Nurturing the marriages of single atoms with atomic clusters and nanoparticles for better heterogeneous electrocatalysis

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Abstract
Single-atom catalysts, featuring some of the most unique activities, selectivity, and high metal utilization, have been extensively studied over the past decade. Given their high activity, selectivity, especially towards small molecules or key intermediate conversions, they can be synergized together with other active species (typically other single atoms, atomic clusters, or nanoparticles) in either tandem or parallel or both, leading to much better performance in complex catalytic processes. Although there have been reports on effectively combining the multiple components into one single catalytic entity, the combination and synergy between single atoms and other active species have not been reviewed and examined in a systematic manner. Herein, in this overview, the key synergistic interactions, binary complementary effects, and the bifunctional functions of single atoms with other active species are defined and discussed in detail. The integration functions of their marriages are investigated with particular emphasis on the homogeneous and heterogeneous combinations, spatial distribution, synthetic strategies, and the thus-derived outstanding catalytic performance, together with new light shined on the catalytic mechanisms by zooming in several case studies. The dynamic nature of each of the active species and in particular their interactions in such new catalytic entities in the heterogeneous electrocatalytic processes are visited, on the basis of the in situ/operando evidence. Last, we feature the current challenges and future perspectives of these integrated catalytic entities that can offer guidance for advanced catalyst design by the rational combination and synergy of binary or multiple active species.

Keywords
atomic clusters, binary/multiple synergy, heterogeneous catalysis, nanoparticles, single atoms
1 | INTRODUCTION

Throughout the long history of catalyst development, research has been driven by the ultimate goal of achieving superior activity, selectivity, stability, and maximizing catalyst utilization at a lowered cost. As those internal atoms in the bulk of a material generally do not contribute to catalytic function, downsizing of the nanoparticles into single atomic units and stabilizing them onto suitable supports has been envisioned as a promising direction and intensively pursued in the past decade. However, when active species get downsized continuously, their structures and catalytic properties experience drastic changes such that they may not be predictable in a simple linear manner. On the road of downsizing the active entities, three distinct categories can be identified, namely nanoparticles, atomic clusters, and single-atom catalysts (including isolated ones, dimers, trimers, and quasi-paired atoms), in light of the nonmonotonic changes in catalytic performance with the entity size.

With their distinct characteristics, nanoparticles, atomic clusters, and single-atoms emerge as three basic building blocks for heterogeneous catalysts. When one takes them as three vertices, a “golden triangle” can be constructed in heterogeneous catalysis to bridge the nano-world with the atomic world in unifying the studies from recent and current progress. To begin with, heterogeneous catalysts based on supported metal nanoparticles have been well-investigated and widely commercialized. For instance, commercial Pt/C catalysts comprise Pt nanoparticles supported on a graphitized carbon substrate and have been used as the performance benchmark for many reactions, such as the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR). Among the three categories, metal nanoparticles exhibit structure-dependent properties which are most resembling that of the bulk metal, with performance most intimately governed by the elemental composition (i.e., type and amount of dopants), crystal structure, exposed facets, and particle size.

The next size level with distinct properties would be atomic clusters that typically consist of fewer than 100 atoms. Such atomic clusters, from atomically precise assemblies of multiple atoms, can possess unique catalytic capabilities as a collective entity, the catalytic performance of which is predominantly affected by their geometric and electronic configurations, among the several structural parameters. Therefore, the basis for understanding the catalytic properties of atomic clusters differs significantly from those of both nanoparticles and single atoms. On the one hand, the atomic clusters differ from nanoparticles and bulk metals/alloys in that they have a significantly higher surface-area-to-volume ratio, quantized electronic structures, and unique atomic packages (due to the need to minimize surface energy). On the other hand, the collective catalytic effort by an atomic metal cluster introduces remarkably different adsorption and activation behavior from those of the single-atom catalysts, especially in reactions that require the synergetic actions of ensemble sites, such as in the breaking of strong O=O double bonds by the dissociative mechanism in the ORR, and the cleavage of C–C or C–H bonds in hydrocarbon oxidation.

Recent advancements in materials synthesis and characterization technologies, both ex-situ and in-situ, have enabled atomically precise tuning and investigation into the catalyst materials at varying scales down to atomic levels, propelling the ultimate downsizing into the realm of single atoms. Catalysts with monodispersed active metal sites are envisioned as a bridge between the traditional homogeneous and heterogeneous catalysts. The term “single-atom catalyst” was first introduced by Zhang and co-workers in 2011, when they reported a single Pt atom catalyst supported on iron oxide for CO oxidation and has since attracted tremendous attention in recent years, although the application of this concept could be further traced back to 1995 when Thomas and co-workers constructed Ti single-site heterogeneous catalyst supported on mesoporous silica for the epoxidation of cyclic alkenes.

So far, single-atom catalysts have been diversely applied in several fields of electrocatalysis (such as in electrocatalytic hydrogen evolution, oxygen evolution, oxygen reduction, etc., which will be further demonstrated in detail in the following sections), photocatalysis (photo-driven CO₂ reduction, hydrogen production, etc.), as well as thermal-catalysis (thermally-driven CO₂ cycloaddition, methane dry reforming, photothermally-driven hydrogenation of acetylene to ethylene, etc.). Atomically precise clusters and single-atom catalysts can potentially expose all the metal atoms on the surface, maximizing the number of active sites. They often demonstrate unique activity and selectivity that are characteristic of their configurations and coordination environment. However, with ultrasmall/ultimate-small size and high surface energy, these atomically precise active species sometimes face stability issues and require extra attention to prevent their agglomerations and sintering during prolonged operation involving relatively high temperatures.

The concept of downsizing has been widely explored for catalysts, and some of the reported single-atom catalysts have enabled much advancement in mechanistic understandings of the chemistry of catalyst materials and catalytic reactions. Nevertheless, single-atom catalysts also have various limitations when acting alone, and on
the other hand, atomic clusters, and nanoparticles each offer unique functions. Recent findings offered by the atomic level understanding are valuable in engineering better single-atom catalysts, and even more important in further inspiring the design of more complex catalysts involving rational combinations of the single atoms, atomic clusters, and nanoparticles.

In this review, we will take an "up-sizing" perspective with the new knowledge acquired from the downsizing strategy, treating single atoms as the simplest building blocks in catalyst systems. Indeed, many of the recently reported electrocatalysts involve a mixture of two or even three entities, including single atoms, atomic clusters, or nanoparticles, due to the actual difficulty in obtaining just one of them during the synthesis process of the catalyst. On the other hand, there have been a number of studies that are designed to purposely combine two or even three of them together, for much better electrocatalytic performance of targeted reactions. Therefore, it would be timely to look into the synergistic functions of integrating single atoms with atomic clusters and nanoparticles within the golden triangle, by focusing on three different combinations: single-atoms in combination with single-atoms, single-atoms in combination with atomic clusters, and single-atoms in combination with nanoparticles. We will also summarize and discuss the dynamic nature of catalytic sites during electrocatalytic processes, based on recently discovered new findings, unveiled by some of the advanced in situ and/or operando investigations. Finally, we will identify the challenges and opportunities for furthering our understanding of the synergy in the above themes.

2 | KEY FUNCTIONS OF BINARY INTEGRATION

To understand the potential interactions between the neighboring catalytic active sites in any binary integration of single atoms with other active species, it would be essential to discuss the distribution effects of the active sites. The distribution of the active sites on a catalyst support surface has profound impacts on the potential spillover of reaction intermediates, shielding from nearby sites, as well as other possible synergistic and/or complementary/supplementary functions between the neighboring sites. When the active sites are sparsely distributed on the catalyst surface and situated far from one another, there is often no or very negligible interaction between the different active sites. However, when they come into close enough proximity with each other, a few interactions become possible (see Figure 1):
reaction intermediates from one site can diffuse more easily to the neighbouring site and get further reacted at the second site (catalysis in tandem), such as in the case of hydrogen spillover; (ii) the reaction intermediates/by-products generated from one site can shield the neighbouring sites from effectively binding the reactants, thus adversely affecting the catalytic performance (catalysis in parallel); (iii) the reaction intermediates are solely adsorbed on one active species while the other adjacent modifiers help to regulate its electronic structure and relevant reaction energy barrier.\textsuperscript{[19]} When the neighbouring active sites are brought even closer, the adjacent active sites may even catalyze the reaction in strong synergy, by binding to a reactant molecule concomitantly and stretching the bonds at both ends.\textsuperscript{[20]} Many catalytic reactions are complex, involving multiple pathways/steps and multiple electron transfers, and several of the abovementioned effects are most likely co-existing in real catalytic reactions, although it is challenging to ascertain the exact mechanism behind any correlation observed between the active site distribution and the catalytic activity/selectivity. Besides this, the distribution of the catalytic active sites, as manifested in the inter-site distance, poses a strong influence on the catalyst stability. During catalysis operation, the supported active species are prone to aggregating and sintering (when involving a relatively high temperature), causing deterioration in the catalyst activity over a prolonged period of operation. As such, more densely populated active sites on a support material usually mean a greater tendency to coalescence, requiring extra care in maintaining the long-term catalytic stability.

Due to the actual difficulty in precisely controlling the distribution of the active sites on a catalyst support, the distribution effect on catalytic activity and selectivity is still in the nascent period of its development. Most theories developed before are based on nanoparticles. For example, Pt nanoparticle-based catalysts have been the most adopted model catalyst in various mechanistic studies of the distribution effect, and the effect of inter-particle separation on the catalytic performance has been investigated for the ORR.\textsuperscript{[21–24]} hydrogen spillover,\textsuperscript{[25,26]} etc. With recent advancements in controlled synthesis, high-resolution characterization, and computational techniques, more atomic insights into the catalytic processes are being increasingly realized, and the theories on the distribution effect have also been expanded to address the different configurations of the single-atomic sites in relation to their neighboring sites.

In a number of the recently published research studies, the term “synergistic effect” has often been used (although quite loosely) to refer to any improvements in catalytic performance by a combined effort from different species which work in tandem (typically i.e., each step in CO\textsubscript{2} reduction reaction to C\textsubscript{2}H\textsubscript{4}), or parallel (typically such as HER vs oxygen evolution reaction, OER, or nitrogen reduction reaction, NRR vs. CER, chlorine evolution reaction), or on a sole reaction site (typical in the case of binary metal centers, where one serves as the true active site while the other modifies its electronic state), which can actually mean a few very different interactions. In this review, we aim to summarize and draw a distinction among four types of interactions, (a) synergistic interactions in parallel, (b) synergistic interactions on a sole reaction site, (c) bifunctional effect; and (d) binary complementary effect, as illustrated in Figure 1.

2.1 Synergistic interactions

Here, a synergistic interaction exclusively refers to the qualitative change in catalytic performance by the combination of two or more different types of active species, enabled by modulation in electronic and geometric structures, or the introduction of any stimulus, such as the strain effect. In the binary combination, one species can modulate the structure and properties of the other, giving rise to improvements in the overall catalytic performance. For example, doping of a Pt atom into the Au\textsubscript{24} cluster induces favorable changes to the electronic structure of the gold cluster, leading to enhanced performance in formic acid oxidation as compared to the Au\textsubscript{25} cluster.\textsuperscript{[27]} In this case, the substitution with a single Pt atom introduces synergistic action to the gold cluster and the Pt atom. In another scenario, the two species modulate the electronic structure of each other and they both synergistically catalyze the scission of a bond. Very recently, we have found the effective elongation of the O–O bond in an *OOH adsorbate over two quasi-paired Pt single atoms supported on a Mo\textsubscript{2}C substrate, as seen in ORR, which proves to be several-fold more effective than by either the single Pt atom or the Pt-Pt dimer.\textsuperscript{[28]}

2.2 Binary complementary effect

The binary complementary effect refers to the combination of the two active species in such a way that they each contribute to different intermediate steps in a specific catalytic reaction and thus enhance the overall reaction by completing the functions of one another. It usually involves the spillover of reaction intermediates from one reaction site to the catalyst support, and eventually further reaction at another site nearby. In binary
combinations of catalytic species involving a single atom and the second type of active sites, such as another single atom, atomic cluster, or nanoparticle, the two different catalytic species favor different steps in a multistep catalytic reaction. When dispersed uniformly on a support material, they can catalyze the different steps independently and speed up the overall reaction collectively.

2.3 | Bifunctional effect

The bifunctional effect is based on a simple addition of the different functions such that the binary integration of active species in the catalytic system can offer, and the enhancement effect is often observed at the device level, where more than one catalytic reaction is taking place. For example, a catalyst material can host several types of active sites that are each highly effective towards water reduction and water oxidation respectively, and as a result, the catalyst material can be conveniently used for overall water splitting due to its bifunctional activity in both HER and OER. Similarly, a bifunctional catalyst for ORR and hydrogen oxidation reaction (HOR) can be applied in both electrodes of a fuel cell device, while a bifunctional catalyst for ORR and OER has promising application potential as a cathode material in rechargeable metal-air batteries. For example, Manthiram and a co-worker have reported a bifunctional catalyst for HER, OER, and ORR based on Ni single atoms and NiFe clusters. However, for such bifunctional or multifunctional catalysts with multiple active species, mechanistic understanding often lags behind the performance evaluation, due to the difficulty in isolating the contribution of each active species in the different functions.

