 V overpotential. While the figure on Pt/C is only 8.2 mA/cm^2 (Figure 14A). The normalized mass activity on ALD50Pt/NGNs is 10.1 A/mg, which is almost 37.4 times higher than Pt/C (Figure 14B). Importantly, no obvious catalytic activity decrease can be found on ALD50Pt/NGNs after 1000 cycles of stability testing, while the Pt/C loses 19% of its initial activity. The XAFS and DFT demonstrated the higher proportional total unoccupied density of states on Pt 5d orbitals on NGN leading to its high catalytic activity.⁶⁰ Liu et al supported Pt single atoms on onionlike nanospheres of carbon (OLC) through ALD. In acidic solution, Pt₁/OLC exhibited great catalytic performance in HER, showing a low overpotential (38 mV) at 10 mA/cm^2 (Figure 14C). The turnover frequency (TOF) is as high as $40.78 \text{ H}_2/\text{s}$ at 100 mV, which is much higher than Pt_1 /graphene SAC (Figure 14D). The theoretical calculation results indicated that the improved catalytic performance can be attributed to the tip-enhanced local electric field on curve-located Pt single atoms.⁸⁷ Deng and coworker prepared Pt single atoms on twodimensional MoS₂ for HER. They demonstrated the in-plane S atoms in MoS₂ can trigger the catalytic activity through the doping of Pt single atoms. STEM and XAFS confirmed that the Pt atoms were doped into MoS₂ with the substitution of Mo atoms. The Pt1/MoS2 showed much improved catalytic activity and stability over that of pristine 2D MoS₂. DFT results indicated that the adsorption behavior of H atom was tuned on the in-plane S atoms, which were close to the doped Pt atoms.⁸⁸

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PGM SACs also showed great potential for the application in HER, such Co and Ni SACs. For instance, Fan and coworkers synthesized Ni single atoms on graphitized carbon through an acid-leaching method for HER. The HCl-Ni@C SAC showed excellent catalytic activity and stability after the activation process (Figure 14E,F). They attributed its high catalytic performance to the unique local structure of Ni atoms, which anchored on the graphitized carbon.²⁶ Fei et al reported a Co-based SAC using N-doped graphene as support for HER. The Co SAC showed great catalytic activity with an overpotential as low as 30 mV, and it also displayed good stability in both acid and alkaline solution, without showing obvious deactivation after 1000 cycles (Figure 14G,H).⁹⁰ Liang et al achieved a Co- N_x/C catalyst using the pyrolysis method. The $Co-N_x/C$ showed high catalytic activity in HER, with current densities of 10 and 20 mA/cm² at overpotentials of 133 and 156 mV, which were the highest among the reported references. The Co- N_x/C also showed excellent stability compared with Co/C catalyst. The Co- N_x/C only showed an 11 mV shift at a



FIGURE 14 A, The HER polarization curves for ALDPt/NGNs and Pt/C catalysts with a scan rate of 2 mV/s in 0.5M H₂SO₄ at room temperature. B, Mass activity at 0.05 V (vs RHE) of the ALDPt/NGNs and the Pt/C catalysts for HER. Reproduced with permission: Copyright 2016, Nature Publishing Group.⁶⁰ C, Polarization curves of Pt₁/OLC (black) in comparison with 5 and 20 wt% commercial Pt/C and Pt₁/graphene (0.33%) (blue) in a 0.5M H₂SO₄ electrolyte. D, Mass activity. Reproduced with permission: Copyright 2019, Nature Publishing Group.⁸⁷ LSV curves (E) and Tafel plots (F) of HCl-Ni@C, A–Ni–C, and Pt/C for HER after activation. Reproduced with permission: Copyright 2016, Nature Publishing Group.⁸⁷ LSV curves (E) and Tafel plots (F) of SO NG, Co-G, Co-NG, and Pt/C in 0.5M H₂SO₄ at scan rate of 2 mV/s. H, Accelerated stability measurements by recording the polarization curves for the Co-NG catalyst before and after 1000 cyclic voltammograms at a scan rate of 50 mV/s under acidic and basic conditions. Reproduced with permission: Copyright 2015, Nature Publishing Group.⁹⁰ ALD, atomic layer deposition; G, graphene; HER, hydrogen evolution reaction; LSV, linear sweep voltammograms; NG, N-doped graphene; NGNs, nitrogen-doped graphene nanosheets; OLC, onion-like nanospheres of carbon; RHE, reversible hydrogen electrode

