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# Synergistic effects of atomically precise Au-based bimetallic nanocluster on energy-related small molecule catalysis

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Utilizing renewable sources to convert small-molecule energy carriers (such as nitrogen, carbon dioxide, water, or oxygen) into high value-added chemicals and fuels is of great significance. Rational design of the catalyst is the key to achieving efficient catalytic performance. Atomically precise metal nanoclusters (NCs) exhibit the advantages of high atomic economy, distinctive discrete electronic energy, and homogeneity in size, composition, structure, and surface environment, not only offering extraordinary catalytic activity but also providing the opportunity to reveal the reaction mechanism. In the metal NC family, Au-based NCs have attracted widespread and sustained interest due to their simple preparation, high stability, easy functionalization, and especially their unique catalytic activity, which once provoked a "gold rush" in academia. The synergistic effect between different metal atoms is regarded as an effective strategy to achieve enhanced catalytic performance, but the underlying mechanism is a puzzle. Recently, abundant, diverse and adjustable atomically precise Au-based bimetallic NCs (doped with Ag, Cu, Pt, Pd, Cd, Hg, Ir etc.) have emerged, which not only provide a bank of materials for highly active catalysts, but also provide feasibility for revealing synergistic effects at the atomic level. This perspective briefly introduces the common synthesis strategy and structural characteristics of atomically precise Au-based bimetallic NCs, summarizes recent advances in their synergistic catalysis in energy-related small-molecule conversion, and proposes insights and advice for future breakthroughs in this field.

## 1. Introduction

In order to actively tackle the current increasingly severe energy crisis and environmental problems, the search for renewable, clean and environmentally friendly new energy resources has become the consensus and the focus of joint efforts of all countries in the world.<sup>1–4</sup> Therefore, the catalytic reaction of small molecules related to new energy storage and conversion technologies, such as the hydrogen evolution reaction (HER), the oxygen evolution reaction (OER), the oxygen reduction reaction (ORR), fuel small-molecule oxidation reactions, the carbon dioxide reduction reaction (CO<sub>2</sub>RR), and synthetic ammonia reactions has aroused great interest and attention in academia and industry.<sup>5</sup> Although some breakthroughs have been achieved after decades of effort and development, these catalytic reactions still face some bottlenecks that need to be overcome. For example, the electrocatalytic water splitting technique for hydrogen production involving HER and OER theoretically requires an applied voltage of 1.23 V in the

standard state (25 °C, 1 atm).<sup>6,7</sup> However, in actual situations, the applied voltage is much higher than the theoretical value. The main reason for this serious deviation from the theoretical voltage phenomenon is that the activity of existing catalysts is not high enough to overcome the reaction energy barrier that OER and HER need to cross as well as solution resistance and contact resistance.<sup>8–10</sup> For full-cells and metal-air batteries, the critical process is ORR, which not only faces the limitation of sluggish kinetics but also faces the problem of selectivity, because it has two possible pathways: one undergoes a 4-electron transfer step to achieve the complete conversion of O<sub>2</sub> to H<sub>2</sub>O, and the other is a 2-electron reaction pathway to generate H<sub>2</sub>O<sub>2</sub>.<sup>11–13</sup> For CO<sub>2</sub>RR, the difficulty in CO<sub>2</sub> activation due to its chemical inertness and the poor product selectivity due to various possible reduction pathways are stumbling blocks to its further development.<sup>14–17</sup> The N<sub>2</sub> reduction reaction (NRR) to synthesize ammonia also faced the N<sub>2</sub> activation problem. In addition, the diversity of by-product type (*i.e.* H<sub>2</sub>, N<sub>2</sub>H<sub>4</sub>, NO<sub>2</sub><sup>−</sup>, etc.) in NRR or NO<sub>3</sub>RR (NO<sub>3</sub><sup>−</sup> reduction reaction) limits the ammonia synthesis efficiency as well.<sup>18–21</sup> The catalyst is the key to the catalytic reaction, where an excellent catalyst can effectively improve catalytic activity, selectivity, and stability by enhancing the adsorption and activation of the reactant, regulating the adsorption ability of the intermediate, reducing the limiting-rate-step barrier, promoting mass transfer, etc.<sup>22–24</sup>

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Therefore, accelerating the development of novel highly-efficient catalysts *via* rational design and precise construction is of great significance.

In order to improve the reactivity per unit volume of the catalyst, there are two main strategies: one is to increase the number of active sites and the other is to improve the reaction rate. Catalyst miniaturization is an effective method to realize the former strategy.<sup>25–29</sup> In recent years, with progress in nano-material preparation methods and the rapid development of fine structure characterization techniques, scientists have been able to achieve the controllable preparation of nanoparticles (NPs), from tens of nanometers to precise nanoclusters (NCs) composed of a few to several hundred atoms, and then to single atom catalysts (SACs), maximizing the utilization rate of atoms and achieving atomic economy.<sup>30–32</sup> The latter is strongly influenced by the adsorption, activation and desorption behaviours of reactants, intermediates and products on the catalyst surface. By using atom doping to exert a synergistic effect between the components, these behaviours can be regulated and optimized to obtain an appropriate and matchable interaction between the reaction molecules and the catalyst, and then realizing an improvement in the catalytic reaction rate.<sup>33–35</sup> Metal NCs, as an emerging type of nanocatalyst, bridging the gap between metal NPs and SACs, has attracted extensive interest due to the characteristic of having a unique molecule-like discrete electronic energy different from those of metal NPs or SACs.<sup>36–39</sup> In addition, compared to its large counterpart metal NPs, metal NCs have relatively small size with higher atomic utilization and abundant surface unsaturated coordination active sites.<sup>40–42</sup> In comparison to SACs, metal NCs exhibit the possibility of a synergistic effect.<sup>43,44</sup> Furthermore, metal NCs show great adjustability in terms of catalytic properties, because at the sub-nanometer scale, even a single atom change will have a huge impact on the properties of the material.<sup>45–47</sup>

In recent years, research on metal NC catalysis has undergone explosive growth, especially, those metal NCs with precise composition and structure, due to the potential opportunity to investigate the catalytic mechanism based on a clear structure–activity relationship.<sup>32,40,48,49</sup> Au has for a long time been considered an unreactive noble metal. In the 1980s, Haruta and Hutching *et al.* discovered that small Au NPs exhibit extraordinary catalytic activity in CO oxidation and acetylene hydrochlorination, which has caused a boom in research into Au catalysis.<sup>50,51</sup> Within the large family of precise NCs, atomically precise Au-based NCs show high stability and ready solubility in various solvents, which is very important for practical catalytic application.<sup>52,53</sup> In addition, the advantages of easy preparation, high yield, and versatile surface functionalization are also the foundation of Au-based NCs as excellent catalysts.<sup>54–63</sup> For example, the typical representative, Au<sub>25</sub> series NCs, can be seen as the standard-bearer of the NC family due to their early discovery (successfully synthesized in 1998 and structurally determined in 2008), and in-depth investigation (properties of optics, chirality, magnetism, electrochemistry, *etc.*), and wide application (catalysis, chemical sensing, imaging, bio-labeling, *etc.*).<sup>64,65</sup> Furthermore, a variety of derivatives with abundant

diversity in terms of properties can be obtained by metal doping, changing ligands, regulating charge states, *etc.*<sup>64–66</sup>

Among various adjustment strategies, heteroatom doping is an effective way to significantly expand the diversity of the composition and structure of NCs and provide a potential synergistic effect for improving catalytic performance. Speaking of a synergistic effect, it is a widely known concept among the public. Simply put, in the field of catalysis, a synergistic effect refers to the catalytic performance produced by the combination of multiple components surpassing that of a single component. It is mainly manifested through synergistic effects between metal atoms, between metals and supports, and between metal atoms and ligands. Here, we focus on the synergistic effects between metal atoms, reflected in the interactions between different metal active centers. Taking the ternary catalyst PtPdRh in automobile exhaust treatment as an example, Pt is mainly responsible for catalyzing the oxidation reaction of CO and CH<sub>x</sub>, converting them into non-toxic CO<sub>2</sub> and H<sub>2</sub>O. Pd also participates in this process, mainly playing a role in heat resistance and improving stability. Rh is mainly responsible for catalyzing the reduction reaction of NO<sub>x</sub>, converting them into N<sub>2</sub> and O<sub>2</sub>. The synergistic effect among the three achieves efficient catalytic activity and stability.

More importantly, the selective and purposeful introduction of foreign atoms into a monometallic NC can rationally optimize catalytic performance *via* modulation of electronic structure, additional active sites, and improvement in structural stability.<sup>43,67,68</sup> Many researches have reported that Au NCs can be partially substituted with Ag, Cu, Pt, Pd, Cd, Hg, or Ir, and the Au-based alloy NCs perform with superior catalytic activity to their parent Au NCs in numerous reactions due to the synergistic effect.<sup>69</sup> Motivated by the current era of rapid development of NC materials and energy catalysis, herein, recent advances in atomically precise Au-based bimetallic NCs in energy-related small-molecule catalytic conversion are reviewed, including a summary of common synthesis strategies and structural characteristic of Au-based bimetallic NCs, and a discussion of the synergistic effect on catalytic activity, selectivity, and stability in HER, OER, ORR, CO<sub>2</sub>RR, NRR, NO<sub>3</sub>RR, *etc.*

## 2. Synthesis strategy and structural characteristic of Au-based bimetallic NCs

This section briefly introduces the general synthetic method for Au-based bimetallic NCs and their structural characteristics, such as heteroatom doping number, type and position. The precise and controllable synthesis of materials with high purity and yield is the basis for a benign industrial catalyst. However, synthesizing clusters with precise structures is not an easy task. After extensive attempts and efforts by researchers, it was not until Zhu *et al.* determined the crystal structure of Au<sub>25</sub>(SR)<sub>18</sub> clusters using X-ray single crystal diffraction in 2008 that the synthesis of atomically precise metal clusters entered a stage of explosive growth.<sup>70</sup> Our previous review summarized several synthesis strategies for atomically precise metal NCs, such as



the direct synthesis method, size-focusing method, ligand-exchange method, chemical etching method, reduction method, metal-exchange method, separation method, inter-cluster reaction method, and anion-template-assisted method.<sup>48</sup> In addition, a lot of cluster-related reviews have summarized synthesis methods.<sup>36–39,71</sup> Besides those mentioned above, others such as mass-selected gas-phase method, template methods, photoreduction method, sonochemical method, microemulsion method, radiolytic method, electrochemical method, and the microwave-assisted method, have also been successfully applied in cluster synthesis. However, not all methods are suitable for the synthesis of bimetallic NCs. Here, we mainly introduce synthesis methods applicable to bimetallic clusters, where common and general methods include the direct co-reduction strategy, cation-assisted strategy, anti-galvanic reduction (AGR) strategy, metal-exchange strategy, and intercluster reaction strategy. The basic principles of these methods are refined and summarized, and corresponding application examples are provided for readers to understand.

**Direct co-reduction strategy:** It usually takes a metal–ligand complex (*i.e.* Au–SR, Ag–SR, *etc.*) as a precursor and directly synthesizes bimetallic NCs with a reducing agent (*i.e.* NaBH<sub>4</sub>, CO, *etc.*); it is also called “*in situ*” or “one-pot” synthesis.<sup>48,69</sup> For example, Au<sub>25–x</sub>Ag<sub>x</sub>(SR)<sub>18</sub> NCs with continuously modulated *x* have been successfully synthesized by this method.<sup>72</sup>

**Cation-assisted strategy:** this refers to the synthesis of bimetallic NCs by the reaction of the existing parent NCs with another metal cation.<sup>69</sup> For instance, Murray *et al.* obtained Au<sub>25–x</sub>Ag<sub>x</sub>(SR)<sub>18</sub> NCs by utilizing Ag<sup>+</sup> ions reacting with Au<sub>25</sub>(SR)<sub>18</sub> NCs.<sup>73</sup>

**Anti-galvanic reduction (AGR) strategy:** Wu *et al.* proposed that the redox potential of the order of metals is no longer the only decisive thermodynamic parameter when the size of NCs is less than 3 nm.<sup>74</sup> They prepared Au–Ag and Au–Cu bimetallic NCs by doping heteroatoms in Au<sub>25</sub>(SR)<sub>18</sub> on the basis of the AGR method.<sup>75,76</sup>

**Metal-exchange strategy:** instead of using an inorganic metal salt, an organic metal–ligand complex is used in the synthesis of bimetallic NCs, and this synthesis process can no longer relate to the rule of metal redox potential.<sup>77</sup> For example, our group utilized Au<sub>25</sub>(SR)<sub>18</sub> as a template to synthesize Cd<sub>1</sub>Au<sub>24</sub>(SR)<sub>18</sub> and Hg<sub>1</sub>Au<sub>24</sub>(SR)<sub>18</sub> by this method.<sup>78</sup>

**Intercluster reaction strategy:** this refers to the preparation of new bimetallic NCs *via* the reaction between two stable NCs.<sup>48,69</sup> For example, (Au<sub>25–x</sub>Ag<sub>x</sub>)(SR)<sub>18</sub> and Au<sub>x</sub>Ag<sub>44–x</sub>(SR)<sub>30</sub> NCs are obtained by spontaneously exchanging metal atoms after mixing Au<sub>25</sub>(SR)<sub>18</sub> and Ag<sub>44</sub>(SR)<sub>30</sub>.<sup>79</sup>

For bimetallic NCs formed by heteroatom doping, the most important considerations are the type, number and position of the doping atoms, because these structural parameters have a great influence on the catalytic performance. Considering that NCs can be viewed as being composed of a metal kernel and a metal–ligand motif, the doping position of the heteroatom can be divided into center doping, kernel doping, kernel surface doping, and motif doping (Fig. 1). For motif doping, the heteroatom is connected with the coordination atom of the

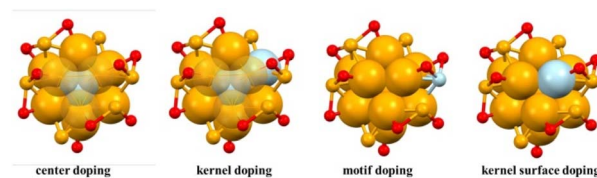


Fig. 1 Schematic diagram of the doping position of the heteroatom in Au-based bimetallic NCs. Atom colors: Au = orange, heteroatom = blue, S = red.

ligand, such as S, P, or N atoms. It is located on the outside of the cluster and has the opportunity to make direct contact with the reactant. For kernel doping (including center doping and kernel surface doping simultaneously) and kernel surface doping, the heteroatom is located at the surface of the metal core. When the catalytic reaction occurs, some ligands will detach due to the weak connection between metal atoms and ligands, and the atoms at the surface of the metal core are exposed as active centers to directly participate in the reaction. For center doping, the heteroatom is located at the center of the metal core, and it seems to have no influence on catalysis due to the indirect contact with the reactant. However, it can participate in the catalytic reaction by modulating the electronic structure of the metal core, regulating the interaction strength with the reactant or intermediate, and optimizing the reaction pathway and kinetics. The synthesis methods and characteristic structural parameters of Au-based bimetallic NCs reported in recent years are summarized in Appendix Table 1.

### 3. Au-based bimetallic NCs in energy-related catalysis

Aiming at current attractive energy-related catalytic reactions, this part classifies, summarizes, and discusses recent progress in the synergistic effects of Au-based bimetallic NCs in the hydrogen evolution reaction, oxygen evolution reaction, oxygen reduction reaction, fuel small-molecule oxidation reaction, carbon dioxide reduction reaction, and synthetic ammonia reaction.

