Microenvironment modulation of single-atom catalysts and their roles in electrochemical energy conversion

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Single-atom catalysts (SACs) have become the most attractive frontier research field in heterogeneous catalysis. Since the atomically dispersed metal atoms are commonly stabilized by ionic/covalent interactions with neighboring atoms, the geometric and electronic structures of SACs depend greatly on their microenvironment, which, in turn, determine the performances in catalytic processes. In this review, we will focus on the recently developed strategies of SAC synthesis, with attention on the microenvironment modulation of single-atom active sites of SACs. Furthermore, experimental and computational advances in understanding such microenvironment in association to the catalytic activity and mechanisms are summarized and exemplified in the electrochemical applications, including the water electrolysis and O₂/CO₂/N₂ reduction reactions. Last, by highlighting the prospects and challenges for microenvironment engineering of SACs, we wish to shed some light on the further development of SACs for electrochemical energy conversion.

INTRODUCTION

Renewable energy conversion and storage devices are critical in the effort to address the global energy consumption and environmental challenges (1, 2). Electrochemical reactions, including the oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), oxygen evolution reaction (OER), nitrogen reduction reaction (NRR), and carbon dioxide reduction reaction (CO₂RR), play key roles in sustainable energy conversion, storage, and utilization (3–8). The noble metals are currently the most frequently used catalysts to drive these reactions; however, the high cost and scarcity of these metals hinder the widespread adoption of these technologies (9–11). Therefore, it is highly desired but still challenging for developing alternative electrocatalysts with earth-abundant metals or reduced loading of precious metals. Furthermore, since the overall electrochemical performance of these reactions is highly sensitive to both the physical and chemical properties of the catalysts, the understanding of the structure-activity relationship of the reactive sites and the underlying reaction mechanism is substantial for the further development of efficient electrocatalysts.

Single-atom catalysts (SACs), with atomically distributed metal centers and maximized atom utilization efficiency, have attracted great attention in catalysis owing to the integrated merits of homogeneous and heterogeneous catalysts (12–17). The distinct atomic micro-environment (defined as a small, specific, and isolated chemical/physical environment, such as the local coordination environment and electronic state of the catalytic center) of SACs offers remarkable advantages to achieve high activity, selectivity, and stability for heterogeneous catalysis (18–22) and electrochemical applications (23–28). Previously, we have thoroughly summarized the advances of supported noble metal SACs for heterogeneous catalysis (15); however, few reports specified and highlighted the microenvironment engineering of SACs for electrochemical applications. Recently, diverse strategies have been developed for rational design of SACs with well-controlled microenvironments, and numbers of experimental and theoretical efforts have been made aimed at in-depth understanding of the microenvironment-activity relationships and the underlying reaction mechanisms in various electrochemical energy conversion reactions (29–37).

In this review, we aim to provide an overview toward the rational design of the microenvironments of SACs for electrochemical energy conversion applications. The recently developed synthetic strategies are thoroughly summarized. The notable breakthroughs that SACs have brought in various electrochemical reactions including OER, HER, ORR, CO₂RR, and NRR are highlighted. In particular, we discuss how different functionalities of SACs can be realized through the rational design and synthesis. Recent experimental and computational achievements in understanding the microenvironment-activity relationships and the associated mechanisms are summarized. In addition, the challenges and future directions for designing SACs with desired electrocatalytic performances for the potential practical energy conversion applications are discussed.

STRATEGIES FOR ALTERING THE MICROENVIRONMENTS OF SACs

The microenvironments of single-atom centers, such as geometric construction, coordination, and electronic structure, are extremely critical in optimizing the physical and chemical properties of SACs. Therefore, fabricating SACs with desired microenvironments while maintaining atomic dispersion of metal species is highly attractive and important. Recently, many synthetic strategies including defect engineering, metal-support interaction (MSI), heteroatom tethering, spatial confinement, atomic alloying, molecular bridging, etc. have been developed for the preparation of SACs with various microenvironments. Besides, metal-organic frameworks, owing to the well-defined structure and flexible adjustability, have attracted great attention in regulating the microenvironments of SACs.

Defect engineering

Controlled construction of surface defects on supports, which serve as “traps” to capture the metal atoms, has been proven effective for developing SACs with a well-defined microenvironment. Typically,
defects such as metal cation, oxygen, sulfur, and carbon vacancies, depending on the types of supports, are the most common sites for altering the microenvironments of single-atom sites.

For the single atoms anchored on metal oxide, cationic vacancies have been widely exploited for developing SACs with well-defined local environments (16–46). For instance, single Pt atoms coordinated by three dangling oxygen atoms supported on hematite could be successfully achieved through the surface Fe vacancies (16). Isolated Pt species with a range of oxidation states and local coordination environments could be hosted by Ti vacancies on anatase TiO$_2$ surface (46). In Pt$_1$/CeO$_2$ SACs, single Pt atoms with a PtO$_4$ core stabilized in Ce vacancies on CeO$_2$ surface was evidenced by density functional theory (DFT) calculations (Fig. 1A) (38). Recently, in the work conducted by Wang and colleagues (47), by electrochemical exfoliation, abundant exposed Mo vacancies in the outer layers of double transition metal MXenes (Mo$_2$TiC$_2$T$_x$) were created and used to immobilize positively charged Pt single atoms through covalent bonding. Defects of surface oxygen vacancies have also been proved as ideal sites to anchor single metal atoms (39, 48, 49). As shown in Fig. 1B, by constructing oxygen vacancies on the surface of TiO$_2$, single Au atoms supported on defective TiO$_2$ nanosheets (Au$_x$/Def-TiO$_2$) with the formation of Ti-Au-Ti structure could be obtained (39). In the work conducted by Li and co-workers (40), Cu atom-pair catalyst (APC) was developed by constructing surface Te defects on Pd$_{10}$Te$_3$ alloy nanowires (Fig. 1C). With the optimal Cu loading ratio of 0.10 weight % (wt %), a stable Cu$_1$Cl$_2$-Cu$_{17}$ atom-pair structure was created and identified.

The important role of sulfur vacancies for trapping single metal atoms has also been revealed in layered transition metal dichalcogenide (MoS$_2$ and WS$_2$) as support (41, 42). For instance, as shown in Fig. 1D, a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the DFT relaxed atomic model of Pt$_1$/MoS$_2$ clearly illustrate that the single Pt atoms are hosted in a 2S vacancy (41). In addition, isolated Co atoms coordinated covalently to sulfur vacancies on MoS$_2$ monolayer sheets (Co$_{1}$/MoS$_2$ SAC) was synthesized by Tsang and colleagues through Li intercalation and chemical exfoliation (42).

For instance, Liang and co-workers (43) and by using porous N,S–co-doped carbon (NSC) matrix as host, Fe-SAs/NSC with well-dispersed FeN$_6$S$_2$ sites could be synthesized (56). In addition, the doping of S atoms in Ni-SAs/NSC and Co-SAs/NSC enabled the formation of NiN$_3$S$_5$ and CoN$_5$S$_5$ sites. All these recent advances clearly demonstrate the feasibility for altering the microenvironments of SACs via MSI; however, besides the carbon–based materials, more studies on many other supports such as metal oxides and polyoxometalates may expand a wider world for the development of SACs.