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current density of 10 mA/cm^2 , while the change on Co/C was higher than 40 mV even after 100 cycles.¹¹⁶

4.3 | Formic acid oxidation reaction

Formic acid, as a chemical fuel source can also be applied to direct formic acid fuel cells. In formic acid oxidation, it can be divided into two reaction pathways, one is the direct dehydrogenation pathway (0.6-0.7 V), and the other is the indirect dehydration pathway (0.9-1.1 V). Pt-based catalysts are one of the best catalysts for FAOR due to their superior performance. Nevertheless, two major factors limit their applications. One is the high cost of Pt metal, the other is carbon monoxide poisoning during FAOR. The generated CO even in trace amounts will strongly adsorb on the surface of Pt NPs, which blocks the active sites and leads to deactivation.^{117,118}

Direct pathway:

$$\text{HCOOH} \to 2\text{H}^+ + \text{CO}_2. \tag{14}$$

Indirect pathway:

$$\text{HCOOH} \to \text{H}_2\text{O} + \text{CO}_{(\text{ads})}.$$
 (15)

Pt SACs with the maximum atomic utilization efficiency greatly decrease the application cost.^{112,119,120} Similarly, the generated CO poisoning in FAOR through indirect dehydrogenation pathway requires at least three to four continuous Pt atoms. Therefore, the CO-induced catalytic deactivation should be greatly depressed on Pt SACs, as the Pt single sites will only oxidize the FA through the direct pathway. Yang and coworkers successfully synthesized Pt single atoms on TiN (Figure 15A). In the FAOR, only one oxidation peak at around 0.7 V can be found on 0.35% Pt/TiN, which has the highest percentage of Pt single atoms, while the other developed catalysts with more or less NPs showed two oxide peaks at 0.7 and 1.0 V, indicating that the Pt single atoms have a very high selectivity to catalyze the FA into direct pathway without CO poisoning (Figure 15B).¹¹² Duchesne et al¹¹⁹ using a solution-phase synthesis method achieved a Pt-Au single alloy catalysts and tested their performance in FAOR. In FAOR, the Pt₄Au₉₆ showed the best catalytic performance compared with other PtAu and Pt/C catalysts. At 0.6 V vs RHE, the mass activity of Pt₄Au₉₆ is about 126 and nine times higher than of Pt₇₈Au₂₂ and Pt/C (Figure 15C). It is worth noting that a significant peak appeared at 0.85 V vs RHE on Pt₇₈Au₂₂ and Pt/C, which can be attributed to the oxidation of adsorbed CO poisoning. However, the lack of this oxidation peak on the other Pt-Au catalysts strongly

indicated their high CO poisoning resistance, which may be the reason for their high catalytic performance. In the theoretical calculation, they found the intensity of near Fermi level DOS increased considerably with the lack of Pt–Pt bonds. They also observed a much weaker CO adsorption on the Pt single atom surface due to the electronic effect and ensemble effect. This high CO poisoning resistance lead to the high performance of Pt_4Au_{96} in FAOR (Figure 15D,E).

4.4 | Oxygen evolution reactions

OER is the half reaction of electrocatalytic water splitting, which is very kinetically sluggish. In the OER theoretical calculation, the highest energy barrier is used as the rate determine step to evaluate the catalytic activity of catalysts. In both acidic and alkaline solution, the OER is a four-electron reaction. The detailed reaction mechanism is shown in the following equations below. However, the breaking of O–H and subsequent formation of O–O are involved, which requires high overpotential to overcome the energy barrier. Therefore, to address the bottleneck of water splitting, designing a highly efficient, stable, and low-cost electrocatalyst for OER is greatly desired.^{121,122}

In acidic electrolyte:

$$M + H_2O \rightarrow MOH + H^+ + e^-, \qquad (16)$$

$$MOH \to MO + H^+ + e^-, \tag{17}$$

$$2\mathrm{MO} \to \mathrm{O}_2 + 2\mathrm{M},\tag{18}$$

or

$$MO + H_2O \rightarrow MOOH + H^+ + e^-,$$
 (19)

