



Controlled synthesis and electrocatalytic applications of atomically precise AuAg nanoclusters: a review

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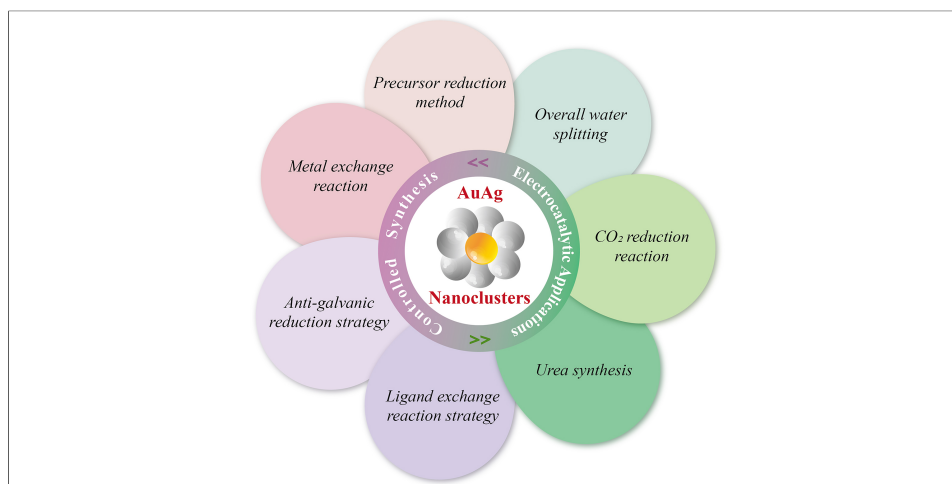
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Abstract

Bimetallic nanoclusters possess tunable physicochemical properties, improved performance, and enhanced stability for versatile applications. Among them, atomically precise AuAg nanoclusters have an important position in the series of bimetallic nanoclusters thanks to the easy preparation and crystallization, unique electronic structure, and robust stability. In this review, the general introduction of bimetallic nanoclusters and the uniqueness of AuAg nanoclusters are first explained. Then, the main strategies for the controlled synthesis of AuAg nanoclusters are summarized, with examples to illustrate the workflow and potential limitations. Following this, atomically precise AuAg nanoclusters for electrocatalytic applications, including overall water splitting, CO₂ reduction reaction, and urea electrosynthesis, are discussed. In this major part, carefully chosen examples are analyzed to reveal the atomic-level structure-performance relationship and to understand the fundamental reaction mechanism. Finally, the current challenges and future outlooks in this field are discussed critically.



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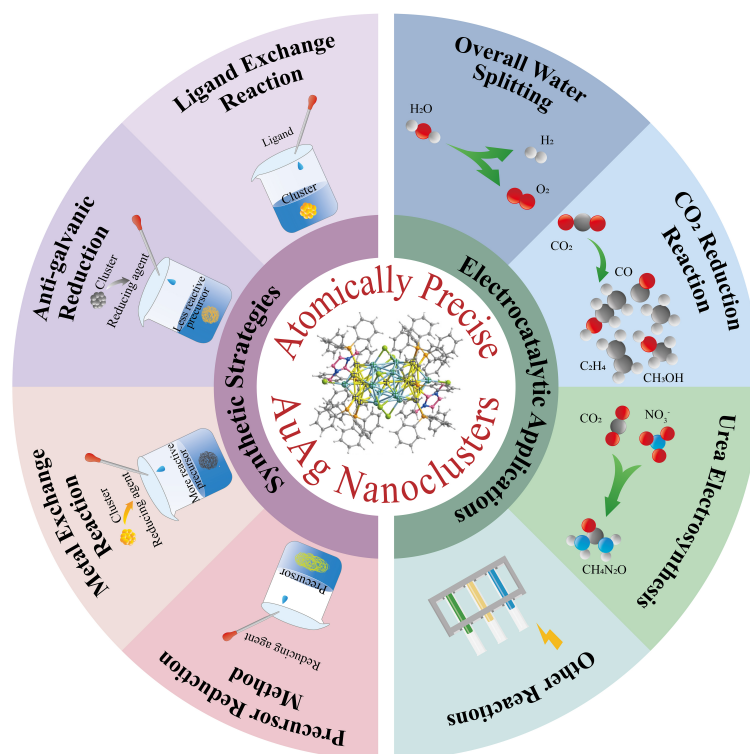
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INTRODUCTION

In the past decade, atomically precise noble metal (e.g., Au, Ag, Cu, and their alloys) nanoclusters have been continuously attracting a great deal of research attention, as they have found versatile applications in various fields such as catalysis^[1-3], sensing^[4,5], optoelectronic^[6-8], imaging^[9-11], and bio-labeling^[12,13]. These nanoclusters typically have ultrasmall sizes, with diameters less than 3 nm, and this ultrasmall size endows them with strong quantum confinement, resulting in physicochemical properties significantly different from those of larger nanoparticles (NPs) or nanocrystals^[14,15]. Note that, by manipulating the reaction kinetics, these metal nanoclusters can be synthetically obtained with high monodispersity of molecular purity^[16,17], with the total structure being resolved by single crystal X-ray diffraction (SC-XRD) once a high-quality single crystal is successfully acquired^[18-20]. The structure-resolved metal nanoclusters can offer unique advantages that are not available from polydisperse metal NPs or nanocrystals. In particular, atomically precise metal nanoclusters have uniform size, composition, charge, morphology, and an identical chemical coordination environment (including geometric configuration, metal coordination number, and metal-metal/metal ligand bond angles/lengths). These structural features are favorable for establishing the structure-performance relationship at the atomic level for various potential applications^[21-23]. Compared to single-metal nanoclusters, introducing another metal to form bimetallic alloy nanoclusters can result in altered electronic structures and improved physicochemical properties, such as absorption, luminescence, and intriguing electrochemical behaviors^[24-29]. Specifically, in the catalytic regime, bimetallic alloy nanoclusters exhibit inter-atomic synergistic effects; that is, the altered geometric configuration can generate new catalytic active sites on the alloy clusters, and the tuned electronic structure can enhance both catalytic activity and stability^[30,31]. Such a synergistic effect is realized through orbital hybridization and charge redistribution between heterometallic atoms^[32,33]. This effect not only optimizes the adsorption strength and configuration of the reaction substrates at active sites but also reduces the key reaction energy barriers through dual-site cooperative activation mechanisms, thereby achieving performance that surpasses that of homometallic nanocluster counterparts.