Spatial confinement

Spatial confinement has been developed as an effective approach to construct SACs with well-defined microenvironments. For the spatial confinement strategy, both selection of supports having uniform pore structures and mononuclear metal precursors with suitable charge state and molecular size are of great significance for altering the microenvironments of single-atom sites. Porous materials including zeolites, covalent-organic frameworks, metal–organic frameworks (MOFs), porous carbon matrix (PCM), etc. have been considered as ideal hosts for encapsulating mononuclear metal precursors. Owing to the microporous diffusion limitation, the spatial confinement strategy ensures uniform dispersion of the precursors. Followed by a posttreatment to remove ligands of precursors, SACs with uniform single metal atoms stabilized by the skeletons of supports could be achieved. For instance, by in situ confining and developing SACs with controlled microenvironments through defect engineering strategy.

Metal-support interaction

Besides the diverse defective sites for stabilizing isolated atoms in SACs, MSI is proposed to modulate the electronic structure of single atoms through the covalent/ionic chemical bonding effect with supports (44). For instance, Qiao and co-workers reported the formation of single Pt atoms on Fe$_2$O$_3$ during methane oxidation through a strong covalent MSI with iron and oxygen atoms, which is not associated with support defects (Fig. 1H) (44). Experimental and DFT studies reveal that the reducibility of iron oxide is crucial for trapping isolated Pt atoms. Recently, a facile dangling bond trapping strategy was developed by Wu and co-workers to construct SACs on graphene oxide (M SAs/GO; M = Fe, Co, Ni, and Cu) (45). The abundant oxygen-containing functional groups on GO have been shown as the main sites to grab the metal atoms (Fig. 1I). In addition, the charge transfer from M$^+$ to the dangling oxygen groups resulted in the isolated M$^{0+}$ (0 < δ < 3) species with the formation of M—O bonds. Despite the recent achievements, more strategies for the precise control of electronic and coordination environment of SACs are highly desired.

Heteroatom tethering

Heteroatom tethering, which provides anchoring sites for fixing metal atoms through MSI, has also attracted great research interests. In carbon–based supports, control over the content of heteroatom such as N, P, S, O, or B provides immense scope for tuning the microenvironments of the single-atom sites within the functionalized carbons (31, 33, 53–55). For instance, Liang and co-workers developed a sulfur-tethering strategy for the synthesis of noble metal SACs with high metal loading up to 10 wt % (33), and the results indicate that the doping of sulfur endows mesoporous carbon with high-density anchoring sites for bonding metal atoms via the strong metal-sulfur interactions. By using porous N,S–co-doped carbon (NSC) matrix as host, Fe-SAs/NSC with well-dispersed FeN$_6$S$_2$ sites could be synthesized (56). In addition, the doping of S atoms in Ni-SAs/NSC and Co-SAs/NSC enabled the formation of NiN$_3$S$_5$ and CoN$_5$S$_5$ sites. All these recent advances clearly demonstrate the feasibility for altering the microenvironments of SACs via MSI; however, besides the carbon–based materials, more studies on many other supports such as metal oxides and polyoxometalates may expand a wider world for the development of SACs.
Fig. 1. Defect and MSI strategy for the synthesis of SACs. (A) DFT atomic model of Pt/\text{CeO}_2 illustrating single Pt atoms with a PtO₄ core anchored on CeO₂, adapted with permission from Bruix et al. (38). (B) Schematic illustration for the synthesis of Au/Def-TiO₂, adapted with permission from Wan et al. (39). (C) Schematic illustration for the synthesis of Cu atom pair anchored on Pd₁₀Te₂ nanowires, adapted with permission from Jiao et al. (40). (D) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and DFT relaxed atomic model of Pt₁/MoS₂ illustrating a Pt atom in a 2S vacancy, adapted with permission from Li et al. (41). (E) HAADF-STEM image, simulated HAADF-STEM image, and atomic model of Co₁/MoS₂, adapted with permission from Liu et al. (42). (F) Schematic of Ni atoms (green balls) stabilized in single-vacancy (SV), double-vacancy (DV), and 5775 (D5775) carbon defects, adapted with permission from Jiang and Wang (30). (G) HAADF-STEM images of graphene defects with or without a trapped Ni atom, adapted with permission from Zhang et al. (43). (H) Dynamic formation of single Pt atoms on Fe₂O₃ during methane oxidation through a strong covalent interaction with oxygen and iron atoms, adapted with permission from Lang et al. (44). (I) Schematic illustration for the stabilization of single Fe atoms coordinated by the surface oxygen dangling bonds on graphene oxide (GO), adapted with permission from Qu et al. (45).
separating a metal-ethylene diamine (M = Pt, Pd, Ru, Rh, Co, Ni, and Cu) complex into the β-cages of Y zeolite during crystallization followed by a thermal treatment process, a series of isolated single metal atomic site catalysts (M-ISA@Y) were synthesized (57). In the work conducted by Lou and colleagues (58), a dynamic reaction strategy to stabilize single Pt atoms in PCM (Pt@PCM) was developed. As shown in Fig. 2A, the dynamic reaction through electrostatic interaction led to the traction and relocation of the single Pt atoms from the surface into the interior of the carbon matrix, which were then converted into Pt@PCM via a stepwise pyrolysis process. Recently, via directly loading Fe species on SBA-15 and a subsequent thermal treatment process (Fig. 2B), Sun and co-workers demonstrated the generation of an SBA-15 confined single–Fe atom catalyst (59). Extended x-ray absorption fine structure (EXAFS) fitting results confirm the presence of atomically dispersed O-Fe sites with an average coordination number of 4.5. In the work performed by Zhang et al. (60), single–Pt atom catalysts were constructed using hierarchical NC nanocages as host. Theoretical simulation revealed that the isolated platinum atoms were confined in the micropores with edge-nitrogen dopants by trapping and anchoring [PtCl6]2− species (Fig. 2C). All these results suggest the versatility of the spatial confinement strategy in designing the local coordination environment of SACs.

**Atomic alloying**

Atomic alloying offers a useful route to tune the bonding geometry and electronic structure of the single-metal sites in single-atom alloys (SAAs) that are composed of one type of metal atoms isolated in an array of atoms of a second metal. Recently, Zhang and co-workers developed a facile colloidal method to synthesize bimetallic Pt-Au SAA and nanoparticle (Fig. 2D) (26). Experimental and theoretical studies evidenced the surface single–Pt atom sites surrounded by Au atoms in Pt4Au96 and Pt3Au86 SAAs and the unique alloy-bonding properties and structure of these single–Pt atom species for the superior catalytic performance. Theoretical predictions carried out by Greiner et al. (25) show the free atom-like electronic structure on the single metal atoms in SAA. As shown in Fig. 2E, the charge-density difference plots clearly indicate the increase of charge density around the Cu ion, behaving like a free atom. The bonding of adsorbates to single metal atoms in SAA resembles the bonding in molecular metal complexes owing to the unusual electronic structure, resulting in unprecedented catalytic properties. Therefore, atomic alloying offers a powerful design strategy to alter the electronic structure of single-atom metal sites.