MOOH +
$$H_2O \rightarrow M + O_2 + H^+ + e^-$$
. (20)

In alkaline electrolyte:

 $M + OH \to MOH, \tag{21}$

$$MOH + OH^{-} \rightarrow MO + H_2O + e^{-}, \qquad (22)$$

$$2\mathrm{MO} \to \mathrm{O}_2 + 2\mathrm{M},\tag{23}$$

or

$$MO + OH^{-} \rightarrow MOOH + e^{-},$$
 (24)

MOOH + OH⁻
$$\rightarrow$$
 M+ O₂ + H₂O + e⁻. (25)

Noble metal-based catalysts such as RuO_2 and IrO_2 show the best catalytic performance in OER. However,



FIGURE 15 A, HAADF-STEM image of 0.35 wt% Pt/TiN. B, Forward scans of cyclic voltammetry using the various samples for formic acid oxidation reaction performed in Ar-saturated 0.5M HCOOH + 0.1M HClO₄ solution. Reproduced with permission: Copyright 2016, Wiley.¹¹² C, Pt mass-normalized anodic sweeps obtained from PtAu nanoparticles catalysts in an electrolyte that contained 0.1M concentrations of both HClO₄ and HCOOH. Predominant formic acid oxidation reaction pathways on few-atom (or greater) (D) and single-atom (E) Pt surface. Reproduced with permission: Copyright 2018, Nature Publishing Group.¹¹⁹ HAADF-STEM, high-angle annular dark-field scanning transmission electron microscopy

the increasing price and low abundance on the earth hinder their large-scale applications. In addition, because of high operating potential of OER, the catalysts are very unstable and easily oxidized. For example, RuO_2 will be oxidized to RuO_4 and then dissolved in the electrolyte. As a result, the catalytic activity will sharply decrease and

finally become inactive. Recently, some reported work showed that the Ru and Ir SACs have potential applications in OER due to the increased catalytic performance. For instance, Luo and coworkers synthesized the Ir single atom anchored on 3D amorphous NiFe nanowire @nanosheet. The NiFeIr_x/Ni NW@NSs exhibited great

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catalytic activity in OER, showing a current density of 10 mA/cm^2 at the overpotential of 200 mV in 1M KOH electrolyte (Figure 16A). It also presented a good stability without showing obvious activity decrease at 10 mA/cm^2 over 12 hours. The DFT results indicated that the promoted activity is due to the introduction of Ir single atoms.¹²³ The lower the Gibbs free energy for the oxidation of O* to OOH* on NiFeIr_x/Ni than NiFe, which suggested the key reason for the high performance of NiFeIr_x/Ni. Apart from the Ir SACs, Ru SACs also exhibited comparable catalytic performance. Cao et al

prepared an Ru SAC with Ru₁-N₄ site on nitrogen-carbon support. The Ru₁-N₄ exhibited a higher catalytic performance than RuO₂ with an outstanding mass activity (3571 A/g_{metal}) under the overpotential of 267 mV at a current density of 10 mA/cm² (Figure 16B). Their operando XAS results demonstrated the adsorption of single O atom on the Ru single site during OER. The DFT further demonstrated that the O-Ru₁-N₄ is an active site for OER.¹⁰¹ Yao and coworkers prepared an Ru₁Pt₃Cu single atom alloy catalyst, which exhibited higher catalytic performance than other Ru or Ir counterparts



FIGURE 16 A, OER polarization curves of NiFe/Ni, NiFeIr_{0.02}/Ni, NiFeIr_{0.03}/Ni, and NiFeIr_{0.05}/Ni NW@NSs catalysts. Reproduced with permission: Copyright 2020, American Chemical Society.¹²³ B, Electrocatalytic OER performances of the Ru–N–C and commercial RuO₂/C in 0.5M H₂SO₄ electrolyte. Reproduced with permission: Copyright 2019, Nature Publishing Group.¹⁰¹ C, LSV curves of Ru₁-Pt₃Cu, Ru₁-PtCu, Cu@Ru₁-Pt₃Cu, and reference samples in an O₂-saturated 0.1M HClO₄ aqueous solution. D, Overpotential to reach 0.1 and 10 mA/cm² for the catalysts. Reproduced with permission: Copyright 2019, Nature Publishing Group.⁹⁹ E, IR-corrected OER polarization curves of S,N-Fe/N/C-CNT, N-Fe/N/C-CNT, S,N-C-CNT samples, and commercial Pt/C, in 0.1M KOH solution. Reproduced with permission: Copyright 2018, Elsevier.⁹² CNT, carbon nanotubes; DG, defective graphene; LSV, linear sweep voltammograms; OER, oxygen evolution reaction; NS, nanosheet; NW, nanowire