#### 3.1 Au-based bimetallic NCs in the hydrogen evolution reaction

The gradual depletion of fossil fuels and consequent environmental and climate concerns have stimulated the development and use of clean and renewable energy sources. Among various clean energy carriers, hydrogen with its high energy density is considered to be one of the promising energy resources for a sustainable society.<sup>80</sup> The hydrogen evolution reaction (HER), which uses the abundant water on Earth as a raw material and is driven by renewable energy, such as hydropower, photovoltaic, wind, or tidal energy, is an ideal method of hydrogen production, which has many advantages, including environmental friendliness, production of high-purity hydrogen, and low carbon emissions.<sup>81</sup> Currently, the mainstream prediction method for the superiority of the HER catalyst is based on the

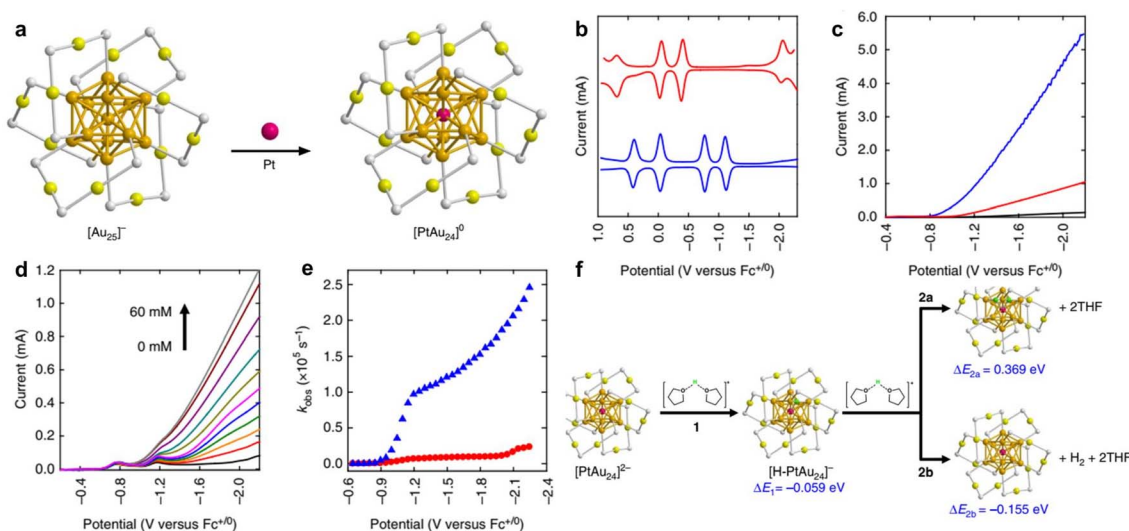


volcano plot, which is constructed by linking the hydrogen adsorption energy with the exchange current.<sup>82</sup> According to the Sabatier principle, a good HER catalyst does not bind the hydrogen too weakly or too strongly; therefore, a nearly thermodynamically neutral hydrogen binding step is assurance of a good HER catalyst.<sup>83</sup>

At present, Pt is recognized as the best-known efficient HER electrocatalyst; however, its high cost and scarce stocks hamper its large-scale industrial application.<sup>84</sup> As the sixth period element in the periodic table next to Pt, the electronic structure of Au is similar to that of Pt, so there is reason to believe that Au NCs have the potential to be an outstanding HER catalyst.<sup>85,86</sup> Kwak *et al.* selectively replaced the center Au atom in Au<sub>25</sub> NCs with a single Pt atom and obtained Pt<sub>1</sub>Au<sub>24</sub> bimetallic NCs (Fig. 2a).<sup>87</sup> Pt doping has little effect on the geometric structure of the NCs; Pt<sub>1</sub>Au<sub>24</sub> almost maintains the configuration of the original Au<sub>25</sub>. However, the electronic structure changes a lot, which is reflected in the surface charge state ([Pt<sub>1</sub>Au<sub>24</sub>]<sup>0</sup> & [Au<sub>25</sub>]<sup>−</sup>), superatomic electronic configuration (Au<sub>25</sub>: 8-electron, Pt<sub>1</sub>Au<sub>24</sub>: 6-electron)<sup>88–90</sup> and optical absorbance spectra (Au<sub>25</sub>: 1.8 eV, Pt<sub>1</sub>Au<sub>24</sub>: 1.1 and 2.1 eV). The redox behavior is also drastically altered. As measured by square-wave voltammetry (SWV), the gaps between the first oxidation (O1) and reduction (R1) potential for Au<sub>25</sub> and Pt<sub>1</sub>Au<sub>24</sub> are 1.67 and 0.73 V, respectively (Fig. 2b). The HOMO–LUMO (highest occupied–lowest unoccupied molecular orbitals) gaps are 1.32 and 0.29 eV for Au<sub>25</sub> and Pt<sub>1</sub>Au<sub>24</sub>, respectively. It is worth noting that the reduction potential of Pt<sub>1</sub>Au<sub>24</sub> is nearly 1 V more positive than that of Au<sub>25</sub>, indicating the possibility of a lower overpotential for the electrocatalytic reduction reaction. This conjecture is further confirmed by the result of linear sweep voltammograms (LSVs). In THF (0.1 M Bu<sub>4</sub>NPF<sub>6</sub>) solution containing 1.0 M trifluoroacetic acid (TFA), Au<sub>25</sub> and Pt<sub>1</sub>Au<sub>24</sub> show onset potentials at −1.10 and −0.89 V, respectively (Fig. 2c).

Notably, the overpotential for Pt<sub>1</sub>Au<sub>24</sub> is ~70 mV (relative to −0.82 V, the thermodynamic reduction potential of a proton in THF with 1.0 M TFA), which is superior to other natural hydrogenase enzymes (~100 mV).<sup>91–93</sup> With an increase in TFA concentration, the current at −0.76 V (the first reduction [Pt<sub>1</sub>Au<sub>24</sub>]<sup>0/−</sup>) of Pt<sub>1</sub>Au<sub>24</sub> shows no significant change, while the current at −1.10 V (the second reduction [Pt<sub>1</sub>Au<sub>24</sub>]<sup>−/2−</sup>) is significantly enhanced, suggesting that Pt<sub>1</sub>Au<sub>24</sub> acts as an electron transfer mediator for HER (Fig. 2d).<sup>94,95</sup> The *k*<sub>obs</sub> (pseudo-first-order rate constant) of Pt<sub>1</sub>Au<sub>24</sub> is calculated to be 121000 s<sup>−1</sup> at  $\eta$  = 650 mV, which is higher than that of Au<sub>25</sub> (8000 s<sup>−1</sup>) or other molecule-like complexes (Co-complex: 700 s<sup>−1</sup> at  $\eta$  = 890 mV, Cu-complex: 11000 s<sup>−1</sup> at  $\eta$  = 720 mV, Ni-complex: 106000 s<sup>−1</sup> at  $\eta$  = 650 mV) (Fig. 2e).<sup>96–98</sup>

In addition, Pt<sub>1</sub>Au<sub>24</sub> shows charge-state-dependent catalytic activity, indicating molecule-like catalytic behavior different from that of the larger-sized metal NPs. The currents at potentials negative to the [Pt<sub>1</sub>Au<sub>24</sub>]<sup>−/2−</sup> all exhibit linear correlation with [Pt<sub>1</sub>Au<sub>24</sub>] and [TFA]<sup>1/2</sup>, suggesting a heterolytic HER mechanism, [H–Pt<sub>1</sub>Au<sub>24</sub>]<sup>−</sup> + H<sup>+</sup> → [Pt<sub>1</sub>Au<sub>24</sub>]<sup>0</sup> + H<sub>2</sub>. In contrast, the current at the potential at which [Pt<sub>1</sub>Au<sub>24</sub>]<sup>−</sup> exists as the predominant form shows linear correlation with [TFA] and [Pt<sub>1</sub>Au<sub>24</sub>]<sup>3/2</sup>, indicating a homolytic HER mechanism, [H–Pt<sub>1</sub>Au<sub>24</sub>]<sup>0</sup> + [H–Pt<sub>1</sub>Au<sub>24</sub>]<sup>0</sup> → 2[Pt<sub>1</sub>Au<sub>24</sub>]<sup>0</sup> + H<sub>2</sub>. The heterolytic HER mechanism over Pt<sub>1</sub>Au<sub>24</sub> is further confirmed by density functional theory (DFT) calculations with an energy change of −0.155 eV, while for Au<sub>25</sub>, the thermodynamically favorable HER pathway is the homolytic mechanism (Fig. 2f). Additionally, an H–Pt bond can spontaneously form. The bond length between adsorbed H and central Pt is shorter than that between adsorbed H and surface Au, indicating that the stronger H–Pt interaction is beneficial for HER energetics on [Pt<sub>1</sub>Au<sub>24</sub>]<sup>2−</sup>. As a result, Pt<sub>1</sub>Au<sub>24</sub> exhibits excellent HER activity whether for homogeneous catalysis in non-aqueous solvent or



**Fig. 2** (a) Structure of Au<sub>25</sub> and Pt<sub>1</sub>Au<sub>24</sub> NC. (b) SWVs of Au<sub>25</sub> (red) and Pt<sub>1</sub>Au<sub>24</sub> (blue) in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M Bu<sub>4</sub>NPF<sub>6</sub>). (c) LSVs in THF (0.1 M Bu<sub>4</sub>NPF<sub>6</sub>) solution containing 1.0 M TFA without a catalyst (black) and with Au<sub>25</sub> (red) and Pt<sub>1</sub>Au<sub>24</sub> (blue). (d) LSVs of Pt<sub>1</sub>Au<sub>24</sub> in THF (0.1 M Bu<sub>4</sub>NPF<sub>6</sub>) with different concentrations of TFA. (e) *K*<sub>obs</sub>–potential plots for Au<sub>25</sub> (red) and Pt<sub>1</sub>Au<sub>24</sub> (blue). (f) Reaction energy calculation for HER on Pt<sub>1</sub>Au<sub>24</sub>. Reproduced from ref. 87 with permission from Springer Nature, copyright 2017.

heterogeneous catalysis in aqueous media, compared to  $\text{Au}_{25}$ , other molecule-like complexes, or commercial Pt/C benchmarking.

Recently, Sun *et al.* revisited the electrocatalytic HER activity origin of  $\text{Pt}_1\text{Au}_{24}$  NCs by a combination of advanced first-principles calculations and attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) experiments.<sup>99</sup> They found that in addition to the central Pt atom, the exposed bridged Au site, due to spontaneous thiolate ligand desorption during the electrochemical process, is also a catalytically active site. The synergistic effect between the two types of active site contributes to the extraordinary HER activity of the  $\text{Pt}_1\text{Au}_{24}$  cluster. As Pt centrally doped  $\text{Pt}_1\text{Au}_{24}$  significantly improves HER activity, it is natural for researchers to ask whether  $\text{Pd}_1\text{Au}_{24}$ , which has a nearly isoelectronic structure and similar redox property, would also exhibit similarly high HER activity. Choi *et al.* systematically compared the HER catalytic activity parameters, such as onset potential ( $E_{\text{onset}}$ ), current density, and turnover frequency (TOF) of  $\text{M}_1\text{Au}_{24}$  and  $\text{M}_2\text{Au}_{36}$  ( $\text{M} = \text{Pt}, \text{Pd}$ ).<sup>100</sup> Compared to non-doped Au NCs, atom doping not only brings about a change in the electrochemical redox property, but also causes an improvement in HER activity.  $E_{\text{onset}}$  is determined by the match between the reduction potential of NC and  $\text{H}^+$ . In both  $\text{M}_1\text{Au}_{24}$  and  $\text{M}_2\text{Au}_{36}$  systems, Pt doping shows higher current density and TOF than Pd doping, which is attributed to the lower H adsorption free energy ( $\Delta G_{\text{H}}$ ) in Pt-doped Au NCs (Fig. 3a). Based on the excellent HER performance of  $\text{Pt}_1\text{Au}_{24}$ , Negishi *et al.* further changed the surface ligand to, for example, C6 = 1-hexanethiolates, TBBT = 4-*tert*-butylbenzenethiolate, PDT = 1,3-propanedithiolate, or PET = 2-

phenylethanethiolate, in pursuit of higher catalytic activity.<sup>101</sup> Due to the differences in the lengths and orientations of -Au(I)-SR-Au(I)- staples between TDT/PDT- and C6/PET-protected NCs, the Au atoms of the  $\text{Pt}_1\text{Au}_{12}$  metal core in TDT/PDT-protected  $\text{Pt}_1\text{Au}_{24}$  NCs are exposed on the outside, resulting in enhanced HER activity. Although Ag is considered to be inactive for HER, obtaining AuAg alloy NCs with comparable HER activity is highly possible *via* a reasonable design. Li *et al.* synthesized  $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$  NCs, which can be regarded as having a trimeric structure, that is with three icosahedral ( $I_h$ ) units face-fused together in a cyclic manner.<sup>102</sup> The unique face-fusion mode in  $\text{Au}_{36}\text{Ag}_2$  endows it with unfilled superatomic orbitals, a low ligand-to-metal ratio, and low-coordinated Au atoms, leading to lower  $\Delta G_{\text{H}}$  and higher electron affinity, thus showing improved HER activity over its counterpart monomeric  $\text{Au}_{25}$  and dimeric  $\text{Au}_{38}$  (Fig. 3b and c).

In addition to the synergies between different metal components within clusters, there are also interactions between NCs and functional carriers, which can be combined in one system to maximize synergies. Du *et al.* designed and synthesized  $\text{Au}_2\text{Pd}_6$  NCs, which can be considered to be two  $\text{Pd}_3$  NCs connected by an  $\text{Au}_2$  unit.<sup>103</sup> On the one hand, after  $\text{MoS}_2$  couple metal NCs, the number of catalytic active sites is increased, and electron transport is promoted, resulting in enhanced HER activity. On the other hand, compared to monometallic  $\text{Au}_2$  and  $\text{Pd}_3$  NCs, and mixed  $\text{Au}_2$ - $\text{Pd}_3$  NCs, bimetallic  $\text{Au}_2\text{Pd}_6$  shows the best HER activity with the lowest overpotential, the smallest Tafel slope and electrochemical resistance, and the largest electrochemically active surface area and TOF value (Fig. 3d-i). X-ray photoelectron spectroscopy and Raman results indicate

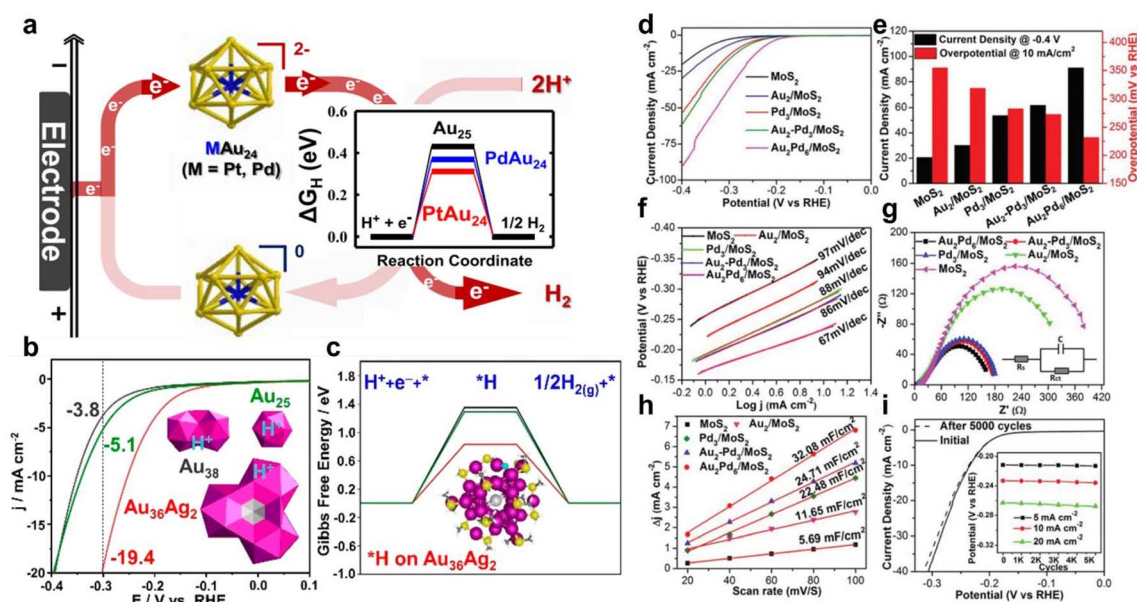


Fig. 3 (a) Schematic diagram of  $\text{M}_1\text{Au}_{24}$  ( $\text{M} = \text{Pt}, \text{Pd}$ ) enhanced HER activity compared to  $\text{Au}_{25}$  NCs. Reproduced from ref. 100 with permission from American Chemical Society, copyright 2018. (b) LSVs and (c)  $\Delta G_{\text{H}}$  of  $\text{Au}_{25}$ ,  $\text{Au}_{38}$ , and  $\text{Au}_{36}\text{Ag}_2$ . Reproduced from ref. 102 with permission from American Chemical Society, copyright 2021. (d) LSVs, (e) current density and overpotential comparison, (f) Tafel slope, (g) electrochemical impedance spectroscopy, and (h) electrochemical double-layer capacitance of  $\text{MoS}_2$ ,  $\text{Au}_2/\text{MoS}_2$ ,  $\text{Pd}_3/\text{MoS}_2$ ,  $\text{Au}_2\text{-Pd}_3/\text{MoS}_2$ , and  $\text{Au}_2\text{Pd}_6/\text{MoS}_2$ . (i) Stability test of  $\text{Au}_2\text{Pd}_6/\text{MoS}_2$ . Reproduced from ref. 103 with permission from Royal Society of Chemistry, copyright 2018.

the strong electronic interaction between NCs and MoS<sub>2</sub>. DFT calculations demonstrate that the largest number of catalytic sites with almost nearly zero  $\Delta G_{\text{H}}$  occur on Au<sub>2</sub>Pd<sub>6</sub>/MoS<sub>2</sub>, further explaining the excellent HER activity of Au<sub>2</sub>Pd<sub>6</sub>/MoS<sub>2</sub> from a theoretical perspective. A similar phenomenon is observed on bimetallic Au<sub>4</sub>Cu<sub>2</sub> NCs, which show better HER activity than that of monometallic Cu<sub>6</sub> or Au<sub>6</sub> NCs.<sup>104</sup> Taking atomically precise alloy NCs as a precursor to proceed with ligand-assisted pyrolysis is a novel method to form nanocluster/single atom (NC/SA) composite systems. Lv *et al.* obtained a hybrid system containing two different active sites types, AuPd alloy NCs and satellite Pd SAs (AuPd<sub>NCs</sub>/Pd<sub>SAs</sub>), by controllable thermal treatment of Au<sub>4</sub>Pd<sub>2</sub>(SC<sub>2</sub>H<sub>4</sub>Ph)<sub>8</sub>.<sup>105</sup> In the hybrid system, the satellite Pd SAs play the role of optimizing the electronic structure, and the Au sites effectively promote the adsorption and dissociation of H<sub>2</sub>O molecules. Thereby, the synergy between Au and Pd promotes the excellent HER activity of AuPd<sub>NCs</sub>/Pd<sub>SAs</sub>-600, which shows one order of magnitude higher mass activity and TOF than commercial Pd/C or Pt/C.