**Molecular bridging**

Molecular bridging including covalent or noncovalent (π stacking, hydrophobic, etc.) approaches has recently been demonstrated as a general method for introducing well-defined single-atom sites on conducting materials. Owing to the high electrical conductivity and surface area, carbon nanotubes and graphene have attracted great interest for this purpose (61–63). For instance, by using the molecular bridging method, a covalent network of cobalt-porphyrin with well-defined CoN4 center on multiwalled carbon nanotube (MWNT) surface (MWNT-CoP) was synthesized by Hijazi et al. (64). As shown in Fig. 2F, coupling of CoP on a MWNT surface provides a robust method for the functionalization of carbon nanotubes with well-defined single-atom species through multiple π–π interactions. In the work conducted by Peng et al. (65), a pyrolysis-free synthetic approach was developed to prepare SACs with atomically well-designed Fe–N–C centers. The fully π-conjugated iron phthalocyanine (FePc) was grafted on the graphene matrix via the intermolecular interactions. Recently, Liu et al. constructed a model single–Ni atom catalyst (Ni SAC) with precise structure via a two-step molecular bridging approach (Fig. 2G). Results from the aberration-corrected HAADF-STEM and x-ray absorption spectroscopy (XAS) measurements clearly confirm the well-defined Ni–N4 moiety on carbon support (66).

Catalysts with atomically dispersed diatomic clusters could also be developed through the preselected metal precursors. For instance, Li and co-workers recently reported the synthesis of a mesoporous carbon nitride (mpg-C3N4)–supported Fe2 cluster catalysts through a “precursor-preselected” wet-chemistry strategy, which could also be applied for producing other diatomic clusters such as Ir2 and Pd2 anchored on mpg-C3N4 (67).

For molecular bridging approaches, the covalent grafting of molecules on carbon materials usually produces robust assemblies; however, the transformation of sp3 hybridized carbon atoms to sp2 leads to the loss of their electronic properties. In contrast, the noncovalent approach can maintain the electronic properties of carbon materials but results in poor stability because of the weak interactions. Therefore, the development of novel techniques that balance both the electronic properties and stability of the atomically dispersed molecular sites is still very challenging.

**Mof derivatization**

MOFs have become the most promising precursors for the construction of SACs over the past few years (29, 68). Owing to the well-defined pore structures and highly ordered arrangements of the metal nodes and organic linkers, atomically dispersed metal sites can be flexibly introduced in pristine MOFs, followed by a thermal or chemical conversion process; SACs with well-controlled microenvironment could be obtained.

Now, a large variety of MOFs have been developed as promising platforms to prepare SACs. For instance, by using the strong coordination between the Ru atoms and free amine groups at the skeleton of derivative MOFs (UiO-66-NH2), a precise control of a single–Ru atom site on nitrogen-doped porous carbon (Ru SAs/N-C) was realized by Li and co-workers (69). As shown in Fig. 2H, the abundant dangling -NH2 groups in UiO-66-NH2 benefit the adsorption of Ru metal ions in the MOF channels via the coordination interaction between the d orbital of Ru atoms and the lone electron pair of nitrogen, which could be further converted to Ru SAs/N-C with abundant single Ru sites coordinated to single-mind N. In the work conducted by Liu and colleagues (70), by pyrolyzing Fe-Co Prussian blue analog (PBA) followed by an acid treatment step, porous N-doped graphene confined single cobalt atoms with CoN4 coordination configuration could be obtained (Fig. 2I).

Besides, more researches are still focusing on ZIF-8, which is constructed with 2-methylimidazolate as the organic linker and Zn cation as the metal node. During pyrolysis at temperatures higher than 900°C, Zn could be evaporated away while M-imidazole-M linkages (M = Fe, Co, Ni, Cu, etc.) would be converted to M–N bonds. SACs with diverse coordination configurations are possible to be prepared through modulation of the organic linkers, metal nodes, and thermal or chemical treatment conditions. For instance, by simply changing the calcination temperature, Li and co-workers realized the flexible regulation of the N coordination number of atomically dispersed Co species.
**Fig. 2. Spatial confinement, atomic alloying, molecular bridging, and MOF derivatization strategies for the synthesis of SACs.** (A) Schematic illustration of the confinement of isolated Pt atoms in PCM (Pt@PCM), adapted with permission from Zhang et al. (58). PDA, polydopamine; PEO, poly(ethylene oxide). (B) Illustration of the decoration of single–Fe atom sites on SBA-15, adapted with permission from Yin et al. (59). (C) Typical configurations of the micropore confined isolated [PtCl$_6$]$^{2-}$ species together with calculated free energies, adapted with permission from Zhang et al. (60). (D) Illustration for the formation of bimetallic Pt-Au single-atom alloy (SAA) and nanoparticle, adapted with permission from Duchesne et al. (26). (E) Calculated charge density difference along the (110) plane in Ag$_{31}$Cu$_1$ SAA, adapted with permission from Greiner et al. (25). (F) Scheme for the synthesis of covalent porphyrin network around multiwalled carbon nanotube (MWNT) surfaces, adapted with permission from Hijazi et al. (64). (G) Synthesis of model Ni SACs on carbon nanotubes, adapted with permission from Liu et al. (66). (H) Scheme for the formation of Ru SAs/N-C and Ru NCs/C, adapted with permission from Wang et al. (69). HF, hydrofluoric acid. (I) Preparation route and model of single–Co atom catalyst from Prussian blue analog (PBA), adapted with permission from Li et al. (70). (J) The formation process of Co-N$_4$ and Co-N, adapted with permission from Wang et al. (71).
shown in Fig. 2J, CoN₄, CoN₃, and CoN₂ with different Co-N numbers were obtained at the calcination temperature of 800°C, 900°C, and 1000°C, respectively (71). Moreover, by introducing multiple types of metal atoms to replace a certain proportion of Zn, atomically dispersed dual-metal sites anchored on NC such as Fe-Co, Fe-Ni dual-atom catalysts could also be developed using this strategy (72–74). The recent advances clearly show the bright prospects for rational design of SACs by integrating the advantages of diverse MOFs.

All these recent advances have clearly demonstrated that the versatile strategies including defect engineering, heteroatom tethering, spatial confinement, atomic alloying, molecular bridging, MOF derivatization, etc. are powerful in altering the microenvironments of SACs. Among them, molecular bridging is shown to be a promising method for designing “model SACs” by introducing well-defined single-atom sites on conducting materials. However, most of these strategies can only realize the “average control” of the geometric and electronic structures of single-atom sites. Further development for the “precise control” of the microenvinronments in SACs is still challenging but highly desired.