To date, various metals - including Au^[34,35], Cu^[36,37], Pd^[38,39], Pt^[40,41], Cd^[42], Rh^[43], *etc.* - have been successfully incorporated into Ag nanoclusters, constructing well-defined Ag-based bimetallic systems. Of all types of Ag-based bimetallic alloy nanoclusters, AuAg nanoclusters have probably gained the most intense research attention, mainly because Au and Ag share an s'd¹⁰ valence electron configuration and have similar atomic radii, resulting in minimal lattice strain during alloy formation^[44]. Meanwhile, the slight difference in electronegativity drives significant interfacial electronic perturbation, which substantially affects the properties of the as-formed AuAg nanoclusters^[45-49]. So far, atomically precise AuAg nanoclusters protected by thiolate ligand^[50,51], alkynyl ligand^[52,53], phosphine ligand^[54,55], halogen^[56], N-heterocyclic carbene (NHC)^[57,58], and other ligands have been well explored. In the past few years, several instructive reviews have been published on the controllable synthesis and electrocatalytic applications of coinage metal(alloy) nanoclusters^[26,29,51,59,60]. However, a comprehensive review on the most widely explored AuAg bimetallic nanoclusters is still missing. This review focuses on the controlled synthesis and electrocatalytic applications of atomically precise AuAg nanoclusters, featuring specific comparative insights into the synthetic strategies and distinctive analysis of the structure-performance relationships in electrocatalysis. In this review, the recent advances in the controlled synthesis of AuAg nanoclusters using various synthetic approaches are first summarized [Scheme 1]. Following that, the electrocatalytic applications - mainly including electrochemical overall water splitting (OWS), CO₂ reduction reaction (CO₂RR), and urea electrosynthesis - catalyzed by atomically precise AuAg nanocluster-based catalysts are discussed, with a focus on elucidating the structure-performance relationship of carefully selected examples [Scheme 1]. Finally, the current challenges and future perspective of this field are analyzed and envisioned.



Scheme 1. Controlled synthesis and electrocatalytic applications of atomically precise AuAg nanoclusters.

CONTROLLED SYNTHESIS OF ATOMICALLY PRECISE AuAg NANOCCLUSERS

Precursor reduction method

The precursor reduction method is quite simple and straightforward, and it is probably the most widely employed method for synthesizing metal nanoclusters including AuAg clusters. In this method, the metal-ligand precursor or complex is first formed through the reaction between the metal salts and the ligand. Followed by the addition of a reducing agent, AuAg nanoclusters were produced. To improve the monodispersity of the obtained nanoclusters, post-reaction treatments or purification steps are necessary in most cases.

One typical example using this method is the synthesis of $[\text{Au}_{34}\text{Ag}_{27}(\text{C}\equiv\text{CR})_{34}](\text{PPh}_4)$ (PPh_4 : tetraphenylphosphonium) cluster with a concentric four-shell structure^[61]. The $\text{Au}_{34}\text{Ag}_{27}$ nanocluster was synthesized by reducing a mixed solution of $\text{AuC}\equiv\text{CR}$ and $\text{AgC}\equiv\text{CR}$ with NaBH_4 in an ice bath. Note that the order of reactant addition can be critical for obtaining specific AuAg nanoclusters. For instance, during the synthesis of $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$ molecule, HAuCl_4 was first treated with PPh_3 (PPh_3 : triphenylphosphine) ligand to form some Au(I) complex, and then AgSbF_6 was added to form AuAg alloy complex^[62]. After filtration to remove the AgCl precipitate, NaBH_4 was added to reduce the filtrate. Once the mixture turned red, it indicated that the Au_8Ag_3 cluster had formed, which is isostructural to the $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$ nanocluster. Notably, if HAuCl_4 and AgSbF_6 were co-mixed with PPh_3 , they react immediately to form the AgCl precipitates; consequently, no AuAg cluster can be obtained. Similarly, the $[\text{Au}_{13}\text{Ag}_{12}(\text{PPh}_3)_{10}\text{Cl}_8]\text{SbF}_6$ nanocluster was fabricated using a nearly identical protocol^[54]. $\text{Au(I)PPh}_3\text{Cl}$ was first prepared and then reacted with AgSbF_6 in an ice bath for 30 min. The mixture was subsequently stirred in the dark for 24 h to yield the $\text{Au}_{13}\text{Ag}_{12}$ nanocluster, which comprises two Au_7Ag_6 icosahedra sharing a central gold atom. Interestingly, this procedure can produce two conformational $\text{Au}_{13}\text{Ag}_{12}$ cluster isomers with complete reversibility by controlling the reaction temperature^[54].

It is worth noting that the precursor reduction method often fails to achieve precise control over the composition and structure of target alloy clusters. This is primarily due to insufficient regulation of metal nucleation and growth kinetics, which in turn leads to poor selectivity and generally low yield^[63].

Metal exchange reaction

The metal exchange reaction usually employs pre-synthesized nanoclusters as the substrate to react with more reactive (or less noble) metal salts. Typically, the as-formed Ag nanocluster can react with Au(I) complex to yield AuAg nanoclusters^[24].

Bootharaju *et al.* fabricated the $\text{Ag}_{24}\text{Au}(\text{SPhMe}_2)_{18}$ (SPhMe_2 : 2,4-dimethylbenzenethiolate) nanoclusters using this method, where the $\text{Ag}_{25}(\text{SPhMe}_2)_{18}$ nanocluster reacts with AuClPPh_3 thanks to the electrochemical redox potential difference between Au(I) and Ag atoms in the Ag_{25} framework^[64]. Interestingly, Au substitution in the Ag_{25} core induces some structural distortion in its icosahedral framework^[64]. In another study conducted by Bootharaju *et al.*, adding AuPPh_3Cl to the $[\text{PdAg}_{24}(\text{SR})_{18}]^{2-}$ (SR: thiolate ligand) nanocluster system controllably generated the mono-gold-substituted $[\text{AuAg}_{24}(\text{SR})_{18}]^-$ nanocluster, where Au replaces Pd at the central position^[65]. The Au-to-Pd substitution can be visually observed by an orange-to-dark-green color transition^[65].

Remarkably, the metal exchange of the Au(I)-to-Ag(I) process can be precisely controlled and directly visualized by mass spectrometry. In 2017, Yao *et al.* documented a surface motif exchange (SME) reaction to selectively replace the surface motifs of $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ nanoclusters, leading to the formation of core-shell structured $[\text{Ag}_{32}@\text{Au}_{12}(\text{SR})_{30}]^{4-}$ nanoclusters^[66]. Such a process was analyzed in detail using mass spectrometry and tandem mass spectrometry. Theoretical calculations also disclosed that the Au@Ag core shell stabilizes the Ag_{20} shell, which can prevent the Au atoms from diffusing inwardly. Such a dedicated SME reaction opens a new door to the precise synthesis of AuAg nanoclusters with pre-designed alloying sites^[66].

Although the metal exchange reaction can achieve atom-level cluster-to-cluster structural transformation, most current examples are limited to single-atom exchanges or involve only a very small number of metal atoms^[64,67]. Customized nanocluster synthesis for regulating the number of doped metal atoms via the metal exchange reaction remains quite challenging. This is predominantly attributed to the inherently uncontrollable galvanic reduction process during the exchange reaction.

Anti-galvanic reduction strategy

Anti-galvanic reduction (AGR) refers to the reaction in which metal ions or complexes are reduced by less reactive (more noble) metal nanoclusters. AGR may seem to contradict the Galvanic theory, but such a reaction occurs on ultrasmall metal nanoclusters due to their quantum confinement effect.

