

Insights into DFT-guided synthesis of atomic clusters for electrocatalysis

Hongyu Jing^{1,§}, Peng Zhu^{2,§}, Han Wu^{3,§}, Chang Cui¹, Nanyu Shao¹, Xinyi Zhang¹, Yu Chen¹, Zihan Zhao¹, Jiaxin Zhou¹, and Zhen Zhao^{1,4}

¹Institute of Catalysis for Energy and Environment, Shenyang Normal University, Shenyang 110034, China

²Interdisciplinary Research Center for Sustainable Energy Science and Engineering (IRC^{SE}), School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, China

³School of Computer Science and Artificial Intelligence, Zhengzhou University, Zhengzhou 450001, China

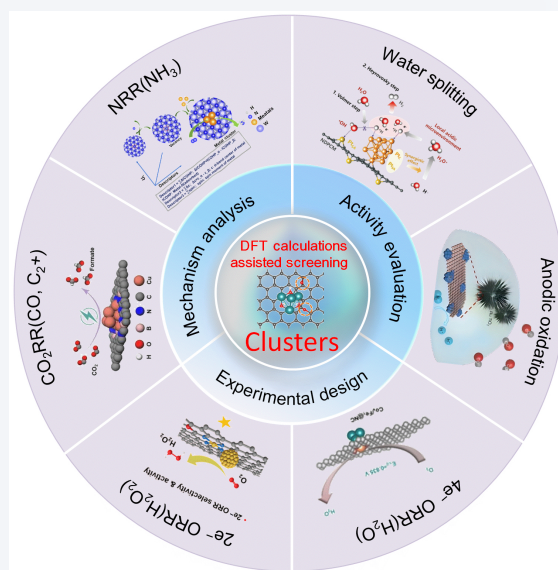
⁴State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China

[§]Hongyu Jing, Peng Zhu, and Han Wu contributed equally to this work.

 Cite this article: Nano Research, 2026, 19, 94908519. <https://doi.org/10.26599/NR.2026.94908519>

ABSTRACT: It is non-trivial to perform density functional theory (DFT) screening for experimental validation that can accelerate qualitative materials discovery to give priority to the top candidates. Cluster catalysts, owing to their adequate active sites, quantum effect, high ratio of volume/surface, excellent activity and selectivity, have garnered widespread attention in various complicated multi-step catalytic reactions. However, the design concept, structure formation principle, electrocatalysis process and potential reaction mechanism are rarely unveiled. This perspective will summarize the DFT calculation-assisted screening concept with emphasis on theoretical calculation descriptor, geometric structures, electronic properties, adsorption behaviors, and reaction mechanism to monitor the cluster catalysis. Thereafter, experimental design of advanced clusters will be presented, including synthetic strategies and various characterization techniques for intrinsic active sites identification. Subsequently, an overview of the structure-property correlation to drive diverse electrochemical reactions will be exemplified and discussed, encompassing cathode reaction of oxygen reduction reaction (ORR), anode oxidation of H₂, alcohols and acids, water splitting, nitrogen reduction reaction (NRR), carbon dioxide reduction reaction (CO₂RR). Finally, a fundamental insight into the existing challenges and perspectives were proposed for rational screening and structural regulation of the advanced clusters for the electrochemical reactions in clean energy conversion devices.

KEYWORDS: density functional theory (DFT) study, cluster catalysts, design strategy, reaction mechanism, structure-property correlation



1 Introduction

Exploring advanced high-performing catalysts with lower

Received: December 9, 2025; Revised: January 21, 2026

Accepted: February 1, 2026

✉ Address correspondence to Hongyu Jing, jinghongyu20121231@163.com; Zhen Zhao, zhaozhen1586@163.com, zhenzhao@cup.edu.cn

environmental impact are desired for sustainable electrochemical energy conversion devices, such as fuel cells, metal-air batteries, water electrolysis, activation and conversion of small molecules (such as N₂/CO₂ to fuel conversion) etc., has become a promising solution to address the energy and environmental crisis [1–3]. In these devices, the catalyst is the engine that determines the overall reaction efficiency to lower the energy barriers. It was demonstrated that noble-metal-based catalysts are considered as the holy grail among other earth-abundant catalyst in many electrocatalytic reactions [4–17]. Nonetheless, the exorbitant price, low stability, and natural scarcity severely restrict their scaling application. Thus,

minimizing the usage of noble metals or exploiting non-noble metal-based alternative catalysts using green and sustainable strategy is of paramount significance [18–26].

Atomically dispersed metal catalysts have aroused worldwide attention due to the quantum size effect, electronic structure effect (e.g. band structures, band gap and density of states), strong metal-support interaction, high atom utilization, and coordination unsaturated center [27–35]. It is well known that the size effect in the range of nanoparticles, clusters, and even to single atoms is tightly associated with the electrochemical activity, which would affect the geometric structure, adjacent coordination environment, and intrinsic electronic property, such as the exposed index planes, the actual active sites, and the binding force of intermediate species. Single-atom catalysts (SACs) possess a broad prospect to achieve high activity toward various reactions [36–50]. But the SACs may raise a risk that the isolated active sites cannot drive the entire catalytic process individually to achieve the desired reaction. Hence, SACs are not the panacea for those reactions requiring continuous active sites. Besides, due to the large size of the nanoparticles (NPs), the reactant substrates will be absorbed onto different sites, such as edge sites, corner sites, and planes of the geometric structures, thereby reducing the catalytic selectivity.

For some intricate catalytic process involving multiple substrates, multiple intermediates and multi-electron transfer, the clusters have become an emerging research hotspot due to the presence of neighboring metal bonds that can trigger synergistic effects [51–56]. Clusters with different symmetry can modify the d band center structure of metal atoms and modulate electronic properties originated from the metal orbital hybridization effect [57–64]. Clusters can provide adjacent atomic sites that may decrease the reaction barrier and improve the catalytic activity. The above of which merits might endow them with many novel physical and chemical properties, new catalytic pathway different from once popular SACs and NPs catalysts in various electrochemical reactions [65–68]. The metal atoms tend to aggregate to NPs or decompose to SACs during the synthesis process. Therefore, it would be challenging to design multi-atom cluster catalysts with desired structures. Recently, strategies such as precursor preselection, coordination stabilization, electrochemical strategies, spatial confinement-pyrolysis, electrospinning, atomic layer deposition, ball-milling, and mass-selected soft landing, etc. have been reported to synthesize cluster catalysts.

However, experimentally synthesizing, characterizing, and predicting the properties of advanced clusters, are a very expensive, labor-intensive, and time-consuming task. Theoretical study based on the density functional theory (DFT) are a promising avenue for reducing the research period and experimental cost of cluster catalysts [69]. DFT calculations can estimate d-band centers, adsorption energies, activation energy barriers, reaction pathways, which are vital parameters to explore the electrocatalytic performance and reaction mechanism. The thermodynamic energy descriptors of catalyst that correlate with activity and selectivity can be predicted by DFT approach, for instance, the descriptor of CO adsorption energy can predict the activity of hydrocarbon generation for the carbon dioxide reduction reaction (CO_2RR) system [70]. Noteworthy, apart from adsorption energy of the intermediates, single descriptor cannot fully determine the electrocatalytic kinetics, which requires analyses of the other critical parameters such as coordination configurations, active centers identifying, surface stability, thermodynamics reaction energy

barriers, transition states, and catalytic reaction mechanism. In addition, the electrocatalytic process of clusters is complicated due to the diversity of reaction pathways and intermediates. The design principle of clusters must give priority to the reaction pathways regulating. For the formic acid oxidation system, it involves the dehydrogenation and dehydration process. The CO^* generated from the dehydration is toxic to the active center. Strong adsorption between CO^* and metal center can make the exposed active site covered by CO^* , which will inhibit the adsorption of other small molecules, leading to low catalytic activity. Clusters with capability of both oxygen reduction reaction (ORR) and OER activities are satisfactory for water splitting, fuel cells and metal-air batteries, etc. For catalyzing the OER, clusters can reduce the reaction barriers for $^*\text{OOH}$, $^*\text{OH}$, and $^*\text{O}$ through synergistic effects to enhance the catalytic activity of the active sites.

Cluster catalysis guided by theoretical calculation is still in its infancy, it is critical to disclose the underlying reaction mechanisms on various active centers. This review aims to systematical summarize the recent research progress on the theory-guided design and experimental discovery of clusters towards various electrocatalytic reactions, as illustrated in Fig. 1. First, we give a precise definition of clusters structure in detail from the theoretical and experimental perspectives. Further, the theoretical principle to rational screen and design clusters catalysts are presented and the corresponding synthesis strategies under the guidance of theoretical calculation are summarized. Thereafter, the recent progress and reaction mechanism of clusters for various energy-related electrocatalytic reaction will be discussed, including cathode reaction of ORR, anode oxidation of H_2 , alcohols and acids, water splitting, nitrogen reduction reaction (NRR), CO_2RR . Finally, conclusions and prospects for the pre-screening, controllable synthesis, characterizations, applications and catalytic mechanism exploration of clusters will be provided. We anticipate to give theoretical and experimental guidelines for scientists to in-depth understanding the structure-property correlation of atomic clusters.

2 Theory-guided clusters design

The traditional trial and error experimental study of clusters is facing the dilemma of low efficiency and lack of evidence. With the rapid development of computer science, theoretical calculations are increasingly important due to the savings in time and higher accuracy. Experimental workflow requires scientific experience to select candidates for clusters synthesis, DFT workflow uses structural optimization to search a balance between structure and activity for near-optimal activity [71]. Ideal adsorption models are searched on catalyst surfaces, which is indicative of catalyst activity. This yields a feedback loop during DFT screening and experimental verification. Based on DFT screening results to guide experimental discovery, a great deal of experimental phenomena can be elucidated at atomic scale. Theoretical calculations have become an indispensable tool in determining catalytic mechanism as well as relationship between cluster structure and catalytic activity.

The development of high-performance electrocatalysts fundamentally relies on establishing robust composition–structure–activity correlations and gaining mechanistic insights into catalytic processes. DFT has evolved into a crucial computational methodology for elucidating the relationship between electrochemical activities and the intrinsic physicochemical properties of catalytic materials. Based on quantum-mechanical

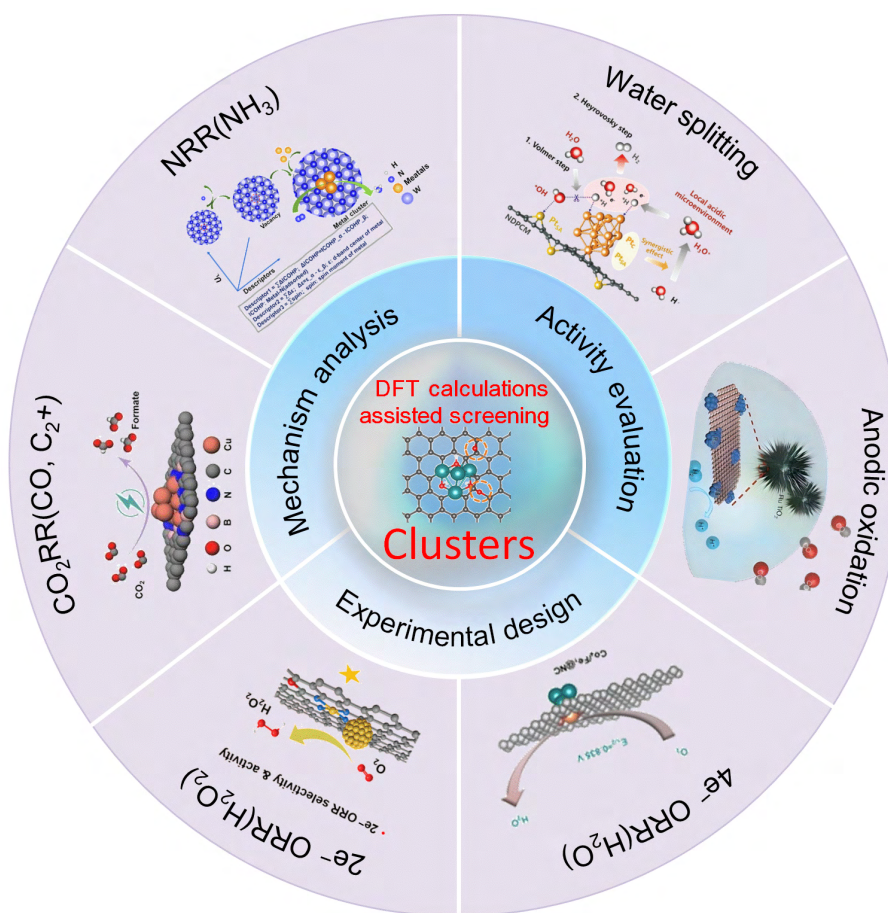


Figure 1 Overview of topics covered in the review on the DFT guidance of designing atomic cluster catalysts towards various electrocatalytic reactions.

theory, DFT approaches reliably determine the ground state energy of atoms in particular configurations, thereby supporting the prediction of catalytic activity and the understanding of reaction mechanisms through an in-depth analysis of electronic structures. The correlation between DFT guided experimental synthesis of clusters is mainly reflected in the structural origins derived from the reconfiguration of d-band structure manipulation, spin state engineering, and tuned charge reconstruction.

Firstly, in terms of experimental synthesis, researchers can adjust the d-band center and d-p hybridization width of clusters by changing the local atomic coordination environment, thereby optimizing the adsorption energy of key intermediates. The position of the center of the d-band directly affects the adsorption strength of the reaction intermediates, and an upward shift will enhance the adsorption energy [72]. The d-band model proposed by Norskov and Hammer has been extensively utilized to correlate the electronic structure of electrocatalysts with the adsorption characteristics of rate-determining intermediates [73, 74]. For atomic clusters, the d-band structure can be characterized by descriptors including the d-band center, width, and the position of the upper edge relative to the Fermi level. Since the electron occupancy in bonding and anti-bonding states is governed by the d-band center position, modulation of this parameter enables precise control over intermediate adsorption strength [75]. The incorporation of another metal atoms introduce additional empty d-orbitals or unpaired d-electrons, which facilitate enhanced orbital hybridization with adsorbates through optimized π/σ donation and

π^* back-donation pathways. This strengthens the metal-adsorbate interaction, promoting both intermediate activation and optimal binding energy. Pan et al. synthesized Pt-based high-entropy alloy clusters supported on super-hydrophilic CeO_2 /porous carbon (Pt-HEA-cluster/ CeO_2 /C) for HER. Synergistic Pt–O–Ce interfacial and Pt–M metallic bonds modulate the Pt d-band center, achieving near-thermo-neutral hydrogen adsorption while concurrently optimizing charge-transfer kinetics and adsorption energy via controlled d-orbital occupancy [76].

Secondly, spin represents an intrinsic property of electrons that has established itself as a cutting-edge research theme across materials science and energy related field [77]. In contrast to precious metal catalysts, which predominantly exhibit a closed-shell electron configuration, 3d metal complexes, particularly those based on iron, demonstrate a comparatively low crystal field splitting energy [78]. This characteristic grants them a tendency to develop open-shell structures and additionally promotes the creation of complex potential energy surfaces through spin transitions. Consequently, such complexes have the capability to display reactivity patterns that significantly differ from those of conventional closed-shell catalysts, indicating the potential for ground breaking advancements in the field of catalysis [79]. Various spin states influence the electronic structure, intermediate binding capacity, and activation energy of the electrocatalyst, consequently affecting the catalytic performance. First-principles simulations by Liu et al. demonstrate that an Fe_3 cluster supported on $\theta\text{-Al}_2\text{O}_3$ (010) serves as an effective heterogeneous catalyst for ammonia

synthesis [80]. Due to the significant spin polarization of the Fe₃ cluster, the adsorbed N₂ is effectively activated, resulting in a high turnover frequency of NH₃. The orbital overlap among metal atoms allows single cluster catalysts to exhibit a specific electronic structure that enhances the interaction with N₂, particularly in terms of donating electrons to the N₂-π* orbitals. Moreover, Jiang et al. put forward an anchored Fe₄ cluster on GaS as ammonia synthesis catalyst. N₂ is fully activated through a side-on adsorption configuration at the hollow site of Fe₄/GaS, where both degenerate N₂-π* orbitals are effectively hybridized with the frontier orbitals of the Fe₄ cluster, as demonstrated by fragment orbital analysis. Furthermore, spin density on activated N₂ reaches 0.40 μB at the hollow site, markedly surpassing values at the top (0.01 μB) and bridge (0.08 μB) sites. Because free N₂ is nonpolar, this spin accumulation further destabilizes the N-N bond [81].

Thirdly, optimized charge transfer between the electrocatalyst and key reaction intermediates has been demonstrated to improve catalytic activity. Theoretical calculations have shown that there are significant interactions between the intermediates during critical reactions and the polarized active sites present on the surface of an electrocatalyst. The spatially uneven charge distribution of atomic clusters is predominantly reflected in the oxidation state. This originates from two coupled mechanisms: (1) electron transfer driven by intrinsic electronegativity differences of the central metal atoms, which modifies oxidation states; and (2) interfacial structural defects that perturb the local coordination environment, coordination number, bond length, and bond angle, relative to ideal lattice parameters, compelling directional reorganization of the electron density. These combined effects ultimately produce a spatially nonuniform charge density profile [82]. For example, Tang et al. reported a Te-N-Pt system (Pt₁₃/Te-N-GMC) as an efficient ORR catalyst. The low electronegativity of Te facilitates electron delocalization, which is stabilized by the unsaturated coordination of the Pt particle center. DFT calculations demonstrate that, in contrast to carbon supports that are either single-heteroatom-doped or undoped, Te-N co-doping enables electron reverse transfer from the Te-N-GMC support to Pt. This charge redistribution enhances electron density at Pt sites and alleviates Pt oxidation under high-voltage conditions, finally boosting its ORR activity [83].

It is of great significance to develop an overview of the general framework and common descriptions for DFT guiding the design of cluster catalysts, in order to facilitate communication between computational and experimental scholars. Combining DFT theory with experimental techniques is a common strategy to improve the accuracy and depth of research. This helps to reduce the time and cost of trial and error in experiments.

The DFT method can be used to calculate the properties and electronic structure of clusters, such as parameters of band structure, electronic density of states, adsorption energy and reaction barriers in catalytic processes [84]. Computational scholars believe that the general framework for DFT guidance typically follows a compute-design-validate process. Firstly, through high-throughput DFT calculations, multiple possible cluster structure models are established. Select the stable structure with the lowest energy by performing geometric optimization and energy calculations. Next, calculate the binding energy and formation energy of the clusters to determine the feasibility of the experimental structure. For the selected stable clusters, determine the active center, calculate its electronic structure and key performance descriptors, simulate catalytic reaction pathways, and

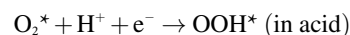
analyze the origin of the activity. Once again, experimental verification will be conducted to test the catalytic activity and selectivity by the experimenters after using the calculated results to guide the synthesis of clusters. In this way, a preliminary structure-descriptor-performance relationship is established. Descriptors are the key bridge connecting cluster structure and performance. Mainly including: (1) geometric structure descriptors, such as bond length and bond angle distribution; (2) electronic structure descriptors, such as transition metal d-band centers and charge distributions; (3) the descriptors of stability between clusters and supports, such as binding energy and cohesive energy; (4) electrocatalytic reaction performance descriptors, such as adsorption free energy, reaction energy barrier/transition state energy [85].

The size of atomic clusters (from dimers to trimers and some tens of atoms) is generally less than about 2 nm, its catalytic behaviors in terms of selectivity and activity will be obviously altered stemming from the quantum effects, electronic effects, geometric effects, synergistic effects between adjacent atoms, and coordination microenvironment effect [86–88]. When the size of bulk metal NP (> 2 nm) is decreased, its electronic structure will be changed from continuous valence bands to a relatively discrete HOMO–LUMO states with a narrow band gap [89]. When the particle size is further decreased to the clusters region, the HOMO–LUMO electronic state is significantly discretized (Fig. 2(a)). The observed difference is mainly attributed to the synergistic effects of additional atoms. The origin of synergistic effects of cluster catalysts usually including d-band filling, spin state, charge difference and electronegativity [90–92]. Clusters may exhibit various configurations, including homo-atom and hetero-atom dimers, bridged dimers, trimers and so on (Fig. 2(b)). When the adsorbate is landed onto the active centers, the additional active site could change the binding pathway, effectively activate the adsorbate, optimize reaction energies, and tune the activity of clusters (Figs. 2(c) and 2(d)) [93]. In addition, clusters with different sizes and structures exhibit different specific surface area, which can expose more surface active sites for the adsorption and activation of multiple substrates or intermediates, and catalyze complex reactions with diverse products.

Due to the unique size effect, distinctive electronic properties, synergistic effects, and excellent catalytic performance of clusters, we have conducted a systematic summary of the key design points and common problems regarding the cluster catalysts towards several typical electro-catalysis processes in the following section in order to gain a deeper understanding of the structure-activity relationship of as-developed clusters.

2.1 Clusters for 2e⁻ ORR to produce H₂O₂

H₂O₂ is a widely used green oxidant in chemical synthesis, wastewater treatment, fiber and paper production, disinfection, medicine, and environmental remediation [94]. The use of 2e⁻ ORR for H₂O₂ electrochemical synthesis is a sustainable alternative technology for industrial energy intensive anthraquinone oxidation process, in which only OOH* intermediate species occurs. In alkaline and acidic conditions, the reactions of 2e⁻ ORR to synthesize H₂O₂ are described as follows [95]



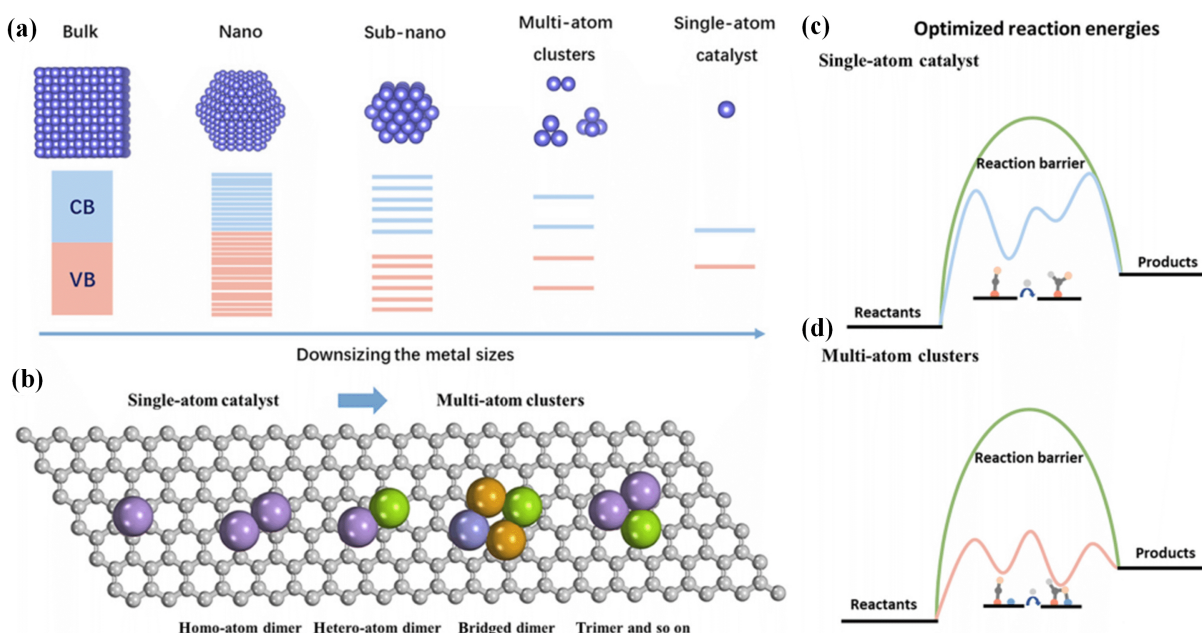
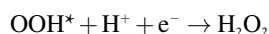
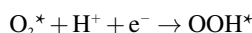
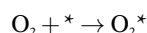


Figure 2 (a) Representative geometric and electronic differences of materials with diverse sizes. (b) Possible multi-atom cluster catalysts. (c) Illustration of optimized reaction energies, and (d) binding and activation of multi-atom cluster catalysts when compared with single-atom catalysts. Reproduced with permission from Ref. [93], © Royal Society of Chemistry 2022.

Therein, H_2O_2 is unstable in alkaline media, thus the direct production of H_2O_2 in acidic conditions is more desirable, the elementary reactions of the 2e^- ORR in acidic environment are given as follows



The limiting potential (U_L) versus ΔG_{OOH}^* shows a volcano plot for the 2e^- ORR. On the left of the volcano, the intermediate of $^*\text{OOH}$ binds too strong, leading to the 4e^- ORR, which means low selectivity but high activity towards the 2e^- ORR. On the right of the volcano, the $^*\text{OOH}$ intermediate binds too weak, representing a high selectivity yet low activity towards the 2e^- ORR. The high 2e^- ORR activity and selectivity are located near the top of the volcano.

Even H_2O_2 is synthesized by the 2e^- route, owing to its high activity of radicals, side reactions of the peroxide reduction may result in the formation of H_2O ($\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$ in acid) and the H_2O_2 decomposition ($2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$). Thus, suitable catalysts that can enhance the activity and selectivity and prevent the H_2O_2 reduction and decomposition are required to be screened via experimental and computational investigations. For the 2e^- ORR to produce H_2O_2 , noble metal alloys of Pt-Hg, Pd-Hg, and Au-Pd [96–98], SACs such as non-precious metals of Fe, Co, Ni, Mn [99–102] and precious metals of Os, Ir, Rh, Ru, Pt, and Pd [103, 104] as well as metal-free heteroatom, for example, B, N, O, F, P, S-doped carbon have been studied [105]. Metal-based SACs, clusters and NPs have been generally reported to be superior electrocatalysts for various reactions [106–108], yet clusters have rarely been developed for 2e^- ORR to produce H_2O_2 .

Theoretical studies indicate that Ag clusters can donate more electrons, which is conducive to the protonation of adsorbed O_2 ,

resulting in a high H_2O_2 selectivity. Liu et al. demonstrated a stable Ag clusters anchored on N-doped hollow carbon spheres (NC-Ag/NHCS), which can catalyze 2e^- ORR with a high H_2O_2 selectivity of 89%–91% in 0.1 M HClO_4 electrolyte [109]. The calculated free energy diagrams of ORR for $2\text{e}^-/4\text{e}^-$ route on NC-Ag/NHCS demonstrate that Ag_{13} cluster possess a lower energy barrier for the 2e^- process rather than the unfavorable 4e^- one, corresponding to $\text{OOH}^* \rightarrow \text{H}_2\text{O}_2$ (Fig. 3(a)). The energy barrier of OOH^* on Ag_{13} cluster is lower than the substrate one, which demonstrates a high selectivity of H_2O_2 resulting from the Ag nanoclusters doping (Fig. 3(b)). For the synthesis of NC-Ag/NHCS, they used resorcinol formaldehyde polymer (RFP) and SiO_2 templates to prepare N-doped hollow carbon spheres (NHCS), AgNO_3 was absorbed on NHCS by wet impregnation, then NC-Ag/NHCS was obtained after the calcination in NH_3/Ar . HAADF-STEM image depicts that Ag clusters were densely dispersed on the hollow carbon shell (Figs. 3(c)–3(f)). XANES spectroscopy was analyzed to conform the atomic structure of NC-Ag/NHCS, two dominant peaks can be respectively assigned to the Ag-N and Ag-Ag (Figs. 3(g) and 3(h)). From the ORR polarization curves showed in Fig. 3(i), it can be found that the ring current density of NC-Ag/NHCS is larger than that of NHCS, demonstrating an enhanced activity to produce H_2O_2 . The selectivity of H_2O_2 and the number of electron transfers (n) are calculated and plotted as a function of different potentials, which displays a high H_2O_2 selectivity of 89%–91% for NC-Ag/NHCS between 0.2 to 0.7 V. And, the corresponding calculated value of n is close to 2, indicating a 2e^- route for ORR (Fig. 3(j)).

Liu and co-workers reported a low-coordinated Mo clusters supported by nitrogen-doped carbon for H_2O_2 electrosynthesis [110]. The H_2O_2 selectivity was higher than 77% with a negligible activity attenuation in an alkaline condition over 10,000 cycles. DFT results revealed that the high H_2O_2 selectivity was due to the ability of Mo clusters can give electrons to activate O_2 and enhancing the binding of $^*\text{OOH}$ on Mo sites. The free energy profiles of ORR

pathways on Mo_4 cluster displayed a free energy barrier (0.17 eV) for the $2e^-$ ORR ($^*\text{OOH} \rightarrow \text{H}_2\text{O}_2$), which was lower than that of $4e^-$ ORR pathway (0.56 eV) (Fig. 4(a)). On the Mo_4 cluster sites, the key intermediate of $^*\text{OOH}$ was much easier to generate compared with the N-G (Fig. 4(b)), which suggested a high H_2O_2 selectivity of $c\text{-Mo/NCPs}$. The catalysts of $c\text{-Mo/NCPs}$ were prepared using a combination process of self-assembly, wet impregnation, and high-temperature calcination (Fig. 4(c)). $c\text{-Mo/NCPs}$ presented apolyhedrons morphology and no crystalline nanoparticles were observed in the TEM image (Figs. 4(d) and 4(e)). Mo clusters were well dispersed on the NCPs surface conformed by HAADF-STEM image (Fig. 4(f)). The Mo 3d XPS spectrum suggested that Mo clusters are in the form of oxidized states, and Mo-N bond was found at the binding energy of 229.0 and 232.8 eV (Fig. 4(g)). In the FT-EXAFS curve, the two peaks at ~ 1.5 and ~ 2.8 Å were attributed to the Mo-N and Mo-Mo (Fig. 4(h)). On the ORR polarization curves (Figs. 4(i) and 4(j)), $c\text{-Mo/NCPs}$ displayed a larger ring current (I_{ring}) with a positive shift of onset potential and 77%–85% H_2O_2 selectivity, indicating an enhanced activity for H_2O_2 electrosynthesis. Chen et al. used a solution-impregnation method

to synthesize partially oxidized amorphous $\text{Pd}^{\delta+}$ clusters ($\text{Pd}_3^{\delta+}$ and $\text{Pd}_4^{\delta+}$) onto oxidized carbon nanotubes ($\text{Pd}^{\delta+}\text{-OCNT}$), achieving nearly 100% selectivity toward H_2O_2 in acidic electrolytes [111]. The free energy diagram and activity volcano plot (Figs. 5(a)–5(c)) suggest that the activity of Pd_3 and Pd_4 with oxygen-containing functional group is further enhanced by two nearby epoxy group, enabling the $\text{Pd}^{\delta+}\text{-OCNT}$ at the peak of the volcano with a overpotential of 0 V. The Pd clusters were obtained with no crystalline lattice in the HRTEM and with a size distribution of 0.61 ± 0.07 nm in the STEM image (Figs. 5(d) and 5(e)). The CV curves of hydrogen adsorption/desorption peak of $\text{Pd}^{\delta+}\text{-OCNT}$, confirming the successful doping of Pd onto the OCNT (Fig. 5(f)).