CHARACTERIZATION OF SACs

Now, many advanced characterization techniques including aberration-corrected HAADF-STEM, XAS, Mössbauer spectroscopy, nuclear resonance vibrational spectroscopy, etc. have been widely used for identifying the precise microenvironment of SACs. Moreover, various in situ/operando characterization techniques have been developed for capturing the reaction intermediates and monitoring the dynamic behaviors of the microenvironment of the catalytic centers. The integrated application of these advanced techniques provides valuable opportunities for designing highly active SACs toward potential practical applications, which has been thoroughly summarized in our recent perspective (75).

ELECTROCHEMICAL APPLICATIONS OF SACs

The atomically dispersed metal atoms with well-defined microenvironments on supports enable SACs as promising advanced materials for various electrochemical energy conversion applications. Through the rational design of microenvironments of single-atom sites, SACs can achieve distinguished activity, stability, and selectivity for a wide variety of electrochemical reactions such as ORR, HER, OER, NRR, and CO₂RR. Below, we will highlight the recent breakthroughs of SACs in these electrochemical reactions. In particular, recent experimental and computational studies on understanding the microenvironment-activity relationships and the catalytic mechanisms will be discussed.

Oxygen reduction reaction

ORR occurring at the cathode is a key reaction in the development of fuel cells and metal-air batteries for green energy conversion. However, due to the sluggish kinetics of ORR, developing efficient catalysts with minimal content of precious metal and high performance is highly demanded.

The ORR follows either a two-electron (2e⁻) or four-electron (4e⁻) pathway, desirable for H₂O₂ production or fuel cell, respectively, which has been found to depend mainly on the microenvironments of SACs. For instance, the S-coordinated single–Pt atom site (PtS₄) was determined to catalyze the ORR via the 2e⁻ pathway (76), while C-coordinated and N-coordinated single–Pt atom sites preferred the 4e⁻ reaction pathway (77–79). In the work conducted by Li et al. (79), Pt₁/α-MoC and Pt₁/MoN SACs, with atomically dispersed Pt atoms anchored on α-MoC and MoN, respectively, were synthesized to study the effect of coordination environment of Pt atoms for ORR. As shown in Fig. 3A, the Pt atoms were demonstrated to be coordinated with Mo atoms in the Pt₁/α-MoC but with N atoms in the Pt₁/MoN. Compared to Pt₁/α-MoC, the weaker adsorption of OH* for Pt₁/MoN resulting from the modified electronic properties of Pt coordinated with N atoms was determined critical for the high ORR catalytic performance. Liu et al. reported the carbon defect-anchored Pt SACs (Pt₁/C) with remarkable ORR performance. DFT calculations indicate that the single Pt atoms coordinated by four carbon atoms in carbon divacancies (Fig. 3B), with optimized adsorption energy for the rate-controlling OH* intermediates, are the main active sites for realizing the excellent ORR performance (78).

Heteroatom coordinated M-N-C SACs (M = Fe, Co, Mn, Cu, etc.) are promising alternatives to Pt-based ORR catalysts (65, 80–86). The intrinsic activity and ORR reaction pathway catalyzed by M-N-C SACs highly depend on the geometrical and electronic environment of the single-atom metal centers. For instance, a wide range tuning of 2e⁻/4e⁻ ORR pathways was achieved in the work conducted by Wang and colleagues (87) via modulating the metal centers or neighboring metalloid coordination of SACs. The single Fe atoms in Fe-C-O species, which generally strengthen the binding of *OOH on C sites, were identified as highly active and selective for the H₂O₂ production via the 2e⁻ pathway. Recently, Liu and co-workers developed a kinetic model that constructs a quantitative relation between the electrochemical kinetic fingerprints and energy profile of oxygen redox (88). As shown in Fig. 3C, Fe-N-C has the optimal binding energy in alkaline media, resulting in the optimum ORR performance near the top of the volcano plot. As a typical Lewis base site, the coordination of N atom can withdraw electrons from single-atom metal sites, which plays a key role in weakening the rate-limited OOH* or OH* bonding energy and, thus, enhancing ORR activity.

In the work conducted by Yang et al. (89), the difference between Gibbs free energies for four-electron and two-electron transfer ORR (ΔG_H₂O₂–ΔG_H₂O) of Fe@pyridinic N, Fe@pyrrolic N, and Pt(111) was found to be consistent with the production of H₂O₂ (Fig. 3D), indicating the Fe-pyrrolic-N species as the main active sites for ORR. However, the Fe-pyridinic-N moieties experience difficulty in adsorbing reaction intermediates because of a lower energy level location of the p band compared to that of Fe-pyrrolic-N moieties. The ORR performance catalyzed by M-N-C could be improved through S doping, which reduced the energy barriers of the reaction intermediates owing to the coordination of S atom (56, 90). For instance, Zhu and co-workers demonstrated that the ORR activity of Fe-N-C could be improved with optimizing the charge and spin distributions of Fe via S doping (90). Further study conducted by Zhang et al. (56) suggests that the S-coordinated Fe atom sites play a vital role in lowering the reaction barrier (Fig. 3E), which is due to the modified Fe d orbitals with the highest occupied states near the Fermi level, boosting the ORR kinetics. Rational tailoring of Fe-N coordination number provides another way to enhance the ORR activity (91). For instance, in the work done by Zhu et al. (91, 92), the Fe-N-C catalyst with FeN₃ active site was found with superior ORR activity owing to the high affinity to O₂ and low energy
barriers for the intermediates and products. In addition, experimental and theoretical results from the work of Wang et al. (92) indicate that the unsaturated Cu$^{I}$-$\mathrm{N}_2$ in Cu-N-C SAC acts as the active site for ORR via a 4$\text{e}^-$ pathway (Fig. 3F). Recently, DFT studies carried out by Zhao et al. (93) suggest that the modification of single-metal atom centers with hydroxyl groups can largely improve the ORR activity of SACs. Furthermore, a self-adjusting mechanism proposed by Wang et al. (94) suggests that the single-atom Fe site in Fe-SAC was intrinsically covered with OH* intermediate existing as Fe(OH)N$_4$ species (Fig. 3G), which can optimize the electronic structure of single Fe atoms and boost the ORR. The construction of dual-metal sites in SACs has been shown with synergistic effects in improving the ORR performance. Recently, DFT studies performed by Hunter et al. (95) demonstrate that the spectating metal
partner in paired SACs can change the reduction potential of the atomically distributed metal atoms. As a result, paired Co and Pt atoms anchored on a N-doped four-atom vacancy graphene ($N_4V_4$) have been proposed as the best-performing system for OER (Fig. 3H). In the work conducted by Xiao et al. (96), a OH-ligand self-binding strategy was proposed for OER with Fe-Co dual-atom active sites for anchoring OH. The anchoring of OH on the triangle FeCoN$_5$ produced the FeCoN$_5$-OH site with optimal geometry configuration and $\epsilon_p$ orbital energy level of Fe, thus enabling easier intermediate desorption and O–O bond scission (Fig. 3I). The magnetic moment and electronic state of single metal atoms in SACs could also be modulated through the incorporation of a second atom, which may change the adsorption energy of intermediates and improve the OER performance. For instance, DFT calculations performed by Sun et al. (97) showed decreased magnetic moment and increased valence electrons of single–Fe atom sites after B doping, thus greatly boosting the OER activity. In the work conducted by Wang and co-workers (98), the incorporation of atomically dispersed Fe and Co dual-atom active sites into two-dimensional (2D) conjugated aromatic networks [CAN–Pc(Fe/Co)] resulted in an increased content of low-spin Fe$^{2+}$ in Fe-N$_4$ moiety (Fig. 3J), which largely facilitated the OER process.