In 2012, Wu first discovered this novel redox phenomenon of $[\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}]$ nanoclusters, which can react with AgNO_3 at a 5.2:1 weight ratio, yielding $[\text{Au}_{22}\text{Ag}_3\text{S}_{12}]^-$ and $[\text{Au}_{23}\text{Ag}_2\text{S}_{12}]^-$ as the dominant products^[68]. Following that, Yao *et al.* systematically studied this reaction, where two Ag atoms can be added onto $[\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}]$ to form $\text{Au}_{25}\text{Ag}_2(\text{SC}_2\text{H}_4\text{Ph})_{18}$ under well-controlled reaction conditions and precise reactant-substrate stoichiometry^[69]. The successful preparation of monodisperse, high-purity $\text{Au}_{25}\text{Ag}_2(\text{SC}_2\text{H}_4\text{Ph})_{18}$ validates the effectiveness of AGR for targeted metal doping.

Beyond simple metal replacement or surface metal addition, the introduction of foreign metal atoms may induce size and structural changes in parent metal nanoclusters, leading to the formation of new nanoclusters. One classic case is the synthesis of the $[\text{Au}_{13}\text{Ag}_{12}(\text{PPh}_3)_8(\text{BIm})_2\text{I}_8]\text{SbF}_6$ (BIm: 1,3-bimethylimidazole) nanocluster with a rod-like carbene structure reported recently by Zhang *et al.*^[70]. By

Table 1. Comparison of the four major nanocluster synthetic methods

Method	Advantages	Limitations	Structural precision	Scalability	Ref.
Precursor reduction method	Fast, simple operation	Non-uniform products, compromised purity	Low	High	[54,61-63]
Metal exchange reaction	Enabling atomic-level structural transformations between clusters; wide applicability	Hard to precisely control reaction rate and exchange extent	High	Medium	[24,64-67]
AGR	Realizing atomic-level incorporation of heterometal atoms while preserving core configuration, high monodispersity	Limited to specific reaction systems with stringent condition requirements	High	Low	[68,69,71,72]
Ligand exchange reaction	Achieving atomic-scale surface engineering and tailorable catalytic properties via functionalized ligands	Hard to precisely control the exchange extent	Medium	Medium	[73-78]

AGR: Anti-galvanic reduction.

reacting the pre-synthesized Au₉ nanoclusters with freshly prepared Ag-BMIm under vigorous stirring in the dark, the [Au₁₃Ag₁₂(PPh₃)₈(BMIm)₂I₈]SbF₆ nanocluster can be obtained within a few minutes.

It is worth noting that the unique physicochemical properties arising from the size and surface effects of metal nanoclusters enable AGR to proceed spontaneously^[23,24], but this reactivity does not apply to all types of noble metal nanoclusters. It is restricted to specific reaction systems and depends on the reaction conditions^[71,72]. Therefore, expanding the universality and applicability of AGR is promising for producing novel atomically precise AuAg and other alloy nanoclusters.

Ligand exchange reaction strategy

Ligand exchange is another effective strategy for fabricating atomically precise AuAg nanoclusters^[73]. It involves partial or complete replacement of the present ligands with incoming ligands on pre-synthesized AuAg nanoclusters. In addition, the extra ligand can initiate etching in the reaction system, leading to size transformation of the parent AuAg nanoclusters.

Au₁₆Ag₁(S-Adm)₁₃ (Adm: Adamantane) was synthesized using this method by Kang *et al.*^[74]. Firstly, a trace amount of Ag(I)(S-C₆H₁₁) was introduced into the Au₁₈(S-C₆H₁₁)₁₄ solution, yielding a mixture of Au₁₇Ag₁(S-C₆H₁₁)₁₄ and residual Au₁₈(S-C₆H₁₁)₁₄. Subsequently, the HS-Adm ligand was added to the mixture. After the reaction was completed, Au₁₆Ag₁(S-Adm)₁₃ was isolated by preparative thin-layer chromatography (PTLC), thanks to the distinct size and surface property differences between the newly generated nanoclusters and the parent nanoclusters^[74]. In another study, Hu *et al.* fabricated the [Au₈Ag₅₅(Dppp)₄(C₆H₁₁S)₃₄](BPh₄)₂ [dppp: 1,3-Bis(diphenylphosphino)propane, BPh₄: tetraphenylborate] nanocluster using this approach; however, a size-expansion process was observed^[75]. Specifically, Au₇Ag₈ nanoclusters were first prepared and dispersed in CH₂Cl₂, after which Dppp and C₆H₁₂SH were introduced into the reaction system. The mixture was stirred for ~12 h, and monodisperse Au₈Ag₅₅ nanoclusters were obtained after completion of the reaction^[75].

It should be noted that the ligand exchange reaction can facilitate atom-precise surface engineering of pre-formed alloy nanoclusters, allowing precise customization toward catalytic^[74,75], optical^[76], or biomedical applications^[77] through functionalized ligands. Nevertheless, during the reaction process, the cluster structure is prone to unintended alterations^[78], imposing fundamental constraints on those applications that require specific atomic structure or configurations.

Overall, the above four most widely employed synthetic methods possess different features. The comparison of their advantages, limitations, structural precision, and scalability is summarized in Table 1.

Other synthetic methods

There are other synthetic approaches that have shown great promise for the synthesis of atomically precise AuAg nanoclusters. For example, photochemical synthesis provides an accessible platform to tailor nanoclusters with specific sizes. In 2023, Wang *et al.* reported the synthesis of atomically precise $[\text{Ag}_{22}\text{Au}_3(4\text{-tBuPhC}\equiv\text{C})_{20}(\text{Dpppe})_3](\text{SbF}_6)_3$ [dpppe: 1, 5-bis(diphenylphosphino)pentane] nanoclusters via this method^[79]. In a typical trial, AgSbF_6 was dissolved in ethanol, followed by the addition of a CH_2Cl_2 solution containing 4-tert-butylphenylacetylene, 1, 5-bis(diphenylphosphino)pentane, and HAuCl_4 . Et_3N was then introduced under vigorous stirring, and the mixture was irradiated with a 5 W white light-emitting diode (LED) at room temperature for 24 h to yield the target nanocluster of $\text{Ag}_{22}\text{Au}_3$ ^[79].

Inter-cluster reactions can form bimetallic nanoclusters through chemical reactions between different cluster molecules, an extremely complex and mysterious process involving atomic exchange and bond reorganization^[80]. For instance, Krishnadas *et al.* documented the fabrication of $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$ superatomic nanoclusters via this method, where the dichloromethane solutions of $[\text{Au}_{25}(\text{FTP})_{18}]^-$ and $[\text{Ag}_{44}(\text{FTP})_{30}]^{4-}$ with precise stoichiometric ratios were mixed and reacted at 30 °C^[81]. Remarkably, the resulting product of $[\text{Au}_{12}\text{Ag}_{32}(\text{FTP})_{30}]^{4-}$ exhibits a geometric and electronic closed-shell configuration, conferring exceptional stability^[81]. Nevertheless, such successful cases of inter-cluster reactions to acquire atomically precise AuAg nanoclusters remain rare, and understanding the complex structural transformation process remains challenging and is still an active area of research in the nanocluster research community.