Transition metal-based catalysts have shown promising application in H_2O_2 synthesis due to their high H_2O_2 selectivity and low price. Among them, Co-based catalysts are beneficial in inhibiting the free radical attack and de-metallization of active sites, which enables them excellent catalytic activity and stability. Cyclodextrin possesses abundant active sites, which can improve the electrocatalytic performance. DFT reveals that the cyclodextrin-mediated $\text{Co}(\text{OH})_2$ structure can optimize the subsequent

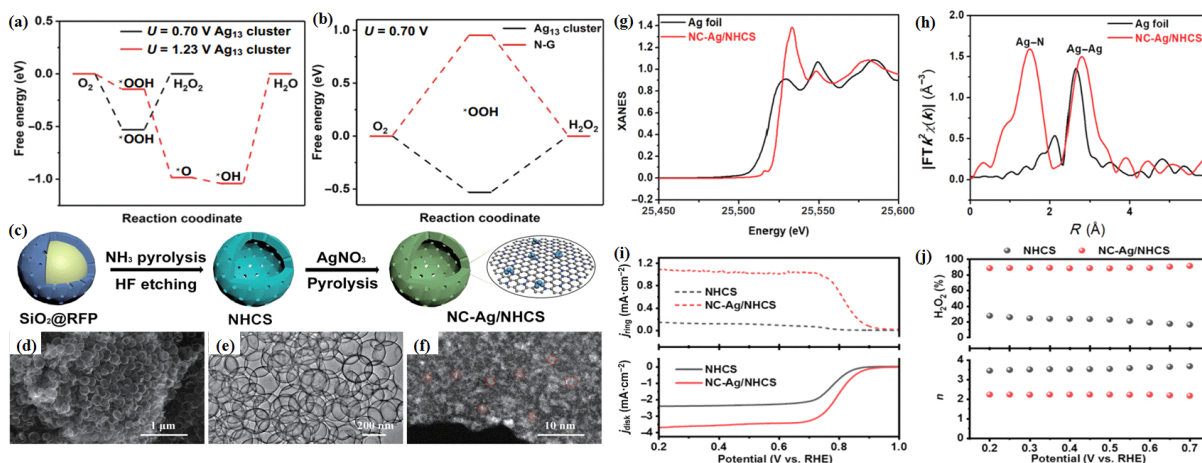


Figure 3 (a) Calculated free energy diagrams for $4e^-/2e^-$ ORR pathways on Ag_{13} cluster. (b) Calculated free energy diagrams for $2e^-$ ORR pathway on Ag_{13} cluster and N-G. (c) Schematic diagram of the synthesis process. (d) SEM image. (e) TEM image. (f) HAADF-STEM image. (g) Ag K-edge XANES profiles. (h) Ag K-edge FT-EXAFS profiles. (i) ORR performance in 0.1 M HClO_4 . (j) Polarization curves, in which j denotes the current density. (k) The calculated H_2O_2 selectivity and n . Reproduced with permission from Ref. [109], © Tsinghua University Press 2022.

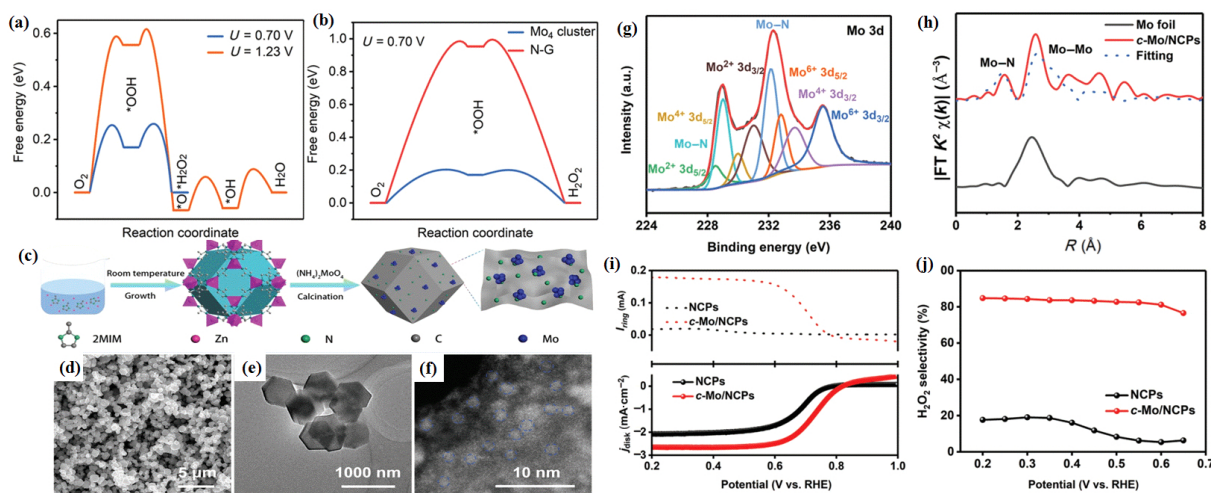


Figure 4 (a) Calculated free energy profiles for $4e^-/2e^-$ ORR pathways on Mo_4 cluster. (b) Calculated free energy profiles for $2e^-$ ORR process on Mo_4 cluster and N-G. (c) The preparation process. (d) SEM, (e) TEM, and (f) HAADF-STEM images of $c\text{-Mo/NCPs}$. (g) High-resolution XPS Mo 3d spectra. (h) Mo K-edge FT-EXAFS profiles. (i) and (j) Electrocatalytic ORR performance of $c\text{-Mo/NCPs}$ in 0.1 M KOH electrolyte. Reproduced with permission from Ref. [110], © Jin, M. M. et al. 2022.

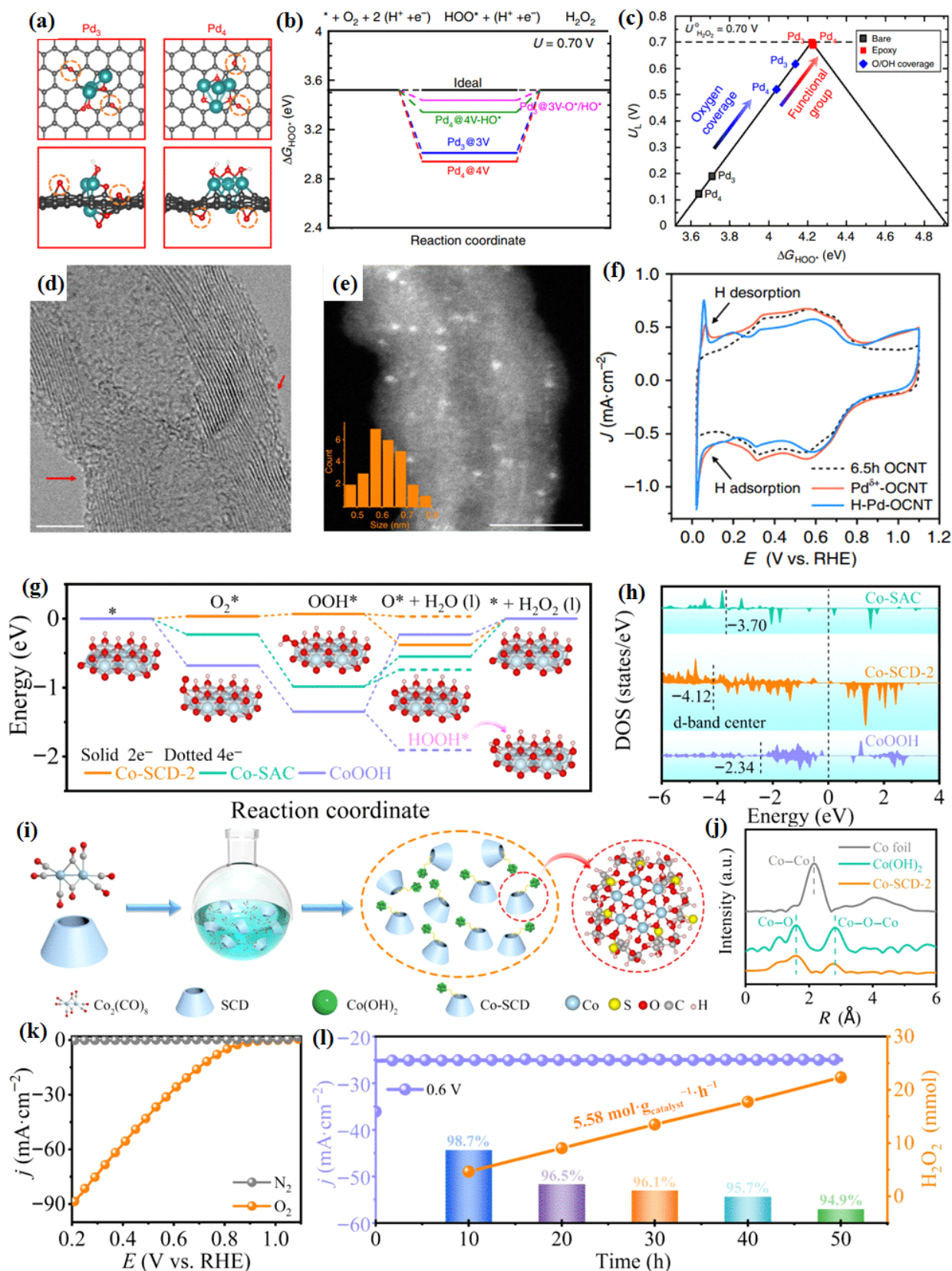


Figure 5 (a) Optimized model with nearby epoxy functional groups on the most stable O*/HO* covered Pd₃ and Pd₄ clusters. (b) Free energy diagram for 2e⁻ ORR at 0.70 V. (c) Activity volcano plot. (d) and (e) HRTEM and STEM images of Pd^{δ+}-OCNT. (f) H adsorption/desorption curves. Reproduced with permission from Ref. [111], © Chang, Q. W. et al. 2020. (g) Free energy change along the reaction pathway. (h) The PDOS of Co-SCD-2, Co-SAC, and CoOOH. (i) The preparation of Co-SCD-2. (j) Fourier transforms of EXAFS spectra. (k) LSV polarization curves and (l) i-t test of Co-SCD-2 for production of H₂O₂ in a three-electrode H-type electrolytic cell. Reproduced with permission from Ref. [112], © Wiley-VCH GmbH 2023.

adsorption of OOH* intermediates and enhances the activation energy barrier for dissociation, leading to the high catalytic activity and selectivity for the 2e⁻ ORR [112]. Co-SCD-2 has the lowest free energy of 0.04 eV for OOH* among the other Co-based catalysts (Fig. 5(g)). The d-band center of Co-SCD-2 shows an obvious left-shift compared to Co-SAC and CoOOH, which weakens the energy of *OOH intermediate and is beneficial for the production of H₂O₂ (Fig. 5(h)). Wang et al. reported a cyclodextrin-supported Co(OH)₂ cluster catalysts by using heptakis-(6-mercapto-6-deoxy)-β-cyclodextrin (SCD) and Co₂(CO)₈ (Fig. 5(i)). The EXAFS spectrum of Co-SCD-2 displays two shells can be ascribed to Co–O and Co–Co scattering paths (Fig. 5(j)). The catalyst exhibited excellent H₂O₂ selectivity and stability, as well as high H₂O₂ yield rate with 5.58 mol·g_{catalyst}⁻¹·h⁻¹ in the H-type cell (Figs. 5(k) and 5(l)).

H₂O₂ electrochemical synthesis is a green and sustainable technology. For the clusters design, introducing atomic vacancies or defects to construct active sites can promote local electron delocalization and enhance conductivity. Constructing synergistic effects between different atomic sites can optimize charge redistribution, and accurately adjust the d-band center and optimize electronic structure through DFT prediction [113].

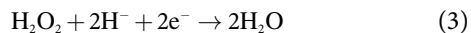
2.2 Clusters for 4e⁻ ORR cathode reaction

The proton exchange membrane fuel cell (PEMFC) or direct methanol fuel cells (DMFCs) with properties of high energy density, low cost and zero-emission of exhaust gas, can provide clean energy by transforming chemical energy into electric energy, which exhibits attractive market prospect [114]. However, the PEMFC or DMFCs is restricted by its sluggish kinetics of cathodic oxygen reduction reaction (ORR). The ORR process is the rate-determining step and has different reaction mechanisms in acid and basic conditions [115].

In acid condition, 4e⁻ transfer pathway



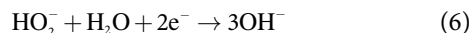
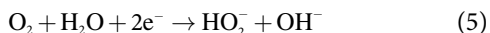
In acid condition, two step 2e⁻ transfer pathway



In basic condition, 4e⁻ transfer pathway

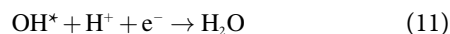


In basic condition, two step 2e⁻ transfer pathway

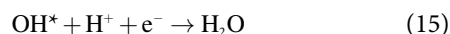


It is worth noting that there are only two processes irrespective of the acidity or alkalinity of the electrolyte. One is the 4e⁻ process to directly generate H₂O in acid or OH⁻ in basic. The other transfer pathway is the two step 2e⁻ process, it undergoes the first 2e⁻ process to generate H₂O₂ or HO₂⁻, and then further undergoes the second 2e⁻ process to produce H₂O or OH⁻. The direct 4e⁻ transfer pathway is required, which can acquire maximum power conversion efficiency.

The 4e⁻ ORR possess the associative and the dissociative mechanism. The elementary reactions of the associative mechanism in acid medium follow the steps below



Besides, the elementary reactions of the dissociative mechanism in acid medium are listed as follows



In the associative mechanism, the intermediates are OOH*, O*, and OH*, here the O–O bond in OOH* will be broken (Eq. (9)), while in the dissociative mechanism, the intermediates are OH* and O*, here the O–O bond in O₂ will be broken (Eq. (13)). Based on the above equations, we can discover that ORR elementary reactions mainly involve two process [116]. One process involves the broken of O–O bond, such as the dissociation of O₂* and OOH*. The other one involves several protonation steps, for example, the protonation of O₂* (Eq. (8)), O* (Eqs. (10) and (14)), and OH* (Eqs. (11) and (15)). It should be noted that too strong bonding of active sites and intermediates will make the activation energy barrier in the protonation processes higher, while too weak bonding will make it difficult to dissociate O–O bond. Therefore, too strong or too weak bonding of the active sites and intermediates are not conducive to the improvement of catalytic activity. The above relations can be described with the volcano curve, in which ORR thermodynamic and kinetic as a function of adsorption energy. Whether the OOH* are dissociated into *O and OH* determines the reaction pathway. The weak adsorption of OOH* leads to a high H₂O₂ selectivity but a low activity, and the strong binding of OOH* leads to the dissociation to *O and OH* resulting in the 4e⁻ ORR. Therefore, OOH* → H₂O₂ is the rate-determining step (RDS) for the 4e⁻ pathway, and O₂ → OOH* is the most sluggish reaction step for the 2e⁻ ORR pathway. The cathode reaction of ORR in the fuel cells remains a bottleneck due to its sluggish kinetics process and large overpotentials. Developing alternatives to substitute precious metal and reducing platinum loading are urgent need for the commercialization because of the scarcity of platinum [117].

Sing-atom Fe-N₄ structure has aroused interest in replacing expensive platinum-based catalysts toward ORR. However, the rigid atomically dispersed Fe-N₄ configuration showed limited activity and serious degradation due to the unsatisfactory adsorption energies to oxygen-containing intermediates in acidic electrolyte. Fe-N₄ SACs modified by clusters, such as Pd clusters [118] or Fe clusters [119], can synergistically maximize the activity and stability of Fe-N₄ SACs for ORR. Wang et al. demonstrated that

adjacent atomic clusters can enhance the ORR activity and stability of single-atom Fe-N₄. The modulation effects of the adjacent Co₄ ACs structure have been demonstrated to improve the ORR activity for Fe-N₄ site through DFT calculations. Co₄/Fe₁@NC and Fe₄/Fe₁@NC showed a longer stretching of O–O bond (ca. 1.30 Å) relative to the Fe-N₄ (1.29 Å) (Fig. 6(a)), implying that O₂ can be more easily broken in Co₄/Fe₁@NC and Fe₄/Fe₁@NC. Figure 6(b) shows the free energy diagrams of OOH*, O* and OH* intermediates and adsorption configurations at U = 1.23 V, the rate-determining step with uphill free energy was the third step from O* to OH*, thus the ORR kinetics and activity was determined by the formation of OH*. Co₄/Fe₁@NC had the lowest free energy change, indicating a more favorable structure to weaken the binding of O* on the Fe-N₄ site. The charge density difference of Co₄/Fe₁@NC demonstrating the electron withdrawing effect from the Fe-N₄ active center to the adjacent Co₄ (Fig. 6(c)). The integration of Fe-N₄ and Co₄ atomic clusters on the N-doped carbon support

(Co₄/Fe₁@NC) was obtained by a “pre-constrained” strategy using Co₄ molecular clusters and Fe(acac)₃ implanted into N-doped carbon precursors derived from ZIF-8. Based on the HAADF-STEM image, the brighter Co/Fe species in the dodecahedral morphologies of Co₄/Fe₁@NC can be observed (Figs. 6(d) and 6(e)). The catalyst exhibits a highest ORR catalytic activity with an onset potential of 0.980 V vs. RHE and a half-wave potential of 0.835 V vs. RHE in acidic electrolyte surpassing the value of Pt/C (*E*_{1/2} = 0.814 V vs. RHE) (Fig. 6(f)) [120].

Modulating the electron redistribution of single metal active sites through multinuclear atomic clusters can optimize the adsorption/desorption process of the intermediates and decrease the energy barrier, which is an effective way to enhance the ORR activity [121–127]. The introduction of adjacent single atoms sites was proved to be a potential way to synergistically boost the ORR activity. The atom-cluster interaction can boost the performance of M-N-C catalysts for ORR. However, how to design atom-cluster

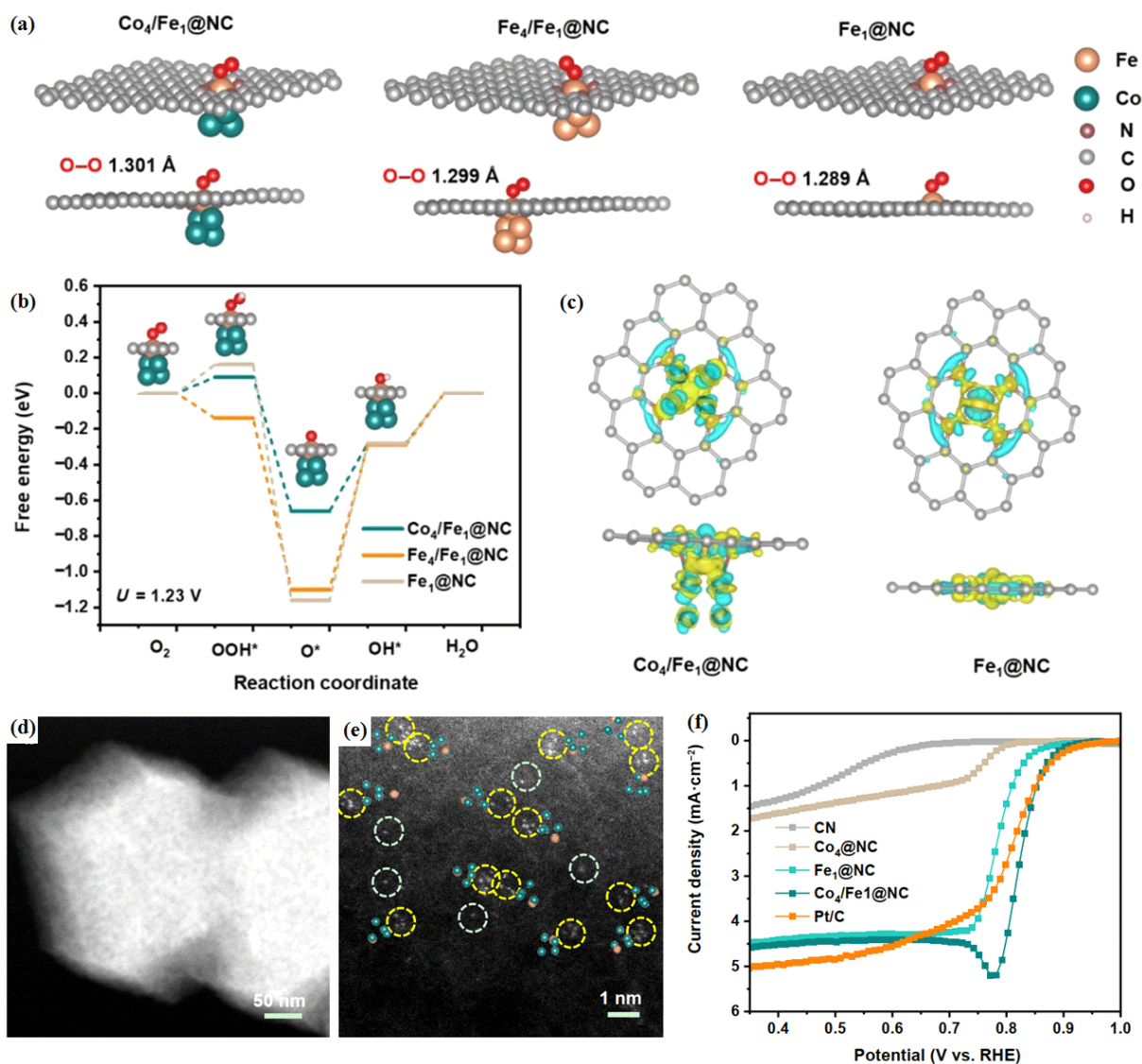


Figure 6 (a) O₂ adsorption models of Co₄/Fe₁@NC, Fe₄/Fe₁@NC and Fe₁@NC. (b) Gibbs free energy diagram for ORR on Co₄/Fe₁@NC, Fe₄/Fe₁@NC, and Fe₁@NC. (c) Charge density of Co₄/Fe₁@NC and Fe₁@NC. (d) Aberration-corrected STEM image of representative Co₄/Fe₁@NC substrates. (e) Atomic-resolution HAADF-STEM image of Co₄/Fe₁@NC revealing the atomically dispersed Co₄ ACs and Fe SACs, which are highlighted by yellow dashed circles. In the corresponding models, orange ball represents Fe atom, green ball represents Co atom. (f) ORR polarization curves of NC, Co₄@NC, Fe₁@NC, Co₄/Fe₁@NC, and Pt/C in O₂-saturated 0.5 M H₂SO₄. Reproduced with permission from Ref. [120], © Wiley-VCH GmbH 2023.

catalysts and revealing their structure-property relations are of great significance and remain a challenge. Luo and coworkers [128] demonstrated that the adjacent Cu-N₄ single atoms can improve the ORR activity through the introduction of atomic cluster (AC) of Fe₅-N-C, in which the Fe center was coordinated with four pyridinic N atoms. DFT studies suggested that Cu-N₄ SAs can serve as a regulator to promote O₂ adsorption and O-O bond cleavage on Fe AC, and optimize the release of OH* intermediates, which can accelerate the entire ORR kinetics. The diagram of Gibbs free energy (ΔG) for the intermediates (Fig. 7(a)), displayed that the rate determining step is OH* $\rightarrow$ H₂O with the lowest energy barrier of 1.06 eV on the Fe₅-Cu-N-C compared to other configurations at the potential of $U = 1.23$ V, demonstrating that the Cu-N₄ sites can

facilitate the release of OH* and accelerate ORR process. The differential charge density distribution (Fig. 7(b)) revealed that the introduction of Cu SAs can significantly induce electronic rearrangement of the Fe AC active sites. The EXAFS fitting results (Figs. 7(c) and 7(d)) indicate that the Fe and Cu atoms exist in the form of Fe-N₄, Fe₄ ACs and Cu-N₄ in Fe₅-Cu-N-mC structure. The Fe₅-Cu-N-mC catalyst exhibited the highest ORR performance with a half-wave potential of 0.92 eV vs. RHE compared with other catalysts, and remained 98.4% of its initial current density in alkali (Figs. 7(e) and 7(f)).

The exploration of the effect of clusters on single-atom sites and the universal synthesis strategy is highly significant but challenging. Peng et al. reported that ORR activity can be effectively modified by

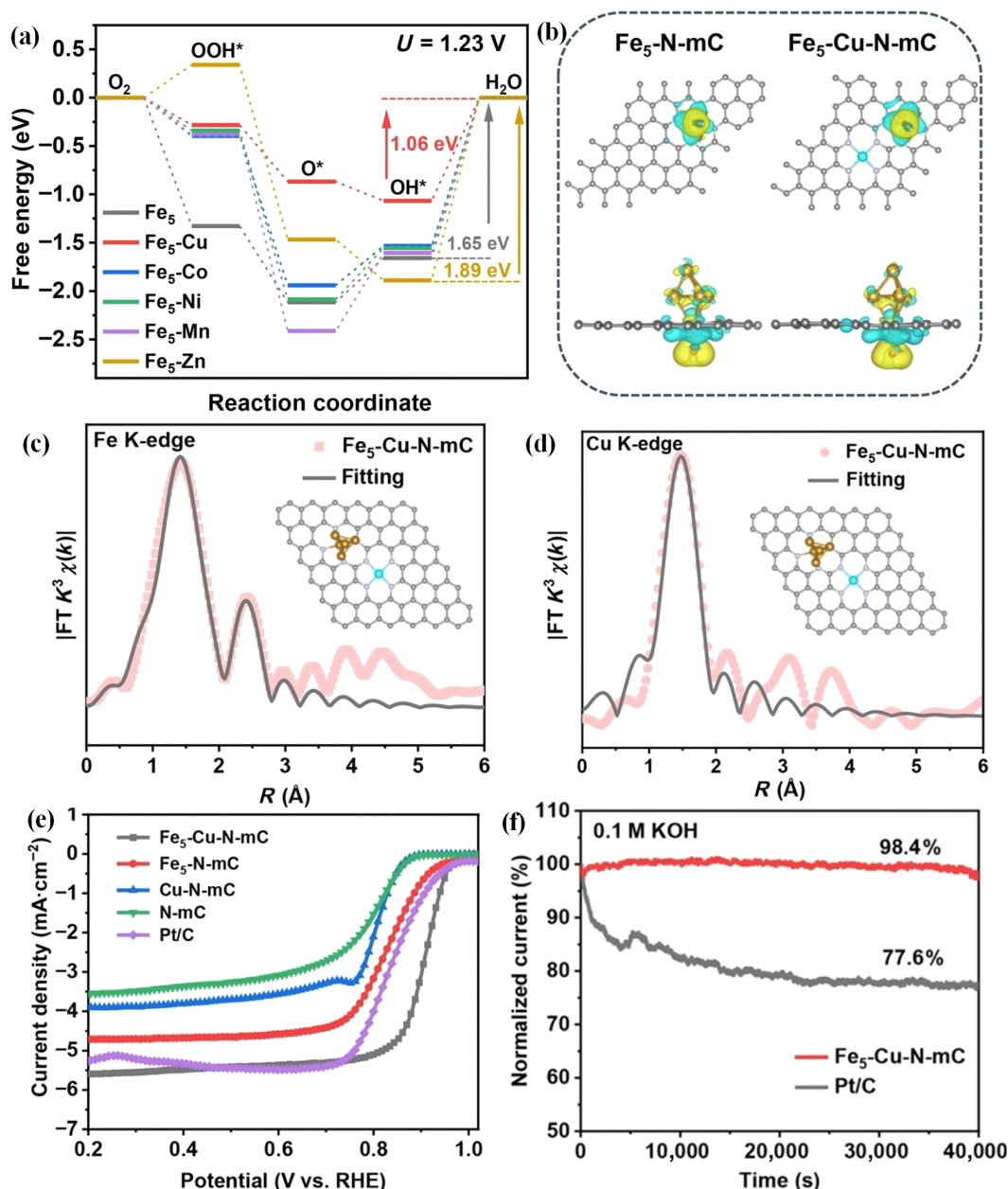


Figure 7 (a) Gibbs free energy diagrams of the models of Fe₅ clusters and the Fe₅ clusters with neighboring secondary metals introduced. (b) Top/side views of the differential charge density of Fe₅-N-mC and Fe₅-Cu-N-mC after *OH adsorption. (c) EXAFS fitting results at R space. (d) EXAFS fitting results at R space. (e) ORR polarization curves of electrocatalysts measured in 0.1 M KOH solution at 1600 rpm. (f) I-t curves at 0.7 V at a rotation speed of 1600 rpm in O₂-saturated 0.1 M KOH for Fe₅-Cu-N-mC and Pt/C. Reproduced with permission from Ref. [128], © Wiley-VCH GmbH 2023.

tuning the electron structure and optimizing the bond lengths of single-atoms via clusters induced electron redistribution. The single-atoms decorated with metal clusters on a nitrogen-doped carbon support (M-ACSA@NC, M = Fe, Co, Ni) was achieved by a coating-pyrolysis-acid etching strategy. Fe-ACSA@NC exhibited a half-wave potential of 0.90 V vs. RHE in alkaline media and delivered remarkable power densities in metal-air batteries. Theoretical analysis further reinforces the significant roles of cluster-induced charge transfer and redistribution between the atomic M-N-C sites and the carbon support, which configuration can facilitate the intermediates desorption for the ORR process [129].