3 | INTEGRATING DIFFERENT SINGLE ATOMS

A brief introduction will be made on the most updated developments in noble and transition metal-based single atoms, atomic dimer, and trimer catalysts, highlighting the effects of bond and coordination chemistry on the catalytic performance. The unique physical and chemical properties of the single atom/dimer/trimer catalysts will be examined to elucidate their distinct catalytic functions and mechanisms. An in-depth understanding will then be given on the distribution, synthesis strategies, and synergistic functions from both homogeneous and heterogeneous combinations of different single atoms. Examples will be given of the typical cases to strengthen the discussion on the interactions among the different mixtures of atomic species (including atomic dimers and trimers) for enhanced heterogeneous electrocatalysis.

3.1 | Homogeneous integrations

A homogeneous integration refers to combining single atoms with the same elemental identity to form monometallic dimer/trimers possessing interatomic interactions, denoted as M_n@support, where M refers to noble/transition metals, n = 2 for the atomic dimer, and n = 3 for atomic trimer.

Recently, there has been reporting on the correlation between the inter-site distance (d_site) of the atomically dispersed sites and intrinsic ORR activity, for example, by Jin et al. The authors successfully obtained the uniformly dispersed Fe SAC via a hydrogel-anchoring approach and realized a precise control in the site density and inter-site distance. According to the series of modeling and experimental evidence, when the Fe-Fe inter-site distance (d_site) was less than about 1.2 nm, strong interactions could be observed between the dispersed iron sites, which modulated their electronic structure and gave rise to an increased intrinsic ORR activity. To this end, although the same kind of metal single atoms was integrated through homogeneous combination, inter-atom distance and the number of atoms in the cluster can impact the bond and coordination chemistry, leading to the modified electronic structure and optimized intermediate adsorption. For instance, Pt_3 trimer was anchored on Co@Pd core@shell support, which induced a particular surface charge localization and weakened the chemisorption, thus catalyzing ORR more efficiently. By virtue of the coordination change, charge transfer between Pd atoms at the Pd_2 dual-site enabled the dimer to possess a moderate adsorption strength of CO*, resulting in excellent CO_2RR performance. Also, a ligand modification was observed over the dual-site catalyst. Interestingly, *OH was found to be formed spontaneously on Co_2 dimers, which could act as a modulating ligand to facilitate the *OH → H_2O reaction in the ORR process. Accordingly, the Co_2 dual-site (Co_2N_5) presented roughly 12 times higher activity compared to the Co_1 isolated site (CoN_2). Moreover, atomic dimer/trimer can possess more anchoring sites for reaction and thus increase atomic utilization. For example, homogeneously integrated dimers exhibit lower dissociation barriers for O_2 than their single-atom counterparts, thereby boosting ORR kinetics. Ye et al. ascribed the driving force for O–O bond cleavage to a “dual-side adsorption”, such that each of the adjacent atoms could bond to an O atom of *OOH.
Another study had attributed it to the tailored O₂ adsorption configurations with various numbers of atoms in the cluster. Specifically, Fe₁ single atom was dominated with a superoxo-like O₂ adsorption, whereas Fe₂ dimer and Fe₃ trimer exhibited peroxo-like O₂ adsorption. According to the experimental and theoretical results reported, the peroxo-like O₂ possessed higher adsorption energy and ORR activity attributed to the lengthened O–O bond.[45] Similar to O₂, CO₂ activation can also be promoted by a dual-site reaction.[46] Dual sites of Ag₂ dimer stabilized the chemisorbed CO₂ by co-interacting with the carbon and an oxygen atom of CO₂, lowering the barrier for the *COOH formation.[37]

### 3.2 Heterogeneous integrations

Heterogeneous integration is aimed at assembling different types of noble/transition metal single atoms into bi/tri-metallic dimer/trimers denoted as MᵢMⱼ(M₃)@support, where M₁, M₂, M₃ refer to different types of noble/transition metal atoms. Herein we mainly focus on atomic dimer catalyst, because most of the reported work concerning trimer electrocatalyst by heterogeneous integration is still in the theoretical stage.

In heterogeneously integrated atomic dimers, the introduction of an adjacent secondary metal atom can modulate the electronic structure, manipulate intermediate interactions, and thus promote electrocatalytic activity. For example, in the HER process, the interplay between the metal-H atoms could be tailored by the neighboring metal in Pt-Ru dimer,[38] and Pt-Cu dimer,[39] largely boosting the HER properties. Also, the spontaneous ligand modification arising from electron redistribution has been investigated. The spontaneously absorbed OH on Fe-Co dual-sites served as ligand modulation, which empowered the dual sites to become more active sites for the ORR.[40] Likewise, a mechanistic study had revealed that the Ni-Fe dual sites exhibited a structural variation upon CO₂ uptake. That is, the spontaneous CO adsorption over the dual sites led to a reduced energetic barrier for both CO desorption and COOH* formation, giving rise to excellent CO₂RR activity.[41] Besides this, electrocatalytic selectivity can be enhanced by providing more active atomic sites in synergy. The reduction in O–O dissociation barrier plays a key role in the selectivity of the 4e⁻ ORR pathway. It is worth mentioning that the barrier of O–O cleavage over dual sites was calculated to be much lower than that over a single site.[40,42] To this end, atomic dimer catalysts, such as Fe-Co,[40,43] Co-Pt,[42] and Zn-Co[44] dual site catalyst, have been successfully synthesized and enabled the 4e⁻ ORR pathway by providing dual sites facilitating the O–O cleavage, supporting this viewpoint.[43]

Moreover, a dual-site catalyst is able to provide a more active site for electrocatalysis, giving rise to a pathway with lower barriers and breaking scaling relations, denoted as the complementary effects. For example, in the Ni-Fe dimer catalyst, Ni and Fe atoms could co-contribute to the OER activity. That is, Fe atop sites facilitated the formation of OH⁺ and O⁺ in succession, whereas Ni sites were inclined to adsorb the OOH*. Such a mechanism was proposed to elaborate reasons for the reduced energy barrier.[45] Furthermore, Han et al.[47] developed an atomic dimer electrocatalyst composed of Co-Ni sites dispersed over the N-doped hollow carbon nano-cubes, which served as a bifunctional catalyst promoting both electrocatalytic ORR and OER processes. The dual site-architecture (Co-Ni-N) in synergy gave rise to a decrease in energy barrier and accelerated the reaction kinetics when compared to the Ni₁ single-atom catalyst and Co-Ni nanoparticle counterparts.[47]

### 3.3 Distribution of single atoms

Ideally, atomic dimer/trimers shall be distributed in the support uniformly, and be stabilized through strong metal-support interactions (SMSI).[48] Such SMSI will affect not only the stability but also the activity nature for surface reactions. To this end, it would be essential to examine the distribution of atomic sites on the supports and figure out their local bond coordination environment.

Among the atomic dimer/trimer catalysts reported so far for electrocatalysis, N-doped carbon materials are mostly exploited as supports, owning to their conductivity, tunable surface chemistry, stability, and generally cost. Our discussion will be done with strong reference to this material. N atom doping can modify the electronic structure of carbon as well as create different functional groups, such as pyridine N, pyrrole N, graphitic N, and oxidized N. Metallic-organic framework (MOF)-derived N-doped carbon,[35,49] N-doped carbon nanotube,[43] N-doped graphene,[31,37] and so forth have been employed as supports to anchor atomic dimer/trimers.

When one studies the atomic distributions, one of the imaging techniques is the HAADF-STEM equipped with EELS, which has been used to observe the atom dispersion and elemental composition. Due to the higher atomic mass than those of the carbon-based matrix, metal atoms are differentiated in magnified HAADF-STEM image as the “dense spots”. For atomic dimers, the atomic “dots” would be in pairs; and a cluster of three for atomic trimers.[18] Usually, inductively coupled plasma mass spectrometry (ICP-MS) is adopted to obtain the information of average metal content. For instance, the weight percentage of Fe in Fe₂-N-C is determined as
0.38 wt% in one report\(^{35}\); The Co and Zn content in ZnCo-N-C is 0.14 wt% and 0.33 wt%, respectively, in another report.\(^{50}\) Generally, the metal loading of single-atom catalyst is below 1%. Dual and even triple-site catalysts lead to an increase in metal content to some extent for more active sites.\(^{49}\)

An accurate determination of the local bond environment and electronic structure of atomic dimer/trimers is the key to understanding their natural properties for catalytic reactions, which can be deduced via X-ray absorption spectroscopy (XAS) aided by the first-principles calculations. To identify the atomic dimer/trimers, the distance between two adjacent atoms in the HAADF-STEM image should be comparable with their bond length; and the metal-metal bond peak should be observed in the corresponding EXAFS spectra.\(^{32}\) Then, the coordination environment and interactions with substrate shall also be further established, e.g., FeCoN\(_6\),\(^{43}\) PdN\(_2\)O\(_3\),\(^{31}\) AgN\(_3\)-AgN\(_3\),\(^{37}\) ZnCoN\(_6\)\(^{50}\) being quoted as examples. Also, an appropriate analysis in the electronic structure is of importance for in-depth understandings of the origin of catalytic activity, which can be tailored by defect engineering (vacancies, heteroatom doping, etc.), ligand modification, geometric strain, and the like.\(^{42}\)

Furthermore, the stability of the distributed atoms should be taken into consideration, from both perspectives of stability during the synthesis process and under the reaction conditions. In the precursor-derived electrocatalysts containing atomic species, there is a common stability issue in the preparation process. For example, the Fe\(_3\) complex was converted to an unstable Fe\(_2\) trimer, which would undergo an aggregation during the subsequent pyrolysis.\(^{51}\) Therefore, a “heteroatom modulator approach (HMA)” was developed to tune the aggregation behavior by replacing one Fe(II) ion of the Fe\(_3\) complex with a thermally removable Zn atom. As such, a stable Fe\(_2\) dimer could be achieved with an optimal coordination configuration (Fe\(_2\)N\(_6\)), and the aggregation of iron atoms could be inhibited during the synthesis process. The same consideration applies to the stability of atomic dimer/trimers under the reaction conditions, where surface oxidation and atom aggregation may well take place.\(^{52}\)

### 3.4 Synthesis strategies

Controlled synthesis methods serve an essential role in the preparation of uniformly dispersed combinations for achieving highly effective electrocatalysts. Herein, we briefly introduce several examples of the preparation methods, including wet-chemistry approaches, high-temperature pyrolysis, atomic layer deposition (ALD), and electrochemical activation.

#### 3.4.1 Wet-chemistry methods

Various wet-chemistry methods have been used to develop atomically dispersed catalysts owing to their simple operation, low cost, and great potential for industrial-scale application. Examples of the wet-chemistry routes include impregnation, chemical reduction, deposition-precipitation, etc., which will be briefly introduced below.

Impregnation is a simple and one-pot technique, where the support material is suspended in a solution containing metal precursors to absorb salt species. For instance, a mixed Ni(NO\(_3\))\(_2\)-6H\(_2\)O and SnCl\(_2\)-2H\(_2\)O solution was dropped into 50 ml of ethanol containing N-doped carbon substrate. Subsequently, the salt-absorbed precursor was converted to Ni-Sn dimer catalyst through pyrolysis treatment (Figure 2A).\(^{53}\) The chemical reduction route is usually adopted to obtain metal/alloy-supported atomic dimer/trimers. For example, an aqueous solution containing H\(_2\)PtCl\(_6\)-6H\(_2\)O was added to a solution containing the metal support and reducing agent. Pt\(_3\) trimer decorated Co@Pd core@shell catalysts were then developed. It is important that the reaction time of this step was restricted to 10 s.\(^{30}\) Cu-Pt dimer alloyed with Pd NRs could be made in a like manner. For example, copper precursor (CuCl\(_2\)-2H\(_2\)O) and platinum precursor (K\(_2\)PtCl\(_4\)) were employed and underwent a chemical reduction process in sequence on the Pd support material.\(^{59}\) A deposition-precipitation method to synthesize Pd\(_2\) dimer electrocatalyst has been reported, where the anion NO\(_3\)\(^-\) of water-soluble precursors of Pd\(_2\) (binuclear Pd(II) complexes) was replaced with PF\(_6\)\(^-\) by using KPF\(_6\) as the precipitant. Therefore, the water-soluble precursor could be precipitated and deposited on the support.\(^{31}\) Indeed, the wet-chemistry method is promising for potentially scaling up production, although it is restricted by the lack of precise controls in some of the key processing parameters.