ATOMICALLY PRECISE AuAg NANOCLUSTERS FOR ELECTROCATALYSIS APPLICATIONS

In the past decade, electrocatalytic science and technology have attracted steadily increasing research interest, particularly in the field of green energy storage and conversion, mainly due to their high efficiency, operation under mild conditions, cost-effectiveness, and extremely low or even zero carbon emissions^[82]. Specifically, electrocatalysis can be regarded as a green technique, especially when intermittent electricity from solar, wind, and other renewable sources is used. Electrocatalysis has opened a sustainable avenue to address the severe carbon emissions and environmental pollution issues worldwide^[83-85].

The ultrasmall size, abundant active sites, precise structure, and Au/Ag synergistic effect have endowed atomically precise AuAg nanoclusters with the ability to serve as model and efficient catalysts in a variety of electrocatalytic reactions^[26]. In recent years, a handful of high-quality reviews focusing on electrocatalysis by metal nanoclusters - including but not limited to AuAg nanoclusters - have been published^[1,2,86-88]. This review mainly discusses the AuAg clusters as electrocatalysts for OWS, CO_2RR , and urea electrosynthesis.

AuAg NCs for OWS

Hydrogen energy, as an ideal energy carrier characterized by its high energy density and combustion product being solely water, has been widely regarded as one of the key renewable energy sources to achieve the carbon neutrality goal^[85,89]. Recently, hydrogen production through electrochemical water splitting has been attracting increasing research attention, not only because it can provide high-purity H_2 gas for direct use, but also because it can fully utilize renewable electricity generated from solar, wind, tidal, and other intermittent sources^[90-93]. Electrochemical water splitting contains two half reactions: the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode. However, for both HER and OER, additional energy input is required to overcome the energy barrier^[94,95]. To facilitate the reaction process, it is essential to lower the energy barriers; therefore, developing efficient and durable catalysts for both the HER and OER is imperative^[96-99].

In the past few years, bimetallic nanoclusters have emerged as model and effective catalysts for both HER and OER, as they have good catalytic performance, and more importantly, their well-defined structure can offer a great platform to unravel the structure-activity relationship at the atomic level^[30,32,100]. Specifically, for

atomically precise AuAg nanoclusters, their uniform size and composition, unique electronic structure, precise Au/Ag stoichiometric ratio, and crystallographically resolved structures endow them with significant advantages as model bimetallic catalysts for gaining deep mechanistic understanding and guiding improved catalyst design^[101]. In 2021, Li *et al.* reported an $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ nanocluster with low thiolate ligand surface coverage, which exhibited ultrahigh HER activity with a very low overpotential to achieve a given current density^[102]. Specifically, $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ consists of three icosahedral (I_h) units, reminiscent of the monomeric $I_h\text{Au}_{25}(\text{SR})_{18}^-$ and dimeric $I_h\text{Au}_{38}(\text{SR})_{24}$, and these tri-units endowed it with a unique geometric and electronic structure. The outstanding HER performance is attributed to the low ligand-to-metal ratio, low-coordinated Au atoms, and the unfilled superatomic orbitals^[102].

Recently, our group investigated the electrocatalytic performance of atomically precise $\text{Au}_{15}\text{Ag}_{23}(\text{tC}\equiv\text{CBu})_{18}\text{Br}_6$ nanoclusters in HER, OER, and OWS^[103]. $\text{Au}_{15}\text{Ag}_{23}$ nanocluster adopts a triple-layered core-shell-shell structure ($\text{Au}_6@\text{Au}_6\text{Ag}_{23}@\text{Au}_3$) with a tetragonal bipyramidal Au_6 core, a middle Au-Ag alloy layer, and an outer Au shell co-protected by 18 bulky alkynyl ligands and 6 Br ligands [Figure 1A and B]. As a 14-electron superatom, its unique electronic configuration and synergistic ligand coordination enable distinct catalytic properties. For HER in 0.5 M H_2SO_4 , the $\text{Au}_{15}\text{Ag}_{23}$ nanoclusters exhibited a low overpotential of 125 mV at $10\text{ mA}\cdot\text{cm}^{-2}$ and negligible current decay over 16 h, outperforming the AuAg NPs (overpotential of 235 mV) [Figure 1C]. In the OER test, the $\text{Au}_{15}\text{Ag}_{23}/\text{NiFe}$ -layered double hydroxide (LDH) composite demonstrated an ultralow overpotential of 250 mV ($10\text{ mA}\cdot\text{cm}^{-2}$) in 1.0 M KOH, with only ~5% current loss over 30 h [Figure 1D]. X-ray photoelectron spectroscopy (XPS) analysis revealed electron transfer from NiFe-LDH to $\text{Au}_{15}\text{Ag}_{23}$, generating high-valent Fe species as the active sites. For OWS, a two-electrode system employing $\text{Au}_{15}\text{Ag}_{23}$ as the cathode catalyst and $\text{Au}_{15}\text{Ag}_{23}/\text{NiFe}$ -LDH as the anode catalyst required an applied voltage of 1.51 V at $10\text{ mA}\cdot\text{cm}^{-2}$ in 1.0 M KOH, surpassing the control system of AuAg NPs paired with NiFe-LDH (1.65 V @ $10\text{ mA}\cdot\text{cm}^{-2}$, Figure 1E). Moreover, the AuAg NC|| $\text{Au}_{15}\text{Ag}_{23}/\text{NiFe}$ -LDH combination exhibited outperformed long-term stability in the 50 h continuous test, manifested by the only ~4% decay of the initial current density, while the AuAg NP||NiFe-LDH combination lost ~30% of the initial current after 50 h [Figure 1F]. The superior catalytic performance was attributed to synergistic co-protection by alkynyl and bromine ligands, which significantly enhanced the electron transfer and active site accessibility. This study highlights the AuAg nanoclusters as multifunctional catalysts to promote HER, OER, and OWS toward hydrogen production.

AuAg NCs for electrochemical CO_2RR

Electrochemical CO_2RR represents a promising approach that can not only mitigate the growing global concern over the harmful effects of excessive CO_2 emissions but also generate value-added carbon-based fuels and chemical feedstocks^[104–106]. However, the development and implementation of CO_2RR is hindered by several serious challenges such as the thermodynamic stability of the CO_2 molecule and the competitive HER reaction. Moreover, CO_2RR involves a very complex reaction pathway with multiple proton/electron transfer steps. Therefore, the CO_2RR catalyst plays a central role in activating the CO_2 molecule, determining the reaction pathway, and governing the catalytic activity and final product selectivity^[107–109].