All these results from recent advances demonstrate the rational manipulation of microenvironment of single-atom sites as an essential way for developing highly efficient single-atom OER catalysts. Moreover, it is of great importance to identify the intrinsic reactive centers in SACs under practical catalysis condition for rational design of high-performance SACs.

**Oxygen evolution reaction**

The OER, which involves multiproton-coupled electron transfer steps, is an essential half-reaction for rechargeable metal-air battery and water splitting. The application of SACs such as SAAs and layered double hydroxide (LDH)/carbon-supported SACs in OER electrocatalysis has been widely reported. Engineering the micro-environment of SACs has been proven as an effective method to boost the sluggish kinetics of OER.

SAAs, with adjustable electronic structure of single-atom sites, have attracted great interest as OER catalysts. In the work conducted by Li et al. (99), a series of PtCu$_x$/Pt$_{\text{skin}}$ core-shell structures with atomically dispersed Ru$_1$ (Ru$_1$-Pt$_{\text{Cu},x}$ SACs) were synthesized and the origin of their enhanced OER performance was unraveled. A volcano relation between the lattice constant and OER activity was demonstrated. The calculated volcano plot of OER overpotential $\eta$ with $\Delta G_{\text{O}} - \Delta G_{\text{OH}}$ and $\Delta G_{\text{OH}}$ on the Ru$_1$-Pt$_{\text{Cu},x}$ (111) SACs is shown in Fig. 4A. A weak binding of adsorbate over the single–Ru atom site increases the dehydrogenation barrier, while a strong binding is detrimental for the formation of $^*$OOH intermediate and the subsequent O$_2$ generation. The projected density of states of Ru$_1$ was found to be shifted gradually toward the Fermi level with increasing Pt-to-Cu ratio in Pt$_{\text{Cu},x}$ owing to the gradual release of compressive surface strain with respect to the pristine Pt (Fig. 4B). As a result, the tailored electronic structure of single Ru sites, which is engineered via the compressive strain of Pt$_{\text{skin}}$ shell, has been proven critical for the optimized binding of oxygenated species and the improved OER activity and stability.

The OER performance could also be tailored through anchoring different metal atoms. For instance, by DFT calculations, Xu et al. screened 28 single metal atoms supported on MoS$_2$ edges as OER catalysts (100). The Pt/T1 vacancy termination in Pt$_1$-doped MoS$_2$ was found to have minimum theoretical overpotential for OER (Fig. 4C and D). In addition, the S coordination environment and electronegativity of the single-atom sites are confirmed as a structure descriptor for the adsorption–activity–structure relationship of MoS$_2$-based SACs. In the work done by Li et al. (101), single Ru atoms dispersed on the surface of CoFe LDHs (Ru$_1$/CoFe-LDHs SAC) were developed for electrocatalytic OER, and the formation of $^*$OOH group was determined as the rate-determining step (Fig. 4E). Further in situ/operando results indicate the strong synergetic electron coupling between LDH substance and single Ru atoms, which avoided the formation of the high oxidation state of Ru and optimized the adsorption free energy of $^*$OOH, boosting the OER activity. Recently, Yan et al. (102) developed a single W atom–doped Ni(OH)$_2$ nanosheet [W$_1$-doped Ni(OH)$_2$] SAC for OER. DFT calculations show that both O–O bond and O radical can be generated at the single–W atom site (Fig. 4F), owing to the low spin population of W$^{6+}$. In addition, DFT calculations carried out by Lai et al. (103) suggest that Ir$_1$@CoO (Ir) in Ir$_1$@Co/NC SAC is responsible for the high OER performance (Fig. 4G). In the work performed by Cai et al. (104), the annealed Au@Ni$_2$P sample with formation of tiny Au clusters and single Au atoms on Ni$_2$P exhibited outstanding OER activity (Fig. 4H).

Carbon as a common support used for preparing SACs with controlled microenvironment for OER. For instance, atomically distributed Ni sites anchored on N-doped hollow carbon matrix with unsaturated coordination geometry show high OER performance with excellent stability (105). The electronic coupling via the Ni–N coordination can move down the Fermi level of single–Ni atom sites, which effectively lowers the adsorption energy of reaction intermediates and, thus, boosts OER kinetics (Fig. 4I). In the work conducted by Cao et al. (106), the O–Ru$_1$–N$_2$ structure formed through pre-adsorption of O atom on Ru–N–C SAC was demonstrated with a low O–O coupling barrier for the formation of $^*$OOH intermediate, which is responsible for the high OER performance (Fig. 4, J and K). In addition, as the synergistic effect of neighboring dual-metal sites helps to optimize the adsorption/desorption of reactive intermediates (Fig. 4, L and M) (107), development of atomically dispersed binary sites on carbon hosts offers another promising way to decrease the overall reaction barrier for OER.

**Hydrogen evolution reaction**

Electrochemical water splitting through HER provides a sustainable and green route to produce molecular hydrogen (H$_2$) for mitigating the global energy crisis; however, the development of active catalysts with minimal overpotential and high efficiency is still urgently demanded for its large-scale application. Recently, SACs supported on various kinds of materials including MoS$_2$, MXene, and carbon-based matrix have been widely used to catalyze HER (108–110). Micro-environment engineering of atomically dispersed active sites, which can result in unique structures and electronic properties of SACs, has been proven as a promising way to dramatically accelerate the reaction kinetics of HER.