#### 3.4.2 High-temperature pyrolysis

High-temperature pyrolysis has been widely used to synthesize atomic electrocatalysts. During the thermochemical process, carbon/metal-containing precursors undergo thermal decomposition at appropriate pyrolysis temperatures in a controlled environment. Atomic metal dimers can be prepared through pyrolysis of a mixture containing the carbon precursor and mixed metal precursors. For example, metal sources (e.g., cobalt nitrate...
and zinc nitrate), nitrogen sources (e.g., carbamide), and carbon sources (e.g., activated carbon black) were mixed, followed by calcination in Ar atmosphere at 700°C. In this way, Zn-Co dimers on N-doped carbon could be developed. Likewise, a mixture of nickel chloride, iron chloride, and dicyandiamide was annealed to obtain Ni-Fe atomic dimers. Liu et al. and Lu et al. adopted chitosan as the C and N sources by pyrolysis to achieve Zn-Co dimers dispersed on the N-doped carbon substrate. During the process, the N atoms on –NH2 of the chitosan chain simultaneously coordinated with Zn2+ and Co2+ to form the N-Zn and N-Co bond, and enabling a uniform distribution of bimetallic dimers in the carbon-based support (Figure 2B). The pyrolysis temperature is an important parameter and needs to be tuned carefully. For instance, the planar-like Fe2N6 structure was synthesized by coupling isolated FeN4 sites through thermal migration on a highly graphitized carbon substrate. In the preparation process, hemin molecules with typical FeN4 moiety were able to couple with each other to generate Fe2N6 dimer under an Ar atmosphere at 650°C. However, pyrolysis at 600 and 800°C led to the formation of Fe SAC and nanoparticles, respectively.

MOF is one of the most common precursors that have attracted extensive attention in the development of porous carbon-supported catalysts. MOFs possess ultrahigh and well-defined porosity as well as compositional and structural tunability, which can serve as platforms to construct atomic dimer/trimers in a controlled manner. Among the large variety of MOFs, the most commonly used precursors in fabrication of atomic dimer/trimer catalysts are zeolitic imidazolate frameworks (ZIFs) and derivatives, such as ZIF-8 and ZIF-67, attributed to their facile synthesis conditions and relatively high N contents in...
the organic ligands.$^{[40]}$ To obtain a dual-site catalyst, a secondary metal site could be fixed on the nodes of MOFs, or confined within the MOF cavity during the synthesis process.$^{[56]}$

For instance, Co$_2$ dimers could be developed by pyrolysis of Zn$_2$Co$_{1-x}$ZIF at 900°C for 1 h, where the target Co metal is anchored on the nodes of ZIFs via partial replacement of Zn atoms.$^{[32]}$ The Zn/Co ion concentration ratio played a key role in the process. That is, the Co final configurations are expected to be tuned into varied degrees of aggregations, depending on the Zn/Co ion concentration ratio before pyrolysis.$^{[32]}$ On the other hand, to achieve Fe$_2$ clusters, a precursor Fe$_2$(CO)$_9$@ZIF-8 composite could be obtained by confining Fe$_2$(CO)$_9$ compound within cavities of ZIF-8. Fe$_2$(CO)$_9$ in the cavity and ZIF-8 were then decomposed into Fe$_2$ dimers and N-doped carbon, respectively, with the evaporation of Zn simultaneously after thermal pyrolysis.$^{[35]}$ For a heterogeneous integration of single atoms by MOF pyrolysis, the preparation involves controls over the bonding between the metal sites, which are fixed on nodes (host) and confined within the MOF cavity (guest). For instance, Fe molecule Fe(acac)$_3$ as the guest metal source was incorporated into the cavity of the as-formed Zn/Co bimetallic metal-organic frameworks.$^{[40]}$ Tailoring in the ratio of Fe/Co precursor concentration and the evaporation of Zn through pyrolysis enabled the successful synthesis of a dual-site FeCo$_2$N$_4$ catalyst rather than the aggregated metal/ alloy nanoparticles.$^{[47]}$ Likewise, in the preparation of the Zn/Ni/Fe ZIF precursors, Fe species were chemically bonded to the organic ligand as the host, where Ni species were confined in cavities as the guest via ion-exchange route. In the end, Ni-Fe dimers were obtained through thermal pyrolysis of the as-synthesized ZIF precursor.$^{[41]}$ Nevertheless, pyrolysis at high temperatures might result in metal atoms agglomeration or generation of complex species.$^{[40]}$

### 3.4.3 Atomic layer deposition

ALD is a vapor-phase deposition process, in which an atomically thin film is deposited via sequential self-limiting surface reaction of selected precursors on the substrate, which so far has evolved beyond the conventional thin-film synthesis. ALD presents surface chemical selectivity and allows atomic-level control of the metal sites, which has been an emerging technique for the synthesis of SAC supported on a defect-rich substrate.$^{[58,59]}$ To synthesize atomic dimers, one shall develop SAC first, and then perform a second ALD cycle on the as-prepared SAC to realize the atom-by-atom construction. For instance, the Pt-Ru dimer was obtained by ALD to anchor Ru on the as-synthesized dispersed Pt single atoms.$^{[58]}$ To achieve the Pt$_2$ dimer, a second Pt ALD cycle was performed on the Pt$_1$/graphene single-atom catalyst (Figure 2C).$^{[60]}$ In previous works, bis(ethylcyclopentadienyl)ruthenium(II), and MeCpPtMe$_3$ were used as the Ru and Pt precursors, respectively. In spite of the merits of being able to give a set of precise controls, the high cost and low throughput of the ALD method hamper its large-scale applications.

### 3.4.4 Electrochemical activation

Electrochemical activation, as a facile and effective method, has been exploited to generate active species via in situ surface reconstruction of precatalysts, including in situ electrochemical incorporations, oxidation, reduction, etching, etc.$^{[61]}$ Bimetallic dimer catalysts can be obtained through an in situ electrochemical incorporation using SAC as the precatalyst. For example, Fe was incorporated into a Co SAC precatalyst through in situ electrochemical activation in an alkaline electrolyte containing iron species, and the Co-Fe dimer could be generated accordingly. Fe-site in Co-Fe dimer contributed to the obvious enhancement in OER activity.$^{[52]}$

Also, an atomic Co-Pt-N-C coordination structure was achieved by 8000-cycle cyclic voltammetry activation using a Co-N-C precatalyst as the working electrode and a Pt wire as the counter electrode (Figure 2D).$^{[42]}$ Nevertheless, several parameters and factors can impact the electrochemical activation, such as the applied potential, temperature, type of the solution, etc., which would require in-depth understanding.

Compared with the synthesis of conventional single-atom catalysts with onefold metal centers, the preparation of binary single atoms requires more concise controls. As for the homogeneous type, the cluster complex with two or three metal atoms, such as binuclear Pd(II) complexes or Fe$_2$(CO)$_9$ compounds, can be directly employed as the precursor. The binding structure in such precursors can be utilized to restrict the metal agglomeration and precisely alter the metal-metal distance and also the local coordination environment. With regard to the heterogeneous interactions, at least two different metal salts should be used during the synthesis process. Similar strategies to those of single-atom catalysts can realize the isolated form, however, the binding structure (M$_1$M$_2$N$_6$ or M$_1$M$_2$N$_8$) can be difficult to accurately control. It can be only identified through subsequent physical characterizations.

Despite several strategies that have been reported to prepare atomic dimer/trimer catalysts, controllable distributions of atomic dimer/trimer sites on targeted locations of the support with uniform and highly dispersion
still pose great challenges. Moreover, as they possess high surface energies, atomic dimer/trimers are susceptible to aggregation and forming alloys, especially under harsh operation conditions during reaction processes, leading to the deactivation of active sites and degradation of catalytic performance.

To this end, the development of synthesis strategies that offer uniformly distributed and stable atomic dimer/trimer catalysts would be essential to be further investigated.

3.5 Case studies in heterogeneous electrocatalysis

3.5.1 Electrocatalysis involving H2 and O2

Electrochemical reactions involving hydrogen and oxygen generation have gained intensive attention more recently in the development of renewable energy. Herein, the development of atomic dimer/trimer catalysts aiming at achieving high reaction rates and low overpotentials for HER, OER, and ORR will be discussed.

Several examples of atomic dimer/trimers have been reported, demonstrating to promote the HER activity. For example, Zhang et al. have successfully prepared an electrocatalyst containing Pt-Ru bimetallic dimers via the ALD process for HER (Figure 3A). The Pt-Ru bonding configuration and interatomic interaction were revealed by XAS, as shown in Figure 3B. Thanks to the synergetic interactions between Pt-Ru dimers, the dxz orbital of Ru became unoccupied upon hydrogen adsorption, thereby optimizing the H atom binding energy (Figure 3C). Figure 3D shows that the activity of Pt-Ru dimers was improved more than 50 times in comparison with the commercial Pt/C catalysts. Chao et al. have reported the successful development of the Cu-Pd dimeric catalyst alloyed with Pd nanorings. As investigated by DFT calculations, the Pt sites functioned as the active sites, and the interaction between Pt-H* was balanced and optimized by the necessary neighboring Cu sites. Consequently, the thus-formed atomically dispersed Cu-Pt dimers on Pd nanorings showed remarkable HER performance, achieving an overpotential of as low as 22.8 mV at the current density of 10 mA cm-2.

For OER, the surface reconstruction of electrocatalyst has been studied as a hot topic over the past several years. For example, *Operando* XAS data indicated that the Co SAC precatalyst underwent structural variations upon immersion into the electrolyte containing Fe species, and was in situ converted into a dimeric Co-Fe structural motif. The incorporated Fe was responsible for the much-improved activity of Co-Fe dimeric catalyst, based on the correlation between the catalytic activity with the amount of Fe, showing the highly efficient OER electrocatalyst composed of atomically dispersed dimers with excellent turnover frequencies.

Moreover, atomic dimer/trimers have been extensively investigated as the ORR electrocatalyst more recently, including both the homogeneous and heterogeneous combinations of single atoms. Taking Pt3 trimer as an example of the homogeneous integration, Dai et al. developed a ternary nanocatalyst composed of Co@Pd core@shell architecture and surface decorated Pt3 trimer with low Pt content (2.4 wt%) to catalyze OER. By virtue of the Pt3 decoration, not only could the induced unique charge localization weaken the chemisorbed anions and improve the ORR properties, but also the highly stable Pt3 endowed the electrocatalyst with excellent stability, which is shown in Figure 3E,F. Accordingly, the catalyst exhibited more than 30-time-increase in the ORR mass activity compared to a commercial Pt electrocatalyst, and outstanding durability with no degradation for more than 322,000 potential cycles. As has been discussed in Section 3.2, a heterogeneous integration of single atoms to form dual sites is able to facilitate O2 dissociation and thereby enhance 4e− ORR pathway selectivity. The strong binding of O2 on the Fe-Co dual-site led to an elongated O−O bond length thus promoted the cleavage of O=O bond. As shown in Figure 3G, the dissociation barrier of O2 and OOH* into O* (0.25 eV) and OH* (0.02 eV) on Fe-Co dimeric catalyst was much lower than those on Fe or Co SACs. A new “quasi-paired single atoms” concept has been proposed, that is in between the isolated single atoms with zero interaction and the closely coupled, bond-forming metal dimers. Like the atomic dimers, such quasi-paired Pt single atoms are also able to facilitate 4e− ORR through inter-site synergistic interactions.

The coordination and local environment of atomic dimer/trimers on the support are important considerations. Interestingly, it has been verified by DFT calculations and in situ XANES spectroscopy that the OH over dual sites could be spontaneously formed and served as the modifying ligands to enable dimers more active. Hence, the most active configuration among different Fe-Co bonding structures was deduced as FeCoN5−OH, which enabled the ORR onset potential and half-wave potential to achieve 1.02 and 0.86 V (vs. RHE), respectively, with the activity being improved by a factor of over 20 in comparison with the FeN4 SAC. In addition, defect engineering is of significance to improve ORR properties. For example, the atomically dispersed Co-Pt dimers were observed to be trapped in vacancies to form Co-Pt-N-C coordination architectures from the HAADF-STEM image. Through a further analysis based on XANES results, the structured environment could be deduced as (Co-Pt)@N8V4 (where N8 refers to the number of nitrogen atoms and V4 represents the number of...
carbon vacancies). DFT calculations on model structures have revealed that atomic coupling at the carbon defects not only could modulate the electronic structure of the metal atoms but also lead to charge redistribution at the coordination structures, boosting the ORR performance.\[42\]

3.5.2 | Electrocatalysis involving N\textsubscript{2}

Electrochemical NRR presents a promising approach to transform N\textsubscript{2} into NH\textsubscript{3}, i.e., N\textsubscript{2} + 6H\textsuperscript{+} + 6e\textsuperscript{-} → 2NH\textsubscript{3}, which can be operated under mild conditions and powered by renewable energies. In spite of the great enthusiasm in developing catalysts for NRR has been aroused, little systematic experimental work has been reported on the atomic dimer/trimer catalysts, although there have been several studies on single-atom electrocatalysts for NRR.