(Figure 16C). At 0.1 and 10 mA cm⁻², Ru₁-Pt₃Cu showed relatively lower overpotentials (Figure 16D). After stability testing, they found only a slight metal loss of Ru and Pt on Ru₁Pt₃Cu through inductively coupled plasmamass spectrometry (ICP-MS). Thanks to the high corrosion-resistance, the Ru₁Pt₃Cu only exhibits a 2.1% activity decrease after 28 hours long-term stability testing. However, the RuO₂ showed almost 100% metal loss through dissolution, thus leading to a significant activity decrease even after only 2 hours. The DFT results indicated that the strain effect optimized the electronic properties and redox behaviors of Ru single atoms, which modulated the binding of O intermediate species and promoted its activity and stability.⁹⁹

Apart from the noble-metal SACs, noble-free SACs also showed great performance in OER. Chen and coworkers synthesized a singly dispersed Fe-N_x species on N and S codecorated hierarchical carbon layers. They further evaluated the S,N-Fe.N/C-CNT catalyst's OER performance in 0.1M KOH. Compared with other counterparts (Pt/C and N-Fe/N/C-CNT), the S,N-Fe.N/C-CNT exhibited a low overpotential (0.37 V) at a current density of 10 mA/cm²⁺ (Figure 16E). The S,N-Fe.N/C-CNT also exhibited an outstanding ORR performance.¹²⁴ Zhang and coworkers prepared Ni single atoms on a defective graphene using an acid-leaching process. Interestingly, the Ni-C configuration was directly observed by the HADDF-STEM technology. The Ni SAC showed high catalytic activity and stability for OER, in which the TOF at 300 mV is as high as $13.4 \text{ seconds}^{-1}$ (Figure 16F). XAS and DFT confirmed the unique structure of Ni1 atoms in the defect of graphene, which optimized the reaction energy barrier of OER.92

4.5 | CO₂ reduction reaction

With the increasing demand for energy, the generated CO₂ from fossil fuels is increasingly problematic. Therefore, electrochemically converting the CO₂ into valueadded chemical products can be a promising way to decrease the CO₂ emission and increase the energy utilization. However, because of the strongly bonded C=O bond, very high overpotential is required to activate the CO₂ molecule. Similarly, the reaction potential window overlaps with HER, which will be a competitive reaction with CO₂RR. Hence, developing a catalyst with high efficiency and selectivity at relatively low overpotentials is needed. SACs with the maximum atomic utilization efficiency are one of the best candidates to meet the high efficiency requirement for CO₂RR. Apart from their high atomic utilization efficiency, SACs also present a highly uncoordinated environment. This unique local structure can result in high selectivity for some reactions through geometric and electronical effects, which modulate the interaction between active sites with reactant, thus providing SACs a great potential for achieving high selectivity in CO_2RR .¹²⁵