The ORR activity of M-N-C in acidic electrolyte remains lower than that of Pt-based catalysts, and the instability of M-N-C in PEMFC mainly originates from the demetalation of M-N_x sites and the oxidation of carbon substrates. Increasing the activity and durability of the M-N-C active sites is essential but remains a challenge. The synergy of single-atom active sites and metal clusters are mostly applied in alkaline electrolyte due to the easily solubility of metal clusters in acids. However, if these clusters chemically bind to the carbon substrate and adjacent metal clusters have stronger electronic interactions with SACs, they will be acid stable in PEMFCs that operating under acid conditions. Shui et al. [130] reported a N-coordinated Fe clusters coupled with satellite Fe-N₄ active sites on 2D porous carbon (Fe_{SA}/Fe_{AC}-2DNPC) for ORR in acidic fuel cells. They found that the Fe clusters can optimize the adsorption strength of intermediates on satellite Fe-N₄ by introducing an OH ligand and shorten the amplitude of Fe-N bonds for ORR, which can reduce the ORR energy barrier. DFT calculations were utilized to study the role of Fe cluster in modulating the Fe-N₄ activity. The hybrid active site was built on graphene with Fe₄-N₆ cluster and an adjacent Fe-N₄-OH site, the distance of Fe SAC and Fe AC is 4.97 Å (Fig. 8(a)). They assumed a 4e⁻ ORR process on the Fe-N₄ site of Fe-N₄-OH/Fe₄-N₆ that proceeds through O₂^{*}, OOH^{*}, O^{*}, and OH^{*} (* denotes the adsorption site, Fig. 8(b)). The free energy diagrams calculated at 1.23 V were displayed in Fig. 8(c). The rate determine step on Fe-N₄ was the OH^{*} formation (O^{*} + H⁺ + e⁻ = OH^{*}), in which the energy

barrier was 0.53 eV. When the Fe cluster was grafted, Fe-N₄/Fe₄-N₆ showed a strong adsorption to OH ligand, the OH can optimize the binding strength of the Fe-N₄ and intermediates that greatly lowering the energy barrier to 0.35 eV.

The modulation of electron distribution of SACs by introduction of atomic clusters as multinuclear sites is an effective way to boost the ORR activity. However, the SACs and atomic clusters with the same metal active centers are mostly focused, and rare works about the atomic clusters and SACs with different metal centers are reported, which may be due to the difficulty in the synthesis. Han and co-workers reported the construction of isolated Mn-N₄ sites coexist with FeMn clusters anchored on defect-rich N-doped carbon support (FeMn_{ac}/Mn-N₄C) [131]. They performed DFT calculations to disclose the synergistic effects of Mn SACs and FeMn clusters on the ORR activity by studying the binding energies and the energy barriers of intermediates for FeMn_{ac}/Mn-N₄C. Three models of Mn-N₅C, Fe-N₅C and FeMn_{ac}/Mn-N₄C anchored on graphene were constructed in Fig. 9(a). The authors depicted the ORR process for FeMn_{ac}/Mn-N₄C under alkaline conditions in Fig. 9(b). From Fig. 9(c), it can be seen that the electron transfer pathways for the three models all displayed a spontaneous downhill free energy at U = 0 V. When increased the potential to U = 1.23 V, the Mn-N₅C and Fe-N₅C occurred endothermic process due to the second ORR step (OOH^{*} + e⁻ + H⁺ → OH^{*} + H₂O) is uphill, demonstrating the broken of O-O bond and the OH^{*} formation was sluggish. Theoretical calculations indicated that the FeMn_{ac}/Mn-N₄C was in favour of the O₂ adsorption and O-O bond broken and further promote the ORR kinetic process. FeMn_{ac}/Mn-N₄C was prepared by a strategy of post-adsorption and secondary pyrolysis using Mn-doped Cd-p-phenylenediamine complexes (CdMn-PPD) as precursor (Fig. 9(d)). The optimal FeMn_{ac}/Mn-N₄C catalyst exhibited an excellent ORR activity with a half-wave potential of 0.79 V vs. RHE in 0.5 M H₂SO₄ and 0.90 V vs. RHE in 0.1 M KOH, respectively (Figs. 9(e) and 9(f)). The above works indicate that the strong coupling effect of SACs and clusters is a potential strategy to improve the ORR activity and stability.

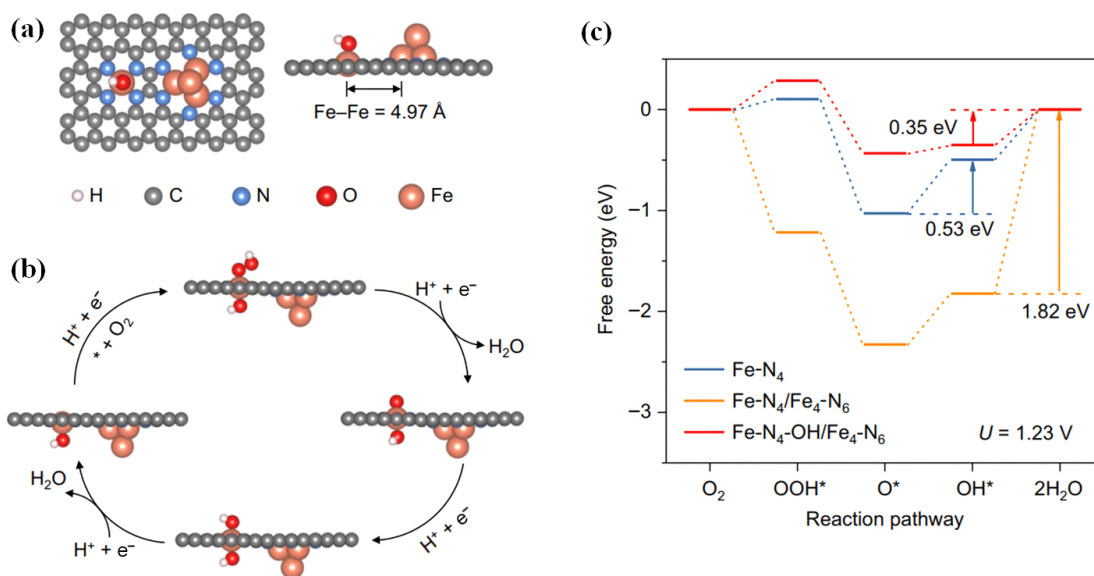


Figure 8 (a) Model structure of Fe-N₄/Fe₄-N₆ used for theoretical calculation with a spontaneously formed OH ligand. (b) Schematic ORR process on the Fe-N₄ site of Fe-N₄-OH/Fe₄-N₆. (c) Free energy diagrams at 1.23 V for ORR over three types of active sites of Fe-N₄, Fe-N₄/Fe₄-N₆, and Fe-N₄-OH/Fe₄-N₆. Reproduced with permission from Ref. [130], © Wan, X. et al. 2022.

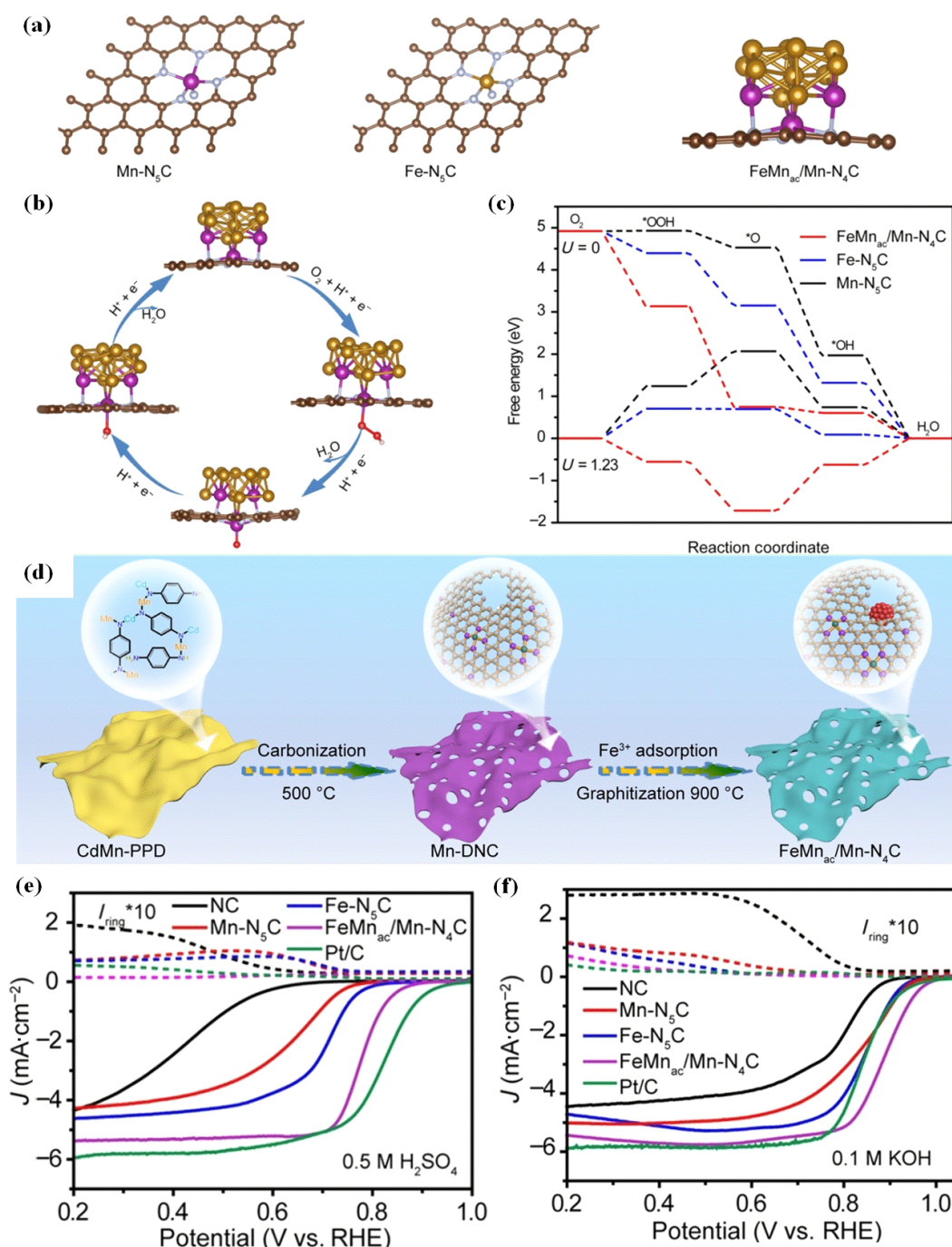


Figure 9 (a) Optimized atomic structures of Mn-N₅C, Fe-N₅C, and FeMn₄/Mn-N₄C. (b) Proposed ORR elemental steps for the FeMn₄/Mn-N₄C. (c) Free energy diagrams for Mn-N₅C, Fe-N₅C, and FeMn₄/Mn-N₄C at 0 and 1.23 V. (d) Schematic illustration for the preparation of FeMn₄/Mn-N₄C. (e) and (f) Electrochemical ORR performance O₂-saturated 0.5 M H₂SO₄ and 0.1 M KOH at 1600 rpm. Reproduced with permission from Ref. [131], © Wiley-VCH GmbH 2022.

2.3 Clusters for anode oxidation of alcohols, formic acids, and hydrogen

Polymer electrolyte membrane fuel cells (PEMFCs) utilizing alcohols and hydrogen as fuel source for anode oxidation have attracted great interest due to their less expensive, environmental friendliness, low operating temperature, low toxicity, portability, and high energy density. In comparison with hydrogen, some alcohols (methanol, ethanol, and polyalcohol or called polyhydric alcohol) are liquid at ambient temperature, which are easy to be transported and stored. However, the challenges remained in

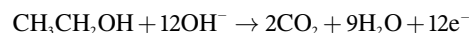
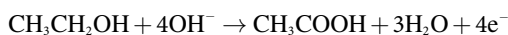
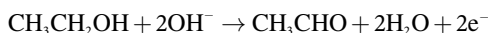
alcohol oxidation in PEMFCs, for example, it is difficult to completely oxidize alcohol due to the presence of C–C bond, and more and more adsorbed intermediates, such as CO, will appear during the anode oxidation process [132].

The commercially available catalysts for direct alcohol fuel cells (DAFCs) are platinum-based materials, but the main issues are the limited reserves, high cost sluggish alcohol oxidation kinetics, poor activity and stability, and poisoning susceptibility of Pt caused by strong adsorption of CO intermediates during the alcohol oxidation process, which can occupy the Pt active site, prevent the active site

from continuing to participate in the reaction, decrease the activity and stability of the overall electrode kinetics and be unfavorable for application prospects of DAFCs. Composite of Pt with other oxygenophilic metals to form Pt-M catalysts have been considered to be a promising strategy, which can not only reduce the amount of noble Pt, but also prevent poisoning effect of intermediates because the introduction of M can generate surface oxygenated species ($M-OH_{ads}$). $M-OH_{ads}$ can react with the CO intermediates, resulting in CO removal, and thus accelerating the reaction kinetics. For example, oxyphilic Ru species can generate adsorbed OH groups ($Ru-OH_{ads}$). $Ru-OH_{ads}$ can greatly accelerate the continued oxidation of toxic intermediates on Pt atoms ($Pt-CO_{ads}$) at lower potential, thereby accelerating the release of occupied active sites on the Pt surface to continue the alcohol oxidation process [133].

2.3.1 Clusters for alcohols oxidation reaction

DAFC, which employs methanol, ethanol, and polyhydric alcohol (such as ethylene glycol and glycerol) as fuels, has become an advanced energy conversion device to solve the energy crisis [134]. Methanol and ethanol are the widely used liquid fuels. The energy in direct methanol fuel cells (DMFCs) is obtained from the methanol oxidation reaction (MOR): $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ in acidic medium and $CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^-$ in basic medium. In the ethanol oxidation reaction (EOR) pathway, the dominant product is acetic acid and the number of electron transfers is $4e^-$ instead of $12e^-$ in the imperfect oxidation [135, 136]



The pyridinic N in g- C_3N_4 can capture Pt clusters by strong metal-support interactions to avoid the agglomeration of Pt. Chen et al. reported a molecular trapping strategy to stabilize Pt clusters on graphitic carbon nitride (g- C_3N_4) modified carbon nanotubes (CNT) for MOR (Fig. 10(a)). The integration of g- C_3N_4 on CNT played a critical role in optimizing the electronic structure and catalytic behavior of Pt catalysts, which can provide sufficient triple-phase boundaries and ensure fast reaction kinetics toward MOR. The CNT can provide fast electronic conductive and diffusive channels. The Gibbs free energies of the pathways during the MOR (Fig. 10(b)) on both Pt-g- C_3N_4 and Pt-CNT demonstrated that g- C_3N_4 could enhance the adsorption strength of intermediates and reduce the energy barriers. The incorporation of CNT can facilitate the accumulation of $-OH$ and reduce the activation energies of the dehydrogenation of CH_3OH , thus the absorbed poisoning intermediates were effectively eliminated. The potential regions between 0.8 and 1.0 V are associated with the CO_{ad} stripping process in 0.5 M H_2SO_4 , and the Pt-g- C_3N_4 -CNT showed a large ECSA values (Fig. 10(c)). Additionally, the Pt-g- C_3N_4 -CNT showed the highest current densities in comparison to Pt-AC and Pt-CNT catalysts, indicating high activities toward MOR in 0.5 M H_2SO_4 and 1 M methanol (Fig. 10(d)) [137].

Carbon dot (CD) can regulate the d-band center of Pt via resonance energy transfer, which promoted electron transfer between the Pt and CD with remarkable electrocatalytic activity. Niu et al. reported a PtRu cluster modified with fluorescent CD for MOR in acidic media [138]. When CH_3OH is adsorbed on the electrocatalyst, the continuous dehydrogenation of CH_3OH ($CH_2OH^* \rightarrow CH_2O^* \rightarrow CHO^*$) will be initiated, and the hydroxyl

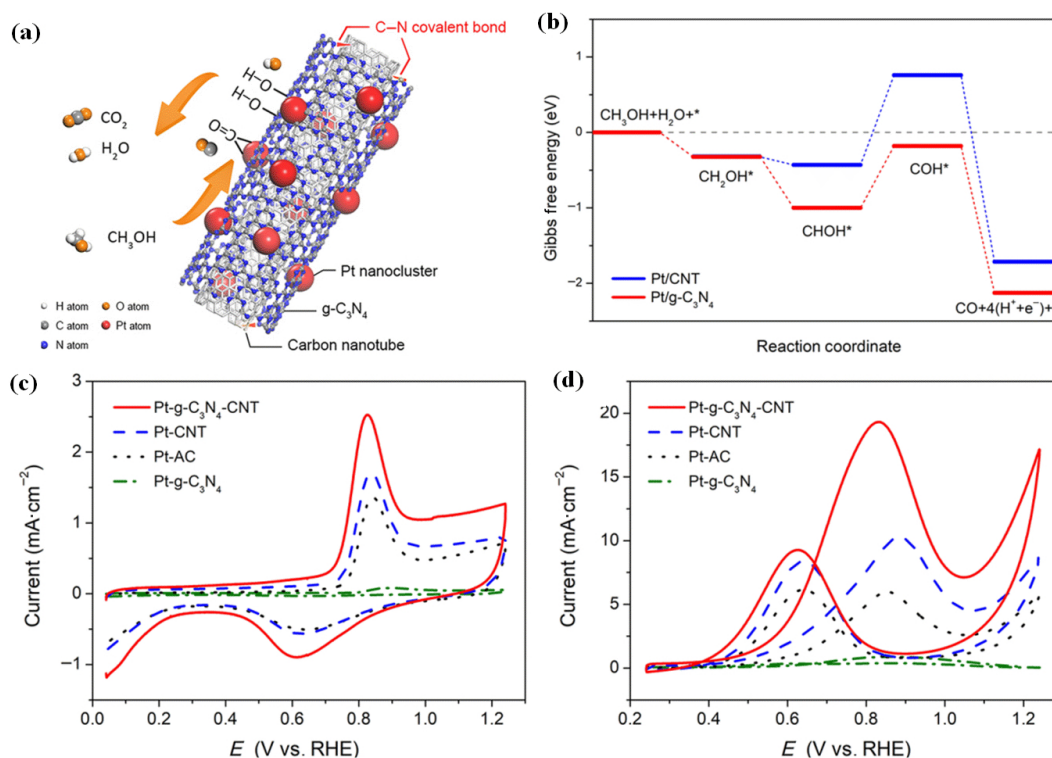


Figure 10 (a) Schematic diagram of the methanol electrocatalytic processes on the Pt-g- C_3N_4 -CNT catalyst. (b) Free energy diagram of methanol oxidation reaction on Pt/CNT and Pt-g- C_3N_4 . Cyclic voltammograms of Pt-g- C_3N_4 -CNT in comparison with Pt-CNT, Pt-AC, and Pt-g- C_3N_4 in (c) 0.5 M H_2SO_4 solution and (d) 0.5 M H_2SO_4 with 1 M methanol solution at a scan rate of $20 \text{ mV} \cdot \text{s}^{-1}$. Reproduced with permission from Ref. [137], © American Chemical Society 2019.

methyl intermediates (CH_3O^*) and H^* (surface adsorption of protons) will be formed. The effective dehydrogenation reaction on the PtRu-CDs (0.21 and -0.40 eV) proving that PtRu clusters are more conducive to forming CHO^* . The oxidation of COOH^* to CO_2 is the rate-determining step for the PtRu-CDs with a low energy of 0.35 eV. DFT calculations revealed that the process of

CO^* oxidation to CO_2 was $\text{CO}^* \rightarrow \text{COOH}^* \rightarrow \text{CO}_2$, with a reduced free energy barrier of 0.59 eV to remove the adsorbed CO^* (Fig. 11(a)). The excellent dehydrogenation and CO^* oxidation ability for the PtRu-CDs indicated good MOR activity. HRTEM image showed two lattice fringes, proving the interaction between CDs and Pt (Fig. 11(b)). The metal clusters were uniformly

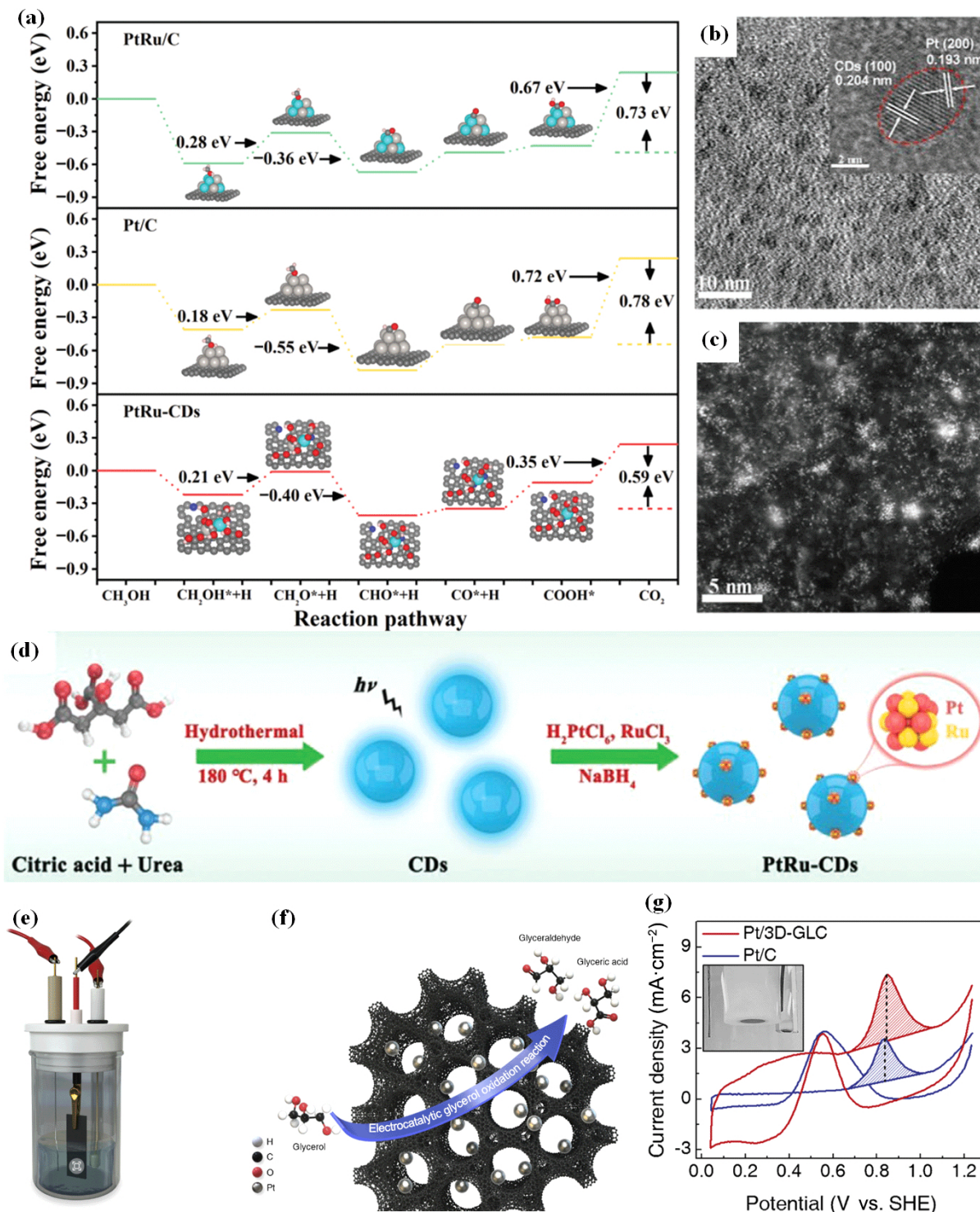


Figure 11 (a) Free-energy profiles recorded for MOR on PtRu/C, Pt/C, and PtRu-CDs (0 V vs. RHE). (b) HRTEM image and (c) HAADF-STEM image of PtRu-CDs-150. (d) Schematic diagram of synthesis of PtRu-CDs. Reproduced with permission from Ref. [138], © Wiley-VCH GmbH 2023. (e) An electrochemical batch reactor system and (f) electrocatalytic GOR over Pt/3D-GLC. (g) CV curves for the electrocatalytic GOR over Pt/3D-GLC and Pt/C in N_2 -purged 2 M glycerol + 0.5 M H_2SO_4 solution. The inset displays an electrochemical half-cell system having a three-electrode configuration. Reproduced with permission from Ref. [142], © Elsevier B.V. 2019.

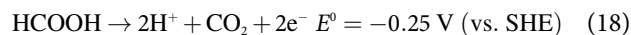
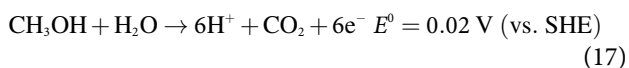
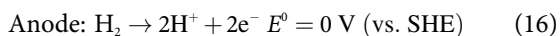
anchored on CDs by HAADF-STEM image (Fig. 11(c)), and Fig. 11(d) displayed the synthetic method of PtRu-CDs.

In addition to methanol and ethanol, DAFCs can also use polyalcohols as fuels to drive the alcohols oxidation reaction (AOR). Polyalcohols, such as ethylene glycol and glycerol, have attracted extensive attention due to its higher energy density, non-volatility and lower cost. However, most of catalysts are kinetically sluggish for the AORs that comprising multi-electron transfer pathways, methanol needs 6e⁻ to be transferred to achieve complete oxidation, not to mention polyalcohol. Due to the large amount of electron transfer and strong C-C bond breakage, the kinetics of polyol oxidation is more sluggish compared with the electrocatalysis process described above. The glycerol oxidation reaction (GOR) can be used as an example. Glycerol as a industrial raw material and a value-added byproduct in the synthesis of fatty acids and biodiesel is widely used in the area of food and pharmaceuticals. The glycerol production exceeds demand, thereby glycerol derivatives such as glyceraldehyde, dihydroxyacetone, glycolic acid, and glyceric acid by electrocatalytic oxidation becoming available. In DAFCs, the GOR can generate valuable chemicals, hydrogen and electrical energy [139, 140].

Single-atomic site decorated with clusters could synergistically boost the electrocatalytic activities. Yu et al. employed intermetallic PtCo integrated with Co single atom (PtCo/Co-N-C) for the aerobic oxidation of glycerol in direct ethanol fuel cell. The PtCo/Co-N-C catalyst exhibited a consistent open-circuit voltage of 0.6 V vs. RHE, demonstrating its promising practical application [141]. Kim et al. reported the Pt clusters loaded on 3D graphene-like carbon (3D-GLC) by zeolite template and Pt impregnation methods (Pt/3D-GLC) (Figs. 11(e) and 11(f)), demonstrating superior electrocatalytic activity for electrochemical GOR than that of commercial Pt/C [142]. The forward peak current density (*I_f*) of Pt/3D-GLC was 1.6-fold higher than that of Pt/C catalyst. The ratio of the *I_f* in the positive sweep and the reverse peak current density in the negative sweep (*I_r*) for Pt/3D-GLC displayed a larger value of *I_f*/*I_r* than that for Pt/C (Fig. 11(g)), demonstrating that the accumulation toxicity of carbonaceous intermediates is relatively low on the surface of Pt/3D-GLC during the GOR process.

2.3.2 Clusters for formic acids oxidation reaction

H₂ has been commonly used as fuel for PEMFCs, but facing the challenges of generation, storage, and handling, which limited its development and motivated researchers to explore liquid fuels for PEMFCs due to the fact that liquid fuels can greatly reduce the storage risks and transportation costs, and have proven the enormous potential in portable devices. Compared with alcohols, formic acid not only possesses the merits of nontoxic, low flammability, fast reaction kinetics and slow crossover rate, but also is a strong electrolyte that can facilitate proton conduction. Additionally, direct formic acid fuel cells (DFAFCs) (Fig. 12(a)) possess a much higher value of theoretical open circuit potential (1.48 V), compared with that of H₂-PEMFCs (1.23 V) and DMFCs (1.21 V) (Eqs. (16)–(19)) [143].



The main challenges in DFAFCs include the stability issue of formic acid oxidation (FAO) activity decay on anode catalysts and crossover effects of electrocatalysts poisoned by the permeated formic acid on cathode catalysts. The most promising FAO electrocatalysts should lean towards the direct pathway with weak binding to CO_{ads}. HCOOH can also be considered as the promising energy carrier for DFAFCs due to it have high volumetric H₂ storage capacity, which is initially decomposed into CO₂ and H₂ under the function of the anode catalyst, then H₂ is sent into a PEMFC system. The chemical energy in HCOOH can be indirectly converted into electrical energy, forming the formic acid-based H₂-PEMFCs (or called indirect formic acid fuel cells, IF AFCs, Fig. 12(b)) [144]. Whereas IF AFCs is confronted with major issues, i.e., contaminants of CO and CO₂ generated from HCOOH decomposition will result in catalyst poisoning effects, leading to a rapid decrease in catalytic activity. The FAO reaction occurred on Pt group metals is considered to through a dual pathway mechanism, including direct paths and indirect paths. In the direct pathway, HCOOH is directly oxidized to CO₂ through a dehydrogenation process forming active intermediates of COOH*. In the indirect pathway, HCOOH is decomposed into CO_{ads} via a dehydration process, which are then oxidized to CO₂. Due to the strong binding between CO_{ads} and Pt, the Pt active sites will be blocked, thereby the catalytic activity will be degraded (Fig. 12(c)) [145]. Thus, it is desirable to develop efficient catalysts to achieve the direct pathway to suppress the dehydration of HCOOH to suppress CO_{ads} accumulation. Developing HCOOH resistant cathode catalysts is a promising approach to address detrimental crossover effect. The strategies to design catalysts resistant to CO_{ads} poisoning including: (1) regulating the electronic structure of the active sites to suppress the production of CO_{ads}, (2) decreasing the binding strength of CO_{ads} to reduce the the occupation of CO_{ads}, and (3) introducing promoters that can facilitate CO_{ads} oxidation at lower potentials to improve anti-poisoning ability. The promoters are usually oxophilic species or elements, such as phosphides, oxides, or hydroxides of transition metals, which have strong affinity for OH_{ads} and the OH_{ads} species can more easily remove CO_{ads} [146, 147].