Understandings on dimer/trimeric catalysts for NRR almost remain at the theoretical stage for catalyst screening or designing by means of DFT simulations. Calculation work has been done to illustrate the importance of atom number control in designing efficient
and economic metal catalysts. For example, an optimal form of Mo species was calculated to be Mo$_0$@GDY among Mo$_x$@GDY ($x = 1–4$), with a low onset potential of $-0.32\,\text{V}$ via the distal mechanism. The activity is beneficial from the moderate energy of *N* adsorption, which balances the PDS steps of N$_2$ adsorption and NH$_3$ desorption reactions.[65] Besides, Deng et al.[66] have worked on N-doped graphene-supported atom-pair catalysts (APCs) for NRR reactivity. According to their calculations, transition metal APCs prefer the enzymatic NRR pathway. Particularly, transition metal APCs presented a unique feature such that the more negative N$_2$ adsorption energies they present, the more capable they suppress HER side reaction.[66] Additionally, Lv et al.[67] have studied the TM APCs as well for the NRR by using high-throughput screening, and demonstrated another unique feature of APCs in comparison with their single atom counterparts. That is, the occupied d orbitals of dimer-atoms can facilitate N$_2$ activation by the donation of more electrons to N$_2$ (Figure 4A). By screening, Fe$_2$ dispersed over graphite carbon nitride was predicted to show the best NRR performance among the 23 transition metal centers, owing to the moderate binding strength with the reaction intermediates, as shown in Figure 4B.[67]

Zheng et al.[68] have investigated 24 transition metal trimers supported on N-doped graphene by using DFT calculations for electrochemical NRR activity. Among these studied trimers, the Ni$_3$, Ru$_3$, and Ir$_3$ were calculated to possess great potential for NRR catalysts considering their low limiting potential, good stability, and excellent selectivity. They demonstrated that the high NRR activity was originated from the pull-push effect, on account of the d-$\pi^*$ acceptance donation mechanism.[68] Also, these authors have tried to bridge the correlation between the NRR activity and intrinsic electronic properties of atomic dimer/trimers by constructing an electronic descriptor like d-orbital electrons, which would need further experimental verification.[66,68]

### 3.5.3 Electrocatalysis involving CO$_2$

Electrochemical reduction of CO$_2$ (CO$_2$RR) into value-added chemicals is a promising and sustainable pathway to achieve carbon neutrality, which has attracted considerable attention more recently.[36] A homogeneous or heterogeneous integration of single atoms into dimer/trimers can promote the multiple-step reactions, where their synergistic interatomic interactions and increased active sites enable the practicality to improve both the CO$_2$RR activity and selectivity.[69]

Zhang et al.[31] developed a Pd$_2$ dimer catalyst and applied it for CO$_2$RR for the first time. As a result of the charge transfer between Pd atoms, the adsorption strength of CO* at the Pd$_2$ dual-site was optimized. Therefore, the Pd$_2$ dimer catalyst exhibited superior CO$_2$RR catalytic properties to the Pd single-atom catalyst, with a FE$_{CO}$ of as high as 98.2% at $-0.85\,\text{V}$ versus RHE.[31] Moreover, the “atom-pair catalyst (APC)” was found to be able to promote CO$_2$ activation. For instance, an alloy supported copper APC was successfully synthesized, which consisted of one Cu atom binding with O and an adjacent Cu to develop a Cu$_1^0$-Cu$_1^{2+}$ APC. Based on the experimental and computational results, the Cu$_1^0$-Cu$_1^{2+}$ pair was the essential active site in CO$_2$RR. Also, a “biatomic activating bimolecular” mechanism was proposed, that is, the Cu$_1^{2+}$ site adsorbed the H$_2$Omolecule, which stabilized the chemisorbed CO$_2$ molecule on the adjacent Cu$_1^0$ site, hence promoting CO$_2$ activation. Such ‘biatomic activating bimolecular’ resulted in an enhanced selectivity with a CO generation of above 92% and suppressed competing H$_2$ evolution reaction.[36]

For heterogeneously integrated dimers, Xie et al. developed a Ni-Sn dual-site catalyst anchored on a carbon nanosheet array structure. A series of characterization and calculation results confirmed the structured environment with an N$_4$-Ni-Sn-N$_4$ configuration, where the adjacent Ni-N$_4$ promoted the charge redistribution of Sn and thus reduced the energy barrier of *OCHO intermediate (Figure 4C-E). The presence and evolvement of *OCHO intermediate were further confirmed by in situ attenuated total reflection-infrared (ATR-IR) spectroscopy, which is shown in Figure 4F. These attributes gave rise to a brilliant selectivity with the yield of formate as high as 36.7 mol h$^{-1}$ g$_{Sn}$ $^{-1}$, superior to previously reported SACs (Figure 4G,H).[53] In addition to the reduced reaction barrier induced by charge redistribution, a mechanistic study revealed the ligand effects as well. It was observed that Ni-Fe dimers exhibited a structural change upon CO$_2$ uptake that could adsorb *CO spontaneously. Such ligand modification resulted in the great CO$_2$RR activity by decreasing the energy barrier for both the COOH* formation and the CO desorption. In this way, the Ni-Fe dimeric electrocatalyst exhibited high selectivity with FE$_{CO}$ achieving above 90% over a wide potential range.[41]
as being smaller than 2 nm or composed of fewer than 100 atoms. In this section, we will focus discussions on the combinations involving single atomic sites and metal clusters with a particular emphasis on their precise structures, geometric configurations, and catalytic properties.

4.1 Homogeneous types

A homogeneous integration of single atoms and atomic clusters consists of homo-metal clusters and single atomic sites with the same metal element. In other words, the two types of active species contain the same metal element but differ in the dispersion state.

Homometal clusters refer to clusters containing only one type of metal element, although sometimes they can also involve the incorporation of nonmetal heteroatoms (e.g., O, S, N, etc.) in compound forms. Such clusters are used extensively as prototypes for mechanistic studies due to their simplicity in the composition coupled with precise tunability in the atomicity and structure. Unlike in nanoparticles, where the atomicity is of less interest as

![Figure 4](image-url)
compared to its composition or the exposed facets, the exact number of atoms in a sub-nano-cluster has an overwhelming impact on its electronic and geometric properties. Instead of adopting a crystalline structure that appears directly truncated from the lattice of bulk particles, atomic clusters tend to undergo rearrangement of atoms to achieve a stable structure by themselves. As a result, a scalable trend of catalytic activity with respect to the cluster size remains elusive. For example, Yamamoto et al.\cite{70} have studied the magic cluster Pt\textsubscript{13} and its nonmagic sibling Pt\textsubscript{12} for the ORR and discovered that Pt\textsubscript{12} exhibited twofold ORR activity as compared to Pt\textsubscript{13}. The notably higher ORR activity of Pt\textsubscript{12} is due to a substantial transition in the structure with the removal of one Pt atom from the icosahedral Pt\textsubscript{13}, and the consequently optimized oxygen-binding strength, which falls near the top of the volcano plot (Figure 5A–C).\cite{70} In another study by Yamamoto et al., the Pt\textsubscript{10} cluster has been demonstrated to possess a rigid pyramidal structure with electron-rich vertices that can activate C\textequiv{}C double bond effectively during the styrene hydrogenation reaction, while Pt\textsubscript{8} and Pt\textsubscript{9} exhibit much more inferior performance due to their nonrigid structures and the lack of electron-rich vertices (Figure 5D,E).\cite{71–73}

Furthermore, given a certain cluster size, the arrangement of atoms can vary, leading to the occurrence of geometric isomers with different energetic properties. For example, Au clusters with atomicity of 18 atoms can adopt two different structures, Au\textsubscript{18a} and Au\textsubscript{18b}.\cite{74} In CO oxidation, these two Au\textsubscript{18} geometric isomers exhibit rather different O\textsubscript{2} absorption abilities. Au\textsubscript{18a} adopts a cage-like structure and shows no O\textsubscript{2} adsorption capability, while Au\textsubscript{18b} has a truncated pyramidal structure and can weakly and exothermically adsorb O\textsubscript{2} (Figure 5F).

In view of the special characteristics of atomic clusters, a proper understanding of the binary integration of single

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**Figure 5**  (A–C) Volcano plots and free-energy diagrams for the oxygen reduction reaction by Pt catalyst. (A) Optimized geometric structures of Pt\textsubscript{12}(C\textsubscript{2v}), Pt\textsubscript{13}(icos), and the FCC (face-centered cubic) nanoparticle are assumed in this investigation. (B) Kinetic current density (j\textsubscript{K}) plotted as a function of the calculated oxygen adsorption energy (\Delta\textsubscript{E\textsubscript{o}}). All data are shown relative to Pt. The predicted j\textsubscript{K} values based on the calculated \Delta\textsubscript{E\textsubscript{o}} for each nonequivalent threefold hollow site on Pt\textsubscript{12}(C\textsubscript{2v}) were plotted as blue circles. The \Delta\textsubscript{E\textsubscript{o}} values for Pt\textsubscript{13}(icos) were out of the range (\textasciitilde{}\textasciitilde{}1.0 eV) of this diagram. (C) A diagram of the relation between the particle size and the relative oxygen binding energy (\Delta\textsubscript{E\textsubscript{o}}). Reproduced with permission.\cite{70} Copyright 2013, American Chemical Society. (D, E) Styrene hydrogenation and its reaction barriers under the existence of platinum catalysts. (D) Hydrogen insertion processes into \alpha{}-carbon and \beta{}-carbon, and the corresponding transition states with Pt\textsubscript{10} catalyst. (E) Calculated reaction barriers under the existence of Pt\textsubscript{8}, Pt\textsubscript{9}, or Pt\textsubscript{10} catalyst. Reproduced with permission.\cite{64} Copyright 2017, Springer Nature. (F) Schematic illustration of adsorption energies of CO and O\textsubscript{2} on anionic and neutral clusters Au\textsubscript{16}–Au\textsubscript{18}, and Au\textsubscript{20}. Adsorption energy color code: dark green, <\textasciitilde{}0.9 eV; green, 0.5 to <\textasciitilde{}0.9 eV; orange, \textasciitilde{}0.2 to <\textasciitilde{}0.5 eV; gold yellow, 0.0 to <\textasciitilde{}0.2 eV; blue, no binding. Reproduced with permission.\cite{74} Copyright 2011, American Chemical Society
atoms and atomic clusters requires highly controllable synthesis techniques and precise characterization of the geometric, electronic, and coordination structures of both the single atoms and the clusters. However, despite the immense efforts to tune and examine the detailed structure of single atomic sites, the precise structure of atomic clusters in these systems is often overlooked, and much too often the clusters are confused with nanoparticles.

Currently, there are two major techniques to synthesize catalysts with a binary integration of homo-metal single atoms and atomic clusters. The first technique involves pyrolysis of a precursor to form single atoms dispersed in a support material (often N-doped carbon), and a subsequent reductive annealing process to convert some of the single atoms into clusters. The degree of dispersion can thus be controlled to a certain extent, by adjusting the temperature and duration of the heat treatment, but the resulting material often contains a range of cluster sizes (sometimes even larger nanoparticles). For example, Li and co-workers have used a Ti MOF precursor to synthesize Pd single atoms and clusters supported on defect-rich TiO₂ (Figure 6A–G).\(^75\) In another work, Pt single atoms were first loaded on defective graphene by impregnation, and the material is then annealed in a reductive atmosphere to form a combination of clusters and single atoms.\(^76\) Another effective technique used to synthesize binary integration of homo-metal single atoms and clusters is ALD. Owing to the sequential and self-limiting surface reactions in ALD, more precise control on the size and distribution of the clusters can be achieved, as exemplified by the work of Sun et al. who have fabricated Pt single atoms and clusters on nitrogen-doped graphene by ALD (Figure 6H–L).\(^77\)

### 4.2 Heterogeneous types

In a heterogeneous integration of single atoms and clusters, the single atoms and clusters contain more than one type of metal element. It can consist of homo-metal clusters and single atomic sites of a second metal element, both dispersed on the same substrate material, or hetero-metal clusters and single atomic sites. In the latter scenario, the single atoms may be supported on the substrate material away from the cluster, or it can be doped as part of the hetero-metal cluster.