Atomically precise AuAg nanoclusters hold great merit as model and effective catalysts for CO_2RR , not only due to their ultrasmall size and high activity and the exclusive selectivity for CO formation, but also because their atom-precise structure provides atomic-level insight into the reaction mechanism^[110,111]. Specifically, with the aid of *in-situ* spectroscopic study and theoretical calculations, such an atomically precise structure is beneficial for identifying the real catalytic activity, elucidating the synergistic effect between Au and Ag, disclosing the surface ligand role, and even understanding the catalyst structure evolution/reconstruction

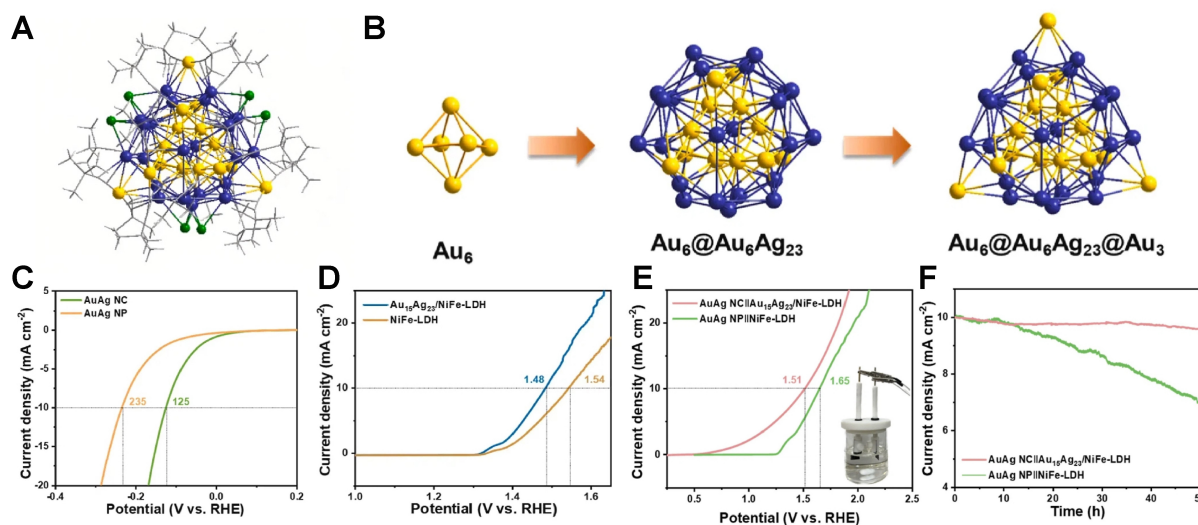


Figure 1. (A) Crystal structure and (B) structure anatomy of the $\text{Au}_{15}\text{Ag}_{23}$ nanocluster. Color labels: Au (gold), Ag (indigo), Br (green), C (25% gray); (C) The HER polarization curves of AuAg NC and AuAg NP in 0.5 M H_2SO_4 ; (D) The OER polarization curves of $\text{Au}_{15}\text{Ag}_{23}/\text{NiFe-LDH}$ and NiFe-LDH in 1.0 M KOH; (E) The OWS performance of the AuAg NC || $\text{Au}_{15}\text{Ag}_{23}/\text{NiFe-LDH}$ assembled electrolyzer and the AuAg NP || NiFe-LDH electrolyzer in 1.0 M KOH; (F) 50 h long-term OWS stability test. Reprinted with permission, copyright 2023 Elsevier Ltd^[103]. HER: Hydrogen evolution reaction; NC: nanocluster; NP: nanoparticle; OER: oxygen evolution reaction; LDH: layered double hydroxide; OWS: overall water splitting; RHE: reversible hydrogen electrode.

mechanism^[75]. For instance, Xu *et al.* reported the evolution from $\text{Au}_{24}\text{Ag}_{20}$ monomer clusters into $\text{Au}_{43}\text{Ag}_{38}$ dimeric nanoclusters, where the $\text{Au}_{24}\text{Ag}_{20}$ kernel of $\text{Au}_{12}@_{\text{Ag}_{20}}$ is assembled into $\text{Au}_{12}@_{\text{Ag}_{19}}\text{-Au-Au}_{12}@_{\text{Ag}_{19}}$, forming the kernel of $\text{Au}_{43}\text{Ag}_{38}$ ^[112]. Interestingly, the monomeric $\text{Au}_{24}\text{Ag}_{20}$ catalysts outperformed dimeric $\text{Au}_{43}\text{Ag}_{38}$ catalysts in CO_2RR ^[112].

The kernel and shell structure in the metal core can significantly affect the CO_2RR catalytic properties of AuAg nanoclusters, including the catalytic activity and stability. In 2022, Seong *et al.* reported a core-shell AuAg nanocluster of $\text{AuAg}_{12}@_{\text{Au}_{12}}(\text{SEtPh})_{18}$ (SEtPh: 2-phenylethanethiolate)^[110]. By engineering the active sites through replacing the $\text{Ag}_{12}(\text{SR})_{18}$ shell of Ag_{25} with an $\text{Au}_{12}(\text{SR})_{18}$ shell, the resulting $\text{AuAg}_{12}@_{\text{Au}_{12}}$ NC exhibited dramatically enhanced performance compared to Au_{25} . $\text{AuAg}_{12}@_{\text{Au}_{12}}(\text{SEtPh})_{18}$ consists of an AuAg_{12} core and an Au_{12} shell protected by 18 phenylethanethiolate (SEtPh) ligands through dimeric staple units. The overall framework of $\text{AuAg}_{12}@_{\text{Au}_{12}}(\text{SEtPh})_{18}$ resembles the icosahedral structure of $\text{Au}_{25}(\text{SEtPh})_{18}$, where the thiolate ligands bond to the metal core-shell via S atoms, and the core-shell interface is stabilized by metal-metal bonds [Figure 2A]. Figure 2B and C demonstrates that the $\text{AuAg}_{12}@_{\text{Au}_{12}}/\text{GDE}$ catalyst exhibits a CO onset potential of 1.62 V and achieves a CO current density (j_{CO}) of $339 \text{ mA}\cdot\text{cm}^{-2}$ at a full-cell potential of 2.66 V in a zero-gap CO_2 electrolyzer, outperforming the Ag NP catalyst. During 24-hour galvanostatic electrolysis at a current density of $200 \text{ mA}\cdot\text{cm}^{-2}$, the full-cell potential remains stable at $2.13 \pm 0.03 \text{ V}$ with an initial CO selectivity of 90% and an energy efficiency of 57%, highlighting its excellent stability and practical applicability^[110]. To better comprehend the reaction mechanism, the authors also performed operando attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) to confirm the active site. During CO_2RR , the $^*\text{CO}$ formation is the key step, and the C=O stretching band of $^*\text{CO}$ for Au_{25} NC is centered at $2,096 \text{ cm}^{-1}$ ^[110]. Interestingly, the $^*\text{CO}$ signal observed for $\text{AuAg}_{12}@_{\text{Au}_{12}}(\text{SEtPh})_{18}$ is located at $2,072 \text{ cm}^{-1}$, which is consistent with that of Au_{25} NC. This indicates that the Au site in $\text{AuAg}_{12}@_{\text{Au}_{12}}(\text{SEtPh})_{18}$ serves as the active site for CO_2RR , and the transplanted Au atoms function as the active site for CO_2 -to-CO electroreduction. These findings demonstrate that atomic-level engineering of metal shells effectively enhances CO_2 -to-CO electroreduction, offering a novel strategy for designing high-performance electrocatalysts.