Thermodynamic analysis demonstrates that with the temperature decreasing, the Gibbs free energy of CO adsorption gets more negative. It means that CO adsorption is favored at low temperature and increasing temperature can dramatically improve CO tolerance, thus alleviating poisoning effect but high temperature will accelerate catalyst degradation. Therefore, electrocatalysts with high thermal stability that can bear elevated temperature are desired. Yan and co-workers synthesized a Pt-C₃N₄@CNT dispersed with triangular clusters of Pt atoms, serving as a FAO catalyst for DFAFCs [148]. The Gibbs free energy profiles of FAO mechanism of HCOOH on Pt-C₃N₄@CNT (Fig. 12(d)) indicated that HCOOH* can spontaneously generates CO* + H₂O(l) in the indirect route, then continuing to form CO* + OH* with endothermic reaction energies of 0.61 eV, finally producing CO₂ with endothermic reaction energies of 1.24 eV, which the two steps are thermodynamically unfavorable, and the rate-determining step is the process of CO₂ formation. In the direct route, the process of HCOOH* to form COOH* requiring a reaction energy of 0.11 eV.

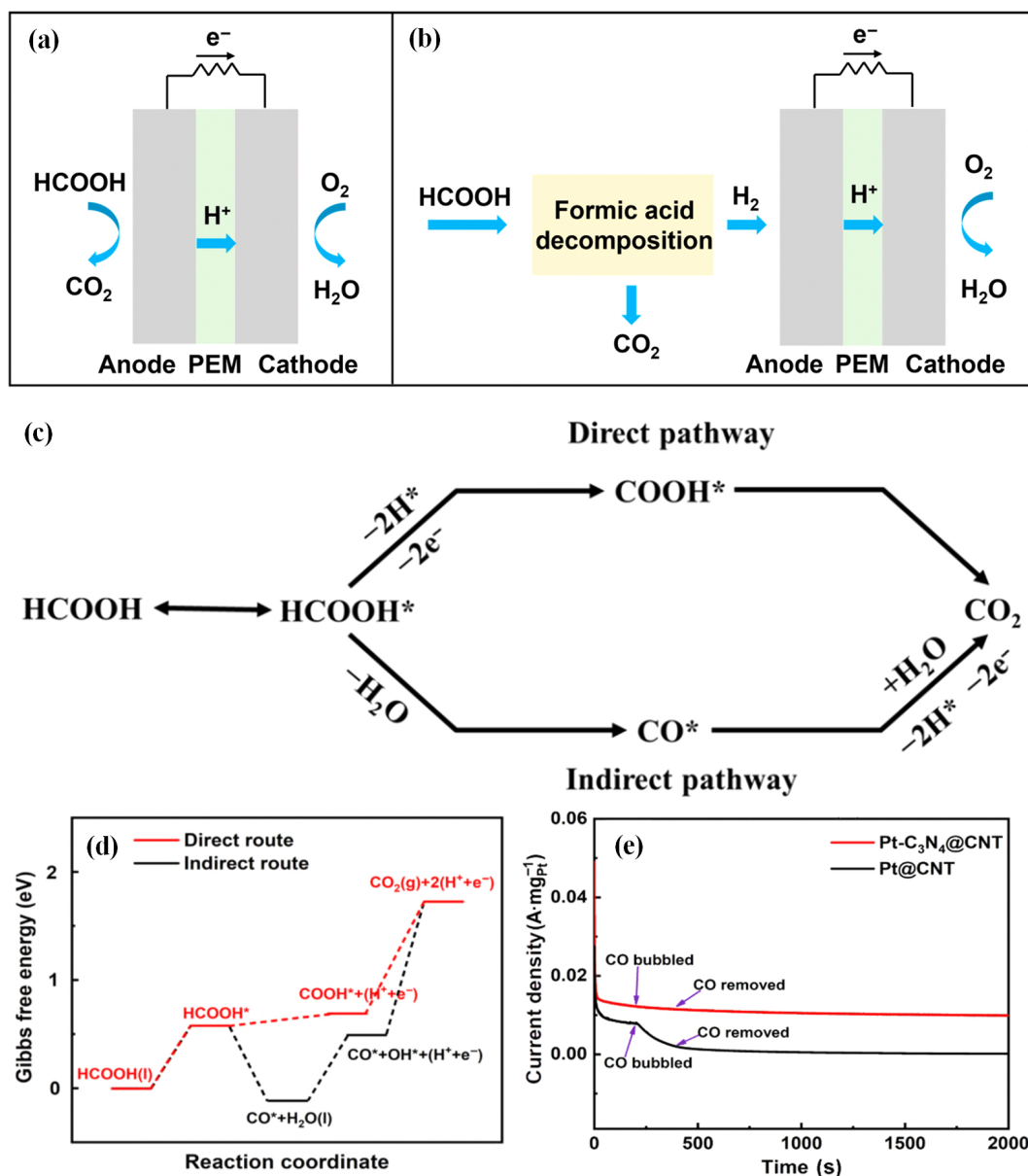


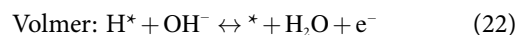
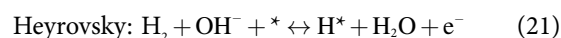
Figure 12 Schemes of (a) DFAFC and (b) IFAFC. Reproduced with permission from Ref. [144], © American Chemical Society 2016. (c) Reaction pathways of FAO on the surface of Pt. (d) Gibbs free energy profiles of formic acid oxidation via indirect and direct routes on the Pt-C₃N₄@CNT site. (e) CO poisoning experiment of Pt-C₃N₄@CNT and Pt@CNT in 0.5 M H₂SO₄ + 0.5 M HCOOH. Reproduced with permission from Ref. [148], © Li, C. et al. 2023.

The final step of COOH* conversion to CO₂ is an endothermic process, requiring a reaction energy of 1.04 eV, which is the rate determining step. The direct route demands less energy than the indirect one, therefore the direct route in Pt-C₃N₄@CNT offers a distinct advantage, and the FAO on the Pt-C₃N₄@CNT mainly follows the direct route with preferred intermediate of COOH*. To evaluate the poisoning resistance, CO was blown into the electrolyte using chronoamperometry (CA) method (Fig. 12(e)). The reduction of mass activity for Pt-C₃N₄@CNT was less than that of Pt@CNT when CO was introduced, proving that Pt-C₃N₄@CNT was an excellent anti-poisoning catalyst for FAO.

2.3.3 Clusters for hydrogen oxidation reaction

H₂ fuel cells are recognized as one of the most promising eco-friendly power supplies. The elementary process of hydrogen oxidation reaction (HOR) in alkaline including three reaction steps

(Eqs. (20)–(22)). In the Tafel–Volmer and Heyrovsky–Volmer mechanisms, H₂ is oxidized to H₂O [149, 150].



Pt-based anodic catalysts suffer from sluggish HOR kinetics in alkaline medium, which decreases the performance of fuel cells compared to acidic medium. Therefore, it is essential to develop effective electrocatalysts while reducing costs for HOR in alkaline medium [151]. The key strategy is to increase the complexity of Pt, especially in terms of composition and morphology. Developing Pt

with less expensive foreign metal atoms, such as Pt-Ru alloy, can significantly boost HOR performance, in which Ru is recognized as a promoter to improve the HOR performance of Pt in alkaline media [152–155]. Ru is much cheaper than Pt [156] and has high anti-CO poisoning capability and O₂ tolerance [157]. However, the passivation caused by excessive adsorption of oxygen species poses a challenge for individual Ru species in maintaining high current densities [158, 159]. Sun and co-workers developed a single atom-cluster multiscale structure (Fig. 13(a)) with isolated Pt single atoms coupled with Ru clusters supported on nitrogen-doped carbon

nanosheets (Pt_i-Ru/NC) enabled robust alkaline HOR performance for anion exchange membrane fuel cells (AEMFCs). The intensity of Pt is significantly heightened compared to adjacent Ru atoms, due to the larger atomic mass of Pt (Figs. 13(b) and 13(c)). Compared with Ru/NC, the current density of Pt_i-Ru/NC is greatly increased, and Pt_i/NC exhibited insufficient HOR kinetics, demonstrating that atomically dispersed Pt atoms served as a promoter in enhancing HOR activity. Meanwhile, when the potential exceeds 0.15 V vs. RHE, the HOR limiting current density of Ru/NC decreases sharply, indicating that the active sites of Ru

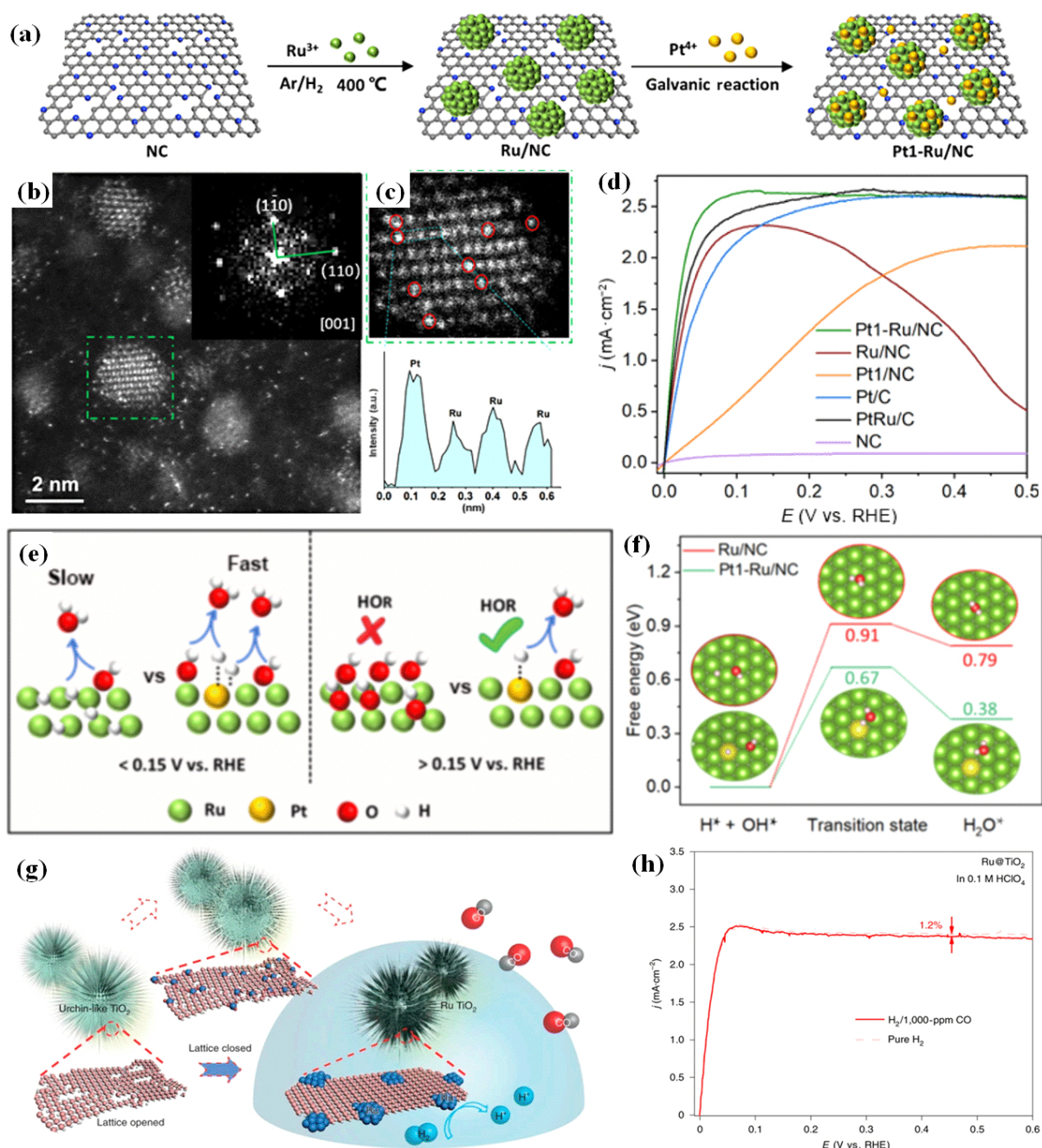


Figure 13 (a) Scheme illustration of the preparation of Pt_i-Ru/NC. (b) The zoom-in HAADF-STEM of Pt_i-Ru/NC and inset in (b) is the FFT pattern. (c) The magnified image in green box of (b). (d) HOR polarization curves of different catalysts in H₂-saturated 0.1 M KOH solution at a rotating speed of 1600 rpm with a scan rate of 2 mV·s⁻¹. (e) Schematic illustration of the enhanced alkaline HOR mechanism of Pt_i-Ru/NC. (f) Free energy diagrams of the elementary step of HOR on pure Ru and Pt_i-Ru. Reproduced with permission from Ref. [160], © Tsinghua University Press 2024. (g) Synthesis of Ru@TiO₂ electrocatalyst. (h) The HOR catalytic performance of Ru@TiO₂ in 0.1 M HClO₄ containing CO. Reproduced with permission from Ref. [161], © Zhou, Y. Y. et al. under exclusive licence to Springer Nature Limited 2020.

are gradually passivated by oxygen-containing species, such as OH^* and O^* . However, the limiting current density of $\text{Pt}_1\text{-Ru/NC}$ remains stable, indicating that the modification of atomically dispersed Pt can effectively protect Ru clusters from the toxicity of excessive oxygen-containing species (Fig. 13(d)). In their work, theoretical calculations demonstrate that the isolated Pt sites can participate in the adsorption of H^* and OH^* , weakening the Ru–H bond strength, and synergistically accelerate the Volmer step, thereby suppressing the over occupation of oxygen-containing species on Ru clusters (Fig. 13(e)). The energy barriers required for the reaction of H^* and OH^* significantly decreases from Ru to $\text{Pt}_1\text{-Ru}$ in the free energy diagrams (Fig. 13(f)) [160]. Wei et al. synthesized Ru clusters stabilized in the urchin-like TiO_2 (Ru@TiO_2), which displayed a higher HOR activity in acidic and alkaline media, and exhibited an excellent CO tolerance with 1000 ppm CO in 0.1 M HClO_4 (Figs. 13(g) and 13(h)) [161]. The blockage of CO adsorption was ascribed to the effective electron transfer from electron-rich TiO_2 to Ru clusters.

Traditional Pt/C catalysts for alkaline HOR are plagued by ultra-low catalytic efficiency, excessively high Pt dosage, poor durability caused by low CO resistance [162, 163]. The competition between the adsorption–desorption of reaction intermediates (such as H^* and OH^*) and CO on the surface of electrocatalysts is the key factor for the low catalytic activity and poor CO resistance [164–166]. Xing et al. developed a highly oxophilic rare-earth lanthanide (e.g. La, Ce, Pr, Nd, and Lu) single-atom embedded into ultrasmall Pt clusters ($\text{Ln}_1\text{Pt NCs}$) electrocatalyst for alkaline HOR by vapor filling and hollow carbon sphere (HCS) limited metal species reduction method. Both Ln_1 single-atom and ultra small size of Pt NCs can improve atomic utilization efficiency. Mechanism studies revealed that oxophilic single-atom Ln_1 can serve as Lewis acid site to selective absorb OH^- and modify the d-band center to adjust the binding strength of H^* and CO intermediates on Pt sites, while Pt NCs can selectively absorb H^* to prevent competitive absorption–desorption behavior. By prompting the removal of H^* and CO , the electron transfer in HOR kinetics and CO oxidation are accelerated, thereby the mass activity of the electrocatalyst is higher than that of

commercial Pt/C with an enhanced CO tolerance [167]. For nanocluster catalysts with precise atomic landing, the adjacent metal sites and synergistic catalytic effects break the limitation of single-site catalysis in SACs, ultimately improving the catalytic performance.

Controlling the preparation of atomically precise multi-nuclear metal precursors while achieving highly uniform dispersion and stable strong interactions of nanoclusters on supports, remains a challenge [168, 169]. It is very meaningful to prepare a unique catalyst with ultra-small size, definitive composition, uniform chemical coordination environment and homogeneous structure. Tian and co-workers designed a Pt_6 nanocluster catalyst stabilized on oxidized carbon nanotubes (Pt_6/OCNT) by a ligand engineering strategy, which exhibited an excellent stability, good CO tolerance and outstanding acidic HOR activity. DFT calculations indicated that Pt_6 cluster can change the hydrogen adsorption energy, thereby reducing the theoretical overpotential of HOR. Their work provides insights into exploration the impact of nanocluster configuration and atomic number on catalytic activity for future exploration [170].

2.4 Clusters for water splitting

Water splitting by electrocatalysis has been acclaimed as a renewable and clean energy conversion technology to generate high-purity H_2 on the cathode and O_2 on the anode (Fig. 14(a)) [171]. However, the key challenges for water splitting requires highly efficient and durable catalysts to lower the energy barrier and the overpotential. Compared to traditional fossil fuels, H_2 produced from electrochemical HER is recognized as one of the most alternative fuels due to the advantage of high energy density and its non-polluting products with the direct use of H_2O as a raw material. SACs have emerged as one of promising candidates for cathodic HER and anodic OER electrocatalysts to replace well-known bench marking Pt/C and $\text{RuO}_2/\text{IrO}_2$, but the simplicity of the active centers limited their electronic properties manipulation to further boost the overall energy efficiency of water splitting. Thus, the synergistic effects of clusters with multiple active centers

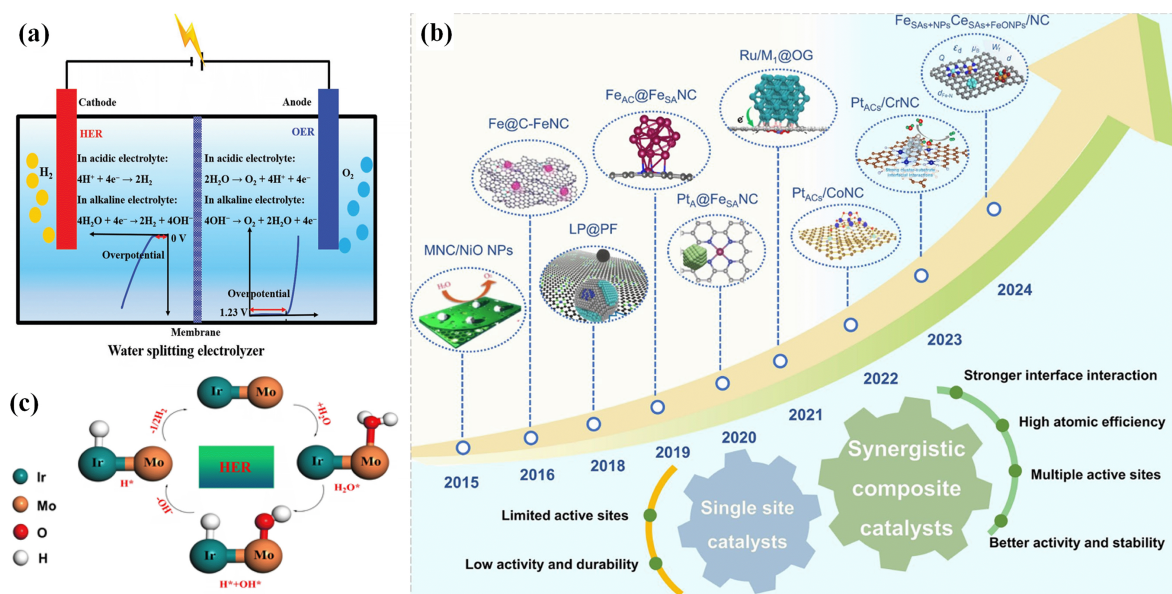


Figure 14 (a) Schematic illustration of water-splitting electrolyzer and related reaction kinetics. Reproduced with permission from Ref. [171], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2019. (b) The progress of synergistic composite catalysts over the past years. Reproduced with permission from Ref. [172], © Luo, G. Y. et al. 2024. (c) Schematic representation of the alkaline HER mechanism for IrMo. Reproduced with permission from Ref. [178], © American Chemical Society 2023.

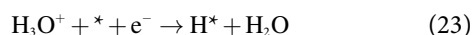
provides a new opportunity to explore efficient HER/OER electrocatalysts (Fig. 14(b)) [172, 173].

2.4.1 Hydrogen evolution reaction (HER)

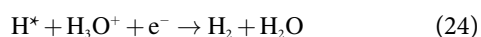
The HER generally proceeds either the Volmer–Heyrovsky or the Volmer–Tafel mechanism. In other words, it firstly proceeds via Volmer reaction, subsequently Heyrovsky or Tafel reaction, as illustrated in the following equations. Both the mechanisms above include two processes: intermediate hydrogen adsorption and desorption of H₂, and the difference between them is the step of H₂ desorption [174–177].

In acidic electrolyte:

The intermediate hydrogen adsorption for Volmer reaction



The desorption of H₂ for Heyrovsky reaction

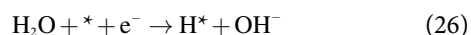


The desorption of H₂ for Tafel reaction

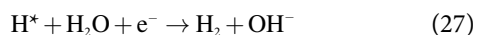


In alkaline electrolyte:

The intermediate hydrogen adsorption for Volmer reaction



The desorption of H₂ for Heyrovsky reaction



The desorption of H₂ for Tafel reaction



Yang and co-workers synthesized a cucurbit[6]uril-derived porous carbon host via a template-free route and loaded it with IrMo clusters for efficient alkaline HER [178]. Because the Mo site binds H₂O more strongly than Ir, water spontaneously anchors at Mo centers within the Ir(111)-Mo surface. Compared with Ir(111), the d-band center of Ir(111)-Mo shifts to a higher energy that lies closer to the Fermi level, enhancing the H₂O adsorption. Finally, the Volmer step is facilitated and the catalytic activity is boosted. The proposed mechanism is illustrated in Fig. 14(c).

Metal–support interaction plays a vital effect in triggering the hydrogen spillover to boost HER. It requires metals with rich electronic state to promote proton adsorption/spillover. However, the rich electronic state is not compatible with the electron-donating OER in proton-poor alkaline conditions. Dai and co-workers supported Ir clusters on NiPS₃ layers (Ir/NiPS₃) to study the Ir electronic states in alkaline hydrogen spillover [179]. As expected, the Ir/NiPS₃ heterostructure shows Pt-beyond activity with a low overpotential of 23 mV at 10 mA·cm⁻² and a small Tafel slope of 32 mV·dec⁻¹ in 1M KOH electrolyte. The Janus electron-rich at the tip and electron-poor states at the interface of Ir clusters facilitate the spillover process. Generally, the HER in alkaline electrolyte involves a slow Volmer step ($\text{H}_2\text{O} + * + \text{e}^- \rightarrow \text{H}^* + \text{OH}^-$), where the adsorption of protons and the generation of H_{ad} should be prerequisites for hydrogen spillover. In order to facilitate proton adsorption, metals in electron-rich states are needed to form electrostatic interactions. Due to the physical tip enhancement effect, electrons will accumulate in the top region of the metal (Fig. 15(a)). Therefore, Janus electronic states will be formed at the

interface (e⁻-deficient) and top (e⁻-rich) of the supported metal Ir clusters, enhancing the spillover effect of alkaline HER.

Lian et al. encapsulated single-atom platinum (Pt_{SA}) and cluster platinum (Pt_C) within a nitrogen-doped porous carbon matrix (Pt_{SA}-Pt_C/NDPCM) to achieve high effective performance across a broad range of pH, particularly in neutral and alkaline solution (Fig. 15(b)) [180]. Through DFT and *operando* Raman characterization, it has been established that the coexistence of Pt_{SA} and Pt_C offers numerous sites for hydrogen adsorption. This results in a localized acidic microenvironment, initiating a unique H₃O⁺-induced water reduction in both alkaline and neutral environments, leading to a remarkably low |ΔG_{Hi}*| for hydrogen adsorption. The Pt_{SA}-Pt_C/NDPCM demonstrated exceptional catalytic performance, achieving an ultra low overpotential of 14 mV vs. RHE at -10 mA·cm⁻² in a 1.0 M potassium phosphate buffer solution (pH = 7), and 20 mV vs. RHE at the same current density in alkaline solution (1 M KOH).

Lu and co-workers incorporated Pt atomic clusters (Pt ACs) into Co/N co-doped carbon (CoNC) substrate as highly efficient electrocatalyst (Pt-ACs/CoNC) for HER in 0.5 M H₂SO₄ [181]. The isolated Co atoms in CoNC serve as the anchoring sites to stabilize Pt ACs (Fig. 15(c)). The charge redistribution in the active moiety Pt-O-Pt of Pt ACs contributes to the enhancement of hydrogen evolution activity. In the Pt-O-Pt unit, the oxidation state of Pt is lower than that of the Pt atoms present in SACs. This phenomenon is due to the lesser extent of charge delocalization from Pt to the neighboring oxygen atoms in the Pt-ACs/CoNC configuration. These Pt atoms are recognized as the primary active sites for hydrogen evolution, while the oxygen linkers further aid in the transfer of adsorbed H⁺ and the desorption of H₂ molecule. The as-designed Pt-ACs/CoNC demonstrates superior catalytic performance for HER, needing only 24 mV vs. RHE of overpotential to reach the current density of 10 mA·cm⁻². Additionally, at an overpotential of 50 mV vs. RHE, the mass activity of Pt-ACs/CoNC is 28.6 A·mg⁻¹, outperforming the commercial 20 wt.% Pt/C catalyst under the same experimental conditions.

Wang and co-workers improve the kinetics of alkaline hydrogen evolution by fine-tuning the microenvironment of Pt species and the heterointerfaces between metal oxide [182]. Isolated PtRu bimetallic clusters were deposited onto the MO_{2-x} (M = Sn and Ce) particles on carbon nanotubes (PtRu/CNT@MO_{2-x}) through an electrochemical reduction process. The enhanced HER activity of platinum clusters compared to platinum single atoms on CNT@MO_{2-x} (M = Sn, Ce) can be attributed to the differing dissociation energy barriers that arise from the configuration of H₂O adsorption. Concurrently, the optimization of the support, regulation of platinum species, and modification with ruthenium facilitated an accelerated Volmer reaction and improved kinetics for H⁺ desorption, effectively balancing the adsorption and dissociation processes of hydrogen and water (Figs. 15(d) and 15(e)). Finally, PtRu/CNT@CeO_{2-x} exhibits outstanding HER activity with an acid-like Tafel slope of approximately 38 mV·dec⁻¹ in 1 M KOH solution. It demonstrates an overpotential of merely 75 mV vs. RHE at the current density of 100 mA·cm⁻². The remarkable mass activity of 12.3 mA·μg⁻¹_{Pt+Ru} are 56 times greater than that observed for commercial 20 wt.% Pt/C at the overpotential of 70 mV.

The catalytic activity of HER mainly depends on the inherent electronic properties, surface structure and active sites of catalysts. Well-designed clusters with controlling morphology and fine-

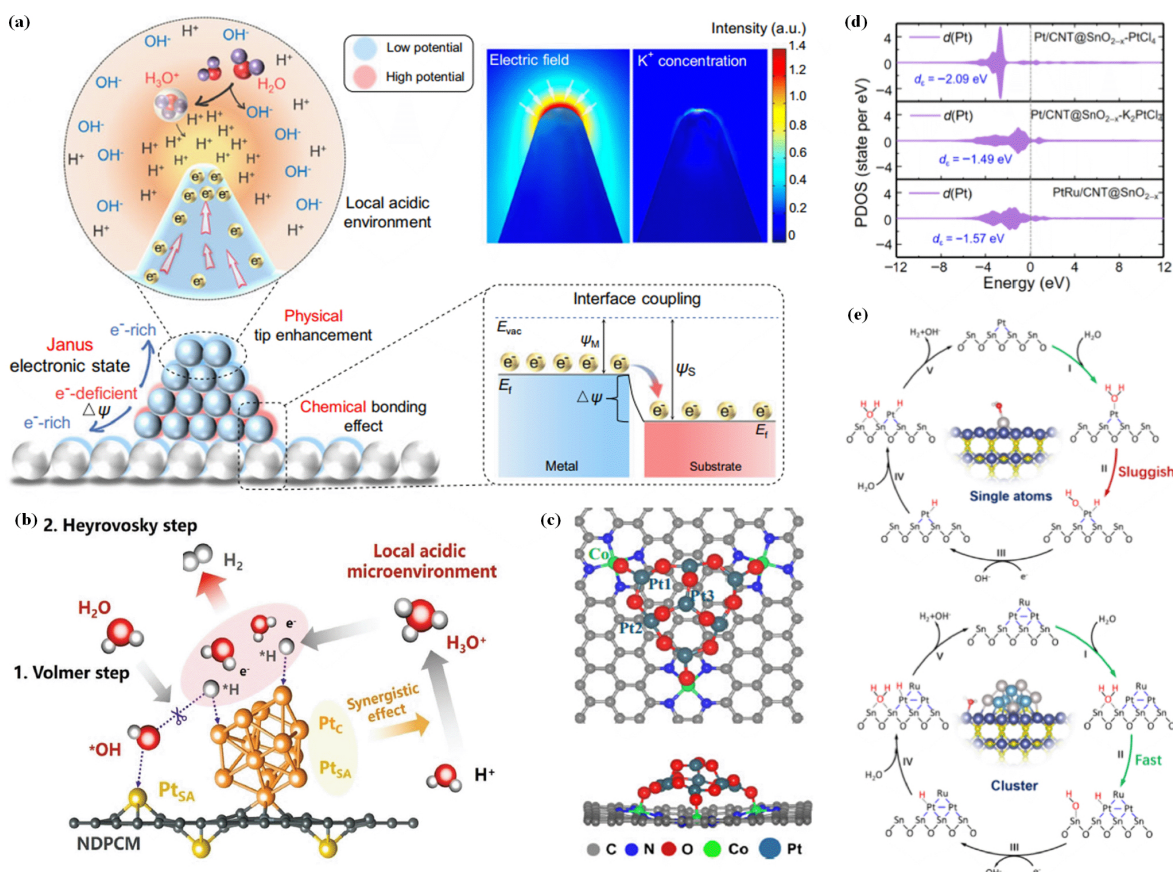


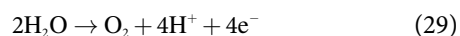
Figure 15 (a) Physicochemical perspective on the Janus electronic state in a metal-support architecture. Reproduced with permission from Ref. [171], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2019. (b) Illustrative diagram of the mechanism in the HER processes of Pt SA-PtC/NDPCM. Reproduced with permission from Ref. [180], © Wiley-VCH GmbH 2023. (c) The top and side view of the atomic structure of Pt-ACs/CoNC. Reproduced with permission from Ref. [181], © Zhao, Y. F. et al. 2022. (d) PDOS of the Pt atoms in Pt/SnO_{2-x}, Pt₁₀/SnO_{2-x}, and Pt₅Ru₅/SnO_{2-x} with aligned Fermi level. (e) Proposed alkaline HER pathways on Pt single-atom catalysts (up) and Pt cluster catalysts (down). Reproduced with permission from Ref. [182], © American Chemical Society 2024.

tuning microenvironment can provide more active sites and increase electrocatalytic reaction rates. Inducing compressive/tensile strain through atomic substitution strategy, the electronic structure can be altered, thereby influencing the electron overlap of the d orbitals and inducing charge redistribution to enhance reaction activity. This not only promotes the electron transfer of d-d orbitals, but also triggers a transition in the spin state of d-orbital electrons.