Among the reported references, Ni and Co SACs showed the most promising applications in CO₂RR. For instance. Li and coworkers first introduce the Ni SACs into the CO₂RR.¹²⁶ In this study, a ZIF-assisted method was used to introduce Ni single atoms on N-doped porous carbon. The Ni SAs/N-C catalyst showed better catalytic performance than the Ni NPs/N-CM and the TOF was as high as 5273 hour^{-1} (Figure 17A). And 71.9% CO selectivity was achieved at 0.89 V. They attributed the high performance of Ni SAC to the increased amount of active sites on the surface, which may promote the electronic conductivity by lowering the CO adsorption energy (Figure 17B).¹²⁶ In Yang and coworkers' work, they reported that an Ni SAC can be achieved through a thermal atomization method. First, they loaded 5-nm-sized Ni particles on ZIF-8-derived N-doped carbon and then thermally treated the sample to 1173 K in Ar. During the pyrolysis process, the Ni NPs disappeared and generated a porous structure. In CO₂RR, the Ni SAC showed over 90% CO selectivity and only less than 10% H₂ was generated at the potential between -0.6 and 1.0 V (Figure 17C,D). While the Ni NPs catalysts only achieved less than 1% CO from -0.7 to -1.2 V; the DFT results indicated that the Ni single atoms have an optimum CO adsorption route that strongly increased its catalytic activity.¹²⁷ Yang et al prepared Ni single atoms on nitrogenated graphene and applied it for CO₂RR. The Ni SAC exhibited a very high CO₂ reduction activity, achieving 97% CO faradaic efficiency and 14 800 hours⁻¹ of TOF at 0.61 V (Figure 17E). It also showed excellent stability with 98% of the initial activity remaining after 100 hours at 22 mA/cm² (Figure 17F). In situ XAS experiments showed that the Ni (+1) are the active sites.¹³⁰ Pan et al supported the Co single atoms on polymerderived hollow N-doped porous carbon spheres. The Co single atoms were confirmed to be bonded with five N atoms through EXAFS analysis. In the CO₂RR, the Co-N₅ showed that the CO faradaic efficiency was higher than 90% between -0.57 and -0.88 V. The Co-N₅ catalyst also exhibited excellent stability without showing any obvious activity decrease even after 10 hours of stability testing. The DFT results demonstrated the faster formation speed of COOH* intermediate and CO desorption on Co-N5 resulted in its high performance in CO₂RR.¹²⁸ Considering that the coordination environment is the key factor for Co SACs in CO₂RR, Wang and coworkers prepared a series of Co₁ SACs with different number of coordinated N atoms. With the increasing pyrolysis



FIGURE 17 A, LSV curves in the N₂-saturated or CO₂-saturated 0.5M KHCO₃ electrolyte at a scan rate of 10 mV/s. B, Proposed reaction paths for CO₂ electroreduction by Ni SAs/N-C. Reproduced with permission: Copyright 2017, American Chemical Society.¹²⁶ C, The measured current density plots recorded in CO₂-saturated 0.1M KHCO₃ solution under different potentials on various electrocatalysts. D, FEs of CO at different applied potentials on various electrocatalysts. Reproduced with permission: Copyright 2018, Wiley.¹²⁷ E, LSV curves. FE_{CO} and FE_{H2} of (F) Co-N₅/HNPCSs and CoPc. Reproduced with permission: Copyright 2018, American Chemical Society.¹²⁸ G, LSV of Co-N₂, Co-N₃, Co-N₄, and Co NPs and pure carbon paper as background. H, CO faradaic efficiencies at different applied potentials. Reproduced with permission: Copyright 2018, Wiley.¹²⁹ FE, faradaic efficiency; HNPCS, hollow N-doped porous carbon spheres; LSV, linear sweep voltammetry; SAs, single atoms

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temperature from 800 to 1000°C, the number of coordinated N atoms increased from two to four. After the synthesis of the catalysts, they evaluated their performance in CO₂RR and found that Co-2N SAC showed much better catalytic activity than other Co SACs with different N coordination numbers (Figure 17G). The Co-2N exhibited a current density of 18.1 mA/cm² and CO conversion of 94% at -0.52 V (Figure 17H). The DFT results indicated that a lower coordination number of N atoms benefitted the activation of CO₂, thus promoting the activity.¹²⁹

4.6 \mid N₂ reduction reaction

While extremely abundant in nature, converting N_2 to NH_3 can be very challenging due to the extremely stable $N\equiv N$ triple bond. In industry, N_2 can be converted to NH_3 through the Haber-Bosch process, which requires harsh conditions (high pressure and high temperature). However, it achieves only 10% to 20% N_2 conversion but costs 1% to 2% of the world's annual energy supply consumption. Similarly, the Haber-Bosch process uses H_2 as the reactant, which normally generated from natural gas

or fossil fuels, along with large amount of CO₂. Due to the rapidly growing consumption of fossil fuels and potential threats of global warming, developing a method to use N₂ and earth-abundant hydrogen sources to produce NH₃ is highly demanded. Among several strategies to convert N₂ to NH₃, the electrochemical N₂RR has attracted considerable attention. In N₂RR, N₂ and H₂O are used as the reactant under ambient atmosphere. Nevertheless, the NH₃ production efficiency through NRR is not satisfactory for widespread adoption as of yet. The key challenge is the low faradaic efficiency in N₂RR, because HER will also occur as a competitive reaction at the same potential reaction window.^{131,132}