In addition to electrocatalytic HER, solar-driven photocatalytic water splitting is a sustainable and clean approach to produce hydrogen. Metal NCs exhibit a molecule-like discrete electronic energy band and strong light absorption in broad spectra, which meet the basic requirements for potential promising photocatalysts.<sup>106</sup> Bootharaju *et al.* synthesized a selenolated [Au<sub>12</sub>Ag<sub>32</sub>(SePh)<sub>30</sub>]<sup>4-</sup> core-shell cluster based on a templated galvanic exchange strategy, which is comprised of an Au icosahedral core and an Ag<sub>12</sub>(SePh)<sub>30</sub> shell.<sup>107</sup> The synergistic effect between the Au core and the Ag shell greatly changes the overall electronic structure, which aligns well with the band structure of TiO<sub>2</sub>, facilitating photogenerated charge carrier separation. Therefore, Au<sub>12</sub>Ag<sub>32</sub>/TiO<sub>2</sub> shows a photocatalytic H<sub>2</sub> production rate of 6810  $\mu\text{mol g}^{-1} \text{h}^{-1}$  under solar irradiation, which is 37.8 and 6 times higher than those of TiO<sub>2</sub> and Ag<sub>44</sub>/TiO<sub>2</sub>, respectively (Fig. 4a and b). Liu *et al.* obtained [Au<sub>x</sub>Ag<sub>25-x</sub>(SR)<sub>18</sub>]<sup>-</sup> series NCs (1 ≤ x ≤ 3, 3 ≤ x ≤ 8, 19 ≤ x ≤ 23, defined as NC-1, NC-2, NC-3).<sup>108</sup> Under visible-light irradiation, the H<sub>2</sub> production rate follows the order: NC-3 > NC-2 > NC-1 > Au<sub>25</sub> > Ag<sub>25</sub>. As revealed by DFT calculation, bimetallic Au<sub>x</sub>-Ag<sub>25-x</sub> shows that the better photocatalytic HER activity is due to the optimization of electronic structure caused by the Au-Ag synergy. The narrowed HOMO-LUMO gap in Au<sub>x</sub>Ag<sub>25-x</sub> partially contributes to the better HER performance. What is more, the microenvironment localized in dual Au-Ag sites benefits the formation of electron-acceptor centers, resulting in photo-generated electrons tending to remain in a cluster to reduce the adsorbed H<sup>+</sup> (Fig. 4c). Additionally, the Au-Ag bimetallic synergistic effect upshifts the D-band centers and balances hydrogen adsorption/desorption dynamics (Fig. 4d and e). Kurashige *et al.* loaded Pd<sub>1</sub>Au<sub>24</sub> and Pt<sub>1</sub>Au<sub>24</sub> on BaLa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> *via* stepwise ligand-exchange, adsorption, and calcination processes, to investigate the effect of heteroatom doping type on photocatalytic HER activity.<sup>109</sup> Although the Pd and Pt atoms are both in the center of M<sub>1</sub>Au<sub>24</sub> when it exists in the form of NCs alone, the positions of Pd and Pt atom are different after depositing them on BaLa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>. As can be rationally inferred from extended X-ray absorption fine structure (EXAFS)

spectroscopy results, Pd is located at the surface of the NCs, while Pt is at the interface between NCs and BaLa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>. Whether Pd or Pt doping is used, the electron density of Au in the NCs is improved. However, for photocatalytic HER activity opposite results are obtained, where Pt doping increases the activity; in contrast, Pd doping causes a decrease in activity, which to a great degree can be attributed to the doping position of the heteroatom (Fig. 4f).

### 3.2 Au-based bimetallic NCs in the oxygen evolution reaction

The oxygen evolution reaction (OER) is an elementary reaction of great importance in the field of energy and the environment. It refers to the half-reaction that occurs on the anode during electrolysis of H<sub>2</sub>O. Because OER involves a four-electron transfer process, it exhibits slow reaction kinetics, and requires higher energy to trigger a reaction; therefore, it is the key factor restricting the efficiency of an overall H<sub>2</sub>O electrolysis device.<sup>110,111</sup> Liu *et al.* synthesized an alkynyl-protected AuAg alloy cluster, Au<sub>15</sub>Ag<sub>23</sub>(<sup>t</sup>BuC≡C)<sub>18</sub>Br<sub>6</sub>, which has a triple-layered core-shell-shell (Au<sub>6</sub>@Au<sub>6</sub>Ag<sub>23</sub>@Au<sub>3</sub>) configuration.<sup>112</sup> Au<sub>15</sub>Ag<sub>23</sub> not only shows excellent electrocatalytic HER activity ( $\eta$  = 125 mV to reach 10 mA cm<sup>-2</sup> current density) but it also displays an outstanding OER property when it is loaded on NiFe layered double hydroxide, whose overpotential is 250 mV to reach 10 mA cm<sup>-2</sup> (Fig. 5a). In an overall water splitting (OWS) system, achieving 10 mA cm<sup>-2</sup> requires only 1.51 V, and it performs for as long as 50 h in a stability test.

The electrocatalytic OWS performance of Au NCs can be regulated by utilizing the electron-attracting ability of an Fe atom to Au NCs. Sun *et al.* synthesized a hybrid system of Au-Fe<sub>1</sub>NCs loaded on Ni foam to act as alkaline HER and OER bifunctional electrocatalysts.<sup>113</sup> The electron structure of H adsorption on the Au NC surface is optimized by the introduction of Fe atoms, manifested by a low overpotential of 35.6 mV to reach 10 mA cm<sup>-2</sup> current density in HER. In addition, the hybrid system Au-Fe<sub>1</sub>NCs display good OER activity with a 246 mV low overpotential at 10 mA cm<sup>-2</sup> oxidation current density. In a two-electrode alkaline OWS device, the cell voltage to reach 10 mA cm<sup>-2</sup> current density is only 1.52 V, and the durability test lasts for 40 h. The synergistic effect in Au-Fe<sub>1</sub>NCs is elucidated by X-ray photoelectron spectroscopy (XPS) experiments and DFT theoretical calculations, mainly reflected in the promotion of electron delocalization and enhancement of O-H bond activation of Au NCs and an upshift in the D-band center of the Fe atom.

The synergistic effect induced by heteroatom doping has shown great improvement in electrochemical activity; however, the understanding of the effect on photo-/photoelectro-catalytic activity, especially that involving charge transfer characteristics, remains blank. Su *et al.* took glutathione-protected Ag-doped Au NCs (Au<sub>1-x</sub>Ag<sub>x</sub>@GSH) and a non-conjugated insulating polymer of poly(diallyl-dimethylammonium chloride) (PDDA), as negatively and positively charged building blocks to elaborately fabricate a spatially multilayered alloy NCs/metal oxide photoanode heterostructure *via* layer-by-layer (LBL) assembly.<sup>114</sup>



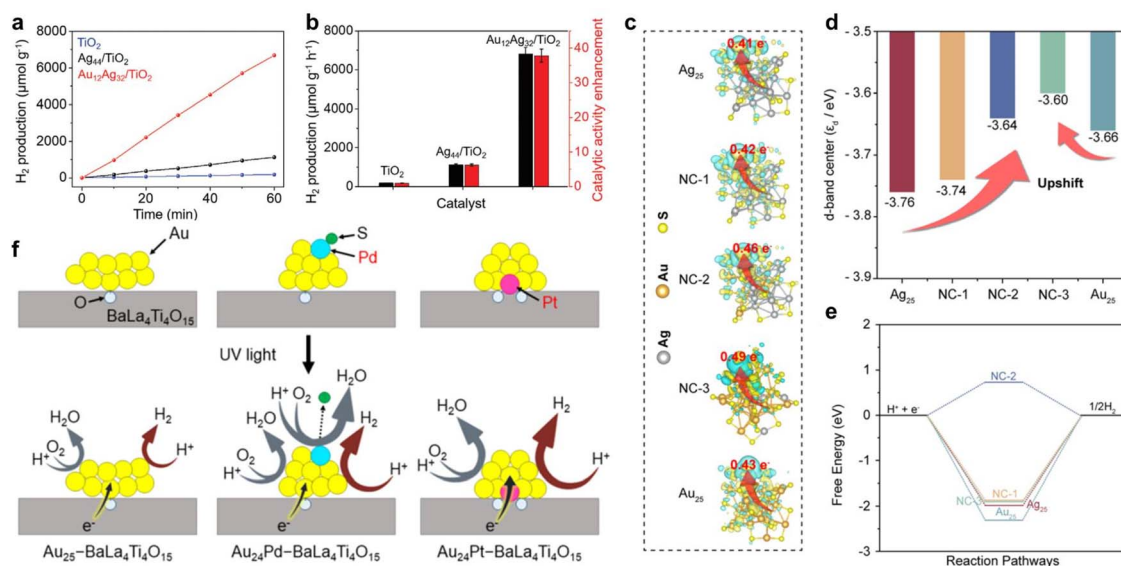


Fig. 4 (a and b) Comparison of photocatalytic HER activity of TiO<sub>2</sub>, Ag<sub>44</sub>/TiO<sub>2</sub>, and Au<sub>12</sub>Ag<sub>32</sub>/TiO<sub>2</sub>. Reproduced from ref. 107 with permission from Wiley-VCH, copyright 2023. (c) The isosurfaces of charge density difference of H<sup>+</sup>-adsorbed NCs. (d) D-band center and (e) ΔG<sub>H</sub> of [Au<sub>x</sub>Ag<sub>25-x</sub>(SR)<sub>18</sub>]<sup>-</sup> series NCs. Reproduced from ref. 108 with permission from Royal Society of Chemistry, copyright 2023. (f) Proposed structures of M<sub>1</sub>Au<sub>24</sub>-BaLa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> for M = (Au, Pd, Pt) before (top) and during (bottom) the water splitting reaction. Reproduced from ref. 109 with permission from American Chemical Society, copyright 2019.

Au<sub>1-x</sub>Ag<sub>x</sub>@GSH acts as a photosensitizer that can be instantly photoexcited to generate e<sup>-</sup> and h<sup>+</sup>, and PDDA plays the role of an electron-withdrawing mediator to accelerate interfacial charge transfer and form a cascade electron transport channel. As a result, LBL-assembled TiO<sub>2</sub>/(PDDA-Au<sub>1-x</sub>Ag<sub>x</sub>)<sub>n</sub> shows good photoelectrochemical H<sub>2</sub>O oxidation performance under visible-light irradiation.

### 3.3 Au-based bimetallic NCs in the oxygen reduction reaction

The electrocatalytic oxygen reduction reaction (ORR) is the process by which oxygen is reduced to water or other oxygen-containing species in an electrochemical system. ORR usually has two reaction pathways, one of which is the 4-electron

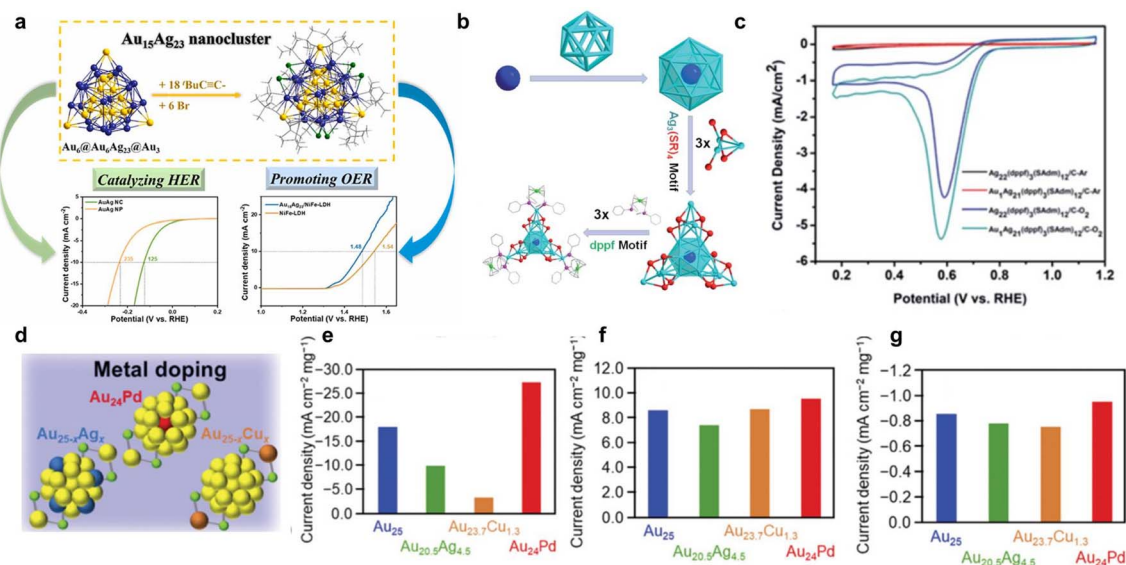


Fig. 5 (a) Schematic diagram of Au<sub>15</sub>Ag<sub>23</sub> NC as efficient HER and OER catalyst. Reproduced from ref. 112 with permission from Elsevier, copyright 2024. (b) Structural analysis of Au<sub>1</sub>Ag<sub>21</sub> NC. (c) Comparison of ORR performance of Au<sub>1</sub>Ag<sub>21</sub> and Ag<sub>22</sub> NC. Reproduced from ref. 124 with permission from Royal Society of Chemistry, copyright 2021. (d) Structural scheme of metal-doped Au<sub>25</sub> NC. Comparison of (e) HER, (f) OER, and (g) ORR activity of Au<sub>25</sub> and different metal-doped Au<sub>25</sub> NCs. Reproduced from ref. 127 with permission from Royal Society of Chemistry, copyright 2020.

reduction process, starting from  $O_2$  to  $H_2O$ , and it is one of the key reactions in energy conversion devices such as fuel cells and metal-air batteries, and its efficiency has a decisive impact on the performance of these devices.<sup>115,116</sup> While the other one is the 2-electron pathway, converting  $O_2$  to  $H_2O_2$ , which can serve as a promising alternative to the traditional energy-intensive anthraquinone process.<sup>117–119</sup>

According to theoretical calculation, the decrease in the core size of Au NPs will result in a narrowed D-band and shift to the Fermi level, which are considered to be beneficial for  $O_2$  adsorption.<sup>120,121</sup> At an early stage, Chen *et al.* utilized two series of Au NCs with different core sizes to investigate the effect of size on ORR activity, and they found the ORR catalytic activity of both follows the trend where a smaller size of NCs results in better ORR reactivity ( $Au_{11} > Au_{25} > Au_{55} > Au_{140}$  and  $Au_{25} > Au_{38} > Au_{144}$ ).<sup>122,123</sup> Besides the core size of the NCs, heteroatom doping is another critical factor influencing the ORR activity of Au NCs. Zou *et al.* synthesized  $M_1Ag_{21}(dppf)_3(SAdm)_{12}(BPh_4)_2$  ( $M = Au/Ag$ ) by introducing 1,1'-bis-(diphenylphosphino)-ferrocene (dppf) as an activating ligand.<sup>124</sup> Dppf is a derivative of ferrocene as well as an electron donor, acting as a common protective ligand used to design and synthesize a metal complex with excellent electrochemical activity. Compared to other Au/Ag NCs without a dppf ligand, the two NCs show better ORR activity. In addition, the two NCs exhibit the same icosahedral  $M_{13}$  ( $M = Au/Ag$ ) kernel with a protective shell of 3  $Ag_3(SR)_4$  motifs and the protection of 3 dppf ligands (Fig. 5b). The identical geometric structure provides an ideal platform to reveal the heteroatom doping effect.  $Au_1Ag_{21}$  shows higher onset potential and diffusion limited current density, indicating better ORR activity than that of  $Ag_{22}$  (Fig. 5c).