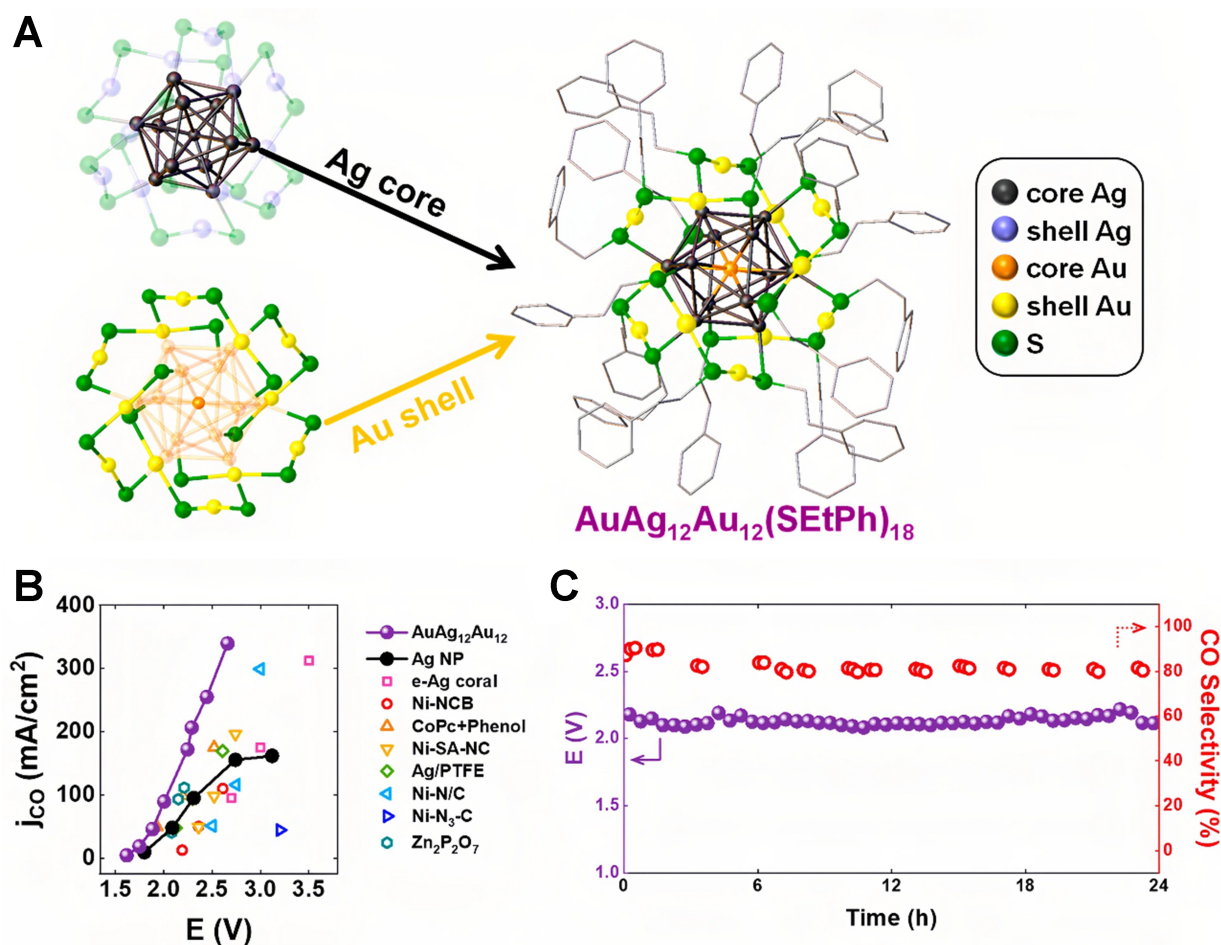


Figure 2. (A) Schematic illustration of the active-site engineering strategy for Ag₂₅ NC and the crystal structure of AuAg₁₂@Au₁₂(SETPh)₁₈, with carbon atoms represented as gray wireframes; (B) Comparison of j_{CO} in the zero-gap CO₂ electrolyzer on the AuAg₁₂@Au₁₂/GDE with other electrocatalysts; (C) Long-term CO₂ electrolysis of the AuAg₁₂@Au₁₂/GDE in a zero-gap cell monitored using the full-cell potential and CO selectivity at 200 mA·cm⁻². Reproduced with permission, copyright 2022 American Chemical Society^[10]. NC: Nanocluster; GDE: glass disk electrode; NP: nanoparticle; NCB: nitrogen-doped carbon black; SA: single atom; PTFE: polytetrafluoroethylene.

Furthermore, by doping Au or Pt atoms into Ag nanoclusters, the as-formed AuAg or PtAg nanoclusters exhibited drastically different CO₂RR properties from the parent Ag nanoclusters. In a recent study, Yoo *et al.* synthesized structurally precise monomeric PtAg₂₄(IPBT)₁₈ (IPBT: 2-Isopropylbenzenethiol) and AuAg₂₄(IPBT)₁₈ nanoclusters, which exhibited different CO₂RR activities^[113]. AuAg₂₄(IPBT)₁₈ exhibits a highly symmetric nanoscale framework, with isopropylphenyl groups of the thiolate ligands exposed on the cluster surface, ensuring good chemical stability and defining its electronic structure [Figure 3A–C]. In a zero-gap membrane electrode assembly (MEA) electrolyzer, the cluster achieves a CO partial current density of -202.2 mA·cm⁻² at -3.6 V with 90.4% Faradaic efficiency of CO (FE_{CO}), while maintaining > 90% FE_{CO} over 24 h at -3.2 V, demonstrating exceptional stability under industrial-relevant current densities [Figure 3D and E]. PtAg₂₄(IPBT)₁₈ displays inferior catalytic activity with a smaller current density and lower FE_{CO}. Operando ATR-SEIRAS measurements were then conducted to investigate the activity differences between the two clusters. The adsorbed CO (*CO) was observed in a range of 1,850–1,810 cm⁻¹ for both PtAg₂₄(IPBT)₁₈ and AuAg₂₄(IPBT)₁₈. However, at a given applied potential, PtAg₂₄ clusters exhibit a red shift of the *CO wavenumber by ~10 cm⁻¹ compared to AuAg₂₄. This suggests a stronger interaction between *CO and the PtAg₂₄ cluster, which is consistent with the slower *CO desorption. AuAg₂₄ exhibits relatively weak *CO adsorption and easier desorption, which contributes to a higher CO current density. Finally, density functional theory (DFT) calculations were performed to elucidate the influence of the central atom on