The HER activity could be improved by designing large numbers of well-defined atomically dispersed active sites hosted over transition metal dichalcogenide materials, such as MoS$_2$ (111–115). For instance, carbonized polyacrylonitrile-immobilized single molecular MoS$_2$ (MoS$_2$–CPAN) was demonstrated with much higher turnover frequency (TOF) to HER than bulk MoS$_2$ (Fig. 5A) (116). Qi et al. (117)
Fig. 4. Applications of SACs in OER. (A) Calculated volcano plot of OER overpotential $\eta$ with $\Delta G^{\circ} = \Delta G_{\text{OH}}$ and $\Delta G_{\text{O}}$ on Ru$_1$-Pt-Cu$_{0.5-2.5}$ (111) SACs. (B) In-plane lattice contraction relative to the Pt(111) pristine surface (red circles) and d-band center of Ru$_1$ (blue squares), together with the corresponding adsorption $\eta$ (blue squares) and energy $E_0$ of the oxygen atoms (red circles), adapted with permission from Yao et al. (99). (C) The hydrogen Gibbs free energy on Pt-doped edge (red bar), Pt top site (blue bar), and pure MoS$_2$ edge (black bar); (D) theoretical overpotentials for the Pt-doped MoS$_2$ terminations as a function of $\Delta G_{\text{OH}*}$ and $\Delta G_{\text{O}*} - \Delta G_{\text{OH}*}$, adapted with permission from Xu et al. (100). (E) Proposed 4$e^-$ OER mechanism on CoFe-LDHs and Ru$_y$/CoFe-LDHs SAC, adapted with permission from Li et al. (101). (F) Proposed OER mechanism on W$_{37}$-doped Ni(OH)$_2$ SAC and bare Ni(OH)$_2$ catalyst, adapted with permission from Yan et al. (102). (G) Proposed OER mechanism on Mn@Co/NC SACs (M = Ir, Fe, Ni, Pt, Ru, and Pd), adapted with permission from Lai et al. (103). (H) OER current density at 1.47 V versus RHE of Ni$_3$P matrix–supported single Au atoms and tiny clusters, adapted with permission from Cai et al. (104). (I) Proposed OER mechanism over HCM@Ni-N SAC and free energy diagram at 0 V versus RHE, adapted with permission from Zhang et al. (105). (J) Proposed OER mechanism over Ru-N-C SAC in acidic electrolyte, (K) free energy diagram for OER on O-Ru$_1$-N$_2$ (blue line), HO-Ru$_1$-N$_2$ (green line), and Ru$_1$-N$_2$ (red line), adapted with permission from Cao et al. (106). (L) Co-Ni-N models. (M) Free energy diagram for OER on NC, Ni-N, and Co-Ni-N, adapted with permission from Han et al. (107).
recently developed an interface SAC with atomic cobalt array bound to distorted 1T MoS$_2$ (Co-MoS$_2$) that achieves Pt-like HER activity with high catalytic stability. DFT calculation results show the ensemble effect via the synergy of S and Co in the distorted 1T MoS$_2$ support (Fig. 5, B and C), which changes the hydrogen-binding mode. In addition, substitution of Mo by Ni in MoS$_2$ with formation of positively charged Ni-S centers greatly modified the electronic structure of Ni-MoS$_2$ SAC and, thus, improved the hydrogen evolution activity (113).

MXenes have been recently applied as promising hosts for anchoring single metal atoms with controlled microenvironment for boosting HER (118, 119). In the work done by Zhang et al. (47), electrochemical, exfoliated, double transition metal MXene nanosheets (Mo$_2$TiC$_2$Tx) were used to immobilize single Pt atoms for enhancing HER performance. The replacement of a Mo atom by a single Pt atom, which causes a reduced charge density around Pt atom due to charge delocalization from Pt to the surrounding atoms (Fig. 5D), greatly reduces the adsorption energy for H$^+$ (Fig. 5E) and, thus, facilitates the formation and release of molecular hydrogen. Recently, a titanium carbide (Ti$_2$C$_2$T$_x$) MXene was used by Ramalingam et al. (120) to host single Ru atoms coordinated with N and S sites (Ru$_{5\times2}$N-S-Ti$_2$C$_2$T$_x$ SAC), which displayed superior HER activity. DFT calculation suggests that the N and S co-coordinated single Ru sites have optimal Gibbs hydrogen adsorption free energy ($\Delta G_{\text{H}^+}$) (Fig. 5F). Furthermore, as demonstrated by Kuznetsov et al. (119), anchoring of isolated Co atoms on Mo vacancies in the oxygen-terminated 2D molybdenum carbide (Mo$_2$CT$_x$) could also tailor the binding of hydrogen and, thus, enhance the HER kinetics.

Recently, many strategies such as construction of nonmetal SACs (121) and SAA catalysts (122) and development of hosts for anchoring single metal atoms (123) have been reported for improving the HER performance. In a recent work done by Jiang et al. (124), single Pt atom embedded in nanoporous cobalt selenide (Pt/np-CO$_{0.45}$Se SAC) was developed as an efficient electrocatalyst for HER. Fourier transform EXAFS result indicates that the Pt atoms, which occupy the Co vacancies and coordinate with Se atoms, have a positive valence state due to the electron transfer from Pt to Se. DFT calculations show that the electronic interactions between np-CO$_{0.45}$Se and atomic-level Pt can largely improve adsorption/desorption of hydrogen, thus reduce the energy barriers for water dissociation, and promote the HER kinetics (Fig. 5G).

Microenvironment engineering of atomically dispersed metal sites anchored on various carbon-based hosts has also attracted great interest in HER (125–133). For instance, Liu et al. (134) developed onion-like nanospheres of carbon (OLC)–supported single Pt atom (Pt$_1$/OLC SAC) as a highly efficient HER catalyst. A remarkable enrichment of protons around single Pt atoms was identified (Fig. 5H). The tip-enhancement effect at the single–Pt atom site, inducing strong localized electric field and extracting electrons from the support, was considered as the main factor for enhancing the HER activity. In the work done by Xue et al. (135), zero valent single Ni/Fe atoms anchored on graphdiyne were developed for hydrogen evolution. The real-space highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) contour plots on Ni-on-GD SAC as shown in Fig. 5I clearly demonstrate the charge density distributions induced by a single Ni$^0$ atom. The strong electronic coupling and chemical interactions between different electronically active C sites of Graphdiyne (GD) and the single Ni/Fe atoms (Fig. 5J) largely improved the HER performance.

Recently, Cao et al. (136) developed a phosphorized carbon nitride–immobilized single–Co atom catalyst (Co$_1$/PCN SAC) with uniform Co$_1$-N$_4$ moiety for HER. Operando XAFS measurements reveal that the formation of high-valence HO-Co$_1$-N$_2$ moiety, followed by the preferred dynamic H$_2$O adsorption as H$_2$O-(HO-Co$_1$-N$_2$), accelerates the H$_\text{ad}$ adsorption.

**CO$_2$ reduction reaction**

The electrochemical CO$_2$RR offers a viable strategy to decrease CO$_2$ emissions and mitigate the energy crisis (4, 12, 137, 138). SACs have shown excellent activity and selectivity in CO$_2$RR for the conversion of CO$_2$ into value-added chemicals such as CO, formic acid, C$_2$ products, etc. (31, 139–143). Microenvironment engineering of SACs offers great opportunities for reducing the overpotential of CO$_2$RR and improving the selectivity for the desired products. Moreover, the SACs with well-controlled coordination environment and electronic state provide a platform to understand the structure-activity relationship of the reactive sites and the underlying reaction mechanism, which is of great importance for practical application of electrocatalytic CO$_2$RR.