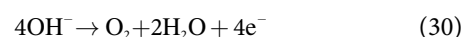
2.4.2 Oxygen evolution reaction (OER)

Exploring high-performance OER electrocatalysts has become imperative for various energy-related electrolysis systems, such as water splitting and rechargeable batteries. OER is key reaction for the electricity-driven water splitting to hydrogen production. However, the OER is more kinetically sluggish than HER, because OER is a multi-step 4e⁻ transfer process (Eqs. (29) and (30)) associated with O-H bond cleavage and O-O bond formation, and involving multiple intermediates (OOH*, OH*, and O*) [183], which is the main bottleneck in improving water splitting efficiency, severely restricting large-scale hydrogen production.

Overall reaction in acidic electrolyte:

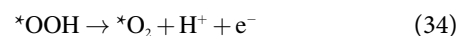
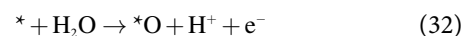
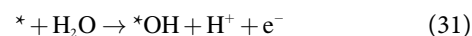


Overall reaction in alkaline or neutral electrolyte:

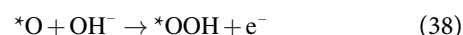
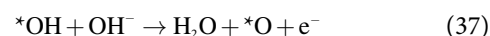
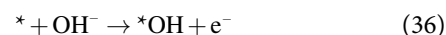


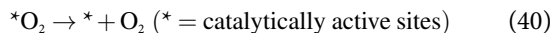
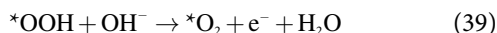
The detailed OER mechanism (Fig. 16(a)) can be described as follows [184–187]

In acidic electrolyte



In alkaline electrolyte





Understanding the OER mechanism is crucial for developing efficient catalysts in order to accelerate reaction kinetics. Adsorbent evolution mechanism (AEM) and lattice oxygen mediated mechanism (LOM) are widely accepted as two OER mechanisms [188, 189]. There is a linear scaling relationship between the free energies of different intermediates, and the thermodynamic and kinetic trends of ORR can be described by the binding energies of intermediates. Moreover, the binding energy is related to the d-band center, which links the electronic structure with catalytic activity. Thermodynamics and kinetic volcano curves are the foundation for understanding the ORR mechanism.

The high cost and restricted availability of precious metal alloys greatly limit their widespread application. Moreover, transition metal compounds with poor conductivity are detrimental to electrochemical reactions. Although single-atom catalysis has great potential for applications due to the high utilization and activity of each atom, SAC is confronted with issues of its simple structure and lack of synergistic effects of catalytic sites in more complicated multi-elementary reactions, due to the different adsorption energies of various intermediates. Due to the high surface free energy of metals in single atoms, they are prone to aggregation. In order to maintain a uniform single atomic structure, the metal loading is strictly limited.

Integrating SACs with clusters into a unified catalyst is an effective strategy to resolve the aforementioned disadvantages through synergistic effects. The advantages of the synergistic effect of SACs coupled clusters are mainly reflected in the following two aspects. Firstly, the coupling of atomic clusters adjacent to the SACs can break the local charge symmetry of M-N_4 , further regulating the electronic configuration, optimizing the binding strength of oxygen intermediates and lowering reaction energy barriers. Secondly, clusters exhibit pinning effects on SACs, inhibiting their demetallation and enhancing the stability of M-N bonds. Small clusters with different coordination structures have shorter interaction distances, resulting in stronger electronic interactions and promoting modulation of electronic structures [190, 191]. As a modifier, the addition of clusters with more exposed active sites can facilitate the redistribution of electronic structure, improve the adsorption/desorption process of reaction intermediates, and accelerate reaction kinetics [192]. However, the physical essence of synergy from the aspects of orbital hybridization, spin coupling and its regulatory mechanism on the reaction pathway are worthy of in-depth study. Through PDOS analysis, Zhang et al. demonstrated that the incorporation of In clusters can induce asymmetrical charge redistribution of FeN_4 sites via p-d orbital hybridization interaction between In 5p and Fe 3d orbital to optimize adsorption/desorption behaviors of key intermediates, thereby achieving superior bifunctional electrocatalytic activity for the ORR and OER. In addition, the asymmetric electron distribution of Fe 3d orbitals indicates the existence of highly active unpaired electrons in the Fe center, thereby reducing the reaction energy barrier and accelerating the reaction kinetics [193].

DFT calculations reveal the synergistic interaction between SACs and clusters in regulating the adsorption/desorption of ORR intermediates. It was demonstrated that Fe_{AC} could influence the electronic properties of Fe-N_4 sites, optimizing the formation energy of OH^* , thus facilitating the ORR process. Sun et al.

demonstrated that $\text{Fe}_{\text{SA}}/\text{Fe}_{\text{AC}}\text{-NC}$ shows typical ferromagnetic properties at 300 K, and the saturation magnetic susceptibility of the $\text{Fe}_{\text{SA}}/\text{Fe}_{\text{AC}}\text{-NC}$ is $0.17 \text{ emu}\cdot\text{g}^{-1}$, in which Fe_{AC} can regulate the spin properties of FeN_4 . The $\text{Fe}_{\text{SA}}/\text{Fe}_{\text{AC}}\text{-NC}$ exhibits pronounced electron density near the Fermi level, indicating the existence of free electrons due to the introduction of Fe clusters. The rate-determining step on the Fe-N_4 for ORR is the formation of OH^* , in which the energy barrier is 0.44 eV. When the Fe cluster was introduced, the adsorption energy of OH^* was enhanced due to the electronic interaction of Fe_{AC} with Fe-N_4 , effectively lowering the energy barrier to 0.31 eV and improving the ORR reaction kinetics [194]. Ni et al. demonstrated that $\text{Fe-N}_4\text{SACs}/\text{Fe}$ atomic clusters coupling active sites play a dominant role in O-O bond cleavage. Based on the PDOS analysis, the d-band center for $\text{CMNCA-Fe}_{\text{SA+AC}}$ is closer to the Fermi level, indicating the optimized orbital hybridization behavior around Fe sites [195]. Hu et al. found that for asymmetrically coupled $\text{Fe}_{\text{AC}}\text{-Fe}_{\text{SA}}\text{-Ni}_{\text{SA}}$ trinuclear centers, Ni_{SA} sites can induce strong electronic coupling, facilitate charge redistribution, elevate the d-band center, and lower the reaction barriers for intermediates, which can rapidly enhance the release of $^*\text{OH}$ towards ORR and the effective conversion of $^*\text{O}$ to $^*\text{OOH}$ towards OER [196].

Bao et al. reported a heterogeneous catalyst integrating Ir single atoms and Co clusters onto a N-doped carbon substrate ($\text{Co}_n\text{Ir}_1/\text{N-C}$) [197], which exhibited a remarkable OER activity compared with single-site catalyst of $\text{Co}_n\text{-(Co}_n/\text{N-C)}$. Ir single atoms and Co clusters are anchored onto the nitrogen-doped carbon support through an electrochemical deposition method. The heterogeneous Ir single atom and Co cluster accelerate OER dynamics through a remote geometric effect that adjusted the configuration of the intermediates. Projected density of state (PDOS) calculation was performed to analyze the electronic structure of Co in $\text{Co}_n\text{Ir}_1/\text{N-C}$ and $\text{Co}_n/\text{N-C}$. The Co d-band center of $\text{Co}_n\text{Ir}_1/\text{N-C}$ was measured at -2.22 eV , while in $\text{Co}_n/\text{N-C}$, it was at -2.22 eV . This elevation of the d-band center in $\text{Co}_n\text{Ir}_1/\text{N-C}$ improves the binding affinity of Co with intermediates during reaction, which then would promote the efficiency of the OER process (Figs. 16(b)–16(d)). As a result, the $\text{Co}_n\text{Ir}_1/\text{N-C}$ revealed superior catalytic activity, requiring a small overpotential about 262 mV vs. RHE at $10 \text{ mA}\cdot\text{cm}^{-2}$ and achieving a TOF of 1.68 s^{-1} at an overpotential of 300 mV in 1.0 M KOH.

Che et al. prepared a composite with Fe clusters and Fe SAs on N-doped carbon nanotubes ($\text{Fe}_3\text{C-NCNTs}$) through chemical vapor deposition [198] as shown in Fig. 16(e). In contrast to the sample without Fe nanoclusters, those with Fe clusters demonstrate strong electron redistribution, as evidenced by off-axis electron holography. This suggests that the synergistic atom-cluster interaction has been modulated. The presence of Fe clusters alters the electron distribution around Fe SACs, accelerates OH^* desorption, and thus enhances the electrocatalytic activity of OER, as demonstrated by DFT. The OER activity is dramatically boosted in contrast with the sample without Fe clusters.

Compared to cathodic HER, anodic OER catalyst has slower reaction kinetics, lower durability under high pressure, and faces issues of over oxidation and dissolution in oxidative environments. The atomic clusters coupling active sites can induce strong electronic spin coupling, facilitate the asymmetric charge redistribution via highly active unpaired electrons, optimize the d-band center via p-d orbital hybridization, and further regulate the adsorption/desorption for intermediates due to the synergistic interaction between SACs and clusters.

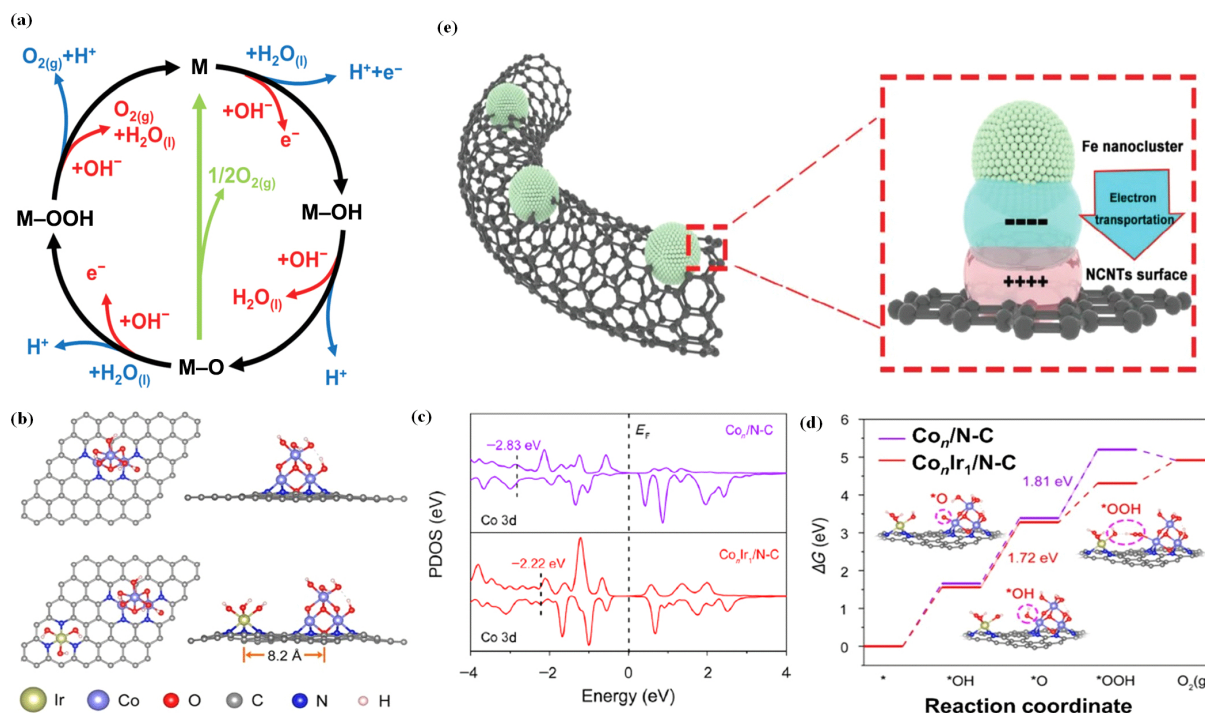


Figure 16 (a) The OER mechanism for acid (blue line) and alkaline (red line) conditions. The black line indicates that the OER involves the formation of a peroxide (M-OOH) intermediate (black line) while another route for direct reaction of two adjacent oxo (M-O) intermediates (green) to produce oxygen. Reproduced with permission from Ref. [184], © Royal Society of Chemistry 2023. (b) Schematic structure of Co_n/N-C and Co_nIr₁/N-C from top and side views. (c) PDOS of Co 3d for Co_n/N-C and Co_nIr₁/N-C. (d) Gibbs free energy of Co_n/N-C and Co_nIr₁/N-C toward OER. Reproduced with permission from Ref. [197], © American Chemical Society 2023. (e) Schematic illustration of the interactions between Fe nanocluster and NCNTs interface. Reproduced with permission from Ref. [198], © Wiley-VCH GmbH 2023.

2.5 Clusters for NRR to produce NH₃

Ammonia plays a crucial role in modern agriculture as it is essential for the synthesis of fertilizers. Apart from its applications in agriculture, ammonia also lays the foundation in the pharmaceutical industry. It serves as a key precursor for the preparation of a great variety of pharmaceutical products, including analgesics, antibiotics, and ant malarial medications [199]. However, the Haber-Bosch process is the mainstay of industrial ammonia production. Harsh industrial circumstances, high energy inputs, and significant CO₂ emissions call for the development of innovative strategies for nitrogen fixation under moderate settings. One avenue to addressing this issue is developing catalysts that can facilitate nitrogen fixation at lower temperatures and pressures. The electrocatalytic nitrogen reduction appears as an attractive strategy for the production of ammonia in a sustainable and environmentally friendly manner under ambient conditions. Nevertheless, this electrochemical method is still far from practical application owing to the extremely strong inert nonpolar N≡N triple bond, the kinetically sluggish NRR process and the low Faradaic efficiency (FE) due to the competing HER. Thereupon, it is imperative to explore effective and robust catalysts to decrease the Gibbs free energy barrier (ΔG), so as to boost the overall performance of NRR while suppressing the HER. Since the appearance of multi-atom cluster catalysts, researchers have dedicated to screen and discover suitable materials for NRR from the theoretical aspect. Recent published works have also demonstrated the viability of multi-atom cluster catalysts for NRR from the perspective of experimental research.

The controllable synthesis of multi-atom clusters can be realized by anchoring metal precursors to a defective substrate. Lu et al.

reported the preparation of Au₄Pt₂(SR)₈ bimetal clusters on the vacancy site of a graphene (denoted as Au₄Pt₂/G) (Fig. 17(a)) [200]. 2-phenylethanethiol was selected as both the ligand and reducing reagent in the preparation of ultrafine bimetallic Au-Pt clusters. The heteroatom dopant serves an essential role in the activation of N₂ through the back donation of electrons transferred from the embedded bimetallic cluster to the N₂ antibonding π^* -orbitals. The Au₄Pt₂(SR)₈ catalyst exhibited a maximum NH₃ yield about 7.9 $\mu\text{g}\cdot\text{mg}^{-1}\cdot\text{h}^{-1}$ at -0.1 V vs. RHE with a faradaic efficiency about 9.7% (Figs. 17(b) and 17(c)). As a contrast, the Au₄Pt₂/G demonstrated a superior NH₃ yield about 23.6 $\mu\text{g}\cdot\text{mg}^{-1}\cdot\text{h}^{-1}$ at -0.1 V vs. RHE, which is three times greater than that of the Au₄Pt₂(SR)₈ catalyst. The catalytic properties of these multi-atom clusters could also be modulated through the substitute of heteroatom dopant like Pd. As expected, Au₄Pd₂/G showed a maximum NH₃ yield about 27 $\text{mg}\cdot\text{h}^{-1}$ with a faradaic efficiency about 12% at -0.2 V vs. RHE.

Liang et al. confined Fe-Cu clusters in the surface cavities of graphitic carbon nitride (denoted as CNT@C₃N₄-Fe&Cu) and used it as a NRR electrocatalyst [201]. CNT@C₃N₄-Fe&Cu was prepared by a "Lyophilization-annealing" process with multi-walled carbon nanotubes selected as the substrate. Dicyandiamide was polymerized into ultra-thin C₃N₄ sheets, which was rich in N atoms on the edge to bind with Fe and Cu clusters. The concept of "sub-nano reactors" was thus proposed as this unique microenvironment can reinforce the interaction between the reaction intermediates and the active sites in this catalyst. Further DFT calculations indicated that the formation of Fe-Cu coordination could help adjust the N₂ absorption, enhance the electron transport, and provide additional redox couples for NRR. The potential-determining step for CNT@C₃N₄-Fe&Cu is the initial hydrogenation step (0.58 eV), much smaller than that of the N₂

adsorption step (0.86 eV) for CNT@C₃N₄-Cu the 5th hydrogenation step (0.71 eV) for CNT@C₃N₄-Fe (Figs. 17(d) and 17(e)). The incorporation of Cu might potentially serve as an electron reservoir, supplying electrons to the Fe atom. This synergistic effect from Cu and Fe atoms in such sub-nano reactors contributes greatly to the enhanced NRR activity. As expected, the prepared CNT@C₃N₄-Fe&Cu delivers a high NH₃ yield about 9.86 mg·mg⁻¹·h⁻¹ and a faradaic efficiency nearly 34%. The NH₃ yield nearly doubles and the faradaic efficiency increases 54% when compared with the corresponding single-metal counterparts.

The NRR process for producing NH₃ has energy-saving and environmental benefits, but the reaction is complex because of three-phases and proton/electron transfer. It is imperative to impede the preferential HER and enhance the selectivity of NRR by exploring effective and robust clusters. Future studies should consider the interactions between clusters and supports to reveal the NRR mechanism, kinetics, thermodynamics, and clusters design. Experimenters can achieve *in-situ* reconstruction of surface atoms by constructing highly active heterointerfaces, thereby promoting interface charge transfer between clusters and support.

2.6 Clusters for CO₂RR to produce value-added multi-carbon products

The electrochemical CO₂ reduction has emerged as a promising approach in addressing both the challenges of climate change and the ever-increasing energy needs [202–206]. By reducing carbon dioxide into value-added products with the usage of renewable electric energy, this technique can help reduce greenhouse gas emissions while also providing a sustainable source of energy. It provides a promising solution for mitigating the environmental impact of carbon dioxide emissions while simultaneously meeting our energy demands. Developing highly active catalysts is crucial

since these catalysts play an important role in lowering the thermodynamic energy barrier and accelerating the reaction dynamics at the same time showing high selectivity in yielding the desired products in CO₂RR. Although lots of researches on single-atom or dual atom catalysts has demonstrated its merits in reducing CO₂ to CO, they are often ineffective in converting CO₂ to more complicated compounds. Therefore, the introducing of extra atoms to create multi-atom cluster catalysts may have the potential to either improve CO₂RR activity or give more sites for catalytic reaction to support complicated processes and efficiently yield C₂H₄, CH₄, CO, HCOOH, etc.

Due to its moderate binding strength with a variety of reaction intermediates, copper-based catalysts are attractive since they can produce different kinds of carbon-based fuels. The copper-based clusters may offer several active sites for intricate reaction pathways while also gaining the merits of high selectivity and activity from SACs. Wang et al. observed the reversible and dynamic transformation of copper(II) phthalocyanine to form metallic copper clusters (~ 2 nm) under the working conditions with the aid of *in-situ* and *operando* X-ray absorption spectroscopy (Fig. 18(a)) [207]. These copper clusters are identified as the active sites for the conversion of carbon dioxide to methane. A similar reversible transformation was also observed by Karapinar et al. using *operando* XAS for the electroreduction of CO₂ to ethanol on the single-site copper [208].

Further, Xu et al. systematically investigated a series of carbon-supported atomically dispersed Cu site catalysts fabricated from an amalgamated Cu-Li approach for CO₂RR [209]. *Operando* X-ray results indicated a reversible restructuring from single atom Cu to Cu_n clusters (*n* = 3 and 4) under CO₂RR potentials (Fig. 18(b)). DFT calculation suggested that Cu clusters formed from Cu single atoms are the active sites in the selective reduction of carbon

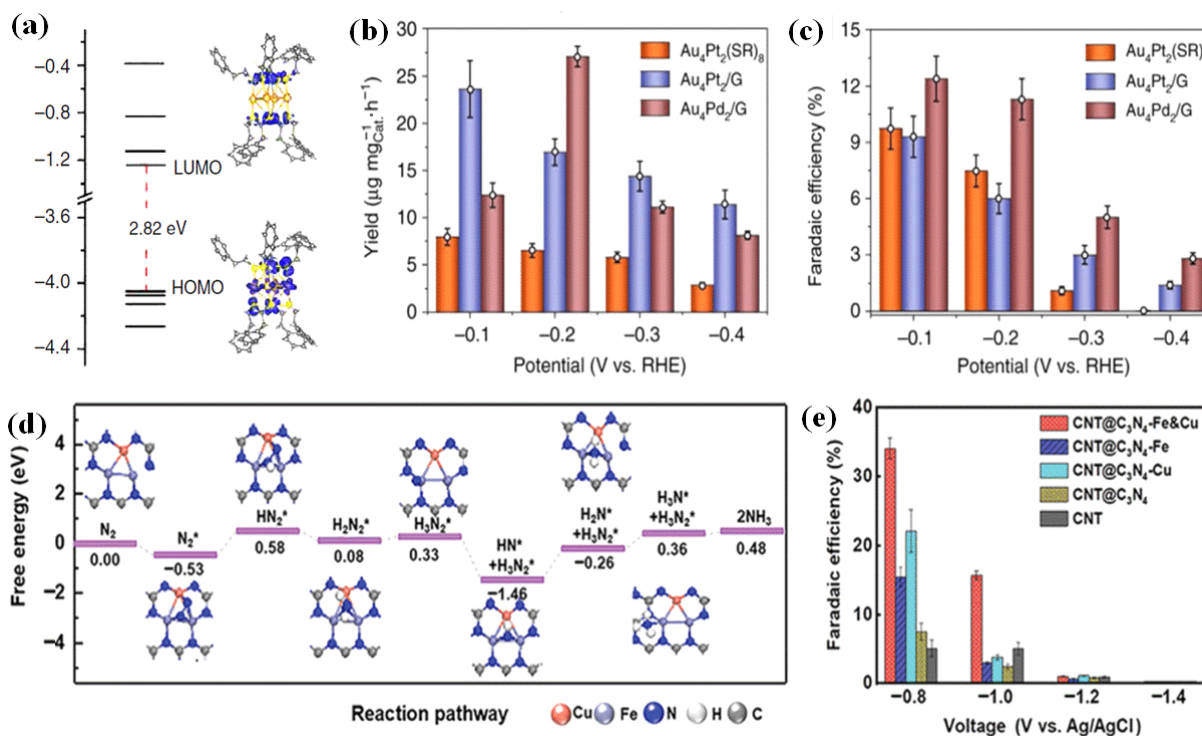


Figure 17 (a) Calculated frontier orbitals for Au₄Pt₂(SR)₈. (b) Ammonia production rate and (c) Faradaic efficiency at various potentials. Reprinted with permission from Ref. [200], © Yao, C. H. et al. 2020. (d) Free energy diagrams of Fe₂Cu clusters for NRR. (e) Faradaic efficiencies of the investigated samples with various potentials. Reproduced with permission. Reproduced with permission from Ref. [201], © Wang, X. W. et al. 2020.

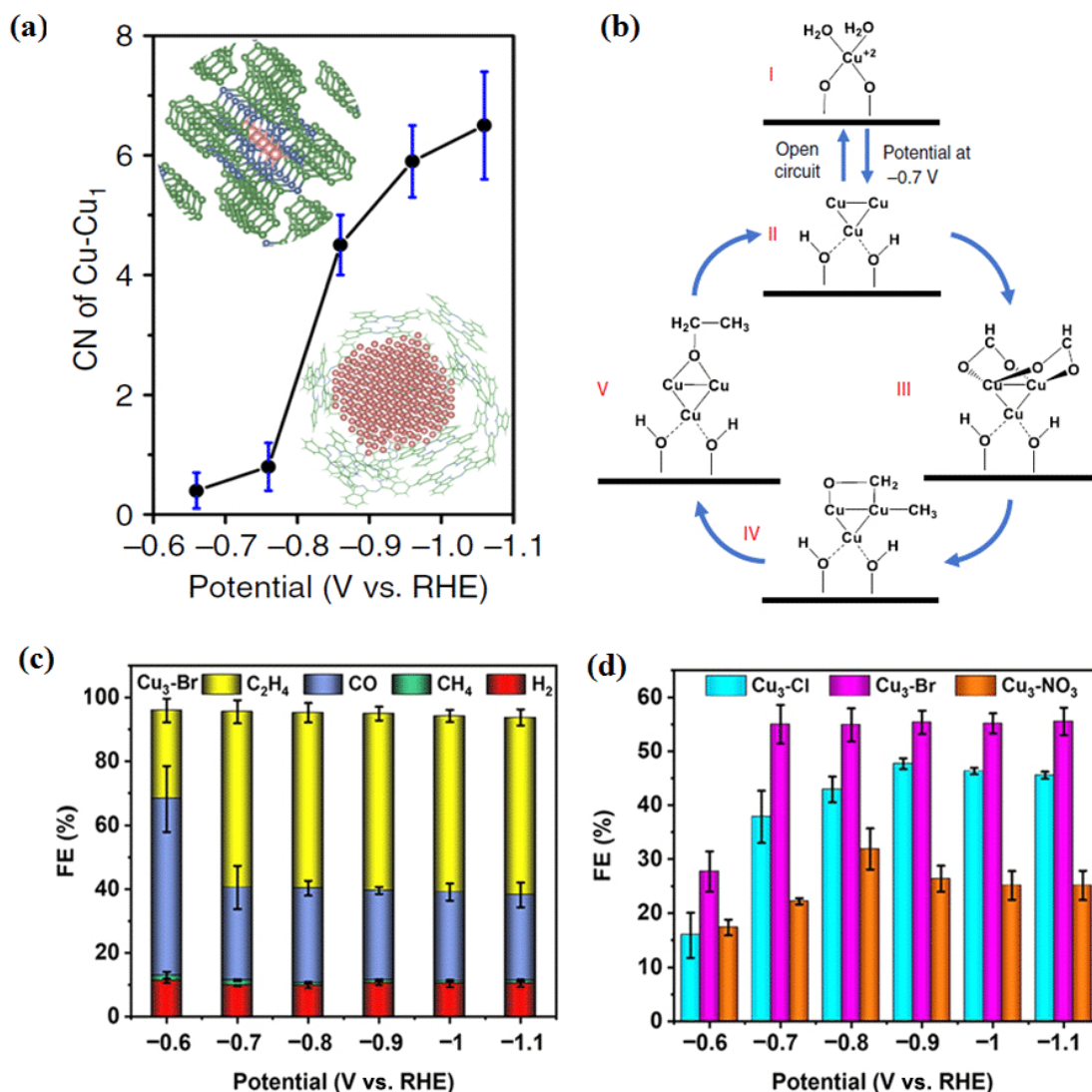


Figure 18 (a) First-shell Cu-Cu coordination numbers of CuPc electrocatalyst at various potentials. Reproduced with permission from Ref. [207], © Weng, Z. et al. 2018. (b) The suggested reaction mechanism proposed by *operando* measurements. Reproduced with permission from Ref. [209], © Xu, H. P. et al. under exclusive licence to Springer Nature Limited 2020. (c) Faradaic efficiency (C₂H₄, CO, CH₄ and H₂) for Cu₃-Br at various potentials (0.6 to 1.1 V). (d) The contrast of faradaic efficiency of Cu₃-X (X = Cl, Br, NO₃) for CO₂RR at various potentials (0.6 to 1.1 V). Reproduced with permission from Ref. [210], © Wiley-VCH GmbH 2021.

dioxide to ethanol. The hydroxyl group on the surface of the electrocatalyst is essential in controlling the contact between the catalytic active center and the substrates, which then influences the catalytic pathway. The as-prepared catalysts showed a quiet low onset potential (-0.4 V vs. RHE) and an extreme high FE (~91% at -0.7 V vs. RHE) during the reduction of carbon dioxide to ethanol.