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**Figure 6**: (A) Schematic diagram for the preparations of Pd\(_{\text{SA}/}\)TiO\(_2\)-VO and Pd\(_{\text{SA+C}/}\)TiO\(_2\)-VO photocatalysts. HRTEM image, AC-HAADF-STEM image, HAADF-STEM image, and corresponding EDS element mappings of (B–D) Pd\(_{\text{SA}/}\)TiO\(_2\)-VO and (E–G) Pd\(_{\text{SA+C}/}\)TiO\(_2\)-VO. Reproduced with permission.\(^75\) Copyright 2021, John Wiley and Sons. (H–K) ADF STEM images of ALD Pt/NGNs samples with (H, I) 50 and (J, K) 100 ALD cycles. Scale bars, 10 nm (H, J), 5 nm (I, K). (L) Schematic illustration of the Pt ALD mechanism on NGNs. The ALD process includes the following: the Pt precursor (MeCpPtMe\(_3\)) first reacts with the N-dopant sites in the NGNs (i). During the following O\(_2\) exposure, the Pt precursor on the NGNs is completely oxidized to CO\(_2\) and H\(_2\)O, creating a Pt-containing monolayer (ii). These two processes (i and ii) form a complete ALD cycle. During the process (ii), a new layer of adsorbed oxygen forms on the platinum surface, which provides functional groups for the next ALD cycle process (iii). Reproduced with permission.\(^77\) Copyright 2016, Springer Nature
The attractive properties of ready mixing between different metals have been found to be a feature unique to the atomic clusters, owing to the finite size effect. For instance, the immiscible pair of Fe and Ag in the bulk alloy form is found to mix readily in a finite-sized cluster.\textsuperscript{[78]} This shines new light on the distinct properties of, and the diverse possibilities enabled by sub-nano hetero-metal clusters. Atomically precise hetero-metal clusters have been typically synthesized by wet-chemistry methods. For instance, the Pt\(\textsubscript{1}\)Au\(\textsubscript{24}\)(SR)\(\textsubscript{18}\) clusters have been synthesized by Chen et al.\textsuperscript{[27]} following a modified method from that for the Au\(\textsubscript{25}\)(SR)\(\textsubscript{18}\) clusters, in which six \([-\text{SR-Au-SR-Au-SR-}]\) oligomers coordinate and stabilize the central icosahedral core of Pt@Au\textsubscript{12}. The clusters are subsequently mixed with and stabilized onto a catalyst support material, in this case on multi-wall carbon nanotubes, to form the final catalyst material. In another work, Yang and co-workers have synthesized Pt\(\textsubscript{1}\)Ag\(\textsubscript{24}\)(SR)\(\textsubscript{18}\) and Ag\(\textsubscript{25}\)(SR)\(\textsubscript{18}\) clusters on g-C\(_3\)N\(_4\) support by a similar method.\textsuperscript{[79]} The wet-chemistry method has also been applied to synthesize Au\(\textsubscript{47}\)Cd\(\textsubscript{2}\)(TBBT)\(_{31}\) through mixing two separate precursor solutions containing respective Au and Cd followed by a solvothermal process, as has been demonstrated by Wu et al.\textsuperscript{[80]}

As compared to their relatively simplistic homo-metal counterparts, the bimetallic or even multimetallic clusters usually show improved stability and catalytic activity arising from metal atoms with complementing size and synergetic chemistry. Nevertheless, a truly rational design of hetero-metal clusters and in-depth understanding of the catalytic mechanism with atomic precision is still in its infancy, as the systems of hetero-metal clusters are much more complicated: a study of the numerous possible compositional isomers and homotops, existing from the combination and permutation of merely two types of metal atoms in a small-sized cluster, is an astounding task even by computational means, let alone by the limited experimental and characterization techniques available to date. Therefore, atomic-scale insight into hetero-metal clusters is an intriguing yet challenging topic, which would need more systematic studies on the combinations of different metal types, the ratio between the multinary components, and the geometric isomers arising from each combination, and the likely different charge states adopted by the clusters.

### 4.3 Distribution of single atoms and clusters

In a binary integration of single atoms and clusters, the two species can assume two types of distribution, which in turn affects the possible interactions between the two players. First, as has been commonly observed for homogeneous combinations of single atoms and clusters, both species are independently supported on a high-surface-area substrate material, following a uniform and random distribution. In this case, the neighboring active sites are often situated sufficiently far from each other such that there is often negligible interaction directly between the different catalytic species. Therefore, the type of interaction present can normally be classified under the binary complementary effect or the bifunctional effect, in which the single atoms and clusters most effectively contribute to different intermediate steps of a certain catalytic reaction, or work on entirely different reactions in the catalytic system.

The spillover effect is one typical example that the single atoms and clusters catalyze in different steps and cooperate to boost the activity of one specific reaction. In many electrocatalytic reactions, such as HER, OER, NRR, CO\(_2\)RR, etc., a major consideration is to ensure fast adsorption and desorption of intermediates on the catalyst active sites. However, the ability to efficiently adsorb and desorb similar intermediate species is commonly contradictory. In this case, the spillover effect becomes important to allow the adsorption and desorption to occur at different active sites and ensure higher overall catalytic activity. Besides the enhancement of activity, the selectivity can also be improved. For instance, a cluster contains many ensemble sites which favor multi-electron reaction pathways, such as the 4-electron ORR pathway or multi-carbon CO\(_2\)RR pathway. By building an appropriate cluster and single atom combination, the selectivity to those reactions can be increased.

The second type of distribution applies to the heterogeneous integration, in which the single atom is directly bonded with the cluster of another metal element, forming one hetero-metal cluster, and such clusters are subsequently stabilized on the substrate material. Due to the direct involvement of the single atom in the cluster, the two species form strong interactions and synergistically catalyze a reaction, via a few mechanisms. First, the hybridization of energy states between the different metal atoms in the heterogeneous single atom-cluster system can modulate the overall electronic structure, and therefore lead to different interactions between the reaction intermediates and the cluster surface. Besides this, the single-atom has different adsorption properties as those atoms in the cluster, which offers different adsorption configuration of the intermediates and affect the selectivity. In addition, the introduction of the foreign single atom can lead to changes in the physical properties such as the strain, electrical conductivity, etc., in turn affecting the catalytic performance.
4.4 | Synthesis strategies

As mentioned above, several synthetic strategies can be employed to obtain high-efficient electrocatalysts with integrated single atoms and atomic clusters as binary active species. As for the homogeneous types, secondary annealing can transform the partial single atoms in the precursor (often N-doped carbon substrate) into tiny atomic clusters. The conversion degree must be well controlled by customizing the pyrolysis temperature and holding time, while the particle size of the as-obtained clusters is hard to control precisely. Another technique is the ALD. The adjustable ALD cycles and time can bring about the controllable size and distribution of the clusters, thus becoming an important technique to integrate binary active species.

With regard to the heterogeneous types, the hetero-metal cluster, namely single-atom alloys are usually prepared by wet-chemistry methods. By controlling the dosage ratio of hetero-metal salt, the single-atom alloys can be well achieved. Besides, the ALD technique can also be utilized to obtain heterogeneous integration of single atoms with atomic clusters. The single-atom catalysts with carbon substrates can be prepared through various methods, and the following ALD of different metal sources can further lead to the generation of hetero-atomic clusters upon the M$_1$-N$_x$-C substrates. Admittedly, many more potential synthetic strategies await to be explored, where the means of more precisely controlling the cluster sizes, the spatial distribution, and content ratio of single atoms to atomic clusters shall be developed.

4.5 | Case studies in heterogeneous electrocatalysis

Binary integrations of single atoms with clusters have demonstrated encouraging prospects in heterogeneous electrocatalysis, including HER, ORR, formic acid oxidation, and CO$_2$RR. The successful improvement in performance and the proposed mechanism are detailed in the following case studies. For example, Li et al. have developed an efficient catalyst consisting of Pt single atoms and nanoclusters supported on defective graphene matrix (PtSA/NC-DG) for HER in alkaline media. Benefiting from their different strength towards water dissociation and hydrogen coupling, the coexistence of Pt single atoms and Pt clusters can decouple the HER reaction, functioning on different steps and improving the overall performance. As compared to Pt single atom and Pt/C, the integration of Pt SA-cluster shows a much smaller overpotential of 41 mV and higher mass activity of 5.40 mA μg$_{Pt}^{-1}$ at 100 mV (Figure 7A,B). The DFT calculation results also suggest that the Pt$_{38}$ cluster has the smallest energy barrier of 0.59 eV for water...
dissociation, and Pt1-C3Ny single atom has the most moderate hydrogen binding energy, which would favor fast hydrogen coupling (Figure 7C–F).\textsuperscript{176}

For applications in ORR, Lee et al.\textsuperscript{81} have found that the integration of clusters together with active single sites can adjust the electronic structure of the single atom. The synthesized FeN₄/Fe₄/C system presents a negatively shifted d-band center of Fe compared to either the single atom or the cluster alone, leading to an optimization in the interaction between the catalyst and the intermediates as well as a better ORR performance. The energy required for the potential determining step for the binary integration is thus smaller than that on the cluster counterpart (Figure 8A–C). The ORR half-wave potential of the FeN₄/Fe₄/C is 0.9 V and the diffusion-limited current density is 4 mA cm\textsuperscript{−2}, which can match up with

![Image](image_url)
those of the Pt/C (Figure 8D).\textsuperscript{[81]} The electron transfer number $n$ for the FeN$_4$/Fe$_d$/C system with sufficient Fe clusters (Fe/NC-3) is between 3.75 and 3.85 in the potential window of 0.2 and 0.8 V, suggesting a higher selectivity towards the 4-electron ORR pathway than the samples with fewer Fe clusters (Fe/NC-1 and Fe/NC-2) (Figure 8E).

For direct formic acid oxidation to carbon dioxide, Chen et al.\textsuperscript{[27]} have synthesized a class of Pt$_1$Au$_{24}$(SR)$_{18}$ clusters and discovered that they exhibit a superior mass activity of 3.7 A mg$^{-1}$, which is 12 and 34 times higher than that from Pt nanocluster and commercial Pt/C, respectively. The Pt$_1$Au$_{24}$ cluster exhibits a similar structure as the Au$_{25}$ cluster with the only difference being that the central Au atom in the Au$_{25}$ cluster is replaced by Pt in Pt$_1$Au$_{24}$. As a result, the overall projected density of states has been shifted and the interaction between the intermediates and the cluster surface has been improved. On the other hand, the gold shell can act as a protecting shell to avoid CO poisoning, leading to synergistically enhanced performance.\textsuperscript{[27]} A similar effect was verified when applying Au$_{47}$Cd$_2$(TBBT)$_{31}$ as the catalyst for CO$_2$ RR.\textsuperscript{[80]}

The above case studies are examples of the decent progress made recently in the fabrication and application of the binary integration of single atoms with clusters. However, a few major issues remain, which have often prevented a more in-depth understanding from being achieved. In many works that have studied the combinations of single atoms and clusters both on the same support material, lack of the proper experimental synthesis techniques often results in products having a range of cluster sizes and atomicity with indeterminable structures. As such, the DFT studies designed to elucidate the mechanism unavoidably rely on over-simplified models, which sometimes make an arbitrary choice that does not correlate with the experimental results. Another major issue is the insufficiency in control groups to establish the real synergistic effect between the single atoms and the clusters. For example, performance enhancements are sometimes established by comparing the combination of single atoms and clusters with another sample consisting of only single atoms. However, without additional control groups that feature only the clusters (without single atoms), it is difficult to ascertain whether the performance enhancement is indeed due to the synergistic effect between the two players, or it is contributed by having clusters alone, or even a merely higher metal loading in the sample. Again, as being limited by synthesis techniques, it is difficult to achieve proper control samples with precisely tunable composition and monodispersing active species.

## 5 Integrating Single Atoms with Nanoparticles

Metal nanoparticles and single-atom sites can be made to coexist by proper controls in the synthesis of electrocatalysts. Large nanoparticles could be leached out by strong acid as has been demonstrated in several studies, to obtain unitary single-atom sites.\textsuperscript{[82,83]} Recently, a co-existence of nanoparticles and single-atom sites has been demonstrated to achieve better electrocatalytic activity than the SACs alone.\textsuperscript{[84,85]} Actually, in many of the systems consisting of nanoparticles assembled on substrates, depending on the synthesis techniques used, some single-atom sites would exist already. Therefore, the presence of potential single-atom sites shall be taken into account, when one studies these catalysts. Synergistic effects shall be among the considerations in leading to superior catalytic activity and selectivity. Hence, it would be of interest to explore the integration of single atoms with nanoparticles.

### 5.1 Homogeneous types

With regard to the cooperative catalysis systems of combining single-atom sites and nanoparticles, a homogeneous type signifies that the central metals on single-atom sites are the same element as the metal component of the nanoparticles. The nanoparticles can be of single metals, alloys, or relevant compounds (oxides, chalcogenides, nitrides, phosphides, carbides, borides, et al.). Lin and co-workers prepared a class of template-free mesoporous carbon nanorods possessing isolated Ni-N$_x$ sites and Ni nanoparticles, by pyrolyzing the rectangular nickel dimethyglyoximate (Ni(dmgH)$_2$) nanorods.\textsuperscript{[86]} Some large Ni particles could be removed by strong acid etching, and a composite-type material with the presence of both single-atom Ni and smaller Ni nanoparticles was obtained. Such a simple synthesis process for achieving dual active species could roughly tune the ratio of single-atom sites to nanoparticles by controlling the leaching time. The method is similar to the “inchoate synthesis method” of carbon-supported metal-based electrocatalysts.