Xu *et al.* simultaneously introduced a dppf surface ligand and a Cd surface doping atom to perform a surface engineering strategy, and then obtained  $Au_{27}Cd_1(SAdm)_{14}(dppf)Cl$  NCs.<sup>125</sup>  $Au_{27}Cd_1$  and  $Au_{38}$  NCs have a similar bi-icosahedral  $Au_{23}$  core, but different surface structures due to surface engineering. The reconstructed surface structure offers enhanced ORR activity for  $Au_{27}Cd_1$ . The synergistic effect between Au and Cd is not only reflected in a comparison of the ORR catalytic activity of  $Au_{27}Cd_1$  and  $Au_{38}$  NCs but is also manifested in the improved ORR activity of  $Au_{22}Cd_1$  compared to that of  $Au_{24}$  NCs. Furthermore, based on the Koutecky–Levich plots, the overall number of electrons transferred for Cd-doped Au NCs is higher than that for bare Au NCs ( $Au_{38}: 2$ ,  $Au_{27}Cd_1: 3.3$ ,  $Au_{24}: 2.2$ ,  $Au_{22}Cd_1: 3$ ), indicating that Cd doping will change the ORR reaction pathway of Au NCs. In addition to Ag/Cd doping, AuPd alloy NCs show better ORR activity than Au NCs. Yan *et al.* synthesized GSH-protected AuPd NCs and tuned the structure and composition with the Pd-to-Au ratio.<sup>126</sup> The AuPd NCs are supported on carbon nanosheets and the protective ligand is completely removed by calcination. The hybrid composite with 30% metal mass loading and Pd-to-Au ratio of 1:2 exhibits optimized ORR activity.

Although there is lots of research into  $Au_n(SR)_m$ -related alloy NCs in electrocatalytic HER, OER, and ORR, the activities are obtained under different experimental conditions, so it is difficult to make a deep comparison and develop a general rule

about the methods needed to achieve high activity. Kumar *et al.* systematically investigated the effect of heteroatom species on the activity of these reactions.<sup>127</sup> Compared to Cu/Ag doping, Pd-doped Au NCs show the highest current density in all three reactions (Fig. 5d–g). Other parameters, such as the number of constituent atoms or ligand functional groups, are also carefully evaluated. The results indicate that the decreased number of constituent atoms and thickness of the ligand layer are helpful for an improvement in activity in all three reactions.

### 3.4 Au-based bimetallic NCs in the fuel small-molecule oxidation reaction

A fuel cell is a chemical device that converts the chemical energy of a fuel directly into electrical energy. Theoretically, it can operate at close to 100% thermal efficiency. It exhibits lots of advantages, such as high economy, low environmental pollution, high reliability, a wide selection of fuels and easy construction.<sup>128–132</sup> Depending on the type of fuel entering at the anode, different types of fuel cells can be obtained. For example, a direct ethanol fuel cell (DEFC) is a device that uses ethanol with its merits of high energy density, low cost and easy storage as a fuel to perform an anodic oxidation reaction and convert it into electric energy.<sup>133–135</sup> Au NCs exhibit excellent performance in the ethanol oxidation reaction (EOR). Tang *et al.* reported alkynyl-protected  $Au_{28}(DMPA)_{20}$  NCs ( $DMPA = 1$ -ethynyl-2,4-dimethylbenzene) synthesized by a direct reduction method.<sup>136</sup> Compared to thiol-ligand-protected  $Au_{28}(SR)_{20}$  (here  $SR = TBBT/CPT$ ,  $TBBT = 4$ -tertbutylbenzenethiol,  $CPT = cyclopentanethiol$ ) with a similar structure,  $Au_{28}(DMPA)_{20}$  shows superior EOR mass activity and specific activity. In order to further improve the EOR activity, commercial Pd and Pt are introduced into Au NCs as heteroatom dopants. Zhang *et al.* synthesized surface-clean  $Pt_3Au$  NCs with a uniform size of 2.1 nm supported on PDDA-functionalized graphene ( $Pt_3Au@PDDA-G$ ) by a CO reduction method.<sup>137</sup> The obtained  $Pt_3Au$  NCs not only effectively suppress Ostwald ripening but also show enhanced EOR activity due to the more efficient removal of the adsorbed CO-like intermediates based on the synergistic effect between Pt and Au. Similarly, Cui *et al.* utilized a wet-chemical method to synthesize AuPd NCs with an average size of 1.0 nm supported on amine-functionalized carbon black ( $AuPd/CB_{H-A}$ ).<sup>138</sup> In EOR,  $Au_{0.4}Pd_{0.6}/CB_{H-A}$  exhibits 5.25 A  $mg_{AuPd}^{-1}$  mass activity and 5.98 mA  $cm_{AuPd}^{-2}$  specific activity, which are 9.7 and 3.4 times greater than those of commercial Pd/C (0.54 A  $mg_{Pd}^{-1}$  and 1.74 mA  $cm_{Pd}^{-2}$ ), respectively.

In addition, direct formic acid fuel cells (DFAFCs) fueled by formic acid are considered to be one of the most promising power sources for portable electronic devices in the future due to their small size, low toxicity and low penetration of Nafion membranes.<sup>139,140</sup> Pt is generally considered to be the most effective catalyst towards the anodic reaction of DFAFCs, formic acid oxidation (FAO). However, due to its poor resistance to CO toxicity, its current development faces a bottleneck. Lu *et al.* synthesized single-Pt-atom-doped  $Au_{25}$  ( $Pt_1Au_{24}(SR)_{18}$ ) NCs.<sup>141</sup> Although only one Pt replaces the central Au atom,  $Pt_1Au_{24}$  shows excellent FAO performance with a high mass activity of



3.7 A  $\text{mg}_{\text{Pt+Au}}^{-1}$ , which is 12 and 34 times higher than that of Pt NCs and commercial Pt/C, respectively. Moreover, the unavailability of adjacent Pt atoms in  $\text{Pt}_1\text{Au}_{24}$  NCs effectively suppresses the poisoning of CO intermediates, which is reflected in the outstanding performance in an accelerated durability test and CO stripping experiment. On the basis of *in situ* electrochemical FTIR observation and thermodynamic and kinetic calculation, the FAO process on  $\text{Pt}_1\text{Au}_{24}$  is speculated to be a direct pathway with  $\text{COOH}^*$  as the preferred reactive intermediate. The introduction of a Pt atom leads to a decreased HOMO–LUMO gap and higher reactivity, and the original Au atomic shell plays a CO anti-poisoning role. The synergistic effect in  $\text{Pt}_1\text{Au}_{24}$  NCs contributes to the high activity and good stability.

### 3.5 Au-based bimetallic NCs in the carbon dioxide reduction reaction

The catalytic conversion of carbon dioxide is the process of converting  $\text{CO}_2$  into chemicals, energy products and functional materials to achieve resource utilization, which has great significance and application prospects for sustainable development. The use of low-grade renewable electricity to reduce  $\text{CO}_2$ , which can both reduce  $\text{CO}_2$  emissions and “turn waste into good”, and convert renewable energy into high energy density fuel storage, is considered a green and promising technique due to its flexible and sustainable method of conversion.<sup>142–146</sup>

At present, the possible main products of  $\text{CO}_2$  electro-reduction include  $\text{C}_1$  products (e.g., carbon monoxide, formic acid, methane, methanol) and  $\text{C}_{2+}$  chemicals (e.g., ethylene, ethanol, ethane, *n*-propanol).<sup>145</sup> Among the different products of  $\text{CO}_2\text{RR}$ , the conversion of  $\text{CO}_2$  to CO is considered to be one of the most promising reactions in the chemical industry due to its technical and economic feasibility.<sup>147</sup> Due to the relatively weak binding of  $^*\text{CO}$  intermediates to Au, Au-based materials show particularly high selectivity for the formation of CO. It is believed that alloying or doping can further improve the  $\text{CO}_2\text{RR}$  efficiency of Au NCs by optimizing the electronic structure and surface geometry. Zhuang *et al.* employed  $\text{Au}_{44}(\text{TBBT})_{28}$  as the parent NCs and chose  $\text{Cd}^{2+}$  as the oxidative ions to prepare  $\text{Au}_{47}\text{Cd}_2(\text{TBBT})_{31}$  NCs by the anti-galvanic reduction (AGR) method in a two-phase system.<sup>148</sup> The doped Cd atoms are on the surface and are coordinated by three thiolates. Compared to  $\text{Au}_{44}(\text{TBBT})_{28}$ ,  $\text{Au}_{47}\text{Cd}_2(\text{TBBT})_{31}$  shows higher faradaic efficiency (FE) for CO over a wide potential range from  $-0.3$  V to  $-0.9$  V, displaying  $\text{FE}_{\text{CO}}$  up to 96% at  $-0.57$  V (Fig. 6a). DFT calculations indicate that introducing Cd atoms results in a change in the adsorption configuration for the  $\text{COOH}^*$  intermediate. Unlike  $\text{Au}_{44}(\text{TBBT})_{28}$ , the O atom of  $\text{COOH}^*$  prefers to bind with Cd, leading to the formation of  $\text{Cd-O-C(OH)-Au}$  and decreased  $\text{COOH}^*$  formation energy, benefiting the enhancement in  $\text{CO}_2\text{RR}$  activity.

In addition, Li *et al.* synthesized Cd-surface-modified Au NCs ( $\text{Au}_{19}\text{Cd}_2(\text{SR})_{16}$ ,  $\text{SR}$  = cyclohexanethiolate) by taking  $\text{Au}_{23}(\text{SR})_{16}$  as the template.<sup>149</sup> Compared to  $\text{Au}_{23}$ , the kernel of  $\text{Au}_{19}\text{Cd}_2$  is maintained, except that two surface Au atoms are replaced by Cd dopants. The introduction of Cd obviously improves the

selectivity and activity of CO formation. The determination of active sites is investigated in detail. Compared to the inactivity of fully ligand-protected NCs, partial ligand detachment is considered a necessity for high catalytic activity. However, it needs to be carefully studied which part ( $-\text{R}$  or  $-\text{SR}$ ) it is reasonable to remove, and which exposure site (S or Au) is the real catalytic site. Through DFT calculations, for both NCs, removing the  $-\text{R}$  group is considered to be more feasible than losing the  $-\text{SR}$  group, and the exposed S site is likely to be the active center for  $\text{CO}_2\text{RR}$ . In contrast, if  $-\text{SR}$  is removed, the exposed Au site is more selective for HER than for  $\text{CO}_2\text{RR}$ . Furthermore, for  $\text{Au}_{19}\text{Cd}_2$  NCs, the S active site ( $\text{Cd-S-Au}$  staple motif) will undergo a dynamic regeneration process during CO formation and desorption, contributing to the different  $^*\text{CO}$  binding mode and leading to the decreased energy for CO formation (Fig. 6b). At the same time, Sun *et al.* investigated the  $\text{CO}_2\text{RR}$  activities of  $\text{Au}_{25}(\text{SR})_{18}$ ,  $\text{Au}_{24}\text{Cd}_1(\text{SR})_{18}$ ,  $\text{Au}_{19}\text{Cd}_4(\text{SR})_{18}$ , and  $\text{Au}_{38}\text{Cd}_4(\text{SR})_{30}$ , and found that Cd doping can selectively control the cleavage of the Au–S or C–S bond.<sup>150</sup> They reached a similar conclusion: that is, the exposed open S site obtained by cleaving the C–S bond is readily bound to  $\text{CO}_2$  and favourable for  $\text{CO}_2\text{RR}$ , while breakage of the Au–S bond leads to the exposure of the metal site, which is preferable for HER. Recognition of the real catalytic site in the two studies perfectly reflects the advantages of atomically precise NCs in revealing the catalytic mechanism and exploring the relationship between structure and activity.

In a comparison of  $\text{CO}_2\text{RR}$  performance between  $\text{Pd}_1\text{Au}_{24}(\text{SR})_{18}$  and  $\text{Au}_{25}(\text{SR})_{18}$  NCs ( $\text{R} = -\text{CH}_2\text{CH}_2\text{Ph}$ ), Li *et al.* found that  $\text{Pd}_1\text{Au}_{24}$  can greatly improve the  $\text{CO}_2\text{RR}$  selectivity, with  $\sim 100\%$   $\text{FE}_{\text{CO}}$ , especially at high potential (up to  $-1.2$  V), while the  $\text{FE}_{\text{CO}}$  of  $\text{Au}_{25}$  NCs starts to decrease at  $-0.9$  V.<sup>151</sup> Theoretical calculations demonstrate that the surface S atom is the active site, and  $\text{Pd}_1\text{Au}_{24}$  can increase the thermodynamic barrier for ligand removal and retain a larger population of S active sites compared to  $\text{Au}_{25}$ , which contributes to the improved  $\text{CO}_2\text{RR}$  selectivity in the extended potential range. As Pd doping can effectively improve the activity of Au NCs in  $\text{CO}_2\text{RR}$ , it is natural to think of two-element doping to form trimetallic Au-based NCs. Zhuang *et al.* utilized the AGR method to synthesize  $\text{Au}_3\text{-AgPd}_6(\text{TBBT})_{12}$  NCs by introducing a kernel Ag single atom on the basis of  $\text{Au}_4\text{Pd}_6(\text{TBBT})_{12}$ .<sup>152</sup> The trimetallic  $\text{Au}_3\text{AgPd}_6$  NCs show higher  $\text{CO}_2\text{RR}$  activity and selectivity than  $\text{Au}_4\text{Pd}_6$  with a similar structure (Fig. 6c). The introduction of Ag causes a significant change in electronic structure, decreases the d-center, weakens  $^*\text{CO}$  adsorption, and promotes the release of CO, thereby improving the  $\text{CO}_2\text{RR}$  activity. Meanwhile, the difficulty of  $^*\text{H}$  desorption is increased, suppressing HER and enhancing  $\text{CO}_2\text{RR}$  selectivity. Pd doping can not only enhance the activity of  $\text{CO}_2\text{RR}$  but also shows the ability to change product type. Cai *et al.* prepared Au-based NCs ( $\text{Au}_9$  and  $\text{Au}_8\text{Pd}_1$ ) confined in a layer of montmorillonite to form NC-based heterogeneous catalysts.<sup>153</sup> Pd doping can reduce the propensity for structural variation induced by the change in coordination number of the surface Au site during the reaction, bringing about multiple benefits to the catalysis. In a traditional fixed-bed reactor,  $\text{Au}_8\text{Pd}_1$  exhibits unique catalytic performance