Up to now, some reported work indicates that SACs are very promising for N₂RR. For example, Geng et al⁵ successfully achieved Ru single atoms on N-doped graphene, which showed remarkable catalytic activity in N₂RR (Figure 18A). The Ru SAC exhibited up to 28.6% faradaic efficiency for NH₃ production at -0.2 V vs RHE (Figure 18B). Surprisingly, the Ru SAC achieved a yield rate as high as 120.9 μ g_{NH3}·mg_{cat}·h, which is the highest among all the reported reference. By scanning at the overpotential at 0.2 V for 12 hours for stability testing, the Ru SAC exhibited extraordinary performance, with less



FIGURE 18 A, Current densities for NH₃ production and (B) FE at different applied potentials on Ru SAs/N-C and Ru NPs/N-C. Reproduced with permission: Copyright 2018, Wiley.⁵ C, Comparison of NH₃ production rate at different pyrolysis conditions at -0.3 V vs RHE in 0.1M KOH solution. D, Comparison of partial current density and FE as a function of pyrolysis condition for Ni_xZn_(1-x) BMOF at -0.3 V vs RHE in 0.1M KOH solution. Reproduced with permission: Copyright 2020, Wiley.⁴ BMOF, bimetallic metal organic framework; FE, faradaic efficiency; NP, nanoparticle; RHE, reversible hydrogen electrode; SA, single atom

than 7% yield rate of NH₃ decline. The DFT results indicated that the variation in Gibbs free-energy for N₂ dissociation, which is the rate-limiting step for N₂RR, on Ru single atoms is lower than Ru(101), thus leading to its high catalytic performance. Instead of Ru SAC, Mukherjee et al⁴ reported an Ni SAC for N₂RR, which exhibited great catalytic activity. In this study, the Ni-N_x-C coordination was formed by controlling the pyrolysis process of an Ni and Zn BMOF ($Ni_xZn_{(1-x)}BMOF$). The Ni will substitute the Zn atoms during crystallization and form Ni single atoms. The XAS results indicated that the Ni single atom exhibited the valance state between 0 and +2 and it bonded with three N atoms. In the N₂RR under 0.1M KOH solution, the Ni SAC showed high faradaic efficiency $(21\% \pm 1.9\%)$ at -0.2 V (Figure 18C,D). In DFT, it indicated that the Ni-N₃-C₁₀ is the most probable configuration in a mixed pathway. Based on this finding, the rate-determining step is the hydrogenation in N₂RR.

5 | SUMMARY AND PERSPECTIVE

SACs with their maximum atomic utilization efficiency and unique coordination environment, lead to their extraordinary catalytic activity and selectivity in electrocatalysis. Regarding their superior catalytic performance, increasing the stability of SACs is an urgent need. In this review, we highlight most of the synthesis strategies to achieve stable SACs. For example, spatial confinement decreases the mobility of single atoms; proximal site modification leads to the strong bonding between single atoms and their neighboring atoms; and thermal treatment on SACs, which have special supports result in thermally stable SACs and stabilized single atoms through EMSI. In addition, we also summarize the application of SACs in electrochemical reactions, including ORR, HER, FAOR, OER, CO₂RR, and N₂RR. Although SACs showed much improved catalytic performance over traditional electrocatalysts, it is still far from the target for practical application. The promising aspects are listed below for future research:

(i) For practical applications: increasing the loading and scaling up synthesizing

The loading of SACs is measured using inductively coupled plasma (ICP) analysis, which can identify the loading amount of elements in samples. Depending on different detection method, they are divided as ICP optical emission spectroscopy (ICP-OES), ICP mass spectrometry (ICP-MS), and ICP atomic emission spectroscopy (ICP-AES). Due to the high surface-free energy of SACs, the metal loadings ARBON ENERGY-WILEY