### 5.2 Heterogeneous types

By definition, a heterogeneous type implies the difference between the central metal atoms in single-atom sites and the metal element of nanoparticles within the nanocomposite. This means that at least two different metal sources should be introduced into the precursor
during the synthesis process. The formation of metal or compound nanoparticles normally requires the use of a high-temperature sintering process, which would raise questions about how to precisely control the monatomic form of one metal while sintering the other metal into nanoparticles. Liu et al. have proposed that the Fe/Co/Ni-Nx sites could regulate the π-conjugated structure of carbon substrate to enhance the interaction with loaded Ru nanoparticles, thereby promoting the electron transfer and enhancing the catalytic activity, from the theoretical viewpoint. But for the synthesis, due to the introduction of two different metal sources, the possibility of existing Fe/Co/Ni-doped Ru nanoparticles and the isolated Ru atoms cannot be ruled out, in addition to the isolated Fe/Co/Ni-Nx sites and Ru nanoparticles. This controversy will be discussed later in the section of synthetic strategies.

5.3 Distribution of single atoms and nanoparticles

To understand the distribution and contribution of single atoms and nanoparticles, one needs to distinguish different situations according to the applied substrates. One case is that the as-formed nanoparticles are directly employed as the substrate, where the extraneous metal atoms are anchored in isolation through strong chemical bonding and serve as the atomic dopants. The other case is that the single metal atoms are anchored on another substrate material, such as a carbon-based framework, by bonding with the heteroatoms from the basement. Meanwhile, the nanoparticles are loaded on the surface of substrates containing single atoms, or wrapped under the thin substrate layer. Next, we will discuss the distribution of single atoms and nanoparticles in line with these two situations.

For the former, nanoparticles serve as the substrate, and the single atoms as dopants are almost uniformly distributed upon the particle substrate. For instance, Tan and co-workers synthesized single-atom platinum incorporated nanoporous Co0.85Se (Pt-np-Co0.85Se) through electrochemical deposition with np-Co0.85Se as the working electrode. As shown in Figure 9A, the partial dissolution of Co atoms from the electrode and consequent cation vacancies provided sufficient anchoring sites for the incorporated Pt atoms. The HAADF-STEM image showed that the bright Pt atoms were separately anchored in the lattice of Co0.85Se, which was confirmed by the separated atomic spacing (Figure 9B,C). With such a high resolution, the single-atom Pt seems to be irregularly distributed on the Co0.85Se, resulting from the restricted observation angle. However, the STEM-EDX elemental mapping with relatively lower magnification exhibited the uniform dispersion of Pt atoms on the ligaments’ surface (Figure 9D). Homogenous distribution of single atoms on the surface of nanoparticles was widely observed in other reported literature, such as Pt1/RuO2, Pt-SAs/MoS2, Mo2TiC2Tx-PSAs, Pt1-Fe/Fe2O3(012), Ni5P2-Ru. For these materials, the active sites can be the isolated metal atoms or the adjoining metals/heteroatoms of the nanoparticle substrates.

The above case studies have mainly focused on the single-phase nanoparticles, and the situations might be different if the nanoparticles are composed of two-phase or even multiple-phase heterostructures. For example, Wang et al. proposed by Bao et al. coupled single-atom platinum within the NiO/Ni heterostructure through stepwise electrodeposition and electroreduction (Figure 9E). The NiO/Ni nanosheets were first electrochemically deposited on the Ag nanowire networks, and then the Pt single atoms were immobilized upon the heterostructure. Interestingly, according to the HAADF-STEM images, the single-atom Pt was mostly anchored alongside the phase interfaces of NiO/Ni (Figure 9F,G). Theoretical simulations had confirmed that the atomically dispersed Pt atoms at the heterogeneous interface acted as more active sites.

As for the latter, due to the presence of another substrate, the single atoms can be considered to be evenly distributed while the nanoparticles are randomly loaded on the substrates. As such, the respective distributions of single atoms and nanoparticles shall be considered, where there can be three types, namely: (i) wrapped type, (ii) anchoring type, and (iii) tandem type, as has been modeled in DFT studies.

(i). Wrapped type

The wrapped type is that the nanoparticles are totally covered with the substrate material containing single-atom sites. One example of the substrate materials is the few-layer graphene with isolated porphyrin-like metal-heteroatom-carbon sites, where the mechanism is similar to the chainmail catalysis proposed by Bao et al. With the wrapped active metal nanoparticles, the electronic states of those surface isolated metal-heteroatom (M-Hx) sites could be optimized through interactions with the active valence electrons from the internal nanoparticles. Thus, the surface M-Hx sites could serve as the more efficient reaction sites in the electrocatalytic reactions. Besides this, the corrosion and deactivation phenomena could be retarded, because the wrapped carbon layers protect the active metal particles from direct contact with corrosive electrolytes. Thereby, the activity and durability were synchronously enhanced.
FIGURE 9  (See caption on next page)
Liu and co-workers have combined the isolated Fe-N₄ sites with Pt-alloy nanoparticles within the MOFs-derived carbon frameworks. To explain the higher electrocatalytic ORR activity of Ptₐ/FeSA-N-C than Ptₐ/FeSA-N-C, DFT calculation was employed. The theoretical models were built, as those defined as the “wrapped type”. The monolayer graphene model with an isolated Fe-N₄ site overlaid the Pt (100) lattice plane (with periodic structure and explicit crystal orientation), as shown in Figure 10A. The interlayer spacing was determined by energy optimization. Taking the Fe atom as the reaction site, the Pt (100)/Fe-N₄ displayed the lowest theoretical overpotential, indicating that the interaction between Pt (100) and Fe-N₄ could effectively enhance the catalytic activity towards ORR (Figure 10C). The further charge density analysis confirmed the charge transfer from Fe atom to Pt atom, consistent with the electronegativity trend. The electron-deficient Fe atoms possessed a weaker adsorption strength towards the key OH* intermediates, thereby reducing the reaction energy barrier. Besides, the interior FeₓC nanoparticles can effectively cooperate with shielded isolated Fe-N₄ sites to modify the electron structure and thus boost the ORR activity. Note that the nanoparticles could adopt the periodic structure, rather than the simplified clusters consisting of several atoms in some works.

(ii). Anchoring type

The anchoring type is the opposite situation to the wrapped type. The active sites in the metal nanoparticles directly participate in the three-phase reactions. Meanwhile, the single-atom sites on the substrate material could anchor the metal moieties through metal-metal bonds. The strong anchoring effect can make the particle size significantly reduced, and inhibit the metal leaching during the electrocatalytic reactions. The single-atom sites would reinforce the interaction with the above metal nanoparticles, and consequently affect the surface adsorption over the active metal atoms of NPs. Taking the Ru nanoparticles coated on the M-Hₓ (M = Fe, Co, Ni) sites as an example, the strong interaction between Ruₜₜ and M₁@OG (O-doped graphene) would result in the regulated charge states as shown in Figure 10D,E. First, the introduction of single metal atoms into O-doped graphene would make the neighboring carbon atoms electron-deficient, which significantly enhances the electron transfer from the loaded Ru nanoparticles to the carbon matrix. The Ru atoms at the interface possess relatively positive charge density, suggesting a weak adsorption strength towards H* species and better catalytic activity (Figure 10F). The density of states also shows that the introduction of single atoms could induce the prominent states at the Fermi level, making the activated graphene layer dramatically interact with Ruₜₜ (see Figure 10G). All these indicate that the single-atom decoration endows the ingenious modulation of charge states and catalytic activity of Ru nanoparticles. The anchoring style has also been extensively studied with the Ni/Ni-N₄, Ru/Fe-N₄, Ru/Ru-N₄. It should be noted that the above cooperative effect of these anchoring-type sites employed simplified theoretical models, which diminish the particle size into cluster model or even atomic aggregation. The adsorption sites were normally chosen as those atoms around the strongly coupled M₁/M₂-Hₓ interfaces.

(iii). Tandem type

Different from the above two types, the tandem type is not concerned with the electronic interaction between vertically arranged single atoms and nanoparticles. In other words, these two active species are spatially adjacent to each other, but with no direct chemical bonding existing. Considering the multiple electron transfer process and complex adsorption/desorption behaviors towards several key intermediates during most complex electrocatalytic reactions, the multiactive sites might undertake their own duties for some of the reaction intermediates, respectively. Concurrently, the intermediates would migrate from upstream active centers to downstream reactive sites through a rapid mass transfer process. The active species in the whole electrocatalytic chain jointly promote catalytic performance. Very recently, our group has systematically studied the synergistic NRR catalysis over the single Mo atoms and Mo₂C nanoparticles. Our DFT calculation results showed that the Mo₂C nanoparticles and isolated MoNC₂ sites were responsible for the respective high NRR and HER activity (Figure 10H–K). In this tandem system, the MoNC₂ with superior HER activity

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**Figure 9**  (A) Schematic of the synthesis of Pt/np-Co₀.₈₅Se. (B) HAADF-STEM images of Pt/np-Co₀.₈₅Se. (C) Line-scanning intensity profile obtained from the area A and B in (B). (D) STEM-EDX elemental mapping of Pt/np-Co₀.₈₅Se. Reproduced with permission. Copyright 2019, Springer Nature. (E) The reaction mechanism of Ptₐ-NiO/Ni in alkaline media. (F) HAADF-STEM image and (G) magnified image of Ptₐ-NiO/Ni. (H, I) Illustrated interface structure by DFT calculation. Reproduced with permission. Copyright 2021, Springer Nature
could construct an $H^*$-rich environment around the Mo$_2$C, thereby activating the inert N$_2$ molecule adsorbed on the surface of nanoparticles. The mutual compensation of MoNC$_2$ sites and Mo$_2$C nanoparticles dramatically elevates the overall NRR catalytic activity. Besides, a Cu-based tandem catalyst has been proposed by Cao et al.\cite{104} when they combined Ni single-atom catalysts with Cu nanoparticles to synergize the CO$_2$ reduction into C$_2$H$_4$. Another similar tandem OER catalytic mechanism was proposed by Cao et al.,\cite{105} where their isolated NiC$_4$ sites and Fe-NiOOH nanoparticles were
embedded on carbon black powder through the strategy of physical adsorption metal ions (PAMIs). In addition, the tandem synergy may not apply to those few-electron electrocatalytic reactions, such as HER. However, the multiple active sites can cooperate to enhance the overall catalytic activity. For example, the isolated Ru-N$_2$C$_2$ sites, nitried Ru nanoparticles, and also the carbon sites in the wrapped graphene layer all possess low HER overpotentials and consequently contribute to the catalytic performance.$^{[106]}$

### 5.4 Synthesis strategies

Synthesis strategies for single-atom sites have been well summarized in several recent reviews of the literature.$^{[107,108]}$ Here we mainly focus on those more specific designs for obtaining the combination of single atoms and active nanoparticles, where the emphasis is on the distribution of active species.

(i). Strategies for single atom-incorporated nanoparticles

For single atom-doped nanoparticles, there are two major synthesis approaches. In the first one, the active nanoparticles are first prepared, and then the single-atom dopants are introduced to the nanoparticles. As shown in Figure 11A, Pt SAs were incorporated into a prefabricated Mo$_2$TiC$_2$Tx MXene through in situ electrochemical deposition.$^{[91]}$ Liquid-phase ion exchange, galvanic replacement, photochemical deposition are the other commonly used methods for uploading single-atom dopants to nanoparticles.

Apart from the posttreatment of nanoparticles, single-atom metal species can also be incorporated in the crystal growth of nanoparticles, where the co-reaction requires a rational selection and low dosage of desired single-atom source, to avoid the aggregation of these single atoms. Hou and co-workers added a small amount of RuCl$_3$·xH$_2$O in the electrodeposition process of NiFeAl LDH on nickel foam, followed by alkaline etching to remove the AI moieties (Figure 11B)$^{[109]}$. Consequently, these Ru dopants were atomically dispersed on the defective NiFe LDH nanosheets. The single-atom tungsten has also been integrated into α-Ni(OH)$_2$ nanosheets.$^{[110]}$

(ii). Strategies for co-loaded single atoms and nanoparticles

For the co-loaded combinations, carbon frameworks have been largely utilized to support single atoms and nanoparticles.$^{[113,114]}$ These carbon substrates usually need to be carbonized at a high temperature, and the metal nanoparticles grow steadily due to the Ostwald ripening, during the pyrolysis process. Single atoms can then be anchored on the carbon substrates through bonding with heteroatoms.$^{[115]}$ By calcining a mixture of metal salts, organic molecules (or other carbon source), metal complexes, or metal-organic frameworks at high temperatures (600–1000°C), there are the nucleation and growth involved to form the nanoparticles. Some metal atoms can be captured by the carbon framework, and bonded with heteroatoms to form isolated M-H$_x$ sites. The particles of large sizes may need to be removed with acid leaching, and the small active metal species are retained to afford a certain activity contribution. A typical synthesis was demonstrated by Wang et al., in which iron nitrate and zinc acetate (sacrificial agent) were added into a chitin solution to form the precursor (Figure 11C)$^{[107,111,112]}$. After that, successive pyrolysis, acid treatment, and secondary annealing processes were conducted to obtain the Fe$_3$C-FeN/NC.