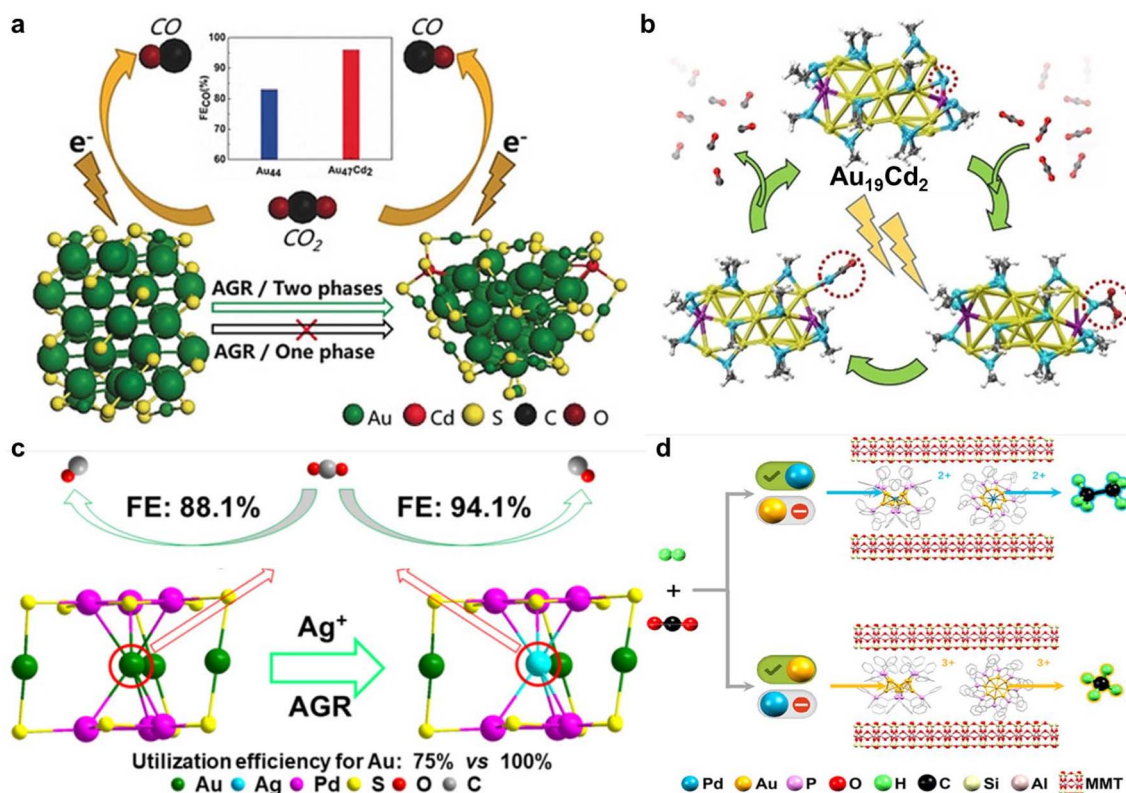


Fig. 6 (a) Schematic diagram of the synthesis and comparison of the CO<sub>2</sub>RR activity of Au<sub>44</sub> and Au<sub>47</sub>Cd<sub>2</sub> NCs. Reproduced from ref. 148 with permission from Wiley-VCH, copyright 2020. (b) Schematic diagram of the structural dynamic evolution of Au<sub>19</sub>Cd<sub>2</sub> during CO<sub>2</sub>RR. Reproduced from ref. 149 with permission from Wiley-VCH, copyright 2021. (c) Synthesis scheme and comparison of the CO<sub>2</sub>RR activity of Au<sub>4</sub>Pd<sub>6</sub> and Au<sub>3</sub>AgPd<sub>6</sub> NCs. Reproduced from ref. 152 with permission from American Chemical Society, copyright 2022. (d) Schematic diagram of tuning selectivity in CO<sub>2</sub> catalytic conversion by Au<sub>5</sub> and Au<sub>5</sub>Pd<sub>1</sub> NCs. Reproduced from ref. 153 with permission from Chinese Chemical Society, copyright 2021.

in the CO<sub>2</sub> hydrogenation reaction, changing the product type from methane to ethane, and improving the catalytic stability as well (Fig. 6d).

Many reports have also shown that AuAg alloy NCs are a highly efficient electrocatalyst for CO<sub>2</sub>RR. Seong *et al.* developed an active-site transplantation strategy to synthesize core-shell AuAg<sub>12</sub>@Au<sub>12</sub>(SETPh)<sub>18</sub> NCs (SETPh = 2-phenylethanethiolate) by replacing the Ag<sub>12</sub>(SR)<sub>18</sub> shell of Ag<sub>25</sub>(SR)<sub>18</sub> NCs with an Au<sub>12</sub>(SR)<sub>18</sub> shell.<sup>154</sup> Compared to Ag<sub>25</sub>(SR)<sub>18</sub> NCs, the active-site-engineered AuAg<sub>12</sub>@Au<sub>12</sub>(SETPh)<sub>18</sub> NCs show significantly improved CO<sub>2</sub>RR activity with a 200 mA cm<sup>-2</sup> industry current density and a 2.1 V full-cell potential in a zero-gap CO<sub>2</sub>-to-CO electrolyzer. Lin *et al.* prepared AuAg<sub>26</sub>(-SAdm)<sub>18</sub>S<sup>-</sup> (HSAdm = 1-adamantanethiolate) NCs composed of an AuAg<sub>12</sub> icosahedron kernel and an Ag<sub>14</sub>(SR)<sub>18</sub>S open shell.<sup>155</sup> Unlike Ag<sub>25</sub>(DMT)<sub>18</sub><sup>-</sup> (DMT = 2,4-dimethylbenzenethiol) and Au<sub>21</sub>(SAdm)<sub>16</sub> with a closed shell, due to the open shell structure in AuAg<sub>26</sub>(SAdm)<sub>18</sub>S<sup>-</sup>, the partial Ag atoms of the AuAg<sub>12</sub> kernel are not protected by thiols, resulting in the exposure of some facets of the kernel. Therefore, owing to the unique open shell structure and Au-Ag synergistic effect, AuAg<sub>26</sub> exhibits lower \*COOH formation free energy and displays increased CO<sub>2</sub>RR activity (98.4% FE<sub>CO</sub> at -0.97 V), compared to Ag<sub>25</sub> and Au<sub>21</sub> NCs (Fig. 7a). Based on the superior CO<sub>2</sub>RR activity of AuAg alloy

NCs, Li *et al.* further investigated the effect of the accessibility of metal sites on the CO<sub>2</sub>RR performance by systematically studying a series of alkynyl-protected AuAg NCs (Au<sub>n</sub>Ag<sub>46-n</sub>-(C≡CR)<sub>24</sub>Cl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>, Au<sub>24</sub>Ag<sub>20</sub>(C≡CR)<sub>24</sub>Cl<sub>2</sub>, and Au<sub>43</sub>(C≡CR)<sub>20</sub>/Au<sub>42</sub>Ag<sub>1</sub>(C≡CR)<sub>20</sub>) of similar size and structure but different surface ligand coverage.<sup>156</sup> Among these NCs, Au<sub>43</sub>(C≡CR)<sub>20</sub> and Au<sub>42</sub>Ag<sub>1</sub>(C≡CR)<sub>20</sub> with the highest number of accessible metal sites exhibit the highest FE<sub>CO</sub> (Fig. 7b). Xu *et al.* utilized two AuAg alloy NCs (Au<sub>24</sub>Ag<sub>20</sub> and Au<sub>43</sub>Ag<sub>38</sub>) to explore how the hierarchical assembly influences CO<sub>2</sub>RR activity.<sup>157</sup> There are some correlations and differences between the two NCs, such as Au<sub>43</sub>Ag<sub>38</sub> maintaining the kernel framework from the parent Au<sub>24</sub>Ag<sub>20</sub> and it can be regarded as a dimeric form of Au<sub>24</sub>Ag<sub>20</sub> monomeric NCs; Au<sub>24</sub>Ag<sub>20</sub> is racemic, while Au<sub>43</sub>Ag<sub>38</sub> is mesomeric; Au<sub>24</sub>Ag<sub>20</sub> exhibits superatomic electronic configurations, while Au<sub>43</sub>Ag<sub>38</sub> has molecule-like characteristics. Possibly due to the different atomic packing structures (individual-core vs. dual-core) and surface motif arrangement (parallel vs. crossed), the Au<sub>24</sub>Ag<sub>20</sub> monomers show better CO<sub>2</sub>RR activity than Au<sub>43</sub>Ag<sub>38</sub> dimers.

Cu is considered as a special element for CO<sub>2</sub>RR due to the suitable adsorption energy for \*CO and \*CH<sub>x</sub>O intermediates; therefore Cu-doped Au NCs have received a lot of attention. Deng *et al.* synthesized [Au<sub>15</sub>Cu<sub>4</sub>(DPPM)<sub>6</sub>Cl<sub>4</sub>(C≡CR)<sub>1</sub>]<sup>2+</sup> NCs



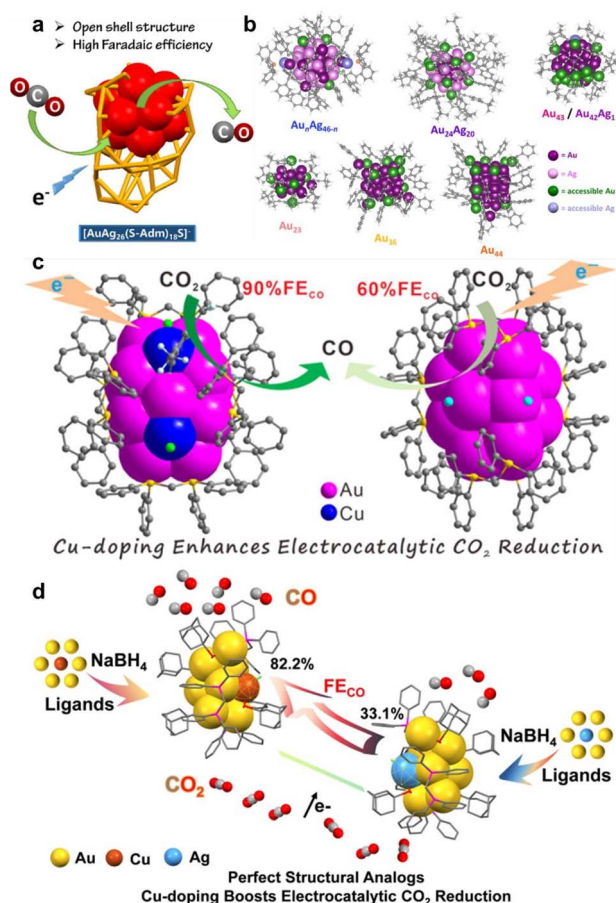


Fig. 7 (a) Schematic diagram of open shell structure of  $\text{AuAg}_{26}(\text{SAdm})_{18}\text{S}^-$  for enhanced CO<sub>2</sub>RR activity. Reproduced from ref. 155 with permission from American Chemical Society, copyright 2021. (b) The metal sites accessible to CO<sub>2</sub> on the surface of different Au/Ag NCs. Reproduced from ref. 156 with permission from Royal Chemical Society, copyright 2023. (c) Schematic diagram of  $\text{Au}_{15}\text{Cu}_4$ -enhanced CO<sub>2</sub>RR activity compared to  $\text{Au}_{18}$  NCs. Reproduced from ref. 158 with permission from American Chemical Society, copyright 2023. (d) Comparison of CO<sub>2</sub>RR activity of structural analogs of  $\text{Au}_8\text{Cu}_1$  and  $\text{Au}_8\text{Ag}_1$  NCs. Reproduced from ref. 160 with permission from Wiley-VCH, copyright 2024.

(DPPM = bis(diphenylphosphino)methane;  $\text{HC}\equiv\text{CR}$  = 3,5-bis-(trifluoromethyl)phenylacetylene) *via* a one-pot method.<sup>158</sup> Compared to the monometallic structural analogue,  $[\text{Au}_{18}(\text{DPPM})_6\text{Br}_4]^{2+}$ ,  $\text{Au}_{15}\text{Cu}_4$  shows a dramatic enhancement in CO<sub>2</sub>RR activity with a high FE<sub>CO</sub> of >90% and an up to industrial CO partial current density of  $-413 \text{ mA cm}^{-2}$  at  $-3.75 \text{ V}$  in a membrane electrode assembly (MEA) cell (Fig. 7c). The exposed Au–Cu dual sites synergistically modulate the d-state shift, contributing to the enhanced catalytic activity. Ding *et al.* also explored the Au–Cu synergistic effect on CO<sub>2</sub>RR activity.<sup>159</sup> They found that  $\text{Au}_1\text{Cu}_{24}$  NCs are preferable for the CO<sub>2</sub>RR, while  $\text{Cu}_{25}$  NCs tends to progress HER, because AuCu synergy can effectively suppress HER due to the contracted electronic distribution. Based on the single Cl-terminated coordination strategy, Su *et al.* obtained a pair of structural analogs,  $[\text{Au}_8\text{Ag}_1(\text{SAdm})_4(\text{Dppm})_3\text{Cl}]^{2+}$  and  $[\text{Au}_8\text{Cu}_1(\text{SAdm})_4(\text{Dppm})_3\text{Cl}]^{2+}$ .<sup>160</sup> Due to the same overall structure and metal

doping number and position, the metal doping type effect can be decoupled from various entangled influencing factors to elucidate metal synergies solely in terms of atomic differences.  $\text{Au}_8\text{Cu}_1$  shows higher FE<sub>CO</sub> than  $\text{Au}_8\text{Ag}_1$  due to the generation of thermodynamically more stable  $^*\text{COOH}$  and lower  $^*\text{CO}$  formation energy (Fig. 7d). The rare structural analogs help us clearly reveal the impact of single-metal change on the catalytic performance. Doping a foreign metal atom to form Au-based alloy NCs can not only regulate the electronic and geometric structure to enhance catalytic activity but also minimize Au usage and reduce the catalyst cost when doping with non-precious metal atoms. Seong *et al.* developed a highly-efficient and economic CO<sub>2</sub>RR catalyst with high mass activity,  $\text{Au}_4\text{Ni}_2$  NCs, by the transplantation of Au active sites into non-precise  $\text{Ni}_4$  NCs (Fig. 8a).<sup>161</sup> In  $\text{Au}_4\text{Ni}_2$  NCs, the Au atoms are the active sites, the Ni atoms mainly play the role of a cost reducer, and thereby the utilization efficiency of the Au atoms is improved. The TOF and mass activity of  $\text{Au}_4\text{Ni}_2$  NCs for CO<sub>2</sub>-to-CO are  $206 \text{ mol}_{\text{CO}} \text{ mol}_{\text{NC}} \text{ s}^{-1}$  and  $25228 \text{ A/g}_{\text{Au}}$ , respectively.

For CO<sub>2</sub>RR, the activation of CO<sub>2</sub> is critical because it is the first step in CO<sub>2</sub> conversion. CO<sub>2</sub> is a linear molecule with high stability, resulting in difficulty in its activation.<sup>162</sup> Constructing asymmetric charge distribution sites is an effective way to activate CO<sub>2</sub>,<sup>163,164</sup> and our previous review introduced several strategies of symmetry-breaking sites in metal NCs for enhancing CO<sub>2</sub>RR activity, including a heteroatom doping induced strategy.<sup>165</sup> For example, Tan *et al.* synthesized a series of  $\text{Au}_{13}\text{Cu}_x$  alloy NCs ( $x = 0-4$ ) with different degrees of symmetry-breaking on the crystal structure by manipulating Cu atom doping (Fig. 8b).<sup>166</sup>  $\text{Au}_{13}\text{Cu}_1$ ,  $\text{Au}_{13}\text{Cu}_2$ , and  $\text{Au}_{13}\text{Cu}_4$  have  $C_{3V}$  symmetry,  $C_{3h}$  symmetry, and  $T_d$  symmetry, respectively, while  $\text{Au}_{13}\text{Cu}_3$  exhibits an asymmetric surface structure with 2 three-coordinate

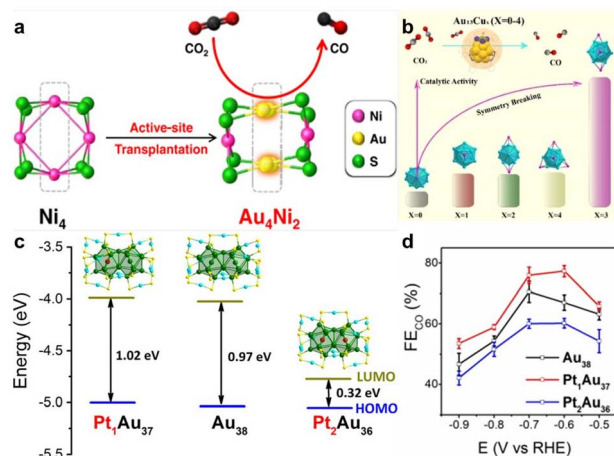


Fig. 8 (a) Schematic diagram of active site transplantation from  $\text{Ni}_4$  to  $\text{Au}_4\text{Ni}_2$  NCs for enhanced CO<sub>2</sub>RR. Reproduced from ref. 161 with permission from American Chemical Society, copyright 2023. (b) Schematic diagram of the different degrees of symmetry breaking in  $\text{Au}_{13}\text{Cu}_x$  ( $x = 0-4$ ) NCs for different CO<sub>2</sub>RR performances. Reproduced from ref. 166 with permission from Wiley-VCH, copyright 2024. (c) Electronic structure energy level and (d) comparison of CO<sub>2</sub>RR activity of  $\text{Au}_{38}$ ,  $\text{Pt}_1\text{Au}_{37}$ , and  $\text{Pt}_2\text{Au}_{36}$ . Reproduced from ref. 167 with permission from Wiley-VCH, copyright 2022.