Fe-based SACs with various microenvironments have been demonstrated to be promising for CO$_2$RR (144–147). For instance, by investigating a series of iron-based catalysts for the electrocatalysis of CO$_2$ to CO, Huan et al. (146) identified the isolated FeN$_4$ sites as the critical catalytic species. In the work performed by Qin et al., by combining DFT calculations and in situ infrared absorption spectroscopy investigations, the edge-hosted Fe$_{2\times2}$ sites embedded in a defective graphitic layer have been shown as the real active sites for CO$_2$-to-CO electrocatalytic conversion (144). The electronic state of the single-atom site is also a main factor determining the electrocatalytic performance of CO$_2$RR. As shown in Fig. 6A, for the Fe-based SACs with Fe$^{3+}$ ions, negligible shift of the Fe K-edge could be observed at −0.4 V (versus Reversible Hydrogen Electrode, RHE), indicating that the oxidation state of Fe$^{3+}$ ions remained unchanged during CO$_2$RR. However, the Fe K-edge shifted to lower energies at −0.5 V (versus RHE) and beyond, the same potential for the deactivation of Fe$^{3+}$-N-C, implying that Fe$^{3+}$ sites in Fe-based SACs are more active for CO$_2$RR (147).

Ni-based SACs with various coordination environments and electronic states have also been demonstrated to be efficient for CO$_2$RR (148–155). The adsorption energies of *CO* and *COOH* on single-atom sites could be largely affected by the microenvironment of single-atom sites, thus determining the CO$_2$RR performance. For instance, DFT calculations carried out by Zhao et al. (156) suggest that the formed *COOH* can be easily reduced to CO* for both NiN$_x$ (x = 1 to 4) and the Ni$_{309}$ cluster (Fig. 6B); however, the *CO* desorption from the Ni$_{309}$ cluster is much more difficult than that from NiN$_x$, indicating NiN$_x$ as the real active species for CO$_2$RR. In the work conducted by Liu and colleagues, atomically dispersed Ni(I) has been proven as the active site for CO$_2$RR (55); the as-developed single–Ni atom catalyst exhibits high intrinsic activity for CO$_2$ reduction, reaching a TOF of 14,800 hours$^{-1}$ with 97% Faradaic efficiency at a mild overpotential of 0.61 V. The following research from the same group further identified the high activity of Ni$^0$ in a model Ni-based SAC for CO$_2$ activation through operando XAS and Raman measurements (Fig. 6C) (66).

Co-based SACs have also been recognized as promising catalysts for CO$_2$RR (4, 157–159). As shown in Fig. 6 (D and E), DFT calculations on well-defined metal N$_4$ sites reveal that CoN$_4$ species...
Fig. 5. Applications of SACs in HER. (A) Immobilized single molecular MoS$_2$ on carbonized polyacrylonitrile for HER, adapted with permission from Zeleke et al. (116). (B) The electron charge of a single Co atom and adjacent S as a function of Co coverage in Co-MoS$_2$ SAC, (C) calculated free energy diagram of HER for Co-MoS$_2$ SAC with different atomic Co loading amounts, adapted with permission from Qi et al. (117). (D) DFT models used to describe Pt-Mo$_2$TiC$_2$O$_2$ SAC, (E) calculated free energy diagram for HER on Pt/C, Pt-Mo$_2$TiC$_2$O$_2$ SAC, and Mo$_2$TiC$_2$O$_2$, adapted with permission from Zhang et al. (47). (F) Calculated free energy diagram of HER for N-S-Ti$_2$C$_2$T$_x$, Ru$_{SA}$-N-S-Ti$_2$C$_2$T$_x$, Ru$_{SA}$-Ti$_2$C$_2$T$_x$, and Ru$_{SA}$-N-S-Ti$_2$C$_2$T$_x$ catalysts, adapted with permission from Ramalingam et al. (120). (G) Schematic illustration of the HER mechanism over single platinum atoms embedded in nanoporous cobalt selenide (Pt/np-Co$_{0.85}$Se SAC) in neutral media, adapted with permission from Jiang et al. (124). (H) HER catalyzed by atomically dispersed Pt, supported on onion-like nanospheres of carbon (Pt$_{1}$/OLC SAC), adapted with permission from Liu et al. (134). (I) Real-space highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) contour plots on Ni-on-GD SAC, and the H$_{C1}$ and H$_{C2}$ denote the active H adsorption sites labeled with C$_1$ and C$_2$, respectively. (J) The free energy profile ($\Delta$G) with respect to the chemisorption energy of H for HER, adapted with permission from Xue et al. (135). (K) Calculated energy diagram for H$_2$O dissociation on HO-Co$_{1}$/PCN SAC and Pt(111), adapted with permission from Cao et al. (136).
exhibit the optimum activity for CO₂ reduction to CO due to the moderate binding energy for both *CO and *COOH on the single-Co atom sites (61). In addition, a volcano trend between the nature of metal N₄ sites and their activities toward CO formation, with Fe and/or Co at the top of the volcano, was identified by Li and co-workers (Fig. 6F) (160). Detailed electronic structure analysis suggests that the enhanced catalytic activity of Co-based SACs with coordinating N atoms substituted by O or C atoms is due to the lack of π bonding in the Co–O bond compared to the Co–N or Co–C bond (158).

Other transition metal–based SACs such as Cu, Zn, Mn, etc. have also been studied for CO₂RR (161–163). Zheng et al. (164)
demonstrated the atomically dispersed Cu-N₂ active sites in ultra-thin Cu-N₅/GN nanosheets as the real active species for CO₂RR. As shown in Fig. 6G, the optimized reaction-free energy for CO₂ activation over Cu-N₅ sites promotes the electron transfer from the single–Cu atom sites to *CO₂, thus boosting the *COOH generation. In the work done by Karapinar et al. (165), Cu-SAC with a CuN₄ coordination environment was developed for CO₂RR, achieving a Faradaic yield of 55% for ethanol under optimized conditions (Fig. 6H). Operando XAS experiments established the very small metallic Cu nanoparticles converted from the CuN₄ sites during electrolysis as the active species for the unique reactivity. Recently, Cu-based SAA has been theoretically shown as a promising catalyst for electrochemical reduction of CO₂ to methanol at a low over-potential (166). As shown in Fig. 6I, the formation of the free atom-like d-band due to the isolated metal atoms could modulate the adsorption strength of reaction intermediates, thus leading to the efficient formation of CH₃OH.

The recent advances for the application of SACs in CO₂RR indicate that the C–C coupling is rather difficult on single active metal sites. Therefore, the rational design SACs with dual active sites has been considered as a promising approach to improve the catalytic performance and generate C₂ products through optimizing the adsorption energies for *CO and *COOH (73). For instance, an APC featuring a stable Cu⁰–Cu^II pair structure was developed for CO₂RR by Li and co-workers (40). Experimental characterization and DFT calculation revealed that the Cu^II site could adsorb H₂O while the Cu⁰ site could adsorb CO₂ (Fig. 6J and K), which boosted the CO₂ activation. In the work conducted by Qiao and co-workers (167), by using C₃N₄ as a molecular scaffold to modify the electronic structure of supported Cu atoms, the adsorption behavior of reaction intermediates could be optimized, which resulted in the unique capability to generate C₂ products. A dual active center mechanism, which illustrates the single Cu active center for carbon and C-containing species adsorption and the adjacent C atom on g-C₃N₄ for bonding reaction intermediates having oxygen (such as *OCH₂*, *OCH₃*, *COO*, and *OH*), was theoretically evidenced.