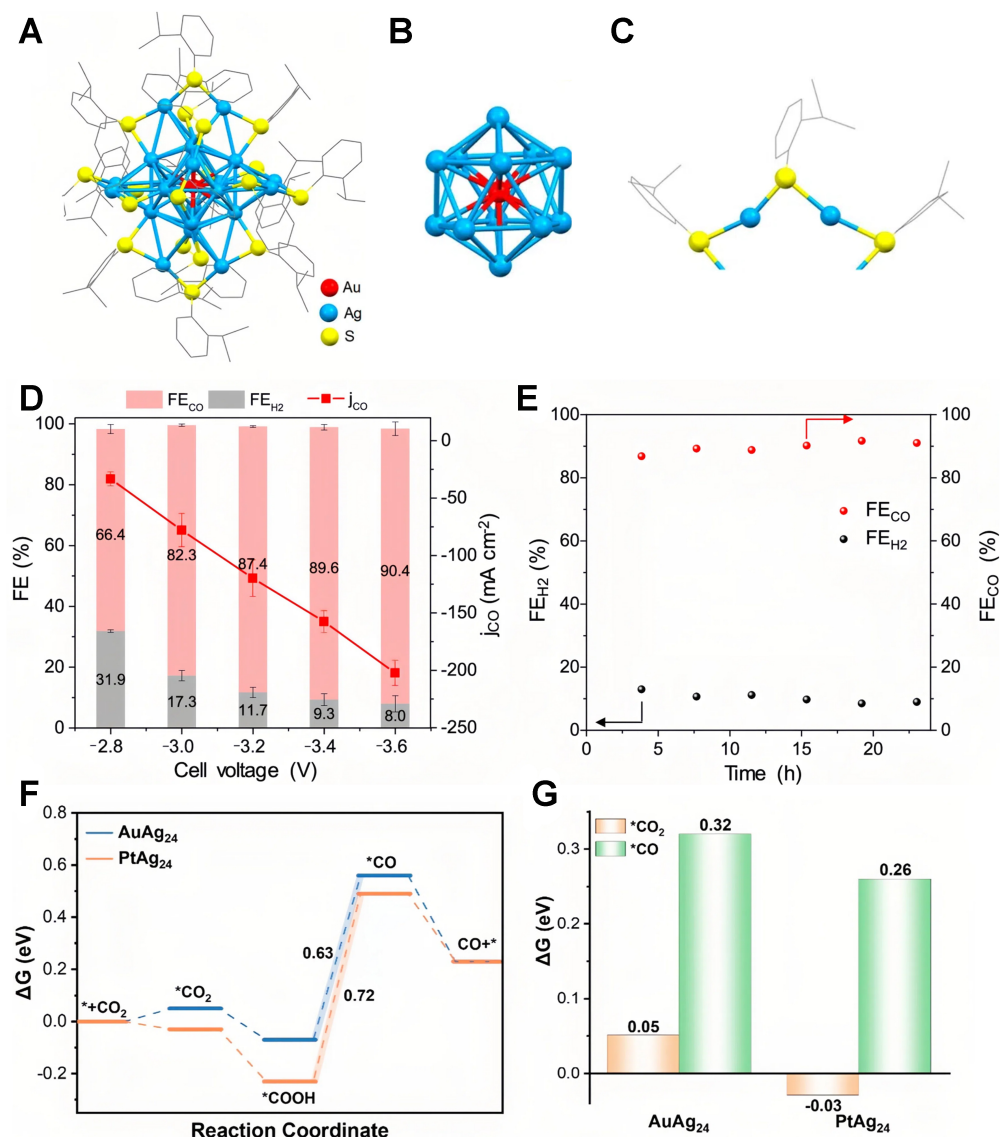


Figure 3. (A) Crystal structure of $[AuAg_{24}(IPBT)_{18}]^-$ NC; (B) Core structures of the dopant-centered $AuAg_{12}$ icosahedra; (C) Surface metal-ligand coordination motifs of $[AuAg_{24}(IPBT)_{18}]^-$ NCs; (D) FE_{CO} and j_{CO} of $AuAg_{24}$ across cell voltages ranging from -2.8 to -3.6 V in a zero-gap MEA cell; (E) Long-term operation of $AuAg_{24}$ at -3.2 V in the MEA cell; (F) Free energy diagram for CO_2 RR and (G) Adsorption free energies of *CO_2 and *CO on $AuAg_{24}$ and $PtAg_{24}$ NCs at $U = 0$ V vs. SHE. Reprinted with permission, copyright 2025 American Chemical Society^[113]. NC: Nanocluster; FE_{CO} : Faradaic efficiency of CO; j_{CO} : CO current density; MEA: membrane electrode assembly; CO_2 RR: CO_2 reduction reaction; SHE: standard hydrogen electrode.

CO_2 RR performance. **Figure 3F** presents the Gibbs-free energy profiles of CO_2 RR on $AuAg_{24}$ and $PtAg_{24}$ nanoclusters, revealing that the $^*COOH \rightarrow ^*CO$ step is the rate-determining step. $AuAg_{24}$ exhibits a lower energy barrier (0.63 eV) compared to $PtAg_{24}$ (0.72 eV), indicating more favorable CO formation kinetics. **Figure 3G** further compares the adsorption Gibbs free energies of *CO_2 and *CO intermediates, showing weaker *CO adsorption on $AuAg_{24}$ (0.32 eV) than on $PtAg_{24}$ (0.26 eV), which facilitates the CO desorption. These theoretical insights align with the experimental observations, confirming that the single Au atom at the core of the icosahedral Ag_{12} unit electronically modulates the Ag shell to optimize the intermediate binding, thereby enhancing both the activity and selectivity for CO_2 -to-CO conversion^[113]. This work showcases the single-atom doping in tuning the electrocatalytic performance of AuAg nanoclusters, and provides a deep mechanistic understanding of the single-atom-doping effect.

It is worth noting that the CO₂RR performance of the AuAg₁₂@Au₁₂, AuAg₂₄ cluster-based catalysts is at least comparable with, if not superior to, most of the recently reported Au/Ag-based nanostructure catalysts under identical or similar conditions, in terms of FE_{CO}, CO current density, and long-term stability [Table 2]. To sum up, for AuAg nanoclusters in CO₂RR, the metal core composition and configuration, as well as the employed surface capping ligands, are the main factors affecting the catalytic properties, as they can significantly tune the active sites, optimize the adsorption of reaction intermediates, and modulate the energy barrier of the rate-determining step.

AuAg NCs for electrocatalytic urea synthesis

Urea is a basic yet important chemical raw material, as it is not only an essential nitrogen fertilizer for crop growth but also serves as a critical feedstock for producing a series of valuable chemicals, such as urea-formaldehyde, barbiturates, and urea-melamine-formaldehyde resins^[120,121]. Currently, the industrial synthesis of urea heavily relies on the reaction between CO₂ and NH₃ at high temperatures (150 °C) and high pressures (150–250 bar). These harsh reaction conditions require expensive equipment and high energy input and, more importantly, generate significant CO₂ emissions, which are a major contributor to global warming^[122,123].

Electrochemical urea synthesis provides a new route for green urea production, as it can operate under mild conditions, utilize renewable electricity, and convert common wastewater contaminants (NO₃[−], NO₂[−], *etc.*) into valuable chemicals^[124–126]. Fundamentally, urea electrosynthesis is an extremely complicated process, and the key lies in the construction of the C–N bond. Atomically precise AuAg nanoclusters offer significant advantages as model catalysts for understanding C–N bond formation, as they provide two neighboring metal sites to stabilize key intermediates for both CO₂RR and nitrogenous compound electroreduction. More significantly, their atomically precise structure enables atomic-level insights into the structure-performance relationship^[127,128].