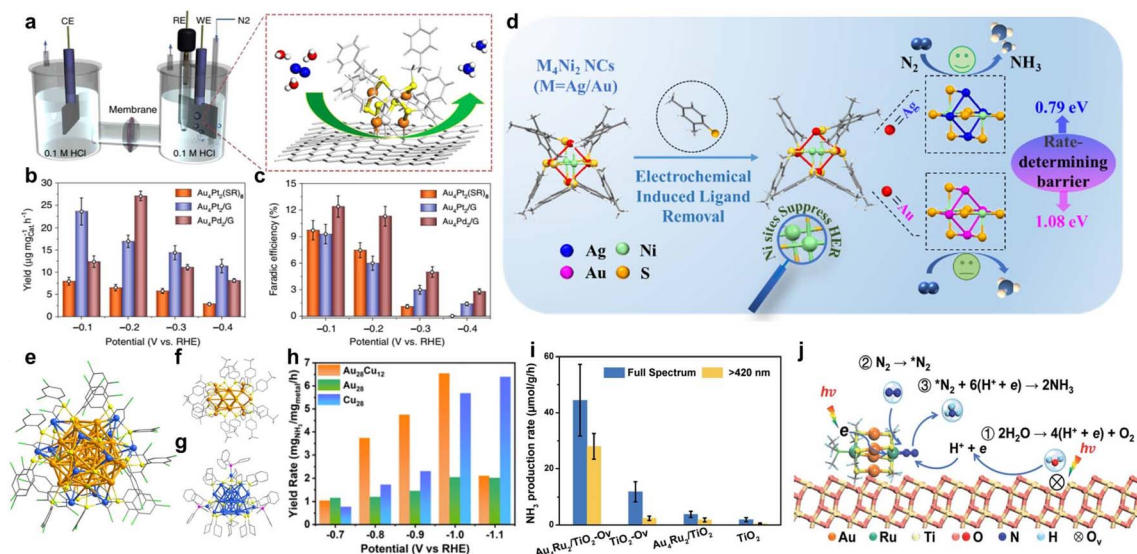


Fig. 9 (a) Schematic diagram of  $\text{Au}_4\text{M}_2/\text{G}$  ( $\text{M} = \text{Pt}, \text{Pd}$ ) for NRR. (b)  $\text{NH}_3$  yield rate and (c) FE of  $\text{NH}_3$  comparison of  $\text{Au}_4\text{Pt}_2$  NC and  $\text{Au}_4\text{M}_2/\text{G}$  ( $\text{M} = \text{Pt}, \text{Pd}$ ). Reproduced from ref. 176 with permission from Springer Nature, copyright 2020. (d) Schematic diagram of regulation of intrinsic activity of  $\text{M}_4\text{Ni}_2$  ( $\text{M} = \text{Au}, \text{Ag}$ ) NCs for NRR. Reproduced from ref. 177 with permission from Wiley-VCH, copyright 2022. (e) Structure of  $\text{Au}_{28}\text{Cu}_{12}$ , (f)  $\text{Au}_{28}$ , and (g)  $\text{Cu}_{28}$  NCs. (h)  $\text{NH}_3$  yield rate comparison of  $\text{Au}_{28}\text{Cu}_{12}$ ,  $\text{Au}_{28}$ , and  $\text{Cu}_{28}$  NCs. Reproduced from ref. 181 with permission from Royal Chemical Society, copyright 2024. (i)  $\text{NH}_3$  yield rate of  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-O}_v$ ,  $\text{TiO}_2\text{-O}_v$ ,  $\text{Au}_4\text{Ru}_2/\text{TiO}_2$ , and  $\text{TiO}_2$  under different sources of light irradiation. (j) Proposed mechanism for photocatalytic NRR on  $\text{Au}_4\text{Ru}_2/\text{TiO}_2\text{-O}_v$ . Reproduced from ref. 182 with permission from Royal Chemical Society, copyright 2020.

$\text{Cu}_1\text{S}_3$  and 1 two-coordinate  $\text{Cu}_1\text{S}_2$  motifs. With the highest asymmetry degree of  $\text{Au}_{13}\text{Cu}_3$ , the unsaturated  $\text{Cu}_1\text{S}_2$  site on the surface more readily coordinates with  $\text{CO}_2$ , promoting  $\text{CO}_2$  adsorption and  $\text{CO}_2\text{RR}$  activity. As a result,  $\text{Au}_{13}\text{Cu}_3$  shows the highest current density of  $70 \text{ mA cm}^{-2}$  within the  $\text{Au}_{13}\text{Cu}_x$  family of NCs ( $\text{Au}_{13}\text{Cu}_x$  ( $x = 1, 2, 4$ ):  $40 \text{ mA cm}^{-2}$ , and  $\text{Au}_{13}$ :  $15 \text{ mA cm}^{-2}$ ). In addition, Liu *et al.* obtained identical geometric structural  $\text{Pt}_1\text{Au}_{37}(\text{SR})_{24}$  and  $\text{Pt}_2\text{Au}_{36}(\text{SR})_{24}$  ( $\text{SR} = 4\text{-tert-butylbenzyl mercaptan}$ ) by the controllable asymmetrical and symmetrical doping of Pt atoms into parent  $\text{Au}_{38}(\text{SR})_{24}$  NCs.<sup>167</sup> The structure of  $\text{Pt}_1\text{Au}_{37}$  is that one Pt atom asymmetrically dopes into one of the two cores of  $\text{Au}_{38}$ , and relative to  $\text{Au}_{38}$ ,  $\text{Pt}_1\text{Au}_{37}$  displays higher HOMO energy with the loss of one valence electron. While the two Pt atoms in  $\text{Pt}_2\text{Au}_{36}$  are symmetrically located in the two cores of  $\text{Au}_{38}$ , and  $\text{Pt}_2\text{Au}_{36}$  exhibits a narrowed HOMO–LUMO gap and loses two valence electrons, compared to  $\text{Au}_{38}$  (Fig. 8c). The difference in doping mode causes the modulation of electronic structure; thereby,  $\text{Pt}_1\text{Au}_{37}$  shows high electron-spin-induced  $\text{CO}_2\text{RR}$  activity, followed by  $\text{Au}_{38}$  and  $\text{Pt}_2\text{Au}_{36}$  (Fig. 8d). Besides, Wang *et al.* utilized an Fe single atom (SA) site to modify  $\text{Au}_8$  NCs and integrate SA and NC into one system.<sup>168</sup> Due to the introduction of Fe SA, asymmetric charge distributed active sites are constructed and the key intermediate  $^*\text{COOH}$  adsorption energy is optimized to benefit an improvement in  $\text{CO}_2\text{RR}$  activity, leading to  $\sim 18.07$ -fold amplification in the FE of  $\text{CO}_2$ -to- $\text{CO}$  compared to isolated  $\text{Au}_8$  NCs.

### 3.6 Au-based bimetallic NCs in the synthetic ammonia reaction

Ammonia is an important industrial raw material that plays an important role in the manufacture of fertilizers, dyes, and

pharmaceuticals. In addition, due to its large hydrogen capacity, high energy density, and ease of transportation, ammonia is considered a potential carbon-free fuel.<sup>169–171</sup> The traditional Haber–Bosch process enables the large-scale industrial production of ammonia, but its production conditions ( $400\text{--}550^\circ\text{C}$ ,  $15\text{--}30 \text{ MPa}$ ) are harsh and are associated with high energy consumption and  $\text{CO}_2$  emissions.<sup>172–174</sup> Using sustainable electric energy, solar energy and other new energy sources as the driving force, abundant  $\text{N}_2$  in the atmosphere or environmentally harmful but highly active nitrogen-containing species (such as  $\text{NO}$ ,  $\text{NO}_2^-/\text{NO}_3^-$ ) are reduced to synthesize ammonia under conditions of ambient temperature and pressure, which is considered to have great application potential.<sup>20,175</sup>

Yao *et al.* firstly synthesized Pt/Pd-doped Au-based NCs ( $\text{Au}_4\text{M}_2(\text{SR})_8$ ,  $\text{M} = \text{Pd}/\text{Pt}$ ) with a precise and controllable size distribution and metal doping and then removed partial ligands by thermal treatment to anchor it onto defective graphene to create a robust supported NC-based catalyst (Fig. 9a).<sup>176</sup> DFT calculations indicate that heteroatom doping plays an essential role in  $\text{N}_2$  activation *via* enhanced electron back donation to  $\text{N}_2$  antibonding  $\pi^*$ -orbitals. By precise metal doping,  $\text{Au}_4\text{Pd}_2$  shows higher  $\text{FE}_{\text{NH}_3}$  and  $\text{NH}_3$  yield at  $-0.2 \text{ V}$  than  $\text{Au}_4\text{Pt}_2$  in the electrocatalytic  $\text{N}_2$  reduction reaction (NRR) (Fig. 9b and c). From the perspective of tuning intrinsic catalytic activity of NCs, Han *et al.* introduced non-precise metal Ni with the ability to suppress HER (the competitive reaction to NRR) to prepare  $\text{M}_4\text{Ni}_2$  ( $\text{M} = \text{Au}/\text{Ag}$ ) NCs.<sup>177</sup> Compared to monometallic NCs ( $\text{Au}_6$ ,  $\text{Ag}_6$ , and  $\text{Ni}_6$ ), bimetallic  $\text{M}_4\text{Ni}_2$  ( $\text{M} = \text{Au}/\text{Ag}$ ) shows better NRR performance. On the one hand, the superior NRR activity is attributed to the effective inhibition of HER by the introduction



of Ni. On the other hand, partial ligand detachment during the electrochemical process provides exposed active sites to access more  $N_2$  reactant and induces reconstruction of the electronic structure, benefiting the NRR (Fig. 9d).

It has been reported that Cu is considered to be a promising candidate for electrocatalytic  $NO_3^-$  reduction ( $NO_3RR$ ) to  $NH_3$ .<sup>178</sup> However, Cu is prone to surface poisoning due to spontaneous oxidative dissolution as well as easy adsorption of other species in the electrolyte.<sup>179,180</sup> Tang *et al.* doped Cu atoms on the surface of  $Au_{28}$  NCs to form stable  $AuCu$  alloy NCs ( $Au_{28}Cu_{12}(SR)_{24}(PPh_4)_4$  ( $SR = 2,4$ -dichlorothiophenol)).<sup>181</sup> Due to the synergistic effect between Au and Cu, the geometric and electronic structure of  $Au_{28}Cu_{12}$  are tailored to be suitable for  $NO_3RR$ . Compared to monometallic  $Au_{28}(TBBT)_{20}$  ( $TBBT = 4$ -*tert*-butylbenzenethiol) and  $Cu_{28}(CHT)_{18}(PPh_3)_3$  ( $CHT =$  cyclohexanethiol), bimetallic  $Au_{28}Cu_{12}$  shows higher  $NH_3$  production activity and stability (Fig. 9e–h).

Sun *et al.* first screened the feasibility of light-driven NRR by a series of  $Au_n$  NCs ( $n = 8, 9, 11, 18, 23, 24, 25, 28, 36, 44$ ).<sup>182</sup> Due to the physical adsorption of  $N_2$  on the surface of  $Au_n$  (the distance between  $N_2$  and  $Au_n$  is longer than 3.2 Å), it is impossible for  $N_2$  to coordinate to  $Au_n$  for activation. Considering Ru is a recognized NRR candidate, Ru-doped Au NCs ( $Au_4Ru_2(-PPh_3)_2(SC_2H_4Ph)_8$ ) are synthesized and then loaded onto the oxygen vacancies of  $TiO_2$  to form an NC-based heterogeneous photocatalyst ( $Au_4Ru_2/TiO_2-O_v$ ) (Fig. 9i). Under light irradiation, both  $Au_4Ru_2$  NCs and  $TiO_2$  can directly generate e–h pairs and photoinduced electron transfer from  $TiO_2$  to  $Au_4Ru_2$  NCs. The introduction of Ru atoms can effectively promote electron injection to adsorbed  $N_2$  and then realize  $N_2$  activation (Fig. 9j). The supported bimetallic  $Au_4Ru_2$  NCs displays better photocatalytic NRR activity than homogold  $Au_n$  NCs (Fig. 9i). This work not only indicates the ability for light harvesting and photogenerating e–h pairs over NCs with non-metallic or excitonic behavior, but also demonstrates a cooperative effect based on heteroatom doping.

## 4. Summary and outlook

Metal NCs not only act as a bridge connecting metal NPs and SACs in terms of their size aspect, it also compensates for their shortcomings in catalysis as a unique type of nanomaterial. First of all, from the perspective of electronic structure, metal NCs have discrete electronic energy levels unlike metal NPs and SACs, and therefore, they show distinctive performance in catalysis. Secondly, compared to metal NPs, the size of the metal NCs is smaller, their atomic utilization is higher, and the number of surface unsaturated coordinated active sites is richer. In addition, the molecule-like high purity and homogeneity in size, composition, structure, and surface environment of atomically precise metal NCs provides the opportunity to reveal the catalytic mechanism and guide catalyst design at the atomic level, which is impossible for metal NPs to achieve. Compared to SACs, metal NCs can effectively exert a synergistic effect between metal atoms, adjusting the composition, geometric configuration and electronic structure of the catalyst,

to realize “1 + 1 > 2” enhancement of catalytic activity, selectivity and stability.

In the metal NC family, Au-based NCs not only exhibit the advantages of simple synthesis, high yield, and easy functionalization but also possess the characteristics of high stability and solubility in various solvents, therefore attracting lots of attention from catalysis researchers. Unlike previous reviews on alloy NCs and NC catalysis (either focusing on the controllable synthesis of NCs or involving general catalytic reactions), this perspective aims at the unsatisfactory activity and dilemma about the unclear reaction mechanism facing the energy-related small-molecule catalytic reaction at the present stage, mainly summarizing the synergistic effect on an enhancement in catalytic performance in atomically precise Au-based bimetallic NCs. From the above summary and discussion, great efforts have been made in this field, and gratifying developments and advances have been achieved. Finally, in this section, some of our own perspectives and insights are put forward, to promote further development, innovation and breakthroughs in this field in the future.