Recently, for the conversion of carbon dioxide to symmetrical C₂₊ products like ethylene, Lan et al. employed crystalline trinuclear copper clusters as the electrocatalyst [210]. To be specific, a kind of trinuclear copper clusters Cu₃-X (X = Cl, Br, NO₃) which contain different types of counter anions were synthesized. These three catalysts share the same coordination environment and appropriate spatial distance. When utilizing Cu₃-X as the catalysts for CO₂RR, the selective control of the transformation of carbon dioxide to ethylene can be simply realized by substituting the counter anions in the structure of these clusters. The DFT calculations illustrated that two adjacent catalytically active Cu centers played an important part in the C-C coupling of the reaction intermediates CH*O and

subsequently promoted the forming C₂H₄. Simply changing the types of counter anions (Cl⁻, Br⁻, or NO₃⁻), the greatest faradaic efficiency be changed from 31.90% to 55.01% of Cu₃-X for the conversion of CO₂ to C₂H₄ (Figs. 18(c) and 18(d)). Among them, Cu₃-Br exhibits the greatest C₂H₄ production activity with notable stability. It showed an excellent FE of C₂H₄ about 55.01% at -0.7 V vs. RHE with the current density about 129.58 mA·cm⁻².

CO₂RR, as a crucial energy conversion technology, has great potential to produce various valuable chemicals, providing a pathway for achieving carbon peak and carbon neutrality goals. However, activating inert CO₂ faces major challenges as it requires electrocatalysts with high selectivity and catalytic activity to overcome huge overpotential. Moreover, different products require different pathways and equilibrium potentials, as competitive HER processes are also prone to occur at high reduction potentials. Due to its moderate binding strength with various reaction intermediates, copper-based multi-atom cluster may be the most promising catalyst for improving CO₂RR activity and selectively producing C₁ and C₂ products in the future.

3 Summary and perspective

DFT calculation-assisted screening atomic clusters can establish the relationship between the intrinsic properties and activities of catalysts at the atomic scale, which can avoid blind trial and error. Whereas, it is still unclear whether single cluster can have a better performance than SACs or nanoparticles materials. The combination of experimental characterizations and theoretical modeling offers complementary means for obtaining a more complete and in-depth understanding of the reaction mechanisms.

In this review, we focused primarily on the recent research progress on the theory-guided design and experimental discovery of clusters towards various electrocatalytic reactions, including cathode reaction of ORR, anode oxidation of H_2 , alcohols and acids, water splitting, NRR, and CO_2 RR. we first demonstrated the definition of clusters structure in detail from the theoretical and experimental perspectives. Then, we also emphasized the theoretical principle to rational screen and design cluster catalysts and presented the corresponding synthesis strategies under the guidance of theoretical calculation. Next, the reaction mechanism of current state of clusters for various energy-related electrocatalytic reaction were systematically exemplified and discussed. Finally, we highlighted rational designing of atomic clusters, and corresponding structure-property correlation guided by theoretical calculations.

Atomic clusters exhibit the synergistic effects between adjacent atoms, abundant coordination microenvironment, and more exposed surface active sites, which has the potential to promote the adsorption and activation of multiple substrates or intermediates, and catalyze complex reactions with diverse products. However, despite the advantages of unique geometric and electronic structures, enhanced catalytic activity, and unusual reaction route, the future holds numerous challenges that require our attention and resolution:

(1) Machine learning should be effectively employed

Although DFT can provide high-precision predictions, it is not suitable for large-scale screening due to the huge computational workload. Its traditional descriptors (such as d-band center, charge, HOMO–LUMO gap, etc.) often fail to capture the intricate electronic interactions in multi-element systems. In addition, the trial-and-error experimental synthesis or pure DFT computational investigations of clusters is infeasible due to time and cost constraints. Clean and renewable energy conversion techniques require the discovery and design of extensive and efficient candidate electrocatalysts, therefore, high-throughput fully automatic theoretical screening method, machine learning (ML) algorithms, have emerged as a popular domain in artificial intelligence (AI), demonstrating its efficacy in guiding DFT calculations to design heterogeneous catalyst, optimize structure, determine the correlations between physical properties and the adsorption energy of intermediates, as well as predict the relationships between intermediate adsorption strengths and catalytic activity.

Utilizing ML algorithms, we can extract the correlation between structure and performance from vast amounts of experimental data and establish predictive models to guide the design of novel clusters. In the future, a big data platform focusing on cluster composition–structure–performance should be built to achieve a closed-loop from theoretical design to experimental verification, thereby significantly shortening the research cycle. Therefore, the synergistic integration of ML and emerging cluster catalysis has opened up a new research horizon. ML has proven to be extremely

valuable in analyzing these complex electronic interactions and enhancing the screening efficiency of vast component databases.

Integrating DFT database with ML techniques can rapidly explore thousands of potential catalysts components through genetic algorithms to identify the optimal model parameters. ML can achieve accurate pattern recognition, classification, and prediction, minimize computational costs, and extract valuable insights from complex datasets. For example, Jiwon Roh et al. [211] proposed an ML framework, which was validated through experimental tests focused on the dry reforming of methane, that not only reduces computational budgets but also overcomes the challenges associated with the absence of interpret ability in black-box models, confirming its potential to significantly accelerate the rational design of catalysts.

Although there is limited research on machine learning-assisted cluster screening in the field of electrocatalysis, we believe that machine learning, as a faster and more precise tool, will greatly expand the application scope of clusters.

(2) AI-driven construction of atomic cluster datasets should be developed

Similar to SACs, atomic clusters are promising candidates for the computational screening of efficient electrocatalysts due to their well-defined, atomically dispersed active sites. Recent theoretical studies on triatomic clusters (e.g., Fe_3 , Co_3 , Ni_3) have demonstrated the feasibility of identifying high-performance electrocatalysts through large-scale simulations and modeling [212, 213]. ML algorithms can analyze large datasets, identify catalyst compositions and predict catalytic activity, which can help accelerate the discovery of novel atomic clusters with higher selectivity and activity, as well as understand complex reaction mechanisms. By integrating ML algorithms with expansive experimental or theoretical datasets, AI rapidly identifies optimal cluster configurations for specific catalytic applications. The workflow for constructing AI models involves generating diverse datasets of atomic clusters, characterized by properties include composition, support type, size, and shape. These datasets are then analyzed to extract features that capture electronic, geometric, and support-related properties.

AI models can subsequently uncover patterns and correlations between cluster structures and reactivity, enabling the design of atomic clusters tailored to desired properties. Nevertheless, there are challenges in developing accurate and reliable machine-learning models. Catalytic systems are complex and diverse, and accounting for this complexity in models is not straightforward. Moreover, interpreting the results guided by AI can be difficult. Further experimental validation is often required to confirm the predicted properties of the atomic clusters. Despite these hurdles, the application of machine learning-based and AI-guided design holds significant promise for advancing the field of atomic cluster catalysis.

A large number of components can be calculated to predict their catalytic properties by AI-driven clusters design. The synergy of ML with the emerging field of AI can open up new frontiers in the design of clusters. These strategies can decipher intricate electronic interactions, and improve the efficiency on screening huge electronic structure libraries to modulate their activity [214]. In the future, efforts should be made to build cluster big data platforms related to composition–structure–performance, in order to achieve a closed-loop cycle from theoretical design to experimental verification and significantly shorten the research and development cycle.

(3) *Advanced computational simulation approaches that are closer to real reaction environments should be considered*

Experimentally, electrocatalytic reactions operate within a complex reaction environment that is surrounded by electrolyte, while DFT calculations are generally conducted in vacuum. This results in a divergence between experimental findings and computational predictions. Furthermore, various electrolyte components, including electrode potential, surface coverage, pH and solvent effects, play a crucial role in determining catalytic efficiency [215]. It is quite difficult to accurately incorporate all these influences into DFT calculations. Substantial research has therefore focused on developing computational protocols that better reflect realistic operating conditions, including charged surfaces and solvent interactions. Advanced computational simulation approaches that are closer to real reaction environments, such as *ab initio* molecular dynamics (AIMD), explicit solvent models, should be considered to decipher catalytic mechanisms and design rational catalyst [216].

Investigating the electronic characteristics of molecular systems requires solving the electronic Schrödinger equation, which furnishes the energies and forces needed to describe reaction dynamics based on explicit electronic structure. This computational methodology is known as AIMD [217]. AIMD represents a significant advancement by combining quantum mechanical calculations with classical molecular dynamics. Unlike traditional force field-based methods that rely on pre-parameterized potentials, AIMD computes electronic structure on-the-fly during simulations, allowing for accurate modeling of chemical bond breaking and formation [218]. AIMD is particularly valuable for studying catalytic processes, electrochemical reactions, and systems where electronic effects dominate the behavior.

Solvation effects can be adequately addressed using either explicit or implicit solvation models [219]. Implicit solvation serves as a highly effective, coarse-grained method in atomic-scale simulations to represent the influence of a surrounding liquid electrolyte as a continuous polarizable medium. The explicit solvent models offer a viable approach to simulate the polarization of electronic density at the electrode surface under applied bias, while simultaneously capturing the capacitive charging of the entire electric double layer-capabilities that extend beyond the inherent constraints of conventional DFT supercells.

(4) *Rigorous experimental verification and precise synthesis of theoretical models are essential*

We should conduct extensive experimental testing to validate the efficacy of the proposed theoretical model simulated from the cluster datasets, which is crucial for the scalability and applicability of the envisioned cluster structure. Future research should focus on employing automation and machine learning to rapidly optimize the synthesis parameters for high-throughput synthesis of cluster catalysts. *In-situ* synthesis of clusters under reaction conditions may generate more active and stable active sites through catalyst reconstruction. Environmentally friendly, sustainable, and scalable synthetic routes, earth-abundant and non-toxic precursors should be developed for industrial applications.

(5) *A workflow of computational guidance-experimental verification-rational design should be formed*

There are still some problems in the study of real electrochemical processes through theoretical calculations, such as the lack of simulation of the external real environment of materials, the inadequacy of existing DFT methods, and the difficulty of describing the properties of complex material systems with simple

material intrinsic properties. All of these problems urgently need to be solved. Developers should investigate a approach of “computational guidance-experimental verification-rational design” to effectively shorten the development cycle of new materials, reduce the research and development costs of subsequent experimental synthesis, and explore the correlation between structure and properties, providing reliable theoretical guidance for subsequent experimental work. In addition, there is still a considerable gap between high-precision calculation methods and experiments. Therefore, theoretical researchers need to develop more effective calculation methods and algorithms, and closely combine experiments to improve the reliability of models.

(6) *In-situ* characterizations for mechanisms should be explored
Theoretical calculations play an essential role in understanding reaction mechanisms, but there are still significant discrepancy between theoretical models and actual catalyst structures. DFT calculations rely on experimental conclusions and characterization results. Simple DFT calculation is difficult to clarify the rationality of the reaction process. Moreover, due to the immediacy of the reaction and the complexity of the environment, detecting the true active sites and capturing reaction intermediates remain highly challenging. Therefore, advanced *in-situ* and *operando* characterization techniques for comprehensively understanding catalytic mechanisms and deciphering the structure-performance relationships should be conducted to identify true active centers, observe structural evolution processes and valence state changes, as well as deeply underlying dynamic behaviour under truly operating conditions.

In-situ characterization technology can monitor and analyze the synthesis and catalytic reaction process of clusters in real time, gaining a deeper understanding of the initial and final states of reactants, as well as reaction pathways and intermediate products [220]. This is crucial for a deeper understanding of the synthesis mechanism, structural characteristics, and catalytic performance of clusters. For example, *in-situ* TEM enables real-time observation of surface atomic reconstruction, diffusion behavior, and sensitive detection of structural changes as well under operating the tracking transformations of the microstructure and the formation and desorption of adsorbed key reaction intermediates formed on the catalyst surface [221]. *In-situ* infrared spectroscopy enables dynamic monitoring of catalytic reactions and provides molecular-level information on reactants and intermediates, as well as surface bonding configurations [222].

Taking OER as an example, to elucidate OER mechanism, it is essential to collaboratively conduct *in-situ* characterization techniques. The ^{18}O isotope labeling with differential electrochemical mass spectrometry (DEMS) was studied by Song et al. to quantitatively analyze the contributions of the AEM and the LOM by tracking the evolution of $^{16}\text{O}_2$, $^{18}\text{O}^{16}\text{O}$ and $^{18}\text{O}_2$. *Operando* X-ray absorption spectroscopy (XAS) allows for tracking the valence state, bond lengths and coordination environments changes of clusters in real time. They believe that the detection of signals of superoxide-like species or metal-oxygen groups can serve as fingerprints of LOM, while the formation of $-\text{OH}$ and $-\text{OOH}$ substances can be used to elucidate the reaction pathways of AEM [223].

(7) *The synergistic effect of coupling active sites should be considered*

Traditional heterogeneous catalysts composed of metal particles of different sizes typically have multiple active sites, and their catalytic activity and selectivity vary. On gold nanoparticles, only a small number of metal atoms can serve as catalytic active species,

resulting in relatively low metal utilization efficiency and insufficient selectivity. The lack of specific active sites may lead to the generation of multiple by-products. The synergistic effect of coupling active sites should be considered, for example, coupling single atoms and clusters, single atoms and nanoparticles. The use of integration strategies can determine feasible combinations and optimal atomic arrangements of metal atoms in coupled systems. The synergistic effect usually promotes activity, but its stability is limited in practical environments due to the coupling catalyst is prone to deactivation over time, thus the trade-off between activity and stability needs to be considered. Future research should focus on developing robust supports, optimizing the interaction between metal atoms and supports in clusters, as well as reducing the cost of experimental synthesis and theoretical calculations. We anticipate the study of in conjunction with DFT-guided engineering of atomic clusters can provide the guidelines and clean up blind areas for various clean energy conversion technologies.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Nos. 22502127, 22301158, and 21871159), Liaoning Provincial Department of Science and Technology Doctoral Research Initiation Fund Project (No. 2022-BS-228), Shenyang Normal University Doctoral Research Initiation Fund Project (No. BS202125), Liaoning Provincial Department of Education Basic Research Project (No. JYTQN2023421), the Science and Technology Project of Henan Province (No. 252102231076), Shenyang Science and Technology Talent Special Project (No. RC230799), Key Discipline Project for Doctoral Program Construction of Shenyang Normal University in 2025 (No. 099-52501002), and the Science and Technology Key Project of Guangdong Province of China (No. 2020B010188002).

Declaration of competing interest

All the contributing authors reports no conflict of interests in this work.

Author contribution statement

H. Y. J., P. Z., and H. W. conceived the topic and co-wrote the manuscript. C. C., N. Y. S., X. Y. Z., Y. C., Z. H. Z. and J. X. Z. contributed to some content and figures. Z. Z. finalized the manuscript. All the authors have approved the final manuscript.

Use of AI statement

None.

References

- [1] Herzing, A. A.; Kiely, C. J.; Carley, A. F.; Landon, P.; Hutchings, G. J. Identification of active gold nanoclusters on iron oxide supports for CO oxidation. *Science* **2008**, *321*, 1331–1335.
- [2] Chen, Y. J.; Li, X. Y.; Chen, Z.; Ozden, A.; Huang, J. E.; Ou, P. F.; Dong, J. C.; Zhang, J. Q.; Tian, C.; Lee, B. H. et al. Efficient multicarbon formation in acidic CO₂ reduction via tandem electrocatalysis. *Nat. Nanotechnol.* **2024**, *19*, 311–318.
- [3] Li, S. F.; Fu, X. B.; Nørskov, J. K.; Chorkendorff, I. Towards sustainable metal-mediated ammonia electrosynthesis. *Nat. Energy* **2024**, *9*, 1344–1349.
- [4] Liu, X.; Meng, J. S.; Zhu, J. X.; Huang, M.; Wen, B.; Guo, R. T.; Mai, L. Comprehensive understandings into complete reconstruction of precatalysts: Synthesis, applications, and characterizations. *Adv. Mater.* **2021**, *33*, 2007344.
- [5] Qi, G. D.; Davies, T. E.; Nasrallah, A.; Sainna, M. A.; Howe, A. G. R.; Lewis, R. J.; Quesne, M.; Catlow, C. R. A.; Willock, D. J.; He, Q. et al. Au-ZSM-5 catalyses the selective oxidation of CH₄ to CH₃OH and CH₃COOH using O₂. *Nat. Catal.* **2022**, *5*, 45–54.
- [6] Chen, J. J.; Liu, C. H.; Pham, H. N.; Toops, T. J.; Dartye, A. K.; Kyriakidou, E. A. Designing ultrastable Pt/CeO₂-Al₂O₃ nanosheet catalysts for three-way catalysts applications. *Chem. Eng. J.* **2023**, *477*, 147086.
- [7] Zhang, S. P.; Bhatta, T.; Rana, S. M. S.; Shrestha, K.; Pradhan, G. B.; Sharma, S.; Jeong, S.; Kim, H. S.; Park, J. Y. Noise-less hybrid nanogenerator based on flexible WPU and siloxene composite for self-powered portable and wearable electronics. *Nano Energy* **2024**, *120*, 109179.
- [8] Qiao, B. T.; Wang, A. Q.; Yang, X. F.; Allard, L. F.; Jiang, Z.; Cui, Y. T.; Liu, J. Y.; Li, J.; Zhang, T. Single-atom catalysis of CO oxidation using Pt₁/FeO_x. *Nat. Chem.* **2011**, *3*, 634–641.
- [9] Ma, R. Z.; Zhang, J.; Gong, J. X.; Lin, Y. X.; Zhang, J. L.; Huang, Z. Q.; Chang, C. R.; Liu, S. J.; Zhu, W.; Wang, Y. X. et al. The cooperative effects of the Rh-M dual-metal atomic pairs in formic acid oxidation. *Angew. Chem., Int. Ed.* **2025**, *64*, e202503095.
- [10] Guan, S. Y.; Liu, Y. Y.; Liu, S. L.; Zhuang, Z. C.; Shen, R. F.; Zhang, H. H.; Liang, E. J.; Fan, Y. P.; Jiang, J. C.; Liu, B. Z. et al. MXene-supported Ru–Ni: A common active site for hydrolysis, hydrogen oxidation, and hydrogenation. *Angew. Chem., Int. Ed.* **2025**, *64*, e202506869.
- [11] Mu, X. Q.; Liu, S. L.; Zhang, M. Y.; Zhuang, Z. C.; Chen, D.; Liao, Y. R.; Zhao, H. Y.; Mu, S. C.; Wang, D. S.; Dai, Z. H. Symmetry-broken Ru nanoparticles with parasitic Ru–Co dual-single-atoms overcome the Volmer step of alkaline hydrogen oxidation. *Angew. Chem., Int. Ed.* **2024**, *63*, e202319618.
- [12] Guan, S. Y.; Yuan, Z. L.; Zhao, S. Q.; Zhuang, Z. C.; Zhang, H. H.; Shen, R. F.; Fan, Y. P.; Li, B. J.; Wang, D. S.; Liu, B. Z. Efficient hydrogen generation from ammonia borane hydrolysis on a tandem ruthenium-platinum-titanium catalyst. *Angew. Chem., Int. Ed.* **2024**, *63*, e202408193.
- [13] Li, Y. P.; Niu, S. W.; Liu, P. G.; Pan, R. R.; Zhang, H. K.; Ahmad, N.; Shi, Y.; Liang, X.; Cheng, M. Y.; Chen, S. H. et al. Ruthenium nanoclusters and single atoms on α-MoC/N-doped carbon achieves low-input/input-free hydrogen evolution via decoupled/coupled hydrazine oxidation. *Angew. Chem., Int. Ed.* **2024**, *63*, e202316755.
- [14] Qin, Y. L.; Yu, K. D.; Wang, G.; Zhuang, Z. C.; Dou, Y. H.; Wang, D. S.; Chen, Z. B. Adjacent-ligand tuning of atomically precise Cu–Pd sites enable efficient methanol electrooxidation with a CO-free pathway. *Angew. Chem., Int. Ed.* **2025**, *63*, e202420817.
- [15] Zhang, Y. F.; Gu, X. R.; Busari, F. K.; Barkaoui, S.; Han, Z. K.; Baiker, A.; Zhao, Z.; Li, G. Size hierarchy of gold clusters in nanogold-catalyzed acetylene hydrochlorination. *Nano Res.* **2024**, *17*, 9594–9600.
- [16] Zhou, S. Y.; Liu, F.; Ran, Y. S.; Wang, J. M.; Wang, H. R.; Yang, T. D.; Wang, X. D. Constructing double-tuned Ru nanoparticles and Co single atoms on MXene/TiO₂ heterojunctions as for efficient oxygen evolution reaction electrocatalyst. *Nano Res.* **2025**, *18*, 94907714.
- [17] Li, R. S.; Wu, D. X.; Rao, P.; Deng, P. L.; Li, J.; Luo, J. M.; Huang, W.; Chen, Q.; Kang, Z. Y.; Shen, Y. J. et al. General approach for atomically dispersed precious metal catalysts toward hydrogen reaction. *Carbon Energy* **2023**, *5*, e294.
- [18] Zhu, C. X.; Yang, J. R.; Zhang, J. W.; Wang, X. Q.; Gao, Y.; Wang, D. S.; Pan, H. G. Single-atom materials: The application in energy conversion. *Interdisc. Mater.* **2024**, *3*, 74–86.
- [19] Chen, S. H.; Ye, C. L.; Wang, Z. W.; Li, P.; Jiang, W. J.; Zhuang, Z.



- C.; Zhu, J. X.; Zheng, X. B.; Zaman, S.; Ou, H. H. et al. Selective CO₂ reduction to ethylene mediated by adaptive small-molecule engineering of copper-based electrocatalysts. *Angew. Chem., Int. Ed.* **2023**, *62*, e202315621.
- [20] Sun, W.; Kuang, T.; Wei, G. Y.; Li, Y.; Liu, Y. Q.; Lyu, S.; Zhang, Y. H.; Li, J. L.; Wang, L. Design and construction of size-controlled CoO/CS catalysts for Fischer–Tropsch synthesis. *Nano Res.* **2024**, *17*, 2520–2527.
- [21] Gao, Y.; Liu, B. Z.; Wang, D. S. Microenvironment engineering of single/dual-atom catalysts for electrocatalytic application. *Adv. Mater.* **2023**, *35*, 2209654.
- [22] Xie, J.; Xi, Y. J.; Gao, W. S.; Zhang, H.; Wu, Y. K.; Zhang, R. H.; Yang, H. F.; Peng, Y.; Li, F. W.; Li, Z. L. et al. Hydrogenolysis of lignin model compounds on Ni nanoparticles surrounding the oxygen vacancy of CeO₂. *ACS Catal.* **2023**, *13*, 9577–9587.
- [23] Tao, Y.; Guan, J. P.; Zhang, J.; Hu, S. Y.; Ma, R. Z.; Zheng, H. R.; Gong, J. X.; Zhuang, Z. C.; Liu, S. J.; Ou, H. H. et al. Ruthenium single atom sites surrounding the support pit with exceptional photocatalytic activity. *Angew. Chem., Int. Ed.* **2024**, *63*, e202400625.
- [24] Gao, Y.; Yang, C. D.; Sun, F. L.; He, D. P.; Wang, X. Q.; Chen, J.; Zheng, X. B.; Liu, R. C.; Pan, H. G.; Wang, D. S. Ligand-tuning metallic sites in molecular complexes for efficient water oxidation. *Angew. Chem., Int. Ed.* **2025**, *63*, e202415755.
- [25] Shao, T.; Geng, W.; Qin, X. P.; Yue, S.; Cao, R.; Cao, M. N. Synergy of sub-nano iridium clusters and cucurbit[6]uril-derived carbon boosts acidic water splitting. *Nano Res.* **2025**, *18*, 94907716.
- [26] Chen, F. R.; Zhao, G. C.; Zhou, G. TiO₂-supported Ni₄ quadruple-atom catalyst: A promising few-atom catalyst with high atomic utilization. *Nano Res.* **2025**, *18*, 94907293.
- [27] Jing, H. Y.; Zhu, P.; Zheng, X. B.; Zhang, Z. D.; Wang, D. S.; Li, Y. D. Theory-oriented screening and discovery of advanced energy transformation materials in electrocatalysis. *Adv. Powder Mater.* **2022**, *1*, 100013.
- [28] Wang, X. Y.; Wei, W. J.; Zhou, S. Y.; Pan, Y. Z.; Yang, J. R.; Gan, T.; Zhuang, Z. C.; Li, W. H.; Zhang, X.; Pan, Y. M. et al. Phosphorus-doped single atom copper catalyst as a redox mediator in the cathodic reduction of quinazolinones. *Angew. Chem., Int. Ed.* **2025**, *64*, e202505085.
- [29] Shen, J.; Tang, M. H.; Shi, Z. H.; Guan, S. Y.; Shi, Y. J.; Zhuang, Z. C.; Li, R. Z.; Yang, J. R.; He, D. P.; Liu, B. Z. et al. Efficient generation of negative hydrogen with bimetallic-ternary-structured catalysts for nitrobenzene hydrogenation. *Angew. Chem., Int. Ed.* **2025**, *64*, e202423626.
- [30] Zhang, M. Y.; Zhu, W.; Liu, Z. Y.; Chen, S. R.; Zhou, D. Y.; Mu, X. Q.; Zhuang, Z. C.; Wang, S. C.; Yang, J. R.; Du, Y. P. et al. Selective sieving effect of multi-atomic bismuth interfaces for efficient formate electrosynthesis and evolution at industrial current density. *Angew. Chem., Int. Ed.* **2025**, *64*, e202510206.
- [31] Yang, J. R.; Zhu, C. X.; Wang, D. S. A simple organo-electrocatalysis system for the chlor-related industry. *Angew. Chem., Int. Ed.* **2024**, *63*, e202406883.
- [32] Yang, J. R.; Zhu, C. X.; Li, W. H.; Zheng, X. S.; Wang, D. S. Organocatalyst supported by a single-atom support accelerates both electrodes used in the chlor-alkali industry via modification of non-covalent interactions. *Angew. Chem., Int. Ed.* **2024**, *63*, e202314382.
- [33] Wang, X. Y.; Pan, Y. Z.; Yang, J. R.; Li, W. H.; Gan, T.; Pan, Y. M.; Tang, H. T.; Wang, D. S. Single-atom iron catalyst as an advanced redox mediator for anodic oxidation of organic electrosynthesis. *Angew. Chem., Int. Ed.* **2024**, *63*, e202404295.
- [34] Zhao, J.; Zhang, Y. X.; Zhuang, Z. C.; Deng, Y. T.; Gao, G.; Li, J. Y.; Meng, A. L.; Li, G. C.; Wang, L.; Li, Z. J. et al. Tailoring d-p orbital hybridization to decipher the essential effects of heteroatom substitution on redox kinetics. *Angew. Chem., Int. Ed.* **2024**, *63*, e202404968.
- [35] Zhang, Y. D.; Sun, Y. J.; Wang, Q. Y.; Zhuang, Z. C.; Ma, Z. T.; Liu, L. M.; Wang, G. M.; Wang, D. S.; Zheng, X. S. Synergy of photogenerated electrons and holes toward efficient photocatalytic urea synthesis from CO₂ and N₂. *Angew. Chem., Int. Ed.* **2024**, *63*, e202405637.
- [36] Xia, J. K.; Xu, J. W.; Yu, B.; Liang, X.; Qiu, Z.; Li, H.; Feng, H. J.; Li, Y. F.; Cai, Y. J.; Wei, H. Y. et al. A metal-sulfur-carbon catalyst mimicking the two-component architecture of nitrogenase. *Angew. Chem., Int. Ed.* **2024**, *63*, e202412740.
- [37] Lv, L. Y.; Tan, H.; Kong, Y.; Tang, B.; Ji, Q. Q.; Liu, Y. Y.; Wang, C.; Zhuang, Z. C.; Wang, H. J.; Ge, M. et al. Breaking the scaling relationship in C–N coupling via the doping effects for efficient urea electrosynthesis. *Angew. Chem., Int. Ed.* **2024**, *63*, e202401943.
- [38] Qiu, W. B.; Qin, S. M.; Li, Y. B.; Cao, N.; Cui, W. R.; Zhang, Z. D.; Zhuang, Z. C.; Wang, D. S.; Zhang, Y. Overcoming electrostatic interaction via pulsed electroreduction for boosting the electrocatalytic urea synthesis. *Angew. Chem., Int. Ed.* **2024**, *63*, e202402684.
- [39] Wang, S. W.; Wang, L. G.; Zhou, X. D.; Fang, J. J.; Deng, C.; Wang, D. S. Design principles of single-atom catalysts anchored over porous materials for green catalysis and conversion. *Nano Res.* **2025**, *18*, 94907137.
- [40] Wang, Y.; Ma, F. Y.; Zhang, G. Q.; Zhang, J. W.; Zhao, H.; Dong, Y. M.; Wang, D. S. Precise synthesis of dual atom sites for electrocatalysis. *Nano Res.* **2024**, *17*, 9397–9427.
- [41] Ye, B. C.; Li, W. H.; Zhang, X.; Chen, J.; Gao, Y.; Wang, D. S.; Pan, H. G. Advancing heterogeneous organic synthesis with coordination chemistry-empowered single-atom catalysts. *Adv. Mater.* **2024**, *36*, e2402747.
- [42] Shen, J.; Chen, J.; Qian, Y. P.; Wang, X. Q.; Wang, D. S.; Pan, H. G.; Wang, Y. G. Atomic engineering of single-atom nanozymes for biomedical applications. *Adv. Mater.* **2024**, *36*, e2313406.
- [43] Zhu, P.; Li, A. L.; Liu, H.; Ouyang, F. P.; Yang, D.; Zhou, Z. Engineering the asymmetric active moiety of Ce–N₃P for efficient selective oxidation of aromatic C–H bonds. *Nano Res.* **2025**, *18*, 94907533.
- [44] Zhu, P.; Xiong, X.; Wang, D. S. Regulations of active moiety in single atom catalysts for electrochemical hydrogen evolution reaction. *Nano Res.* **2022**, *15*, 5792–5815.
- [45] Gan, T.; Wang, D. S. Atomically dispersed materials: Ideal catalysts in atomic era. *Nano Res.* **2024**, *17*, 18–38.
- [46] Zhu, L. Z.; Feng, S. Z.; Wang, L. L. Triple-atom catalysts: Atomic-level engineering for next-generation catalytic energy conversion. *Nano Res.* **2026**, *19*, 94907826.
- [47] Zhang, H.; Zhang, N.; Xi, B. J.; Wan, F.; Song, K. P.; An, X. G.; Xiong, S. L.; Li, X. G. Boosted electrosynthesis of hydrogen peroxide on isolated metal sites through second-shell modulation. *Nano Res.* **2025**, *18*, 94907211.
- [48] Lee, J. W.; Din, H. U.; Im, T.; Hwang, C. K.; Kim, J. M.; Lee, J. H.; Jeong, S. Coordination tailoring of Pt single-atom catalysts at room temperature and their exceptional performance in hydrogen evolution reaction. *Carbon Energy* **2025**, *7*, e720.
- [49] Li, J. J.; Zhang, L.; Doyle-Davis, K.; Li, R. Y.; Sun, X. L. Recent advances and strategies in the stabilization of single-atom catalysts for electrochemical applications. *Carbon Energy* **2020**, *2*, 488–520.
- [50] Zhu, P.; Xiong, X.; Wang, D. S.; Li, Y. D. Advances and regulation strategies of the active moiety in dual-atom site catalysts for efficient electrocatalysis. *Adv. Energy Mater.* **2023**, *13*, 2300884.
- [51] Lin, J. J.; Yang, J.; Li, T.; Zhao, S. Q.; Huang, W. H.; Chen, C. L.; Zhao, Y.; Liu, S. M.; Gu, L.; Yang, L. N. et al. Surface structure engineering of PtCu clusters enhances the performance of propane dehydrogenation. *Nano Res.* **2025**, *18*, 94907357.
- [52] Liu, Z. J.; Yang, X. M.; Wang, Y. Y.; Wang, S. Y. Atomically precise coinage metal nanoclusters with defects in catalysis. *Nano Res.* **2025**, *18*, 94907141.
- [53] Song, Y. X.; Shen, Y. L.; Zhang, W.; Li, L. N.; An, C. H. Engineered