Unlike the homogeneous types, it is difficult to maintain a monoatomic configuration of one metal, while sintering another metal into nanoparticles for the heterogeneous types. Certain single-function isolating factors, such as the use of specific chelating agents, can be introduced into the precursor to restrict the migration of one metal source spatially, while is not applicable to the other metal source. Thereout, the distinct components of heterogeneous active species can be generated after the calcination process. Another feasible approach is to construct these two active species step by step, e.g., the single-atom configuration is first built, and the then heterogeneous metal nanoparticle is constructed. For instance, the porphyrinic triazine framework could first afford isolated Ni sites, on which the Cu nanoparticles were loaded through reduction with ascorbic acid (Figure 11D)$^{[104]}$. Pt alloys can be electrodeposited on the pre-synthesized FeSA-N-C framework.$^{[86]}$

As discussed above, categorized by the configurations adopted in the binary integration of single atoms with nanoparticles, several synthetic strategies are commonly employed. To prepare single atom-incorporated nanoparticles whereby the nanoparticles act as the substrate/matrix for the single atoms, the single atoms can be loaded either by posttreatment of the as-synthesized nanoparticles or in a one-pot co-reaction process with the rational design of the reactants. On the other hand, a more common configuration of the binary integration involves a mixture of the single atoms and nanoparticles co-loaded on another support material. This is achieved through controlled pyrolysis of precursor material, for example, optionally with a subsequent acid leaching step to remove excess nanoparticles or a reduction step to induce the formation of more nanoparticles.
5.5 | Case studies in heterogeneous electrocatalysis

Having discussed the types, distribution, or spatial configuration, commonly-used synthesis strategies for electrocatalysts with both single atoms and nanoparticles, in this section, we look into the performance and reaction mechanism in several types of heterogeneous electrocatalysis.

5.5.1 | Electrocatalysis involving O₂

Several of the above-mentioned electrocatalysts are identified to be active in oxygen electrocatalysis. For example, Sun and co-workers prepared an electrocatalyst with CoN₄ and CoNP-CoN₄ sites, where the SiO₂ coating layer generated localized stress on the internal ZnCo-ZIF framework, deforming the isolated Co-N₄ sites.

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**Figure 11** (A) Schematic of the in situ electrochemical deposition process of Mo₂TiC₂Tx-PtSA. Reproduced with permission.[91] Copyright 2018, Springer Nature. (B) The schematic of electrodeposition process of Ru₁/D-NiFe LDHs. Reproduced with permission.[109] Copyright 2021, Springer Nature. (C) Schematic of synthetic methods of Fe₃C-FeN/NC. Reproduced with permission.[97] Copyright 2021 Royal Society of Chemistry. (D) Schematic of synthesis of PTF(Ni)/Cu. Reproduced with permission.[104] Copyright 2021, John Wiley and Sons.
in geometry structure. A metalorganic gaseous doping approach was utilized to deposit Co nanoparticles onto the surface of deformed CoSA-N-C (d-CoSA-N-C). The HAADF-STEM images and corresponding EDX elemental mapping demonstrate the coexistence of Co nanoparticles, abundant Co SAs, and also the CoNP-CoN4 composite sites (Figure 12A,B). The XANES spectrum gave further proof for the Co cations and nanoparticles, verified by the Co-Co and Co-N scattering paths (Figure 12C). With the coordination of Co-N (4) and Co-Co (1) (Figure 12D), the CoNP-CoN4 composite sites and deformed Co-N4 sites enhance the activation of oxygen molecules, strengthen the adsorption of key oxygenic intermediates, and inhibit the formation of H2O2. The synergistic effect endows it with excellent catalytic activity (E1/2 = 0.83 V) and durability (only 12 mV decline of E1/2 after 50,000 cycles) in acidic media (Figure 12E).

For OER, single nickel atoms and Fe-doped NiOOH species were concurrently embedded into the conductive carbon black (Figure 12F). The obtained Ni SAs/Fe-NiOOH could achieve the current density of 10 and 50 mA cm−2 with a low overpotential of 269 and 293 mV, respectively (Figure 12G). Supported by DFT calculations, a tandem catalytic mechanism was proposed (Figure 12H). Specifically, the formation of OH* and O* took place on the Fe-NiOOH with a thermodynamically favorable pathway, and then the formed O* could migrate to the surface of Ni-C4 sites, to accomplish the subsequent transformation and desorption (Figure 12I). With the tandem catalytic mechanism, the overpotential could reduce to 0.15 V, which is much smaller than that of pure NiC4 site (0.32 V) and Fe-NiOOH (0.34 V). Interestingly, the dual-phasic carbon framework with isolated Co-Nx sites and Co nanoparticles (CNT@SAC-Co/NCP) exhibit bifunctional electrocatalytic activity for...
ORR ($E_{1/2} = 0.870 \text{ V}$) and OER ($\eta_{10} = 380 \text{ mV}$) in alkaline media.\textsuperscript{[118]}

5.5.2 Electrocatalysis involving H$_2$

HER is an important electrocatalytic reaction for green production of hydrogen. A NiO/Ni heterostructure incorporated with single platinum atoms has been demonstrated to effectively accelerate the sluggish alkaline HER kinetics.\textsuperscript{[94]} Those coupled Pt SAs along the heterointerface could induce the charge delocalizing from Pt atom to the adjoining O atom, as well as charge localization from surrounding Ni atom to Pt atom, which formed a half-moon shaped enhanced electric field (Figure 12J). Such inductive effect is much stronger than those from the Pt$_{\text{SA}}$-doped NiO or Ni, and can lead to a higher occupation at the Fermi level of PDOS (Figure 12K). Consequently, the reaction energy barrier of water dissociation and the hydrogen generation were all optimized on the Pt$_{\text{SA}}$-NiO/Ni models (Figure 12L). Therefore, it exhibited excellent HER activity ($\eta_{10} = 26 \text{ mV}$, $\eta_{100} = 85 \text{ mV}$) in alkaline media (Figure 12M), together with the initial catalytic activity being retained for about 30 h operation or after 5000 CV test cycles. Impressively, the integration of Co SAs and Co$_9$S$_8$ nanoparticles in the hollow carbon nanotubes gave a trifunctional catalyst for the electrocatalytic ORR, OER, and HER, and it could be employed in overall water splitting devices driven by Zn-air batteries.\textsuperscript{[119]}

5.5.3 Electrocatalysis involving N$_2$ and CO$_2$

CO$_2$RR and NRR are among the frontier research field of heterogeneous electrocatalysis. Hou and co-workers utilized the Ni@NiNCM as an efficient synergistic catalyst for electrochemically catalyzing CO$_2$ into the CO product.\textsuperscript{[100,117]} Compared with NiNCM with one-fold Ni-N$_x$ sites, the Ni@NiNCM with additional Ni active species could achieve a much higher current density towards CO$_2$RR (Figure 12N). The product was dominant CO without any liquid product. The specific activity normalized to the double-layer capacitance of Ni@NiNCM also surpasses NiNCM and Ni NPs. The high selectivity (FE >90%) of Ni@NiNCM could be maintained until the current density exceeded 100 mA cm$^{-2}$ (Figure 12O). The DFT calculations uncovered that the Ni nanoparticles were favorable for the water dissociation process (the generation of adsorbed H), and thus accelerated the intermediate protonation step over the adjacent Ni-N$_x$ sites (Figure 12P,Q).

6 DYNAMIC NATURE OF CATALYTIC SITES

All types of active species (nanoparticles, clusters or single atoms) would undergo the potential structural or component evolvement during the operation process with a strong electric field and corrosive electrolyte. Here, we analyze the dynamic nature of various catalytic sites by ex situ or in situ/operando means for helping understand the actual active centers and dynamic reaction mechanism in a proper manner.

6.1 Dynamic nature of nanoparticles or atomic clusters

The dynamic evolution of nanoparticles, as well as the tiny clusters, has been studied for a long period of time. The reconstruction phenomenon on these particles would prominently induce the surface and even complete transformation of physicochemical properties. The reconstruction of nanoparticles can include both the topological deformation and compositional variation.

The topological deformation typically involves surface roughening, change in porosity, and microstructure.\textsuperscript{[120]} In general, the as-synthetic catalyst possesses a relatively smooth surface and therefore suffers from a rapid roughening during the electrochemical process.\textsuperscript{[121]} Besides, due to the gradual change of microstructure, nanoparticles might be condensed into a bulk catalyst layer.\textsuperscript{[122]} A highly developed porous structure would be then shrunk to restrict the mass transfer. Topological deformation can be normally attributed to the intrinsic compositional variation. Owing to the agglomeration state of nanoparticles, the electrochemical corrosion and dissolution effects induced by the high voltages and harsh electrolytes are the most important dynamic nature. The dissolution of components for the nanoparticles can be commonly analyzed by off-line monitoring the changes in elemental composition during the electrochemical reactions. Therefore, in situ/operando studies on both of them are still lacking nowadays although they are highly required. Lotsch and co-workers have studied the dynamic activity enhancement and inherent structural transformation of Pd-based delafossites.\textsuperscript{[123]} The as-prepared PdCoO$_2$ catalyst exhibited a gradually enhanced HER activity in acidic media with the increasing cathodic cycling numbers (Figure 13A,B). Rapid dissolution of Co and the formed Pd-rich surface was identified by monitoring the mass of Co ions in the post-reaction electrolyte from the ICP-OES results. As compared to the smooth surface of the initial PdCoO$_2$, the catalyst surface after the HER test was strongly roughened and modified with the cracks and nanoparticles over the Pd-rich
capping layer. HAADF-STEM images further confirmed that Pd nanocrystals of 2–10 nm were formed in the Pd capping layer (about 30 nm thick), and a tensile strain existed in the in situ grown Pd capping layer (Figure 13C,D). The strong capacitance effect suggested the active hydrogen adsorption on the capping layer, which was favorable for the formation of isotropically strained interstitial hydrides (β-PdHx) as the actual active species.

Partial dissolution can trigger several subsequent dynamic evolution phenomena. Thus, monitoring the ion content of these dissolved elements with in-situ means can help one understand the initial motivation of dynamic evolution. Xu et al. [127] integrated single-molecule fluorescence microscopy with an electrochemical working station to monitor the real-time deactivation behavior of Pt/C catalyst during the HOR. The decline of catalytic activity was mainly imputed to the electrochemical
leaching of Pt nanoparticles, and the spontaneous activity regeneration could be also observed at the single-particle level. To inhibit the dissolution, a protective layer, such as a conductive carbon layer, can be constructed on the surface of nanoparticles to avoid direct contact with the harsh electrolyte and thereby retard the deactivation phenomenon.

Another type of compositional variation is related to phase transformation, which is also referred as reconstruction chemistry. Mai and co-workers utilized the thermally induced complete reconstruction (at the industrial 51.9°C) to convert the crystalline nickel molybdate into polycrystalline nickel (oxy)hydroxide with abundant grain boundaries and vacancies (Figure 13E–G). Note that the reconstruction with the same crystal characteristics is concentrated in the surface layer at the ambient temperature. Currently, such complete or surface reconstruction has been extensively explored in the OER. Besides, the amorphous species can be also obtained by activating the pristine crystalline metal compounds. For example, Xu et al. imbedded the iron atoms into the inactive spinel CoAl2O4 to accelerate the surface reconstruction into highly active amorphous Co oxyhydroxides. The rapid surface reconstruction would bring about excellent OER activity after several CV cycles (Figure 13H–J). In addition, the amorphous materials would also recrystallize to form the low-crystalline active species. Yu et al. utilized the in situ HRTEM to track the reconstruction process of amorphous CoSx precatalyst into low-crystalline CoOOH. The Co(OH)2 served as the reconstruction intermediate during the stepwise oxidation evolution, and also transformed the initial morphology. The final CoOOH gave the real active species (Figure 13K–N). In brief, these low- or poly-crystalline, and even amorphous reconstruction products usually own massive vacancies, crystal defects, and unsaturated coordinated metal atoms, which resulted in sufficient active sites for electrocatalytic reactions.

6.2 Dynamic nature of single atoms

It is generally understood that single metal atoms have better long-term corrosion resistance than metal nanoparticles. The strong coupling effect between isolated central metal atoms with coordinated atoms alleviates the leaching and dissolution phenomena. Hence, the dynamic nature of single atoms has focused on the changes/transformations at the atomic level. Based on the published literature, we summarized the dynamic evolution of single atoms into the following four types: (i) variation in geometry configuration and valence state, (ii) Transition to near-free state, (iii) emergence of reversible cluster species, and (iv) generation of irreversible cluster species.

(i). Variation in geometry configuration and valence state

Single atoms are often chosen as the adsorption site towards multiple reaction intermediates. Owing to these adsorption behaviors, the initial coordination structure will be changed with the stretching or contraction of chemical bonds. Furthermore, an applied electric field can also induce the distortion of geometry configuration. Such configurational transformation is normally accompanied with the charge transfer, therefore altering the valence state of central metals.