(1) The synthesis range of doped metal NCs needs to be further expanded. It is not limited to bimetallic NCs. At present, there have been reports on trimetallic alloy NCs. We can learn from ideas about the preparation of high-entropy alloy NPs,<sup>183,184</sup> to try to synthesize polymetallic alloy NCs, and perhaps some novel and unexpected phenomena or properties will appear in the subnanometer region. In addition, as far as synthesis is concerned, the rapid development of society no longer allows us to continue to blindly use the “trial and error” approach, which is too inefficient. We can use the advanced scientific and technological achievements of computer science, allowing chemistry, catalysis, computer technology and other interdisciplinary subjects to cross-fertilise and integrate, use artificial intelligence to predict the kind of doping, the amount of doping, and the position of doping for the best catalytic performance, which can greatly improve preparation efficiency.<sup>185,186</sup> Additionally, they can be combined with a high-throughput NC synthesis technique to quickly prepare multiple types of NCs at one time in order to quickly screen their catalytic properties.<sup>187</sup>

(2) Considering future practical application scenarios, the cost-effectiveness of catalysts is an important consideration. It is necessary to develop non-noble metal clusters, such as transition metal clusters (iron-based, cobalt-based, nickel-based, copper-based clusters, *etc.*). However, due to their inherent instability (easily reacting with oxygen and water), the synthesis conditions are relatively harsh, and the purity and yield of the obtained product are unsatisfactory. Therefore, it is necessary to choose more suitable protective ligands to stabilize the transition metal core. In addition, synthesis can also be considered in an anhydrous and oxygen-free environment in a glove box. The large-scale preparation of cluster-based catalysts also needs to be given attention. Currently, chemical synthesis methods are relatively mature, and there are many types of clusters that can be prepared by this method, and high-purity and high-yield products can be obtained through precise control over chemical reaction conditions. However, the synthesis of cluster-based catalysts is still in the laboratory stage, and there are only a few



reports in the literature where the yield of one-time synthesis reaches the gram level.<sup>188–191</sup> There is still a long way to go to achieve industrial-scale preparation. Furthermore, for the recycling and recovery of clusters after catalytic reaction, one strategy with the most potential and promise is the construction of cluster-based composites. Due to the small size of the clusters, a support is required to load them, while avoiding aggregation or mass loss after the reaction. Porous materials are good candidates due to their abundant and adjustable pores and channels. If the surface of the material could be modified with various functional groups, it would be even better because it could solidly connect with clusters, and various types of surface groups may also bring about unexpected improvements in catalytic performance.

(3) For bimetallic NCs, and even for polymetallic NCs that may be used in the future, the enhancement in their catalytic performance is mainly attributed to the synergistic effect between metal atoms, but this statement is very general. Specifically, it is not particularly clear how the components affect each other or regulate each other, and how they play a synergistic role. Do the different metal atoms regulate each other's electronic structure, jointly affect the adsorption, activation and desorption behaviour of reaction molecules/intermediates/product molecules, and then realize synergistic catalysis? or is it tandem/cascade catalysis? for example, in CO<sub>2</sub>RR, in an Au–Cu alloy, the Au site usually plays the role of converting CO<sub>2</sub> into CO, and then CO reduction and coupling continue to occur at the Cu site, achieving efficient tandem/cascade catalysis.<sup>192</sup> This is a scientific question worthy of detailed discussion and careful investigation.

(4) An NC is a complex system involving an inner core of metal atoms and outer organic ligands, each of which plays a role in catalysis. In some catalytic cases, it has been found that it is not only the surface atoms that participate in the catalytic reaction; even the metal atoms at the center of the metal core also contribute to catalysis.<sup>153,167</sup> Additionally, in cases of the Au–Cd NCs catalysis of CO<sub>2</sub>RR, the real catalytically active center (the exposed Au site with –SR detachment, or the exposed S site with –R removal) has been investigated in detail.<sup>149,150</sup> All these inspire us to make more careful explorations in the future to determine the real active sites. In addition, for an expansion of types of energy catalysis, especially those involving multiple reactants and

steps, it will be meaningful and useful to clarify the real role each component plays in catalysis to guide catalyst design in the future.

(5) Although most current energy catalytic reactions are still laboratory-level, the future will certainly tend toward industrialization, and there are already some reports about HER, ORR, CO<sub>2</sub>RR, *etc.* at industrial current density at this stage.<sup>193–195</sup> As mentioned above, using NCs alone still faces the problem of easy aggregation and declining activity. Therefore, in industrial catalysis, functional supports are needed to load NCs to strengthen their stability and increase service lifetime. Therefore, it is necessary to clarify the interface and interaction between NCs and supports, so as to purposefully select appropriate supports and form supported NC-based catalysts with high activity for target reactions.

Overall, atomically precise bimetallic NCs have unique advantages in energy-related catalysis not only reflecting their extraordinary activity but also providing the opportunity to build structure–activity correlation; therefore, it deserves much more effort for further in-depth exploration and wide application, and the insights and general rules obtained from it that can be extended to other alloy materials and more types of catalytic reaction in the future.

## Data availability

All data in this perspective were cited from other references.

## Author contributions

Y. X. Du and M. Z. Zhu conceived the topic and structure of the article. Y. Fang and P. Wang conducted the literature research and designed the figures and tables. All authors were responsible for reviewing, editing and developing the perspective.

## Conflicts of interest

The authors have no competing interests to declare.

## Appendix

Table 1 Summary of representative Au-based bimetallic NCs

| Series NC <sub>s</sub> name               | NC <sub>s</sub> formula                                                                             | Synthesis method             | Structural characteristic |               |                       | Reference |
|-------------------------------------------|-----------------------------------------------------------------------------------------------------|------------------------------|---------------------------|---------------|-----------------------|-----------|
|                                           |                                                                                                     |                              | Doping type               | Doping number | Doping position       |           |
| M <sub>1</sub> Au <sub>3</sub> series NCs | [(Audppy) <sub>3</sub> AgO](BF <sub>4</sub> ) <sub>2</sub>                                          | Metal-exchange strategy      | Ag                        | 1             | Kernel surface doping | 196       |
| M <sub>2</sub> Au <sub>4</sub> series NCs | Au <sub>4</sub> Ni <sub>2</sub> (PPh <sub>2</sub> ) <sub>2</sub> S <sub>2</sub> (PCP) <sub>2</sub>  | Direct co-reduction strategy | Ni                        | 2             | Kernel surface doping | 197       |
|                                           | Au <sub>4</sub> Pd <sub>2</sub> (SR) <sub>8</sub> , SR = SC <sub>2</sub> H <sub>4</sub> Ph          | Direct co-reduction strategy | Pd                        | 2             | Kernel surface doping | 105       |
|                                           | Pt <sub>2</sub> Au <sub>4</sub> L <sub>8</sub> , L = C <sub>21</sub> H <sub>28</sub> O <sub>2</sub> | Direct co-reduction strategy | Pt                        | 2             | Kernel surface doping | 198       |



Table 1 (Contd.)

| Series NC <sub>s</sub> name               | NC <sub>s</sub> formula                                                                                                                                                             | Synthesis method               | Structural characteristic |               |                                     | Reference |
|-------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------|---------------------------|---------------|-------------------------------------|-----------|
|                                           |                                                                                                                                                                                     |                                | Doping type               | Doping number | Doping position                     |           |
| M <sub>4</sub> Au <sub>4</sub> series NCs | [Au <sub>4</sub> Cu <sub>4</sub> (π-CH≡Cp-C <sub>6</sub> H <sub>4</sub> R)],<br>R = H, Cl, CH <sub>3</sub>                                                                          | Direct co-reduction strategy   | Cu                        | 4             | Kernel surface doping               | 199       |
|                                           | Au <sub>4</sub> Cd <sub>4</sub> (2, 4-DMBT) <sub>12</sub>                                                                                                                           | Cation-assisted strategy       | Cd                        | 4             | Kernel surface doping               | 200       |
|                                           | [Au <sub>4</sub> Cu <sub>4</sub> (DPPM) <sub>2</sub> (S-Adm) <sub>5</sub> ] <sup>+</sup> Br <sup>−</sup>                                                                            | Direct co-reduction strategy   | Cu                        | 4             | Kernel surface doping               | 201       |
| M <sub>2</sub> Au <sub>6</sub> series NCs | [Au <sub>6</sub> Ag <sub>2</sub> (C)(L <sub>2</sub> ) <sub>6</sub> ](BF <sub>4</sub> ) <sub>4</sub> , L <sub>2</sub> =<br>2-(diphenylphosphino)-5-<br>pyridinecarboxaldehyde        | Direct co-reduction strategy   | Ag                        | 2             | Kernel surface doping               | 202       |
|                                           | [Au <sub>6</sub> Ag <sub>2</sub> C(dppy) <sub>6</sub> ](BF <sub>4</sub> ) <sub>4</sub>                                                                                              | Direct co-reduction strategy   | Ag                        | 2             | Kernel surface doping               | 203       |
| M <sub>6</sub> Au <sub>2</sub> series NCs | Au <sub>2</sub> Cu <sub>6</sub> (PPh <sub>2</sub> Py) <sub>2</sub> (S-Adm) <sub>6</sub> ,                                                                                           | Direct co-reduction strategy   | Cu                        | 6             | Kernel surface doping               | 204       |
|                                           | Au <sub>2</sub> Cu <sub>6</sub> (PPh <sub>2</sub> Py) <sub>2</sub> (TBM) <sub>6</sub>                                                                                               | Direct co-reduction strategy   | Cu                        | 6             | Kernel surface doping               | 205       |
|                                           | Au <sub>2</sub> Cu <sub>6</sub> (S-Adm) <sub>6</sub> [P(Ph-OMe) <sub>3</sub> ] <sub>2</sub> ,                                                                                       | Direct co-reduction strategy   | Cu                        | 6             | Kernel surface doping               | 205       |
| (M-Au) <sub>9</sub> series NCs            | Au <sub>2</sub> Cu <sub>6</sub> (S-Adm) <sub>6</sub> (PPh <sub>3</sub> ) <sub>2</sub> ,                                                                                             | Direct co-reduction strategy   | Cu                        | 6             | Kernel surface doping               | 205       |
|                                           | Au <sub>2</sub> Cu <sub>6</sub> (S-Adm) <sub>6</sub> [P(Ph-F) <sub>3</sub> ] <sub>2</sub>                                                                                           | Direct co-reduction strategy   | Cu                        | 6             | Kernel surface doping               | 205       |
| (M-Au) <sub>9</sub> series NCs            | [PdAu <sub>8</sub> (PPh <sub>3</sub> ) <sub>8</sub> ] <sup>2+</sup>                                                                                                                 | Direct co-reduction strategy   | Pd                        | 1             | Center doping                       | 206       |
|                                           | Au <sub>4</sub> Ag <sub>5</sub> (dppm) <sub>2</sub> (S-Adm) <sub>6</sub> -(BPh <sub>4</sub> )                                                                                       | Direct co-reduction strategy   | Ag                        | 5             | Kernel surface doping               | 207       |
| (M-Au) <sub>10</sub> series NCs           | Au <sub>4</sub> Pd <sub>6</sub> (TBBT) <sub>12</sub>                                                                                                                                | Direct co-reduction strategy   | Pd                        | 6             | Kernel surface doping               | 152       |
|                                           | [PdAu <sub>9</sub> H(PPh <sub>3</sub> ) <sub>8</sub> Cl] <sup>+</sup>                                                                                                               | Direct co-reduction strategy   | Pd                        | 1             | Center doping                       | 208       |
| (M-Au) <sub>12</sub> series NCs           | [Au <sub>10</sub> Ag <sub>2</sub> (2-py-C=                                                                                                                                          | Direct co-reduction strategy   | Ag                        | 2             | Kernel surface doping               | 209       |
|                                           | C) <sub>3</sub> (dppy) <sub>6</sub> ](BF <sub>4</sub> ) <sub>5</sub>                                                                                                                | Direct co-reduction strategy   | Ag                        | 2             | Kernel surface doping               | 209       |
|                                           | [Au <sub>11</sub> Cu <sub>1</sub> (PPh <sub>3</sub> ) <sub>7</sub> (SPy) <sub>3</sub> ] <sup>+</sup>                                                                                | Direct co-reduction strategy   | Cu                        | 1             | Kernel surface doping               | 210       |
| (M-Au) <sub>12</sub> series NCs           | Au <sub>6</sub> Cu <sub>6</sub> MBT <sub>12</sub> , Au <sub>6</sub> Cu <sub>6</sub> PET <sub>12</sub>                                                                               | Metal-exchange strategy        | Cu                        | 6             | Kernel surface doping               | 211       |
|                                           | AuCu <sub>11</sub> [S <sub>2</sub> P(OiPr) <sub>2</sub> ] <sub>6</sub> (C≡CPh) <sub>3</sub> Cl                                                                                      | Intercluster reaction strategy | Cu                        | 11            | Kernel surface doping               | 212       |
| (M-Au) <sub>13</sub> series NCs           | [AuCu <sub>12</sub> (SR) <sub>6</sub> (C≡CPh) <sub>4</sub> ] <sup>+</sup> ,<br>SR = S <sub>2</sub> P(C <sub>2</sub> H <sub>4</sub> Ph) <sub>2</sub>                                 | Direct co-reduction strategy   | Cu                        | 12            | Kernel doping                       | 213       |
| (M-Au) <sub>15</sub> series NCs           | [Au <sub>7</sub> Ag <sub>8</sub> ( <sup>t</sup> BuC≡C) <sub>12</sub> ] <sup>+</sup>                                                                                                 | Direct co-reduction strategy   | Ag                        | 8             | Kernel surface doping               | 214       |
| (M-Au) <sub>16</sub> series NCs           | [Au <sub>7</sub> Ag <sub>9</sub> (dppf) <sub>3</sub> (CF <sub>3</sub> CO <sub>2</sub> ) <sub>7</sub> BF <sub>4</sub> ] <sub>n</sub>                                                 | Direct co-reduction strategy   | Ag                        | 9             | Kernel surface doping, Motif doping | 215       |
| Au <sub>13</sub> Cux series NCs           | [Au <sub>13</sub> Cu <sub>4</sub> (PPh <sub>2</sub> Py) <sub>4</sub> (SC <sub>6</sub> H <sub>4</sub> - <i>tert</i> -<br>C <sub>4</sub> H <sub>9</sub> ) <sub>8</sub> ] <sup>+</sup> | Intercluster reaction strategy | Cu                        | 4             | Motif doping                        | 216       |
|                                           | Au <sub>13</sub> Cu <sub>4</sub> (PPh <sub>2</sub> Py) <sub>3</sub> (SePh) <sub>9</sub>                                                                                             | Direct co-reduction strategy   | Cu                        | 4             | Motif doping                        | 217       |
|                                           | [Au <sub>13</sub> Cu <sub>2</sub> (DPPP) <sub>3</sub> (SPy) <sub>6</sub> ] <sup>+</sup>                                                                                             | Direct co-reduction strategy   | Cu                        | 2             | Motif doping                        | 218       |
|                                           | [Au <sub>13</sub> Cu <sub>2</sub> (PPh <sub>3</sub> ) <sub>6</sub> (SPy) <sub>6</sub> ] <sup>+</sup>                                                                                | Intercluster reaction strategy | Cu                        | 2             | Motif doping                        | 216       |
| (M-Au) <sub>17</sub> series NCs           | Au <sub>16</sub> Ag <sub>1</sub> (S-Adm) <sub>13</sub>                                                                                                                              | Direct co-reduction strategy   | Ag                        | 1             | Center doping                       | 219       |
|                                           | Au <sub>4</sub> Ag <sub>13</sub> (DPPM) <sub>3</sub> (SR) <sub>9</sub> , SR =<br>C <sub>8</sub> H <sub>10</sub> S                                                                   | Direct co-reduction strategy   | Ag                        | 13            | Kernel surface doping, Motif doping | 220       |
|                                           | Au <sub>x</sub> Ag <sub>17-x</sub> N <sub>3</sub> (TBBT) <sub>12</sub> , N =<br>a counter cation, x = 0, 1                                                                          | Direct co-reduction strategy   | Ag                        | 16, 17        | Kernel doping                       | 221       |
| (M-Au) <sub>18</sub> series NCs           | Au <sub>15</sub> Ag <sub>3</sub> (SR) <sub>14</sub> SR=SC <sub>6</sub> H <sub>11</sub>                                                                                              | Intercluster reaction strategy | Ag                        | 3             | Kernel surface doping               | 222       |
| (M-Au) <sub>19</sub> series NCs           | [Ag <sub>x</sub> Au <sub>18-x</sub> (Dppm) <sub>6</sub> Br <sub>4</sub> ](BPh <sub>4</sub> ) <sub>2</sub><br>(x = 1, 2)                                                             | Metal-exchange strategy        | Ag                        | 1, 2          | Kernel surface doping               | 223       |
|                                           | [Au <sub>7</sub> Cu <sub>12</sub> (dppy) <sub>6</sub> (TBBT) <sub>6</sub> Br <sub>4</sub> ] <sup>3+</sup>                                                                           | Direct co-reduction strategy   | Cu                        | 12            | Kernel surface doping               | 224       |