- metal-atom aggregates enable selective ethylene glycol production through photocatalytic methanol C–C coupling. *Nano Res.* **2025**, *18*, 94907765.
- [54] Ji, J. P.; Hou, Y. P.; Zhou, S. Y.; Qiu, T.; Zhang, L.; Ma, L.; Qian, C.; Zhou, S. D.; Liang, C. D.; Ling, M. Oxygen-coordinated low-nucleus cluster catalysts for enhanced electrocatalytic water oxidation. *Carbon Energy* **2023**, *5*, e216.
- [55] Zhou, T. Y.; Guan, Y.; He, C. J.; Zhang, L.; Sun, X. L.; Song, Z. X.; Zhang, Q. L.; He, C. X.; Jiang, X. T.; Luo, Z. Y. et al. Building Fe atom-cluster composite sites using a site occupation strategy to boost electrochemical oxygen reduction. *Carbon Energy* **2024**, *6*, e477.
- [56] Shao, G. L.; Xu, J.; Gao, S. S.; Zhang, Z.; Liu, S.; Zhang, X.; Zhou, Z. Unsaturated bi-heterometal clusters in metal-vacancy sites of 2D MoS₂ for efficient hydrogen evolution. *Carbon Energy* **2024**, *6*, e417.
- [57] Feng, X.; Ling, L. X.; Cao, Y. T.; Zhang, R. G.; Fan, M. H.; Wang, B. J. A DFT study on the catalytic CO oxidative coupling to dimethyl oxalate on Al-doped core-shell Pd clusters. *J. Phys. Chem. C* **2018**, *122*, 1169–1179.
- [58] Tang, M. H.; Shen, J.; Zhang, F. T.; Zhao, Y. F.; Gan, T.; Zeng, W.; Li, R. X.; Wang, D. S.; Han, B. X.; Liu, Z. M. Upcycling of polyamide wastes to tertiary amines using Mo single atoms and Rh nanoparticles. *Angew. Chem., Int. Ed.* **2025**, *64*, e202416436.
- [59] Liu, Y. C.; Wang, X. C.; Lang, Z. L.; Li, Y. Q.; Yu, F. Y.; Dong, H. L.; Yao, R. Q.; Geng, S.; Liu, Z. X.; Tan, H. Q. et al. Pd⁰-polyoxometalates cluster-cluster catalyst for efficient selective hydrogenation of olefins. *Nano Res.* **2025**, *18*, 94907437.
- [60] Li, X.; Lei, Y. T.; Gao, Y.; Shang, H. S.; Yang, F.; Li, Y. F. Nitrogen-free charge-asymmetric indium cluster catalyst for efficient CO₂ electroreduction to formate. *Nano Res.* **2025**, *18*, 94907370.
- [61] Wang, Y. N.; Jia, H. Y.; Lu, D. Y.; Wang, J. G.; Peng, T. Y. *In situ* fabrication of Cu^{II}-tetrapyrrolylporphyrin derived single-atom Cu_N cluster-modified TiO₂ for efficient hydrogen evolution reaction. *Nano Res.* **2025**, *18*, 94907499.
- [62] Li, Z. M.; Li, X. Y.; Ma, H. Q.; Ye, C. L.; Yu, H.; Nie, L.; Zheng, M.; Wang, J. Anchoring Ru clusters to highly defective N-doped carbon nanotubes via a thermal-shock strategy for stable industrial hydrogen evolution. *Nano Res.* **2024**, *17*, 5261–5269.
- [63] Bieniek, J.; Baek, W.; Lorenz, S.; Münzer, F.; Fainblat, R.; Hyeon, T.; Bacher, G. Impact of exciton fine structure on the energy transfer in magic-sized (CdSe)₁₃ clusters. *Nano Res.* **2024**, *17*, 10669–10676.
- [64] Li, B. W.; Kang, L. M.; Lun, Y.; Yu, J. L.; Song, S. Q.; Wang, Y. Structure-performance relationship of Au nanoclusters in electrocatalysis: Metal core and ligand structure. *Carbon Energy* **2024**, *6*, e547.
- [65] Rong, H. P.; Ji, S. F.; Zhang, J. T.; Wang, D. S.; Li, Y. D. Synthetic strategies of supported atomic clusters for heterogeneous catalysis. *Nat. Commun.* **2020**, *11*, 5884.
- [66] Yang, H. C.; Duan, P. F.; Zhuang, Z. C.; Luo, Y. W.; Shen, J.; Xiong, Y. L.; Liu, X. W.; Wang, D. S. Understanding the dynamic evolution of active sites among single atoms, clusters, and nanoparticles. *Adv. Mater.* **2025**, *37*, 2415265.
- [67] Liu, X. Y.; Wang, Y.; Su, J. Y.; Wang, L. L. Synergistic effects of single atoms and nanoparticles: Emerging opportunities for electrocatalysis. *Nano Res.* **2025**, *18*, 94907441.
- [68] Deng, Z. W.; Guo, Y. X.; Sun, Z. Y.; Lin, J.; Zhai, H. Z.; Chen, W. X. Electrocatalytic organic transformation reactions in green chemistry: Exploring nanocrystals and single atom catalysts. *Nano Res.* **2024**, *17*, 9326–9344.
- [69] Wang, L. G.; Wu, J. B.; Wang, S. W.; Liu, H.; Wang, Y.; Wang, D. S. The reformation of catalyst: From a trial-and-error synthesis to rational design. *Nano Res.* **2024**, *17*, 3261–3301.
- [70] Liu, X. Y.; Xiao, J. P.; Peng, H. J.; Hong, X.; Chan, K.; Nørskov, J. K. Understanding trends in electrochemical carbon dioxide reduction rates. *Nat. Commun.* **2017**, *8*, 15438.
- [71] Tran, K.; Ulissi, Z. W. Active learning across intermetallics to guide discovery of electrocatalysts for CO₂ reduction and H₂ evolution. *Nat. Catal.* **2018**, *1*, 696–703.
- [72] Han, F. F.; Zhang, L. R.; Jin, Q.; Ma, X. Z.; Zhang, Z. G.; Sun, Z. H.; Zhang, X. T.; Wu, L. L. High rate and long-cycle life of lithium-sulfur battery enabled by high d-band center of high-entropy alloys. *ACS Nano* **2025**, *19*, 9182–9195.
- [73] Nørskov, J. K.; Abild-Pedersen, F.; Studt, F.; Bligaard, T. Density functional theory in surface chemistry and catalysis. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 937–943.
- [74] Hammer, B.; Nørskov, J. K. Why gold is the noblest of all the metals. *Nature* **1995**, *376*, 238–240.
- [75] Shi, Z. S.; Yang, W. Q.; Gu, Y. T.; Liao, T.; Sun, Z. Q. Metal-nitrogen-doped carbon materials as highly efficient catalysts: Progress and rational design. *Adv. Sci.* **2020**, *7*, 2001069.
- [76] Wang, H. Y.; Wang, X. Q.; Gao, F.; Chen, J. B.; Ren, X. R.; Shen, Z. C.; Wang, K.; Qi, F. L.; Liu, Y. X.; Gao, Y. et al. Synergistic catalysis of Pt-based high-entropy clusters coupled with super-hydrophilic CeO₂ enables efficient anion exchange membrane water electrolysis. *Adv. Mater.* **2026**, *38*, e14269.
- [77] Suntivich, J.; May, K. J.; Gasteiger, H. A.; Goodenough, J. B.; Shao-Horn, Y. A perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles. *Science* **2011**, *334*, 1383–1385.
- [78] Hwang, J.; Rao, R. R.; Giordano, L.; Katayama, Y.; Yu, Y.; Shao-Horn, Y. Perovskites in catalysis and electrocatalysis. *Science* **2017**, *358*, 751–756.
- [79] Xue, D. P.; Zhao, Y.; Cao, J. L.; Wang, Y.; Li, X. N.; Ma, T. Y. Spin engineering of dual-atom site catalysts for efficient electrochemical energy conversion. *Adv. Mater.* **2025**, *37*, 2504213.
- [80] Liu, J. C.; Ma, X. L.; Li, Y.; Wang, Y. G.; Xiao, H.; Li, J. Heterogeneous Fe₃ single-cluster catalyst for ammonia synthesis via an associative mechanism. *Nat. Commun.* **2018**, *9*, 1610.
- [81] Dai, T. Y.; Lang, X. Y.; Wang, Z. L.; Wen, Z.; Jiang, Q. Rational design of an Fe cluster catalyst for robust nitrogen activation. *J. Mater. Chem. A* **2021**, *9*, 21219–21227.
- [82] Zhang, M. Y.; Luo, X.; Zhou, D. Y.; Wang, S. C.; Chen, S. R.; Du, Y. P.; Zhuang, Z. C.; Yang, J. R.; Zhu, W.; Liu, S. L. et al. Multiscale manipulation of functional imperfection atomic interfaces. *Acc. Chem. Res.* **2026**, *59*, 322–336.
- [83] Chen, Y. X.; Meng, Z. H.; Wei, X. L.; Wu, M. J.; Xiong, Y. F.; Tang, H. B.; Wang, R.; Tian, T.; Wang, D. S.; Tang, H. L. Tellurium-nitrogen-carbon support boosting platinum catalysis in high-efficiency proton exchange membrane fuel cells. *Angew. Chem.* **2025**, *137*, e202512315.
- [84] Hammes-Schiffer, S.; Galli, G. Integration of theory and experiment in the modelling of heterogeneous electrocatalysis. *Nat. Energy* **2021**, *6*, 700–705.
- [85] Huang, H. W.; Zhao, J. W.; Guo, H. L.; Weng, B.; Zhang, H. W.; Saha, R. A.; Zhang, M. L.; Lai, F. L.; Zhou, Y. F.; Juan, R. Z. et al. Noble-metal-free high-entropy alloy nanoparticles for efficient solar-driven photocatalytic CO₂ reduction. *Adv. Mater.* **2024**, *36*, 2313209.
- [86] Beniya, A.; Higashi, S.; Ohba, N.; Jinnouchi, R.; Hirata, H.; Watanabe, Y. CO oxidation activity of non-reducible oxide-supported mass-selected few-atom Pt single-clusters. *Nat. Commun.* **2020**, *11*, 1888.
- [87] Tyo, E. C.; Vajda, S. Catalysis by clusters with precise numbers of atoms. *Nat. Nanotechnol.* **2015**, *10*, 577–588.
- [88] Abbet, S.; Sanchez, A.; Heiz, U.; Schneider, W. D.; Ferrari, A. M.; Pacchioni, G.; Rösch, N. Acetylene cyclotrimerization on supported size-selected Pd_n clusters (1 ≤ n ≤ 30): One atom is enough! *J. Am. Chem. Soc.* **2000**, *122*, 3453–3457.

- [89] Liu, L. C.; Corma, A. Metal catalysts for heterogeneous catalysis: From single atoms to nanoclusters and nanoparticles. *Chem. Rev.* **2018**, *118*, 4981–5079.
- [90] Yang, Y. Q.; Zhang, H.; Liang, Z. F.; Yin, Y. R.; Mei, B. B.; Song, F.; Sun, F. F.; Gu, S. Q.; Jiang, Z.; Wu, Y. E. et al. Role of local coordination in bimetallic sites for oxygen reduction: A theoretical analysis. *J. Energy Chem.* **2020**, *44*, 131–137.
- [91] Gao, X. P.; Mei, L.; Zhou, Y. N.; Shen, Z. M. Impact of electron transfer of atomic metals on adjacent graphyne layers on electrochemical water splitting. *Nanoscale* **2020**, *12*, 7814–7821.
- [92] He, F.; Wang, Z. X.; Wei, S. Q.; Zhao, J. X. Adsorption and catalytic activation of N₂ molecule on iron dimer supported by different two-dimensional carbon-based substrates: A computational study. *Appl. Surf. Sci.* **2020**, *506*, 144943.
- [93] Sun, L. B.; Reddu, V.; Wang, X. Multi-atom cluster catalysts for efficient electrocatalysis. *Chem. Soc. Rev.* **2022**, *51*, 8923–8956.
- [94] Tong, Y. Y.; Liu, J. X.; Su, B. J.; Juang, J. Y.; Hou, F.; Yin, L. C.; Dou, S. X.; Liang, J. High-rate electrochemical H₂O₂ production over multimetallic atom catalysts under acidic-neutral conditions. *Carbon Energy* **2024**, *6*, e378.
- [95] Kulkarni, A.; Siahrostami, S.; Patel, A.; Nørskov, J. K. Understanding catalytic activity trends in the oxygen reduction reaction. *Chem. Rev.* **2018**, *118*, 2302–2312.
- [96] Siahrostami, S.; Verdager-Casadevall, A.; Karamad, M.; Deiana, D.; Malacrida, P.; Wickman, B.; Escudero-Escribano, M.; Paoli, E. A.; Frydendal, R.; Hansen, T. W. et al. Enabling direct H₂O₂ production through rational electrocatalyst design. *Nat. Mater.* **2013**, *12*, 1137–1143.
- [97] Verdager-Casadevall, A.; Deiana, D.; Karamad, M.; Siahrostami, S.; Malacrida, P.; Hansen, T. W.; Rossmeisl, J.; Chorkendorff, I.; Stephens, I. E. L. Trends in the electrochemical synthesis of H₂O₂: Enhancing activity and selectivity by electrocatalytic site engineering. *Nano Lett.* **2014**, *14*, 1603–1608.
- [98] Jirkovský, J. S.; Panas, I.; Ahlberg, E.; Halasa, M.; Romani, S.; Schiffrin, D. J. Single atom hot-spots at Au–Pd nanoalloys for electrocatalytic H₂O₂ production. *J. Am. Chem. Soc.* **2011**, *133*, 19432–19441.
- [99] Jiang, K.; Back, S.; Akey, A. J.; Xia, C.; Hu, Y. F.; Liang, W. T.; Schaak, D.; Stavitski, E.; Nørskov, J. K.; Siahrostami, S. et al. Highly selective oxygen reduction to hydrogen peroxide on transition metal single atom coordination. *Nat. Commun.* **2019**, *10*, 3997.
- [100] Jung, E.; Shin, H.; Lee, B. H.; Efremov, V.; Lee, S.; Lee, H. S.; Kim, J.; Hooch Antink, W.; Park, S.; Lee, K. S. et al. Atomic-level tuning of Co–N–C catalyst for high-performance electrochemical H₂O₂ production. *Nat. Mater.* **2020**, *19*, 436–442.
- [101] Gao, R. J.; Pan, L.; Li, Z. W.; Shi, C. X.; Yao, Y. D.; Zhang, X. W.; Zou, J. J. Engineering facets and oxygen vacancies over hematite single crystal for intensified electrocatalytic H₂O₂ production. *Adv. Funct. Mater.* **2020**, *30*, 1910539.
- [102] Ma, F. H.; Wang, S. H.; Liang, X. Z.; Wang, C.; Tong, F. X.; Wang, Z. Y.; Wang, P.; Liu, Y. Y.; Dai, Y.; Zheng, Z. K. et al. Ni₃B as a highly efficient and selective catalyst for the electrosynthesis of hydrogen peroxide. *Appl. Catal. B: Environ.* **2020**, *279*, 119371.
- [103] Shen, R. A.; Chen, W. X.; Peng, Q.; Lu, S. Q.; Zheng, L. R.; Cao, X.; Wang, Y.; Zhu, W.; Zhang, J. T.; Zhuang, Z. B. et al. High-concentration single atomic Pt sites on hollow CuS_x for selective O₂ reduction to H₂O₂ in acid solution. *Chem* **2019**, *5*, 2099–2110.
- [104] Kim, J. H.; Shin, D.; Lee, J.; Baek, D. S.; Shin, T. J.; Kim, Y. T.; Jeong, H. Y.; Kwak, J. H.; Kim, H.; Joo, S. H. A general strategy to atomically dispersed precious metal catalysts for unravelling their catalytic trends for oxygen reduction reaction. *ACS Nano* **2020**, *14*, 1990–2001.
- [105] Sun, F.; Yang, C. W.; Qu, Z. B.; Zhou, W.; Ding, Y. N.; Gao, J. H.; Zhao, G. B.; Xing, D. F.; Lu, Y. F. Inexpensive activated coke electrocatalyst for high-efficiency hydrogen peroxide production: Coupling effects of amorphous carbon cluster and oxygen dopant. *Appl. Catal. B: Environ.* **2021**, *286*, 119860.
- [106] Byeon, A.; Yun, W. C.; Kim, J. M.; Lee, J. W. Recent progress in heteroatom-doped carbon electrocatalysts for the two-electron oxygen reduction reaction. *Chem. Eng. J.* **2023**, *456*, 141042.
- [107] Wang, Y.; Zheng, X. B.; Wang, D. S. Design concept for electrocatalysts. *Nano Res.* **2022**, *15*, 1730–1752.
- [108] Hu, Y. M.; Chao, T. T.; Dou, Y. H.; Xiong, Y. L.; Liu, X. W.; Wang, D. S. Isolated metal centers activate small molecule electrooxidation: Mechanisms and applications. *Adv. Mater.* **2025**, *37*, 2418504.
- [109] Jin, M. M.; Liu, W.; Sun, J. Q.; Wang, X. Z.; Zhang, S. S.; Luo, J.; Liu, X. J. Highly dispersed Ag clusters for active and stable hydrogen peroxide production. *Nano Res.* **2022**, *15*, 5842–5847.
- [110] Jin, M. M.; Liu, S.; Meng, G.; Zhang, S. S.; Liu, Q.; Luo, J.; Liu, X. J. Low-coordinated Mo clusters for high-efficiency electrocatalytic hydrogen peroxide production. *Adv. Mater. Interfaces* **2023**, *10*, 2201144.
- [111] Chang, Q. W.; Zhang, P.; Mostaghimi, A. H. B.; Zhao, X. R.; Denny, S. R.; Lee, J. H.; Gao, H. P.; Zhang, Y.; Xin, H. L.; Siahrostami, S. et al. Promoting H₂O₂ production via 2-electron oxygen reduction by coordinating partially oxidized Pd with defect carbon. *Nat. Commun.* **2020**, *11*, 2178.
- [112] Qi, D. F.; Xu, J.; Zhou, Y. T.; Zhang, H.; Shi, J. Q.; He, K.; Yuan, Y. F.; Luo, J.; Wang, S.; Wang, Y. Cyclodextrin-supported Co(OH)₂ clusters as electrocatalysts for efficient and selective H₂O₂ synthesis. *Angew. Chem., Int. Ed.* **2023**, *62*, e202307355.
- [113] Zhang, H. Y.; Wang, H.; Duan, P. Y.; Lei, Q.; Li, B. B.; Zhu, D. M.; Tian, M.; Sun, J. Y.; Sun, J. H.; Wang, Y. F. Harmonizing cobalt atom-cluster moieties with selective oxygen functional groups for augmented electrocatalytic H₂O₂ production. *Adv. Funct. Mater.* **2025**, *35*, 2417090.
- [114] Tang, B.; Ji, Q. Q.; Zhang, X. L.; Shi, R. C.; Ma, J.; Zhuang, Z. C.; Sun, M.; Wang, H. J.; Liu, R. Q.; Liu, H. J. et al. Symmetry breaking of FeN₄ moiety via edge defects for acidic oxygen reduction reaction. *Angew. Chem., Int. Ed.* **2025**, *64*, e202424135.
- [115] Shao, M. H.; Chang, Q. W.; Dodelet, J. P.; Chenitz, R. Recent advances in electrocatalysts for oxygen reduction reaction. *Chem. Rev.* **2016**, *116*, 3594–3657.
- [116] Duan, Z. Y.; Wang, G. F. Comparison of reaction energetics for oxygen reduction reactions on Pt(100), Pt(111), Pt/Ni(100), and Pt/Ni(111) surfaces: A first-principles study. *J. Phys. Chem. C* **2013**, *117*, 6284–6292.
- [117] Alemany-Molina, G.; Quílez-Bermejo, J.; Navlani-García, M.; Morallón, E.; Cazorla-Amorós, D. Efficient and cost-effective ORR electrocatalysts based on low content transition metals highly dispersed on C₃N₄/super-activated carbon composites. *Carbon* **2022**, *196*, 378–390.
- [118] Wei, X. Q.; Song, S. J.; Cai, W. W.; Luo, X.; Jiao, L.; Fang, Q.; Wang, X. S.; Wu, N. N.; Luo, Z.; Wang, H. J. et al. Tuning the spin state of Fe single atoms by Pd nanoclusters enables robust oxygen reduction with dissociative pathway. *Chem* **2023**, *9*, 181–197.
- [119] Ao, X.; Zhang, W.; Li, Z. S.; Li, J. G.; Soule, L.; Huang, X.; Chiang, W. H.; Chen, H. M.; Wang, C. D.; Liu, M. L. et al. Markedly enhanced oxygen reduction activity of single atom Fe catalysts via integration with Fe nanoclusters. *ACS Nano* **2019**, *13*, 11853–11862.
- [120] Han, A. L.; Sun, W. M.; Wan, X.; Cai, D. D.; Wang, X. J.; Li, F.; Shui, J. L.; Wang, D. S. Construction of Co₃ atomic clusters to enable Fe–N₄ motifs with highly active and durable oxygen reduction performance. *Angew. Chem., Int. Ed.* **2023**, *62*, e202303185.
- [121] Ying, Y. R.; Luo, X.; Qiao, J. L.; Huang, H. T. “More is Different.” Synergistic effect and structural engineering in double-atom catalysts. *Adv. Funct. Mater.* **2021**, *31*, 2007423.
- [122] Kong, F. P.; Si, R. T.; Chen, N.; Wang, Q.; Li, J. J.; Yin, G. P.; Gu,

- M.; Wang, J. J.; Liu, L. M.; Sun, X. L. Origin of hetero-nuclear Au–Co dual atoms for efficient acidic oxygen reduction. *Appl. Catal. B: Environ.* **2022**, *301*, 120782.
- [123] Tong, M. M.; Sun, F. F.; Xie, Y.; Wang, Y.; Yang, Y. Q.; Tian, C. G.; Wang, L.; Fu, H. G. *Operando* cooperated catalytic mechanism of atomically dispersed Cu–N₄ and Zn–N₄ for promoting oxygen reduction reaction. *Angew. Chem., Int. Ed.* **2021**, *60*, 14005–14012.
- [124] Chen, M. X.; Zhu, M. Z.; Zuo, M.; Chu, S. Q.; Zhang, J.; Wu, Y. E.; Liang, H. W.; Feng, X. L. Identification of catalytic sites for oxygen reduction in metal/nitrogen-doped carbons with encapsulated metal nanoparticles. *Angew. Chem., Int. Ed.* **2020**, *59*, 1627–1633.
- [125] Li, P.; Qiang, F. Q.; Tan, X. H.; Li, Z.; Shi, J.; Liu, S.; Huang, M. H.; Chen, J. W.; Tian, W. Q.; Wu, J. Y. et al. Electronic modulation induced by decorating single-atomic Fe–Co pairs with Fe–Co alloy clusters toward enhanced ORR/OER activity. *Appl. Catal. B: Environ.* **2024**, *340*, 123231.
- [126] Chen, C. J.; Wu, Y. L.; Li, X. L.; Ye, Y. T.; Li, Z. L.; Zhou, Y. F.; Chen, J.; Yang, M. Z.; Xie, F. Y.; Jin, Y. S. et al. Modulating Fe spin state in FeNC catalysts by adjacent Fe atomic clusters to facilitate oxygen reduction reaction in proton exchange membrane fuel cell. *Appl. Catal. B: Environ.* **2024**, *342*, 123407.
- [127] Wang, H.; Yin, F. X.; Liu, N.; Kou, R. H.; He, X. B.; Sun, C. J.; Chen, B. H.; Liu, D. J.; Yin, H. Q. Engineering Fe–Fe₃C@Fe–N–C active sites and hybrid structures from dual metal-organic frameworks for oxygen reduction reaction in H₂–O₂ fuel cell and Li–O₂ battery. *Adv. Funct. Mater.* **2019**, *29*, 1901531.
- [128] Qi, C. H.; Yang, H. Y.; Sun, Z. Q.; Wang, H. F.; Xu, N.; Zhu, G. H.; Wang, L. J.; Jiang, W.; Yu, X. Q.; Li, X. P. et al. Modulating electronic structures of iron clusters through orbital rehybridization by adjacent single copper sites for efficient oxygen reduction. *Angew. Chem., Int. Ed.* **2023**, *62*, e202308344.
- [129] Huang, H. J.; Yu, D. S.; Hu, F.; Huang, S. C.; Song, J. N.; Chen, H. Y.; Li, L. L.; Peng, S. J. Clusters induced electron redistribution to tune oxygen reduction activity of transition metal single-atom for metal-air batteries. *Angew. Chem., Int. Ed.* **2022**, *61*, e202116068.
- [130] Wan, X.; Liu, Q. T.; Liu, J. Y.; Liu, S. Y.; Liu, X. F.; Zheng, L. R.; Shang, J. X.; Yu, R. H.; Shui, J. L. Iron atom-cluster interactions increase activity and improve durability in Fe–N–C fuel cells. *Nat. Commun.* **2022**, *13*, 2963.
- [131] Liu, H.; Jiang, L. Z.; Khan, J.; Wang, X. X.; Xiao, J. M.; Zhang, H. D.; Xie, H. J.; Li, L. N.; Wang, S. Y.; Han, L. Decorating single-atomic Mn sites with FeMn clusters to boost oxygen reduction reaction. *Angew. Chem.* **2023**, *135*, e202214988.
- [132] Huang, Y. F.; Wu, P.; Ma, Y. Y.; Tang, J. P.; Zhou, X. W.; Ma, X. Z.; Li, W.; Zhao, X. L.; Chen, C.; Shih, W. et al. Single atom iron carbons supported Pd–Ni–P nanoalloy as a multifunctional electrocatalyst for alcohol oxidation. *Int. J. Hydrogen Energy* **2023**, *48*, 13972–13986.
- [133] Siller-Ceniceros, A. A.; Sánchez-Castro, M. E.; Morales-Acosta, D.; Torres-Lubian, J. R.; Martínez G., E.; Rodríguez-Varela, F. J. Innovative functionalization of Vulcan XC-72 with Ru organometallic complex: Significant enhancement in catalytic activity of Pt/C electrocatalyst for the methanol oxidation reaction (MOR). *Appl. Catal. B: Environ.* **2017**, *209*, 455–467.
- [134] Pei, L. J.; Xie, S. L.; Guo, H.; Li, X. Q.; Xie, H. D.; Tang, Z. B.; Han, G. H.; Xia, Z. H.; Li, M. G.; Liu, H. Ultrathin porous PdPtNi nanosheets as efficient electrocatalysts for alcohol oxidation reactions. *Chem. Eng. J.* **2024**, *483*, 149113.
- [135] Zhao, X.; Liu, Q. M.; Li, Q. X.; Chen, L. Y.; Mao, L.; Wang, H. Y.; Chen, S. W. Two-dimensional electrocatalysts for alcohol oxidation: A critical review. *Chem. Eng. J.* **2020**, *400*, 125744.
- [136] Sun, Y. C.; Huang, L. Q.; Shan, Q. H.; Li, G.; Zheng, Z. P.; Jiang, Q. R.; Jiang, Y. Q.; Xie, Z. X. Interstitial hydrogen atom modified PdPt nanosheets for efficient ethanol electro-oxidation with high C–C bond cleavage selectivity. *ACS Appl. Energy Mater.* **2022**, *5*, 10907–10914.
- [137] Zhang, W. Y.; Yao, Q. S.; Jiang, G. P.; Li, C.; Fu, Y. S.; Wang, X.; Yu, A. P.; Chen, Z. W. Molecular trapping strategy to stabilize subnanometric Pt clusters for highly active electrocatalysis. *ACS Catal.* **2019**, *9*, 11603–11613.
- [138] Liang, J. H.; Cheng, H. Y.; Zhao, B. L.; Hu, Q.; Xing, Z. H.; Zhang, Y. W.; Niu, L. Boosting the methanol oxidation reaction activity of Pt–Ru clusters via resonance energy transfer. *Small* **2023**, *19*, 2302149.
- [139] Zhang, Z. Y.; Xin, L.; Li, W. Z. Electrocatalytic oxidation of glycerol on Pt/C in anion-exchange membrane fuel cell: Cogeneration of electricity and valuable chemicals. *Appl. Catal. B: Environ.* **2012**, *119–120*, 40–48.
- [140] Sanati, S.; Morsali, A.; García, H. Metal-organic framework-based materials as key components in electrocatalytic oxidation and reduction reactions. *J. Energy Chem.* **2023**, *87*, 540–567.
- [141] He, Z. Y.; Yang, G. X.; Wang, H. J.; Dai, F. Y.; Peng, F.; Yu, H. Co–N–C-supported platinum catalyst: Synergistic effect on the aerobic oxidation of glycerol. *ACS Sustain. Chem. Eng.* **2020**, *8*, 19062–19071.
- [142] Lee, D.; Kim, Y.; Kwon, Y.; Lee, J.; Kim, T. W.; Noh, Y.; Kim, W. B.; Seo, M. H.; Kim, K.; Kim, H. J. Boosting the electrocatalytic glycerol oxidation performance with highly-dispersed Pt nanoclusters loaded on 3D graphene-like microporous carbon. *Appl. Catal. B: Environ.* **2019**, *245*, 555–568.
- [143] Fukuzumi, S. Production of liquid solar fuels and their use in fuel cells. *Joule* **2017**, *1*, 689–738.
- [144] Czaun, M.; Kothandaraman, J.; Goeppert, A.; Yang, B.; Greenberg, S.; May, R. B.; Olah, G. A.; Prakash, G. K. S. Iridium-catalyzed continuous hydrogen generation from formic acid and its subsequent utilization in a fuel cell: Toward a carbon neutral chemical energy storage. *ACS Catal.* **2016**, *6*, 7475–7484.
- [145] Gao, W.; Song, E. H.; Jiang, Q.; Jacob, T. Revealing the active intermediates in the oxidation of formic acid on Au and Pt(111). *Chem.—Eur. J.* **2014**, *20*, 11005–11012.
- [146] Gao, D. W.; Li, S. N.; Lv, Y. P.; Zhuo, H. Y.; Zhao, S.; Song, L. H.; Yang, S. H.; Qin, Y. C.; Li, C. C.; Wei, Q. et al. PtNi colloidal nanoparticle clusters: Tuning electronic structure and boundary density of nanocrystal subunits for enhanced electrocatalytic properties. *J. Catal.* **2019**, *376*, 87–100.
- [147] Cheng, H. F.; Wang, J.; Wu, C.; Liu, Z. L. Electrocatalysts for formic acid-powered PEM fuel cells: Challenges and prospects. *Energy Mater. Adv.* **2023**, *4*, 0067.
- [148] Li, C.; Tang, Z.; Shi, L. L.; Li, Y. J.; Ji, Y. J.; Zhang, K. X.; Yang, Z. Y.; Yan, Y. M. Constructing a triangle ensemble of Pt clusters for enhanced direct-pathway electrocatalysis of formic acid oxidation. *Chemistry* **2023**, *5*, 1621–1633.
- [149] Su, L. X.; Gong, D.; Jin, Y. M.; Wu, D. A.; Luo, W. Recent advances in alkaline hydrogen oxidation reaction. *J. Energy Chem.* **2022**, *66*, 107–122.
- [150] Oshchepkov, A. G.; Braesch, G.; Bonnefont, A.; Savinova, E. R.; Chatenet, M. Recent advances in the understanding of Nickel-based catalysts for the oxidation of hydrogen-containing fuels in alkaline media. *ACS Catal.* **2020**, *10*, 7043–7068.
- [151] An, L. L.; Zhao, X.; Zhao, T. H.; Wang, D. L. Atomic-level insight into reasonable design of metal-based catalysts for hydrogen oxidation in alkaline electrolytes. *Energy Environ. Sci.* **2021**, *14*, 2620–2638.
- [152] Wang, Y. H.; Wang, X. T.; Ze, H. J.; Zhang, X. G.; Radjenovic, P. M.; Zhang, Y. J.; Dong, J. C.; Tian, Z. Q.; Li, J. F. Spectroscopic verification of adsorbed hydroxy intermediates in the bifunctional