Yao et al. have investigated the dynamic evolution of atomically dispersed Ru1-N4 sites during the operation of acidic OER, with operando synchrotron radiation XAS and Fourier transforming infrared spectroscopy (SR-FTIR). The SR-FTIR spectra revealed that the reversible key reaction intermediate, namely single oxygen adsorption species, emerged during the electrocatalytic OER process (Figure 14A). Besides, the negative shift and enhanced peak intensity of the first coordination peak at the catalytic voltage showed the contracted pristine Ru-N coordination and further anchored central Ru atom (Figure 14B). As shown in Figure 14D, the strengthened pre-edge peak at the operation voltage of 1.5 V signified the distortion of coordination structure of central Ru atom and consequent escape of more electrons from Ru 4d state, therefore resulting in the increased valence state of central Ru atoms (+3→+4). The adsorbed oxygen intermediates made the Ru 4d state of Ru-N-C catalyst downshift and delivered electrons to the coordinated N and adsorbed O atoms, therefore possessing moderate binding energy with key intermediates (Figure 14C). Such a phenomenon was also verified in Co-N4 and Cu-SIN3 coordinates.

In short, the high coverage of intermediates on the central metal atoms and the applied electric field would render the coordination structure transformed. In different cases reported, the coordination bonds might be stretched or contracted, and the oxidation state of central metal atoms would be promoted or reduced. The transformation of geometry configuration can be tracked with the in situ/operando EXAFS by its fitting results of coordination bond length, while the change of oxidation state is able to be explored with operando XANES spectra. Normally, such changes in microstructures are reversible once the electrocatalytic reactions are completed.
lowered coordination number. These near-free metal atoms will form the authentic active centers with the assistance of adsorbed species. For example, Yao et al.\textsuperscript{139} have reported the dynamic nature of near-free single platinum atoms during HER reaction. With the negatively shifted potential, the decreased d-band holes and mean valence state of central Pt atoms in as-prepared Pt\textsubscript{1}/N-C catalyst implied their less interaction with coordinated N-C substrate and transformation to near-zero metallic state. The operando EXAFS further confirmed the apparently altered local geometric configuration and enhanced structural disorder upon these initial Pt\textsubscript{1}-C\textsubscript{3}N\textsubscript{1} sites during the HER reaction (Figure 14E). At the applied voltage of +0.15 V, the coordination number of the central Pt atom decreased to two, along with one accessional Pt-O coordination with adsorbed water molecule from alkaline electrolyte (Figure 14F). This corresponds to the dissociation of adsorbed water at this stage. Only the two-fold Pt-C/N
coordination could be detected at the applied voltage of \(-0.07\) V, while the Pt-H coordination with adsorbed H* could scarcely be discerned. Such dynamic evolution to near-free single atoms during the electrocatalytic process is also reported in Cu\(_1\)-N\(_4\).\(^{140}\) Fe-N\(_4\)^{141}\) and Ni-N\(_4\)^{142}\) coordinates.

(iii). Emergence of reversible cluster species

With the progress in bond-breaking, the free atoms with relatively close interval can regather to form the atomic clusters. Such atomic restructuring can be reversible and will recover to single-atom state after the electrocatalytic reaction. Thus, its dynamic evolution is generally imperceptible, and shall be detected by in situ/operando characterization means. For example, Fu and co-workers analyzed the actual action and dynamic nature of binary metal centers in Cu/Zn-NC catalyst.\(^{143}\) The operando Zn K-edge XANES spectra exhibited no significant change at various applied voltages, and its bond length and coordination number remained stable as well. It indicated that the Zn-N\(_4\) sites only transferred partial electron to adjacent Cu-N\(_4\) sites, and did not participate in the practical catalysis. Conversely, a reversible valence change of Cu atom could be observed from the round-trip shift of the absorption peak. Besides, a new Cu-Cu coordination could be found at the applied voltage of 0.4 or 0.3 V, along with the decreased intensity of Cu-N coordination (Figure 14G–J). Meanwhile, the coordination number of Cu-N bond was reduced to two at the ORR operation voltage. These results indicated that the free single Cu atoms tended to gather into atomic clusters under the applied ORR potential, and they would return to the pristine single-atom state once the electric field was removed. Such invertible structural reform of isolated Cu atoms is also reported in the field of electrocatalytic CO\(_2\)RR reaction,\(^{144,145}\) single atom Ni supported on the 1T-MoS\(_2\) catalyst.\(^{146}\)

(iv). Generation of irreversible cluster species

Inevitably, some atomic clusters, formed during the electrocatalytic process, cannot recover to the initial states. These unrecoverable cluster species can lead to the deactivation of original active single-atom sites, or bring about new active species with higher or lower activity. For example, Jaouen et al.\(^{167}\) utilized the in situ Fe Mössbauer spectroscopy to identify the high-spin S1 site (pyrrolic-N coordinated single Fe atom) and medium-/low-spin S2 site (pyridinic-N coordinated single Fe atom) in the Fe-N-C catalysts (Figure 14K).\(^{147}\) Both of them belonged to the Fe\(_1\)-N\(_4\) species, but were embedded into the carbon framework in different coordination types (S1: Fe\(_1\)-N\(_4\)-C\(_{12}\); S2: Fe\(_1\)-N\(_4\)-C\(_{10}\)). With the extension of operation time, the electrocatalytic activity declined slowly but steadily. Meanwhile, the content of S1 sites was decreased, while the S2 remained stable. Their operando investigations suggested that the S1 sites would be subjected to oxidation-state transformation (Fe(II) \(\rightleftharpoons\) Fe(III)), and the S2 sites only contained Fe (II) species. At first, both of them have contributed to the overall ORR activity of Fe-N-C catalyst in acidic media. But during the operation of PEMFC, the S1 sites would be soon gathered and oxidated into inactive Fe\(_2\)O\(_3\) clusters, resulting in the reduced catalytic activity. Relatively, S2 sites showed excellent configurational stability in acidic media. However, Chen and co-workers found the structural reconstruction of single atoms into clusters could generate more active species.\(^{148}\)

During the electrocatalytic reactions, a strong coupling effect between single atoms and nanoparticles can effectively retard the corrosion and dissolution of metal nanoparticles, but the surface reconstruction cannot be avoided. Besides, due to the inherent structural distortion, the single-atom sites are prone to undergo further changes in geometric configuration and valence states, possibly resulting in the breakage of coordination bonds and the formation of reversible/irreversible cluster species. Unfortunately, the current researches are still lack of in-depth investigation into the synergistic dynamic nature of such hybrid sites. A few reports have focused on the single atom-doped metal compounds, and argued that their dynamic natures are similar to those of the simplex single atoms or nanoparticles.\(^{108,110}\)

Investigations into the dynamic nature of multiple active species is of great significance for accurately identifying the practical active centers, understanding the adsorption pathway of intermediates, comprehending the reaction mechanism, and acquiring the thermodynamic/kinetic characteristics during the electrocatalytic reactions.\(^{149}\) If the geometric configuration and electronic structure of catalytic sites change irreversibly, the phase/microstructure can be tracked by virtue of ex situ characterization. However, it is difficult to obtain a set of critical information about reaction intermediates and the evolution process. On the condition that the changes are irreversible, the dynamic catalytic surfaces must be monitored with advanced in situ/operando apparatus. For the clusters or nanoparticles, in situ XRD can realize the surveillance of the phase transformation process during the real-time catalytic reaction. The information about the chemical bond changes and corresponding required conditions can be revealed by in situ Raman spectra, to confirm the true catalytic species. Besides, the quasi-operando XPS is a method for studying the evolvement of metallic valence states. With regard to
the single atoms, the surface adsorbed species can be analyzed with operando SR-FTIR spectroscopy. The configurational deformation and valence change of the single-site atoms are usually disclosed with synchrotron-radiation EXAFS and XANES spectra, respectively. In addition, the in-situ electron microscopy, quasi-operando identical location electron microscopy can realize the visualization of the dynamic evolution of active species. And the catalytic kinetics and properties of the three-phase interface can be monitored in real-time with in situ EIS analysis. Once successfully identifying the dynamic structure of active sites and the adsorbed reaction intermediates during the electrochemical process, the theoretical models can be built to match the actual configuration. Ultimately, the reaction pathway and mechanism can be deduced based on the adsorption free energy calculations.

7 | CONCLUSIONS AND PERSPECTIVES

Among the three basic building blocks in the vertices of the catalysts “golden triangle”, namely single atoms, atomic clusters, and nanoparticles, each possesses its own distinct characteristics and metrics. Most of the previous studies have largely focused on the individual activation and optimization of the respective active species involved. Recently, several breakthroughs have emerged when combining single atoms with one of the three into a single catalytic entity for much-enhanced electrocatalysis. Their synergistic functions dramatically affect electrocatalytic activity, selectivity, and stability. These combined catalytic entities, composed of two or more types of active species, are of particular advantages for a number of reactions involving multiple pathways or steps. This review comprehensively summarizes the current advances on the integrations of single atoms respectively with other single atoms, atomic clusters, and nanoparticles, and the unique catalytic trios and mechanisms thus derived in various heterogeneous electrocatalysis. The key synergistic functions, component type, spatial distribution, designed strategies, and unique catalytic mechanisms of integrated catalytic entities are elucidated in detail by zooming in several typical case studies. Besides this, the dynamic nature and evolution of these active species, when they are together during the electrocatalytic processes, is systematically expounded. Despite several of the impressing breakthroughs for such integrated catalytic entities, not only several challenges but also opportunities still exist.

(i). The uniformity/purity of each of the binary or multiple active species should be considered by employing more controllable construction strategies, for the sake of eliminating the side effect of other latent components. For example, for the binary or multiple isolated metal atoms, the existence of particle-type impurities should be strictly avoided in the synthesis, electrocatalysis, and characterizations. And for the concomitant single atoms and metal nanoparticles/clusters, especially for the heterogeneous types, the simplex and pure active species should be well-identified. Currently, it is actually challenging to distinguish the heterogeneous types by electron microscopy or spectroscopy means. Thus, it must be considered in the pivotal synthetic strategies, where strategies such as the stepwise constructions of multiple active species can be more feasible than those one-step synthesis methods.

(ii). The relative space distributions of the constituent components in any of the collective catalytic entities should be properly stipulated so as to guide the succedent analysis of the catalytic mechanism. The elemental type and relative spacing between two metal atoms must be discerned, for example, by using aberration-corrected electron microscopy combined with electron energy loss spectroscopy. Recently, various metal dimers, trimers, and quasi-paired atoms have been employed to ensure the monodispersity, uniformity, as well as spacing interval of catalytic units. However, the spatial arrangement of these metal species with single atoms, including wrapped, anchoring, and tandem types, must be clarified with intuitive electron microscope observation. The actual configurations shall match with the anticipated results from the synthesis strategies.

(iii). The rationality of theoretical modeling shall be consistent with the actual characterization results. Otherwise, it not only poses a challenge to the analysis of the active species but also increases the difficulty of theoretical modeling. In many of the studies reported, the theoretical calculations are the simplified simulations of material structure and composition. But a more matched theoretical model can help the researchers to better understand the real changes in the electronic structures and adsorption behaviors upon such integrated catalytic entities. In particular, the dynamic nature of each of the catalytic species and their interactions during the reaction adds huge challenges to the theoretical investigations for simulating authentic situations.

(iv). Although several studies have focused on identifying the reaction mechanism(s) of binary/multiple combinations of single atoms with other active
species, deep analysis about the respective roles and synergistic effects of these binary/multiple active species are still lacking, especially for their shows in experiments. With regard to heterogeneous electrocatalysis, the reaction is generally accompanied by a set of complicated multiple electron-proton coupled transfer steps. Thus, one-fold active species do not always contribute to some or all these sub-steps. A synergistic interaction or complementary effect, even a bifunctional effect on the complex catalytic system could produce new opportunities and therefore deserve to be explored in detail. The key intermediates adsorption can be online identified with in situ advanced spectroscopies, such as SR-FTIR. And the DFT calculations can predict the modulation of electronic state and fundamental catalytic mechanisms by virtue of the adsorbed configuration. Different from the simplest adsorption on onefold sites, the synergistic interactions or tandem mechanisms on the collective catalytic entities are more controversial but worth pursuing.

(v). By far, the investigation into the dynamic nature of such binary/plural catalytic entities during the practical catalytic conditions is still at the early stage, although the evolution of some nanoparticles or single atoms has been widely studied individually. Understanding the mutual influence of these binary/plural active species on the respective evolution process during heterogeneous catalytic reactions can deeply deduce the real catalytic process. The confinement effect of single-atom sites on atomic clusters or even nanoparticle might retard their dissolutions, while the interaction would induce the stretch/constriction of atomic configuration, thereby leading to the likely atom release/fastening.

By virtue of the respective unique characteristics of the three vertices in the “golden triangle”, the synergistic natures of binary/multiple integrations of single atoms with atomic clusters and nanoparticles could well meet the requirements of complex electrocatalytic applications in the targeted specific reaction pathway, with higher activity and selectivity. Considering the excellent prospect of collective catalytic entities in heterogeneous electrocatalysis, this review is aimed at offering timely guidance and enlightenment for the rational construction, meticulous characterizations, dynamic evolution, and elaborated structure-activity relationships of the binary/multiple combination systems.

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CONFLICT OF INTEREST

The authors have no conflict of interest to declare.

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