of SACs are kept low to reduce aggregation. Still, most SACs cannot be achieved in industrial production but only at laboratory scale, which limits their commercial applications. As a result, increasing the loading and scaling up the synthesizing of SACs can be quite challenging. The interaction between single atoms and the substrate are one of the most important factors to achieve high loading SACs. With the increased interaction, the single atoms will be trapped or stabilized on the support through EMSI or strong metal-support interaction (SMSI). In this case, the mobility of single atoms will be sharply reduced, thus limiting the possibility of aggregation. In other case, during the synthesis process, the ligand of metal precursor will detach from the center metal, therefore, the ligand-free species may form clusters and NPs. Therefore, developing and finding suitable substrate is critical to increase the loading of SACs. Besides, efficient and suitable synthesis methods are also important to increase the loading and scaling up synthesizing of SACs. Very recently, some reported reference showed the strategies to scale up the synthesis of SACs. For instance, mixing Ni salt with activated carbon black, gram-scale Ni SACs can be achieved by ion adsorption.¹³³ A "precursor-dilution" strategy can achieve kilogram-scale noble metal SACs.^{133,134} These methods would be very promising for scaling up the production of SACs.

(ii) Beyond the single atom: dimeric or diatom catalysts

Because of the unique local structure of SACs, their electronic properties are tremendously affected by their neighboring atoms. Thus, modifying their most closely neighboring sites may lead to favorable geometric and electronic effects. One of the most promising way is to introduce another single atom, which would form a dimeric or diatom structure. Because the second atom will bond with the first atom through the direct metal-metal bond or the indirect bonding through the bridge atoms, the modulated charge transfer between two single atoms should lead to a high catalytic activity by optimization of the adsorption of reactants. Due to the strong interaction between the two single atoms, the stability of said catalyst would also be improved. However, to get high purity dimers are very challenging. There are two ways, which can be considered to increase the proportion of dimers. The first one is to directly use the precursors, which are already in dimeric state. For example, Zhao et al¹³⁵ successfully achieved Ir₂ diatom catalysts using Ir homodimers. The other method is to selectively deposit the second metal onto the first achieved single atoms.

However, this method specifically requires that the second metal cannot be deposited on the substrate. Therefore, the selection of substrate is quite important. Recently, Pt_2 and Pt- Ru dimers have been successfully achieved by ALD, which can be a promising method to synthesize dimers.^{136,137}

(iii) Deeper understanding of SACs in electrochemical reaction: in situ or operando XAS study

SACs have seen sufficient development in recent years, including the elements from noble metal to nonnoble metal, gas-phase reaction to electrocatalysis, and low loading (<1 wt%) to high loading (>5 wt%). Although there are lots of theoretical calculations toward understanding the behavior of SACs under reaction, direct observation of the chemical state of SACs is still lacking. Insight into the real behavior of SACs under realistic reaction will give us the opportunities to understand the catalysis mechanism for the rational design of SACs. In situ or operando techniques such as in situ or operando XAS study can be a very promising technique to study the real reaction behavior of SACs, especially for electrochemical reactions. For example, some work related to the in situ or operando XAS on SACs showed that the valence states of SACs differs from the ex situ cauterization, and the local structure are highly dependent on the reaction conditions.²³ Therefore, unveiling the "real world" of SACs through in situ or operando investigations is highly desired.

So far, although SACs have seen plenty of growth during the past few years, SACs still have broader development, especially in the electrocatalysis, with a focus on understanding the performance mechanisms and industrial scaling. We believe that with unceasing effort, the practical application of SACs will come true in the future.

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ORCID

Xueliang Sun D http://orcid.org/0000-0003-0374-1245

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AUTHOR BIOGRAPHIES



Junjie Li is currently a PhD candidate in Prof Xueliang (Andy) Sun's Group at the University of Western Ontario, Canada. He received his MS degree in physical chemistry from the University

of Science and Technology of China in 2017. Currently, he is working on the synthesis of advanced nanomaterials for fuel cell applications.



Xueliang Sun is a Canada Research Chair in Development of Nanomaterials for Clean Energy, fellow of the Royal Society of Canada and Canadian Academy of Engineering, and full professor at the

University of Western Ontario, Canada. Dr Sun received his PhD in materials chemistry in 1999 from the University of Manchester, UK, which he followed up by working as a postdoctoral fellow at the University of British Columbia, Canada and as a research associate at L'Institut National de la Recherche Scientifique (INRS), Canada. His current research interests are focused on advanced materials for electrochemical energy storage and conversion, including all-solid-state batteries, lithium-ion batteries, lithium-sulfur batteries, metal-air batteries, and electrocatalysis in fuel cells.

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