- mechanism of the hydrogen oxidation reaction. *Angew. Chem., Int. Ed.* **2021**, *60*, 5708–5711.
- [153] Ma, M.; Li, G.; Yan, W.; Wu, Z. Z.; Zheng, Z. P.; Zhang, X. B.; Wang, Q. X.; Du, G. F.; Liu, D. Y.; Xie, Z. X. et al. Single-atom molybdenum engineered platinum nanocatalyst for boosted alkaline hydrogen oxidation. *Adv. Energy Mater.* **2022**, *12*, 2103336.
- [154] Ni, W. Y.; Meibom, J. L.; Hassan, N. U.; Chang, M. Y. O. N.; Chu, Y. C.; Krammer, A.; Sun, S. L.; Zheng, Y. W.; Bai, L. C.; Ma, W. C. et al. Synergistic interactions between PtRu catalyst and nitrogen-doped carbon support boost hydrogen oxidation. *Nat. Catal.* **2023**, *6*, 773–783.
- [155] Wang, S. P.; Fu, L. H.; Huang, H. P.; Fu, M.; Cai, J. L.; Lyu, Z. X.; Wang, Q. X.; Kuang, Q.; Xie, Z. X.; Xie, S. F. Local oxidation induced amorphization of 1.5-nm-thick Pt–Ru nanowires enables superactive and CO-tolerant hydrogen oxidation in alkaline media. *Adv. Funct. Mater.* **2023**, *33*, 2304125.
- [156] Mu, X. Q.; Zhang, X. Y.; Chen, Z. Y.; Gao, Y.; Yu, M.; Chen, D.; Pan, H. Z.; Liu, S. L.; Wang, D. S.; Mu, S. C. Constructing symmetry-mismatched Ru₃Fe₃O₄ heterointerface-supported Ru clusters for efficient hydrogen evolution and oxidation reactions. *Nano Lett.* **2024**, *24*, 1015–1023.
- [157] Zhang, X. Y.; Xiao, X. Z.; Chen, J.; Liu, Y. F.; Pan, H. G.; Sun, W. P.; Gao, M. X. Toward the fast and durable alkaline hydrogen oxidation reaction on ruthenium. *Energy Environ. Sci.* **2022**, *15*, 4511–4526.
- [158] Zhang, X.; Xia, L. X.; Zhao, G. Q.; Zhang, B. X.; Chen, Y. P.; Chen, J.; Gao, M. X.; Jiang, Y. Z.; Liu, Y. F.; Pan, H. G. et al. Fast and durable alkaline hydrogen oxidation reaction at the electron-deficient ruthenium–ruthenium oxide interface. *Adv. Mater.* **2023**, *35*, 2208821.
- [159] Li, Y. B.; Yang, C. Y.; Yue, J. C.; Cong, H. J.; Luo, W. Polymorphism-interface-induced work function regulating on Ru nanocatalyst for enhanced alkaline hydrogen oxidation reaction. *Adv. Funct. Mater.* **2023**, *33*, 2211586.
- [160] Wang, J. M.; Zhang, B. X.; Zheng, X. Z.; Liu, X. R.; Guo, W.; Luo, Z. X.; Liu, Y. F.; Gao, M. X.; Chen, J.; Zhuang, Z. B. et al. Pt single atoms coupled with Ru nanoclusters enable robust hydrogen oxidation for high-performance anion exchange membrane fuel cells. *Nano Res.* **2024**, *17*, 6147–6156.
- [161] Zhou, Y. Y.; Xie, Z. Y.; Jiang, J. X.; Wang, J.; Song, X. Y.; He, Q.; Ding, W.; Wei, Z. D. Lattice-confined Ru clusters with high CO tolerance and activity for the hydrogen oxidation reaction. *Nat. Catal.* **2020**, *3*, 454–462.
- [162] Han, L. L.; Ou, P. F.; Liu, W.; Wang, X.; Wang, H. T.; Zhang, R.; Pao, C. W.; Liu, X. J.; Pong, W. F.; Song, J. et al. Design of Ru–Ni diatomic sites for efficient alkaline hydrogen oxidation. *Sci. Adv.* **2022**, *8*, eabm3779.
- [163] Wei, J. X.; Xiao, K.; Chen, Y. X.; Guo, X. P.; Huang, B. L.; Liu, Z. Q. *In situ* precise anchoring of Pt single atoms in spinel Mn₃O₄ for a highly efficient hydrogen evolution reaction. *Energy Environ. Sci.* **2022**, *15*, 4592–4600.
- [164] Li, L. G.; Liu, S. H.; Zhan, C. H.; Wen, Y.; Sun, Z. F.; Han, J. J.; Chan, T. S.; Zhang, Q. B.; Hu, Z. W.; Huang, X. Q. Surface and lattice engineered ruthenium superstructures towards high-performance bifunctional hydrogen catalysis. *Energy Environ. Sci.* **2023**, *16*, 157–166.
- [165] Yao, Z. C.; Tang, T.; Jiang, Z.; Wang, L.; Hu, J. S.; Wan, L. J. Electrocatalytic hydrogen oxidation in alkaline media: From mechanistic insights to catalyst design. *ACS Nano* **2022**, *16*, 5153–5183.
- [166] Su, L. X.; Jin, Y. M.; Gong, D.; Ge, X.; Zhang, W.; Fan, X. R.; Luo, W. The role of discrepant reactive intermediates on Ru–Ru₂ P heterostructure for pH-universal hydrogen oxidation reaction. *Angew. Chem., Int. Ed.* **2023**, *62*, e202215585.
- [167] Wang, X. N.; Tong, Y. F.; Feng, W. T.; Liu, P. Y.; Li, X. J.; Cui, Y. P.; Cai, T. H.; Zhao, L. M.; Xue, Q. Z.; Yan, Z. F. et al. Embedding oxophilic rare-earth single atom in platinum nanoclusters for efficient hydrogen electro-oxidation. *Nat. Commun.* **2023**, *14*, 3767.
- [168] Yan, L.; Li, P. P.; Zhu, Q. Y.; Kumar, A.; Sun, K.; Tian, S. B.; Sun, X. M. Atomically precise electrocatalysts for oxygen reduction reaction. *Chem* **2023**, *9*, 280–342.
- [169] Gu, J.; Xu, Y. X.; Lu, J. L. Atom-precise low-nuclearity cluster catalysis: Opportunities and challenges. *ACS Catal.* **2023**, *13*, 5609–5634.
- [170] Yan, L.; Wang, D. C.; Li, M.; Lu, R. H.; Lu, M. G.; Li, P. P.; Wang, K. Y.; Jin, S.; Wang, Z. Y.; Tian, S. B. Hexa-atom Pt catalyst fabricated by a ligand engineering strategy for efficient hydrogen oxidation reaction. *Angew. Chem., Int. Ed.* **2024**, *63*, e202410832.
- [171] Zhang, J.; Zhang, Q. Y.; Feng, X. L. Support and interface effects in water-splitting electrocatalysts. *Adv. Mater.* **2019**, *31*, 1808167.
- [172] Luo, G. Y.; Song, M.; Zhang, Q.; An, L. L.; Shen, T.; Wang, S.; Hu, H. Y.; Huang, X.; Wang, D. L. Advances of synergistic electrocatalysis between single atoms and nanoparticles/clusters. *Nano-Micro Lett.* **2024**, *16*, 241.
- [173] Zeng, L. Y.; Zhao, Z. L.; Huang, Q. Z.; Zhou, C. H.; Chen, W. X.; Wang, K.; Li, M. G.; Lin, F. X.; Luo, H.; Gu, Y. et al. Single atom Cr–N₄ sites with high oxophilicity interfaced with Pt atomic clusters for practical alkaline hydrogen evolution catalysis. *J. Am. Chem. Soc.* **2023**, *145*, 21432–21441.
- [174] Li, Y.; Li, R. P.; Wang, D.; Xu, H.; Meng, F.; Dong, D. R.; Jiang, J.; Zhang, J. Q.; An, M. Z.; Yang, P. X. A review: Target-oriented transition metal phosphide design and synthesis for water splitting. *Int. J. Hydrogen Energy* **2021**, *46*, 5131–5149.
- [175] Zhu, J.; Hu, L. S.; Zhao, P. X.; Lee, L. Y. S.; Wong, K. Y. Recent advances in electrocatalytic hydrogen evolution using nanoparticles. *Chem. Rev.* **2020**, *120*, 851–918.
- [176] Ekka, J.; Upadhyay, S. N.; Keil, F. J.; Pakhira, S. Unveiling the role of 2D monolayer Mn-doped MoS₂ material: Toward an efficient electrocatalyst for H₂ evolution reaction. *Phys. Chem. Chem. Phys.* **2022**, *24*, 265–280.
- [177] Zhang, G.; Feng, Y. S.; Lu, W. T.; He, D.; Wang, C. Y.; Li, Y. K.; Wang, X. Y.; Cao, F. F. Enhanced catalysis of electrochemical overall water splitting in alkaline media by Fe doping in Ni₃S₂ nanosheet arrays. *ACS Catal.* **2018**, *8*, 5431–5441.
- [178] Xiao, X.; Li, Z.; Xiong, Y.; Yang, Y. W. IrMo nanocluster-doped porous carbon electrocatalysts derived from Cucurbit[6]uril boost efficient alkaline hydrogen evolution. *J. Am. Chem. Soc.* **2023**, *145*, 16548–16556.
- [179] Liu, Y. D.; Li, L.; Wang, L.; Li, N.; Zhao, X. X.; Chen, Y.; Sakthivel, T.; Dai, Z. F. Janus electronic state of supported iridium nanoclusters for sustainable alkaline water electrolysis. *Nat. Commun.* **2024**, *15*, 2851.
- [180] Yang, W. W.; Li, M. Y.; Zhang, B. K.; Liu, Y. Z.; Zi, J. Z.; Xiao, H.; Liu, X. Y.; Lin, J. K.; Zhang, H. Y.; Chen, J. et al. Interfacial microenvironment modulation boosts efficient hydrogen evolution reaction in neutral and alkaline. *Adv. Funct. Mater.* **2023**, *33*, 2304852.
- [181] Zhao, Y. F.; Kumar, P. V.; Tan, X.; Lu, X. X.; Zhu, X. F.; Jiang, J. J.; Pan, J.; Xi, S. B.; Yang, H. Y.; Ma, Z. P. et al. Modulating Pt–O–Pt atomic clusters with isolated cobalt atoms for enhanced hydrogen evolution catalysis. *Nat. Commun.* **2022**, *13*, 2430.
- [182] Zhou, C. A.; Ma, K.; Zhuang, Z. C.; Ran, M. L.; Shu, G. Q.; Wang, C.; Song, L.; Zheng, L. R.; Yue, H. R.; Wang, D. S. Tuning the local environment of Pt species at CNT@MO_{2-x} (M = Sn and Ce) heterointerfaces for boosted alkaline hydrogen evolution. *J. Am. Chem. Soc.* **2024**, *146*, 21453–21465.
- [183] Song, J. J.; Wei, C.; Huang, Z. F.; Liu, C. T.; Zeng, L.; Wang, X.; Xu, Z. J. A review on fundamentals for designing oxygen evolution electrocatalysts. *Chem. Soc. Rev.* **2020**, *49*, 2196–2214.

- [184] Suen, N. T.; Hung, S. F.; Quan, Q.; Zhang, N.; Xu, Y. J.; Chen, H. M. Electrocatalysis for the oxygen evolution reaction: Recent development and future perspectives. *Chem. Soc. Rev.* **2017**, *46*, 337–365.
- [185] He, H. Z.; Zhang, Y.; Li, Y. Y.; Wang, P. Recent innovations of silk-derived electrocatalysts for hydrogen evolution reaction, oxygen evolution reaction and oxygen reduction reaction. *Int. J. Hydrogen Energy* **2021**, *46*, 7848–7865.
- [186] Qin, L. B.; Ma, G. Y.; Wang, L. K.; Tang, Z. H. Atomically precise metal nanoclusters for (photo)electroreduction of CO₂: Recent advances, challenges and opportunities. *J. Energy Chem.* **2021**, *57*, 359–370.
- [187] Yang, L.; Guo, Z. L.; Huang, J.; Xi, Y. N.; Gao, R. J.; Su, G.; Wang, W.; Cao, L. X.; Dong, B. H. Vertical growth of 2D amorphous FePO₄ nanosheet on Ni foam: Outer and inner structural design for superior water splitting. *Adv. Mater.* **2017**, *29*, 1704574.
- [188] Gou, W. Y.; Wang, Y. C.; Zhang, M. K.; Tan, X. H.; Ma, Y. Y.; Qu, Y. Q. A review on fundamentals for designing stable ruthenium-based catalysts for the hydrogen and oxygen evolution reactions. *Chin. J. Catal.* **2024**, *60*, 68–106.
- [189] Zhang, N.; Chai, Y. Lattice oxygen redox chemistry in solid-state electrocatalysts for water oxidation. *Energy Environ. Sci.* **2021**, *14*, 4647–4671.
- [190] Yu, F. S.; Zhan, J. Y.; Chen, D. T.; Guo, J. Y.; Zhang, S. B.; Zhang, L. H. Electronic states regulation induced by the synergistic effect of Cu clusters and Cu–S₂N₃ sites boosting electrocatalytic performance. *Adv. Funct. Mater.* **2023**, *33*, 2214425.
- [191] Xie, Y. H.; Chen, X.; Sun, K. A.; Zhang, J. Q.; Lai, W. H.; Liu, H.; Wang, G. X. Direct oxygen-oxygen cleavage through optimizing interatomic distances in dual single-atom electrocatalysts for efficient oxygen reduction reaction. *Angew. Chem.* **2023**, *135*, e202301833.
- [192] Zhu, E. Z.; Zheng, T. L.; Yu, J.; Shi, C. Y.; Zhou, L. X.; Jin, H. D.; Yang, J. R.; Luo, G. T.; Wei, D. Y.; Yang, X. K. et al. Electron redistribution and proton transfer induced by atomically fully exposed Cu–O–Fe clusters coupled with single-atom sites for efficient oxygen electrocatalysis. *Energy Storage Mater.* **2024**, *69*, 103410.
- [193] Shu, X. X.; Cao, X. Y.; He, B. W.; Chen, X. Y.; Zhao, L. L.; Yang, C. D.; Ma, J. Z.; Zhang, J. T. Coupling of indium clusters with atomic Fe–N₄ on carbon for long-term rechargeable Zn-air batteries. *Energy Environ. Sci.* **2025**, *18*, 1262–1271.
- [194] Li, Y. Y.; Jiang, H. M.; Lin, L.; Sun, Z. M.; Sun, G. B. Single-atomic iron synergistic atom-cluster induce remote enhancement toward oxygen reduction reaction. *J. Energy Chem.* **2025**, *102*, 413–420.
- [195] Sun, J. J.; Shen, M. X.; Chang, A. J.; Cui, S. Q.; Xiu, H.; Wang, P. B.; Li, X.; Ni, Y. H. Biological neural network-inspired micro/nano-fibrous carbon aerogel for coupling Fe atomic clusters with Fe–N₄ single atoms to enhance oxygen reduction reaction. *Small* **2025**, *21*, 2500419.
- [196] Xu, Q. L.; Zhang, L.; Li, L. H.; Zhang, S. J.; Zhou, Y. T.; Hu, G. Z. Harnessing multi-asymmetric engineering: A new horizon in bifunctional oxygen electrocatalysis with iron-group atom-cluster nanohybrid. *Adv. Funct. Mater.* **2025**, *35*, 2414379.
- [197] Ding, X. L.; Jia, C. Y.; Ma, P. Y.; Chen, H. H.; Xue, J. W.; Wang, D. D.; Wang, R. Y.; Cao, H.; Zuo, M.; Zhou, S. M. et al. Remote synergy between heterogeneous single atoms and clusters for enhanced oxygen evolution. *Nano Lett.* **2023**, *23*, 3309–3316.
- [198] Chen, G. Y.; Liu, Y. H.; Xue, S. Y.; Zhang, R. X.; Lv, H. L.; Zhang, J. C.; Wu, L. M.; Che, R. C. Exceptionally bifunctional ORR/OER performance via synergistic atom-cluster interaction. *Small* **2024**, *20*, 2308192.
- [199] Liu, G. Q.; Zhang, H.; Wang, P. F.; Gao, C.; Zhuang, Z. C.; Wang, D. S.; Zhan, S. H. Atomic-level design of acid–base pairs in oxides for selective catalytic reduction of nitrogen oxides with ammonia. *Angew. Chem., Int. Ed.* **2025**, *64*, e202509362.
- [200] Yao, C. H.; Guo, N.; Xi, S. B.; Xu, C. Q.; Liu, W.; Zhao, X. X.; Li, J.; Fang, H. Y.; Su, J.; Chen, Z. X. et al. Atomically-precise dopant-controlled single cluster catalysis for electrochemical nitrogen reduction. *Nat. Commun.* **2020**, *11*, 4389.
- [201] Wang, X. W.; Qiu, S. Y.; Feng, J. M.; Tong, Y. Y.; Zhou, F. L.; Li, Q. Y.; Song, L.; Chen, S. M.; Wu, K. H.; Su, P. P. et al. Confined Fe–Cu clusters as sub-nanometer reactors for efficiently regulating the electrochemical nitrogen reduction reaction. *Adv. Mater.* **2020**, *32*, 2004382.
- [202] Yang, Y.; Zhang, W. J.; Wu, G. C.; Huang, Q.; Wen, J. H.; Wang, D. S.; Liu, M. Y. Electronic structure tuning in Cu–Co dual single atom catalysts for enhanced COOH* spillover and electrocatalytic CO₂ reduction activity. *Angew. Chem., Int. Ed.* **2025**, *64*, e202504423.
- [203] Chen, S. H.; Zheng, X. B.; Zhu, P.; Li, Y. P.; Zhuang, Z. C.; Wu, H. J.; Zhu, J. X.; Xiao, C. H.; Chen, M. Z.; Wang, P. S. et al. Copper atom pairs stabilize *OCCO dipole toward highly selective CO₂ electroreduction to C₂H₄. *Angew. Chem., Int. Ed.* **2024**, *63*, e202411591.
- [204] Ma, F. Y.; Zhang, P. F.; Zheng, X. B.; Chen, L.; Li, Y. R.; Zhuang, Z. C.; Fan, Y. M.; Jiang, P.; Zhao, H.; Zhang, J. W. et al. Steering the site distance of atomic Cu–Cu pairs by first-shell halogen coordination boosts CO₂-to-C₂ selectivity. *Angew. Chem., Int. Ed.* **2024**, *63*, e202412785.
- [205] Guan, M. L.; Lu, N.; Zhang, X.; Wang, Q. W.; Bao, J.; Chen, G. Y.; Yu, H.; Li, H. M.; Xia, J. X.; Gong, X. Z. Engineering of oxygen vacancy and bismuth cluster assisted ultrathin Bi₁₂O₁₇Cl₂ nanosheets with efficient and selective photoreduction of CO₂ to CO. *Carbon Energy* **2024**, *6*, e420.
- [206] Peng, W. K.; Li, F. F.; Kong, S. Y.; Guo, C. X.; Wu, H. T.; Wang, J. C.; Shen, Y.; Meng, X. G.; Zhang, M. X. Recent advances in nickel-based catalysts in eCO₂RR for carbon neutrality. *Carbon Energy* **2024**, *6*, e498.
- [207] Weng, Z.; Wu, Y. S.; Wang, M. Y.; Jiang, J. B.; Yang, K.; Huo, S. J.; Wang, X. F.; Ma, Q.; Brudvig, G. W.; Batista, V. S. et al. Active sites of copper-complex catalytic materials for electrochemical carbon dioxide reduction. *Nat. Commun.* **2018**, *9*, 415.
- [208] Karapinar, D.; Huan, N. T.; Ranjbar Sahraie, N.; Li, J. K.; Wakerley, D.; Touati, N.; Zanna, S.; Taverna, D.; Galvão Tizei, L. H.; Zitolo, A. et al. Electroreduction of CO₂ on single-site copper-nitrogen-doped carbon material: Selective formation of ethanol and reversible restructuring of the metal sites. *Angew. Chem., Int. Ed.* **2019**, *58*, 15098–15103.
- [209] Xu, H. P.; Rebollar, D.; He, H. Y.; Chong, L. N.; Liu, Y. Z.; Liu, C.; Sun, C. J.; Li, T.; Muntean, J. V.; Winans, R. E. et al. Highly selective electrocatalytic CO₂ reduction to ethanol by metallic clusters dynamically formed from atomically dispersed copper. *Nat. Energy* **2020**, *5*, 623–632.
- [210] Lu, Y. F.; Dong, L. Z.; Liu, J.; Yang, R. X.; Liu, J. J.; Zhang, Y.; Zhang, L.; Wang, Y. R.; Li, S. L.; Lan, Y. Q. Predesign of catalytically active sites via stable coordination cluster model system for electroreduction of CO₂ to ethylene. *Angew. Chem., Int. Ed.* **2021**, *60*, 26210–26217.
- [211] Roh, J.; Park, H.; Kwon, H.; Joo, C.; Moon, I.; Cho, H.; Ro, I.; Kim, J. Interpretable machine learning framework for catalyst performance prediction and validation with dry reforming of methane. *Appl. Catal. B: Environ.* **2024**, *343*, 123454.
- [212] Liu, J. C.; Xiao, H.; Zhao, X. K.; Zhang, N. N.; Liu, Y.; Xing, D. H.; Yu, X. H.; Hu, H. S.; Li, J. Computational prediction of graphdiyne-supported three-atom single-cluster catalysts. *CCS Chem.* **2023**, *5*, 152–163.
- [213] Liu, N.; Ma, X. L.; Li, J.; Xiao, H. Singly dispersed bimetallic sites

- as stable and efficient single-cluster catalysts for activating N_2 and CO_2 . *J. Phys. Chem. C* **2021**, *125*, 27192–27198.
- [214] Zhang, X. L.; Li, C.; Wu, W. B.; Li, W. W. High-entropy electrocatalysts toward high-performance oxygen evolution reaction: A perspective from atomic-scale electronic structure modulation. *Electron. Struct.* **2025**, *7*, 043001.
- [215] Liao, X. B.; Lu, R. H.; Xia, L. X.; Liu, Q.; Wang, H.; Zhao, K.; Wang, Z. Y.; Zhao, Y. Density functional theory for electrocatalysis. *Energy Environ. Mater.* **2022**, *5*, 157–185.
- [216] Yao, Y. G.; Dong, Q.; Brozena, A.; Luo, J.; Miao, J. W.; Chi, M. F.; Wang, C.; Kevrekidis, I. G.; Ren, Z. J.; Greeley, J. et al. High-entropy nanoparticles: Synthesis-structure-property relationships and data-driven discovery. *Science* **2022**, *376*, eabn3103.
- [217] Piccini, G.; Lee, M. S.; Yuk, S. F.; Zhang, D. F.; Collinge, G.; Kollias, L.; Nguyen, M. T.; Glezakou, V. A.; Rousseau, R. *Ab initio* molecular dynamics with enhanced sampling in heterogeneous catalysis. *Catal. Sci. Technol.* **2022**, *12*, 12–37.
- [218] Pastore, G.; Smargiassi, E.; Buda, F. Theory of *ab initio* molecular-dynamics calculations. *Phys. Rev. A* **1991**, *44*, 6334–6347.
- [219] Ringe, S.; Hörmann, N. G.; Oberhofer, H.; Reuter, K. Implicit solvation methods for catalysis at electrified interfaces. *Chem. Rev.* **2022**, *122*, 10777–10820.
- [220] Ganesan, S.; Bhatt, D.; Satheesh, D.; Kokulnathan, T.; Pant, P.; Bharathi, D. S.; Baskar, L.; Sahoo, N. G.; Palaniappan, A.; Manavalan, K. High entropy alloys: A comprehensive review of synthesis, properties, and characterization for electrochemical energy conversion and storage applications. *J. Mater. Chem. A* **2025**, *13*, 37663–37699.
- [221] Wen, B. Y.; Chen, Q. Q.; Radjenovic, P. M.; Dong, J. C.; Tian, Z. Q.; Li, J. F. *In situ* surface-enhanced Raman spectroscopy characterization of electrocatalysis with different nanostructures. *Annu. Rev. Phys. Chem.* **2021**, *72*, 331–351.
- [222] Zhu, K. Y.; Zhu, X. F.; Yang, W. S. Application of *in situ* techniques for the characterization of NiFe-based oxygen evolution reaction (OER) electrocatalysts. *Angew. Chem., Int. Ed.* **2019**, *58*, 1252–1265.
- [223] Liu, L. Y.; Ding, X.; Qin, H. T.; Tang, S. Y.; Xu, L. L.; Song, F. Z. High-entropy alloys for electrocatalytic water oxidation: Recent advances on mechanism and design. *Chemistry* **2025**, *7*, 190.



This is an open access article under the terms of the Creative Commons Attribution 4.0 International License (CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>).

© The Author(s) 2026. Published by Tsinghua University Press.