Table 1 (Contd.)

| Series NC <sub>s</sub> name                | NC <sub>s</sub> formula                                                                                                                                                                                                        | Synthesis method               | Structural characteristic |               |                                     | Reference |
|--------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------|---------------------------|---------------|-------------------------------------|-----------|
|                                            |                                                                                                                                                                                                                                |                                | Doping type               | Doping number | Doping position                     |           |
| (M-Au) <sub>21</sub> series NCs            | [Au <sub>19</sub> Cd <sub>2</sub> (SR) <sub>16</sub> ] <sup>−</sup> , SR = C <sub>6</sub> H <sub>11</sub> S                                                                                                                    | Direct co-reduction strategy   | Cd                        | 2             | Motif doping                        | 225       |
|                                            | [Au <sub>9</sub> Ag <sub>12</sub> (SR) <sub>4</sub> (dppm) <sub>6</sub> X <sub>6</sub> ] <sup>3+</sup> , SR = S-Adm/S- <sup>t</sup> Bu, X = Cl/Br                                                                              | Direct co-reduction strategy   | Ag                        | 12            | Kernel surface doping, Motif doping | 226       |
|                                            | Au <sub>20</sub> Ag <sub>1</sub> (S-Adm) <sub>15</sub>                                                                                                                                                                         | Direct co-reduction strategy   | Ag                        | 1             | All                                 | 227       |
|                                            | Au <sub>20</sub> Ag <sub>1</sub> (SR) <sub>15</sub> , Au <sub>21−x</sub> Ag <sub>x</sub> (SR) <sub>15</sub> (x = 4–8), Au <sub>21−x</sub> Cu <sub>x</sub> (SR) <sub>15</sub> (x = 0–5), SR = SC <sub>4</sub> H <sub>10</sub> O | Direct co-reduction strategy   | Ag, Cu                    | 0–8           | Kernel surface doping/Motif doping  | 228       |
| (M-Au) <sub>23</sub> series NCs            | Au <sub>23−x</sub> Cu <sub>x</sub> (SR) <sub>16</sub> , SR = SC <sub>6</sub> H <sub>12</sub> O                                                                                                                                 | Direct co-reduction strategy   | Cd                        | 2             | Motif doping                        | 225       |
| M <sub>1</sub> Au <sub>24</sub> series NCs | [Au <sub>24</sub> Pd(PPh <sub>3</sub> ) <sub>10</sub> (SR) <sub>5</sub> Cl <sub>2</sub> ], SR = SC <sub>2</sub> H <sub>4</sub> Ph                                                                                              | Direct co-reduction strategy   | Pd                        | 1             | Center doping                       | 229       |
|                                            | Au <sub>24</sub> M <sub>1</sub> (SR) <sub>18</sub> , SR = SC <sub>2</sub> Ph/PET                                                                                                                                               | Direct co-reduction strategy   | Hg, Cd, Pt, Pd            | 1             | Kernel surface doping/Center doping | 230–232   |
|                                            | [Ag <sub>24</sub> Au(SR) <sub>18</sub> ] <sup>−</sup> PPh <sub>4</sub> <sup>+</sup> , SR = SPhMe <sub>2</sub>                                                                                                                  | Direct co-reduction strategy   | Ag                        | 24            | Kernel surface doping, Motif doping | 233       |
| M <sub>24</sub> Au <sub>1</sub> series NCs | [Au <sub>1</sub> Ag <sub>24</sub> (Dppm) <sub>3</sub> (SR) <sub>17</sub> ] <sup>2+</sup> , SR = C <sub>6</sub> H <sub>12</sub> S                                                                                               | Direct co-reduction strategy   | Ag                        | 24            | Kernel surface doping, Motif doping | 234       |
|                                            | AuCu <sub>24</sub> H <sub>22</sub> (PPh <sub>3</sub> ) <sub>12</sub> , AuCu <sub>24</sub> H <sub>22</sub> ( <i>p</i> -FPh) <sub>3</sub> P) <sub>12</sub>                                                                       | Direct co-reduction strategy   | Cu                        | 24            | Kernel surface doping               | 189       |
|                                            | [Cu <sub>13</sub> Au <sub>12</sub> (PPh <sub>3</sub> ) <sub>10</sub> (SR) <sub>5</sub> Cl <sub>2</sub> ] <sup>2+</sup> , SR = PhC <sub>2</sub> H <sub>4</sub> S                                                                | Direct co-reduction strategy   | Cu                        | 13            | Kernel surface doping               | 235       |
|                                            | Au <sub>22</sub> Ir <sub>3</sub> (PET) <sub>18</sub>                                                                                                                                                                           | Intercluster reaction strategy | Ir                        | 3             | Kernel doping                       | 236       |
| (M-Au) <sub>25</sub> series NCs            | Pd <sub>2</sub> Au <sub>23</sub> (PPh <sub>3</sub> ) <sub>10</sub> Br <sub>7</sub>                                                                                                                                             | Direct co-reduction strategy   | Pd                        | 2             | Center doping                       | 237       |
|                                            | [Au <sub>4</sub> Ag <sub>23</sub> (C≡C <sup>t</sup> Bu) <sub>10</sub> (dppf) <sub>4</sub> Cl <sub>7</sub> ](PF <sub>6</sub> ) <sub>2</sub>                                                                                     | Direct co-reduction strategy   | Ag                        | 23            | Kernel surface doping, Motif doping | 238       |
|                                            | Au <sub>25</sub> Ag <sub>2</sub> (SR) <sub>18</sub> , SR = SC <sub>2</sub> H <sub>4</sub> Ph                                                                                                                                   | Direct co-reduction strategy   | Ag                        | 2             | Motif doping                        | 239       |
| (M-Au) <sub>29</sub> series NCs            | Ag <sub>29−x</sub> Au <sub>x</sub> (SR) <sub>12</sub> (pph) <sub>4</sub> , SR = S <sub>2</sub> C <sub>6</sub> H <sub>6</sub> (x = 1–5)                                                                                         | Direct co-reduction strategy   | Ag                        | 24–28         | Kernel surface doping, Motif doping | 240       |
|                                            | [Au <sub>5</sub> Ag <sub>24</sub> (C≡CC <sub>6</sub> H <sub>4</sub> <sup>−</sup> <i>p</i> - <sup>t</sup> Bu) <sub>16</sub> (dppf) <sub>4</sub> Cl <sub>4</sub> ](PF <sub>6</sub> ) <sub>3</sub>                                | Direct co-reduction strategy   | Ag                        | 24            | Kernel surface doping, Motif doping | 238       |
|                                            | Au <sub>24</sub> Cu <sub>6</sub> (SPh <sup>t</sup> Bu) <sub>22</sub>                                                                                                                                                           | Intercluster reaction strategy | Cu                        | 6             | Motif doping                        | 241       |
| (M-Au) <sub>30</sub> series NCs            |                                                                                                                                                                                                                                |                                |                           |               |                                     |           |
|                                            |                                                                                                                                                                                                                                |                                |                           |               |                                     |           |
| (M-Au) <sub>34</sub> series NCs            | [Ag <sub>33</sub> AuS <sub>2</sub> (SR) <sub>18</sub> (CF <sub>3</sub> COO) <sub>9</sub> (DMF) <sub>6</sub> ]                                                                                                                  | Direct co-reduction strategy   | Ag                        | 33            | Kernel surface doping, Motif doping | 242       |
|                                            | [AuAg <sub>33</sub> (BTCA) <sub>3</sub> (C≡Cbu <sup>t</sup> ) <sub>9</sub> <sup>−</sup> (tfa) <sub>4</sub> (CH <sub>3</sub> OH) <sub>3</sub> ]SbF <sub>6</sub>                                                                 | Direct co-reduction strategy   | Ag                        | 33            | Kernel surface doping, Motif doping | 243       |
| (M-Au) <sub>38</sub> series NCs            | Au <sub>38−x</sub> Cu <sub>x</sub> (2,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> S) <sub>24</sub> (x = 0–6)                                                                                               | Intercluster reaction strategy | Cu                        | 0–6           | Motif doping                        | 244       |
| M <sub>2</sub> Au <sub>36</sub> series NCs | M <sub>2</sub> Au <sub>36</sub> (SR) <sub>24</sub> , SR = SC <sub>2</sub> H <sub>4</sub> Ph/SC <sub>6</sub> H <sub>13</sub>                                                                                                    | Direct co-reduction strategy   | Pd, Pt                    | 2             | Center doping                       | 245–248   |
| (M-Au) <sub>40</sub> series NCs            | AuAg <sub>39</sub> (TBBM) <sub>21</sub> (CH <sub>3</sub> COO) <sub>11</sub>                                                                                                                                                    | Intercluster reaction strategy | Ag                        | 39            | Kernel surface doping, Motif doping | 249       |
| (M-Au) <sub>41</sub> series NCs            | [Au <sub>3</sub> Ag <sub>38</sub> (SR) <sub>24</sub> X <sub>5</sub> ] <sup>2−</sup> (X = Cl or Br), SR = SCH <sub>2</sub> Ph                                                                                                   | Direct co-reduction strategy   | Ag                        | 38            | Kernel surface doping, Motif doping | 250       |
| (M-Au) <sub>42</sub> series NCs            | Au <sub>38</sub> Cd <sub>4</sub> (DMBT) <sub>30</sub>                                                                                                                                                                          | Metal-exchange strategy        | Cd                        | 4             | Kernel surface doping               | 251       |
| (M-Au) <sub>44</sub> series NCs            | Au <sub>12</sub> @S <sub>8</sub> @Ag <sub>32</sub> (PS) <sub>24</sub> ] <sup>2+</sup>                                                                                                                                          | Direct co-reduction strategy   | Ag                        | 32            | Kernel surface doping               | 252       |
|                                            | [Au <sub>12+x</sub> Cu <sub>32</sub> (SR) <sub>30+x</sub> ] <sup>4+</sup> , SR = SPhCF <sub>3</sub>                                                                                                                            | Direct co-reduction strategy   | Cu                        | 32            | Motif doping                        | 253       |
|                                            | Au <sub>24</sub> Ag <sub>20</sub> (2-SPy) <sub>4</sub> (PhC≡C) <sub>20</sub> Cl <sub>2</sub>                                                                                                                                   | Direct co-reduction strategy   | Ag                        | 6             | Kernel surface doping               | 254       |
|                                            | Au <sub>2</sub> Ag <sub>42</sub> (S-Adm) <sub>27</sub> (BPh <sub>4</sub> )                                                                                                                                                     | Direct co-reduction strategy   | Ag                        | 42            | Kernel surface doping, Motif doping | 255       |



Table 1 (Contd.)

| Series NC <sub>s</sub> name                 | NC <sub>s</sub> formula                                                                                                                                                                                    | Synthesis method             | Structural characteristic |               |                                     | Reference |
|---------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|---------------------------|---------------|-------------------------------------|-----------|
|                                             |                                                                                                                                                                                                            |                              | Doping type               | Doping number | Doping position                     |           |
| M <sub>32</sub> Au <sub>12</sub> series NCs | [Au <sub>12</sub> Ag <sub>32</sub> (FTP) <sub>30</sub> ] <sup>4-</sup>                                                                                                                                     | Metal-exchange strategy      | Ag                        | 32            | Kernel surface doping, Motif doping | 256       |
| (M-Au) <sub>45</sub> series NCs             | Au <sub>12</sub> Ag <sub>32</sub> (SR) <sub>30</sub> SR = SPhF/SPhF <sub>2</sub> /SPhCF <sub>3</sub>                                                                                                       | Direct co-reduction strategy | Ag                        | 32            | Kernel surface doping, Motif doping | 190       |
| (M-Au) <sub>45</sub> series NCs             | Au <sub>9</sub> Ag <sub>36</sub> (SR) <sub>27</sub> (PPh <sub>3</sub> ) <sub>6</sub> , SR = SPhCl <sub>2</sub>                                                                                             | Direct co-reduction strategy | Ag                        | 36            | Kernel surface doping, Motif doping | 257       |
| (M-Au) <sub>48</sub> series NCs             | Au <sub>26</sub> Ag <sub>22</sub> (TBBT) <sub>30</sub>                                                                                                                                                     | Direct co-reduction strategy | Ag                        | 22            | Kernel surface doping, Motif doping | 258       |
| (M-Au) <sub>49</sub> series NCs             | [Au <sub>19</sub> Cu <sub>30</sub> (C=CR) <sub>22</sub> (Ph <sub>3</sub> P) <sub>6</sub> Cl <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub> , RC=C=H <sub>3</sub> C <sub>4</sub> S <sub>3</sub> -C≡CH/PhC≡CH | Direct co-reduction strategy | Cu                        | 30            | Kernel surface doping               | 259       |
| (M-Au) <sub>50</sub> series NCs             | [Au <sub>2</sub> Ag <sub>48</sub> (S <sup>t</sup> Bu) <sub>20</sub> (Dppm) <sub>6</sub> Br <sub>11</sub> ]                                                                                                 | Direct co-reduction strategy | Ag                        | 48            | Kernel surface doping, Motif doping | 255       |
| (M-Au) <sub>62</sub> series NCs             | Au <sub>34</sub> Ag <sub>28</sub> (PhC≡C) <sub>34</sub>                                                                                                                                                    | Direct co-reduction strategy | Ag                        | 28            | Kernel surface doping               | 260       |
| (M-Au) <sub>70</sub> series NCs             | [Ag <sub>46</sub> Au <sub>24</sub> (S <sup>t</sup> Bu) <sub>32</sub> ](BPh <sub>4</sub> ) <sub>2</sub>                                                                                                     | Direct co-reduction strategy | Ag                        | 46            | Kernel doping                       | 261       |
| (M-Au) <sub>110</sub> series NCs            | [Au <sub>80</sub> Ag <sub>30</sub> (C≡CPh) <sub>42</sub> Cl <sub>9</sub> ]Cl                                                                                                                               | Direct co-reduction strategy | Ag                        | 30            | Kernel surface doping               | 262       |
| (M-Au) <sub>124</sub> series NCs            | Au <sub>57</sub> Ag <sub>53</sub> (C≡CPh) <sub>40</sub> Br <sub>12</sub>                                                                                                                                   | Direct co-reduction strategy | Ag                        | 53            | All                                 | 263       |
| (M-Au) <sub>124</sub> series NCs            | [Au <sub>52</sub> Cu <sub>72</sub> ( <i>p</i> -MBT) <sub>55</sub> ] <sup>+</sup> Cl <sup>-</sup> , <i>p</i> -MBT = SPh- <i>p</i> -CH <sub>3</sub>                                                          | Direct co-reduction strategy | Cu                        | 72            | Kernel doping                       | 264       |
| (M-Au) <sub>130</sub> series NCs            | Au <sub>130-x</sub> Ag <sub>x</sub> (TBBT) <sub>55</sub>                                                                                                                                                   | Direct co-reduction strategy | Ag                        | 98            | All                                 | 265       |

| Ligand abbreviations | Formula                                          |
|----------------------|--------------------------------------------------|
| dppy                 | C <sub>17</sub> H <sub>14</sub> NP               |
| pph                  | C <sub>18</sub> H <sub>15</sub> P                |
| dppm                 | C <sub>25</sub> H <sub>22</sub> P <sub>2</sub>   |
| S-Adm                | C <sub>10</sub> H <sub>16</sub> S                |
| 2,4-DMBT             | C <sub>8</sub> H <sub>10</sub> S                 |
| TBM                  | C <sub>22</sub> H <sub>18</sub>                  |
| py                   | C <sub>5</sub> H <sub>5</sub> N                  |
| TBBT                 | C <sub>10</sub> H <sub>14</sub> S                |
| S- <i>t</i> Bu       | C <sub>4</sub> H <sub>10</sub> S                 |
| dppf                 | C <sub>34</sub> H <sub>28</sub> FeP <sub>2</sub> |
| PET                  | C <sub>8</sub> H <sub>10</sub> S                 |
| CHM                  | C <sub>6</sub> H <sub>12</sub> S                 |
| SSR                  | C <sub>6</sub> H <sub>6</sub> S <sub>2</sub>     |
| BTCA                 | C <sub>8</sub> H <sub>10</sub> O <sub>8</sub>    |

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