Nitrogen reduction reaction

The electrocatalytic NRR has been considered as an attractive route for nitrogen fixation and ammonia production. However, the large overpotential and low faradic efficiency toward NH₃, as two major issues, largely limit the further development of NRR. Owing to the unique structural and electronic features, SACs have attracted increasing attention in exploring advanced NRR electrocatalysts and revealing the underlying mechanisms. By rationally designing the microenvironment of different metal centers with diverse supports, SACs are promising to improve the catalytic performance and understand the microenvironment-activity relationships for efficient NRR.

Recently, by using DFT calculations, Qiao and co-workers built up a library of different transition metal centers anchored on various NC as NRR catalysts, which illustrates the electronic origins, activity trends, and design strategies of SACs for electrocatalytic N₂ reduction (168). As shown in Fig. 7A, the maximum activity for NRR, marked by the red region, could be possibly achieved by independently tuning ΔG*NH₃* and ΔG*N₂*. Since the supports or ligands of the active centers could regulate the scaling relations for intermediate adsorption, the rationally designed SACs with controlled microenvironment is shown to be critical for improving the catalytic activity. In addition, the stability of the ligands should also be considered to ensure the durability of NRR SACs. As shown in Fig. 7B, the decomposition potentials for g-C₃N₄ four coordinating nitrogen atoms (N₄), and three coordinating nitrogen atoms (N₂) were calculated to be −0.81, −1.03, and −0.71 V (versus Standard Hydrogen Electrode, SHE), respectively, indicating the high stability of SACs supported on the NC substrate under moderate NRR potential. Results of this work predicted Ru@g-C₃N₄ close to the ideal region as a promising candidate for NRR, which has been experimentally verified (169–171). As evidenced by Yu et al. (169), the doping of single Ru atoms could lead to notable electronic rearrangement of both g-C₃N₄ and Ru atoms (Fig. 7C), which led to stronger N₂ adsorption on Ru SAs/g-C₃N₄ compared to that on Ru bulk surface and, thus, improved the catalytic activity and selectivity for NH₃ formation. In the work conducted by Sun and colleagues (170), the single Ru atoms anchored in oxygen vacancies have been shown as the main active centers for NRR, which enable the stabilization of *NH2 and enhance the N₂ adsorption (Fig. 7D). Both Ru@Zr₃O₆₃ and Ru/NC₂ SACs were demonstrated to be highly active for NRR because of the reduced free energy for *NNH formation (Fig. 7, E and F), which is considered as the most energy-consuming step in electrochemical NRR.

SACs with other single-atom centers (Fe, Co, Mo, B, etc.) have also been investigated in NRR (172–180). For instance, Ou et al. (181) systematically studied the Gibbs free energies for *H (ΔG*H) and *N₂ (ΔG*N₂) on various Mo-based SACs. As shown in Fig. 7G and H, Mo₃N₃ anchored on N-doped black phosphorus, with extremely low overpotential (0.02 V) and fast removal of the NH₃ molecule, is proposed as a compelling highly efficient catalyst for NRR. Recently, a type of SACs with single V atoms anchored on boron monolayer (V/B₁₂–BM) was theoretically evidenced as a promising catalyst for NRR (182). As shown in Fig. 7I and J, by calculating the free energy change of each elementary step over V/B₁₂–BM SAC during NRR, an “acceptance-donation” interaction between the V atom and N₂ was proposed. The ionization of 1π orbital of N₂, which greatly elongates the N–N bond length, leads to the enhanced activity for electrocatalytic N₂ reduction. In the work conducted by Sun and co-workers (183), single B atoms anchored on different 2D materials were theoretically studied as electrocatalysts for NRR (Fig. 7K). The volcano diagrams for NRR over different B-based SACs as shown in Fig. 7L indicate that the catalytic activity of boron is highly correlated with the charge transfer degree between the substrate and the boron atom. Results of this work identified the single boron atoms substituted into h-MoS₂ (hS-1) and supported on graphene (G-A) as the most promising NRR catalyst. All these results provide a general guideline for the rational design of efficient SACs for electrocatalytic N₂ reduction through microenvironment engineering.

SUMMARY AND OUTLOOK

In summary, we have witnessed the fast development of SACs in both their preparation strategies and application field in electrochemical energy conversion. A number of synthetic strategies including defect engineering, spatial confinement, atomic alloying, molecular bridging, MOF derivatization, etc. have been categorized for the synthesis of SACs with various microenvironments. The distinct atomic local microenvironment of SACs offers remarkable advantages of distinguished activity, selectivity, and stability for a wide variety of electrochemical reactions such as ORR, HER, OER, NRR, and CO₂RR. Furthermore, the microenvironment modulation...
of SACs would provide great help in the deep understanding of the microenvironment-activity relationships and underlying catalytic mechanisms associated to different electrochemical reactions.

However, the research of microenvironment engineering of SACs for electrochemical energy conversion is still at its infancy stage. First, although many advanced strategies have been proven to be powerful for altering the microenvironments of SACs, the development of novel synthesis strategies for the “precise control” of the microenvironments in SACs is still challenging but highly desired. Second, despite the fact that many efforts have been devoted to studying the carbon-based SACs, microenvironment engineering of single atoms on many other types of hosts, such as MXenes, transition metal dichalcogenide materials, defective metal oxides, as well as single atom alloys, deserves more attention. Third, theoretical study of SACs would provide great help in the deep understanding of the microenvironment-activity relationships and underlying catalytic mechanisms associated to different electrochemical reactions.
prediction based on computational modeling has been proven useful in discovering SACs for electrochemical applications. Strategies for the rational design of model SACs with a well-controlled microenvironment based on the DFT studies are still highly desired. Last, SACs provide an ideal platform for investigating the microenvironment-activity relationships and the underlying reaction mechanisms of various electrochemical energy conversion reactions. In most cases, although the catalytic center is stable during the reaction, the microenvironment of SACs would undergo a dynamic cycle with in situ formation of intermediate species; therefore, the integrated utilization of in situ/operando techniques is of significance but still under development.

As a conclusion, despite that the exciting advances have been achieved in the microenvironment engineering of SACs for electrochemical energy conversion, opportunities and challenges are both to be faced. Therefore, microenvironment engineering of SACs with a well-controlled coordination environment and electronic state, integrated with the advanced in situ/operando techniques as well as DFT theoretical studies, shall pave the way for both fundamental research and the future industrial applications of SACs for various electrochemical energy conversion fields.

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