In 2024, Chen *et al.* reported two Ag-based bimetallic clusters - Ag₁₄Pd(PTFE)₆(TPP)₈ (Ag₁₄Pd) (PTFE: pentafluorothiophenol, TPP: triph-enylphosphine) and Ag₁₃Au₅(PTFE)₁₀(DPPP)₄ (Ag₁₃Au₅) [dppp: 1,3-Bis(diphenylphosphino)propane] - and their catalytic performance toward urea electrosynthesis^[129]. Figure 4A and B presents the crystal structures of the Ag₁₄Pd and Ag₁₃Au₅ clusters, respectively. Ag₁₄Pd consists of a Pd@Ag₁₂ icosahedral center capped by two AgS₃P units and eight TPP molecules. The electrocatalytic urea synthesis was then carried out in 1 M KOH containing 200 ppm NO₃[−] with CO₂ gas flowing over the chamber. The urea Faradaic efficiency (FE_{urea}) and yield rate in the potential range of −0.076 to −0.576 V are illustrated in Figure 4C and D. When the applied potential becomes more negative, the FE_{urea} for both Ag₁₄Pd and Ag₁₃Au₅ first increases and then decreases. The urea yield rate of Ag₁₄Pd exhibits a similar trend, whereas the urea yield of Ag₁₃Au₅ continuously increases. Ag₁₄Pd achieves the highest FE_{urea} of 15.8% and urea yield rate of 143.3 mg·h^{−1}·g^{−1} at −0.276 V, surpassing that of Ag₁₃Au₅. The authors then employed DFT calculations to elucidate the underlying reaction mechanism. Figure 4E displays the Gibbs-free energy profile for urea production on Ag₁₄Pd and Ag₁₃Au₅. It can be noted that Ag₁₄Pd possesses a lower energy barrier of 0.63 eV in the rate-determining step of NO → NOH during nitrate reduction to [•]NH₂, while Ag₁₃Au₅ has a much higher energy barrier of 0.81 eV. Additionally, Ag₁₄Pd stabilizes the key intermediates through lower adsorption energies: [•]NH₂ at −2.49 eV *vs.* −2.42 eV in Ag₁₃Au₅, and [•]CO at −0.19 eV compared to 0.01 eV for Ag₁₃Au₅. This enhanced adsorption capability facilitates the C–N coupling with a lower energy barrier of 0.48 eV from Ag₁₄Pd against that of Ag₁₃Au₅ (0.58 eV). Notably, Ag₁₃Au₅ exhibits stronger Ag → Au electron transfer of 0.81 e[−], which elevates the Ag oxidation state to +0.09 *vs.* +0.04 in Ag₁₄Pd. Such electronic polarization weakens the intermediate interactions and promotes the [•]NH accumulation, shifting the selectivity toward CO₂ reduction. By reducing the energy barriers, strengthening the intermediate adsorption, and regulating charge polarization, Ag₁₄Pd emerges as a high-performance catalyst for urea electrosynthesis^[129]. However,

Table 2. Comparison of the CO₂RR performance between AuAg₁₂@Au₁₂, AuAg₂₄ and other top-level Au/Ag-based nanocatalysts

Electrocatalyst	Electrolyte	Cell type	FE _{CO} (%)	J _{CO} (mA·cm ⁻²)	Stability (h)	Ref.
AuAg ₁₂ @Au ₁₂	1.0 M KOH	MEA-cell	90	206	24	[110]
AuAg ₂₄	0.1 M KHCO ₃	MEA-cell	90.4	-202.2	24	[113]
Au ₂₄	0.1 M KHCO ₃	MEA-cell	90	-90	100	[114]
Ag ₁₅	0.5 M KHCO ₃	H-cell	95	-13.0	10	[115]
Hollow Au-Cu NP/C	0.5 M KHCO ₃	MEA-cell	53.3	~-16.5	12	[116]
D-100 Ag NWs	0.1 M KHCO ₃	GCE-cell	88.1	0.35	24	[117]
Ag-900D NNAs	0.5 M KHCO ₃	H-cell	91.4	43.41	~11.7	[118]
Au ₂₂	0.5 M KHCO ₃	H-cell	92.7	~-7.0	10	[119]

CO₂RR: CO₂ reduction reaction; FE_{CO}: Faradaic efficiency of CO; j_{CO}: CO current density; MEA: membrane electrode assembly; NP: nanoparticle; NWs: nanowires; GCE: glass carbon electrode; NNAs: nano-array architectures.

Ag₁₃Au₅ has demonstrated great potential for urea electrosynthesis, and through composition optimization and ligand engineering, improved catalytic performance toward urea electrosynthesis might be achieved^[129].

Recently, Zhang *et al.* reported a carbene-ligand-protected AuAg nanocluster of [Au₁₃Ag₁₂(PPh₃)₈(BMIm)₂I₈]SbF₆ (Au₁₃Ag₁₂), and studied the influence of the carbene ligand on the electrocatalytic urea synthesis^[70]. The overall structure of Au₁₃Ag₁₂ is shown in Figure 5A and B. The Au₁₃Ag₁₂ nanocluster features a metal core of two vertex-sharing icosahedra in an S-configuration. Au atoms occupy the core, and they are bonded to the NHC ligands via shorter Au–C bonds (2.075 Å vs. Au–P: 2.30–2.34 Å), while Ag atoms at axial positions coordinate with the iodine ligands through Ag–I bonds (2.624 Å). Interestingly, when anchored on NiFe-LDH, the Au₁₃Ag₁₂ nanoclusters exhibited outstanding electrocatalytic performance for urea synthesis, achieving a urea production rate of 29.5 mmol·g_{cat}⁻¹·h⁻¹ with a Faradaic efficiency (FE) of 34% at -0.5 V vs. reversible hydrogen electrode (RHE) [Figure 5C]. Such remarkable performance substantially surpasses that of AuAg nanoclusters stabilized by conventional ligands such as DPPP or Ph₃P. Furthermore, the electrospray ionization mass spectrometry (ESI) results confirmed that the CO₂ molecules can be chemically bonded onto the cluster surface [Figure 5D]. The authors also used the DFT calculations to study the electronic structure of the Au₁₃Ag₁₂ nanoclusters. Figure 5E–H presents the DFT-simulated l-Au-BMIm and l-Au-PPh₃ and their bond properties. It can be noted that the carbene ligands can strengthen the Au–C bonds (2.01 Å bonding length vs. Au–PPh₃: 2.30 Å) with higher bond energy (74.1 vs. 60.1 kcal/mol). There are frontier orbital overlaps between the Au orbitals and the carbene orbitals, specifically highest occupied molecular orbital (HOMO)-9 and HOMO-3, where HOMO-3 has an s character and HOMO-9 exhibits a p character. Specifically, a constructive overlap exists between Au's *d*_{xz} orbital and C's *p*_z orbital in the HOMO-9 orbital, while the HOMO-2 orbital has an s character similar to that of the HOMO-3 orbital in l-Au-BMIm. The orbital overlap between Au and carbene indicates strong electron delocalization, which can optimize the *CO and *NH₂ adsorption, reduce the energy barrier of C–N coupling, and eventually enhance the NO₃⁻/HCO₃⁻ conversion synergistically^[70]. This study highlights the crucial role of electronic structure tuning of atomically precise AuAg nanoclusters in boosting both the activity and selectivity in electrocatalytic urea synthesis.

As a note, the electrocatalytic activity of the Au₁₃Ag₁₂, Ag₁₄Pd cluster-based catalysts toward urea electrosynthesis - including the FE_{urea} and the urea yield rate - is comparable to that of other Au/Ag-based nanostructure electrocatalysts, as compiled in Table 3.

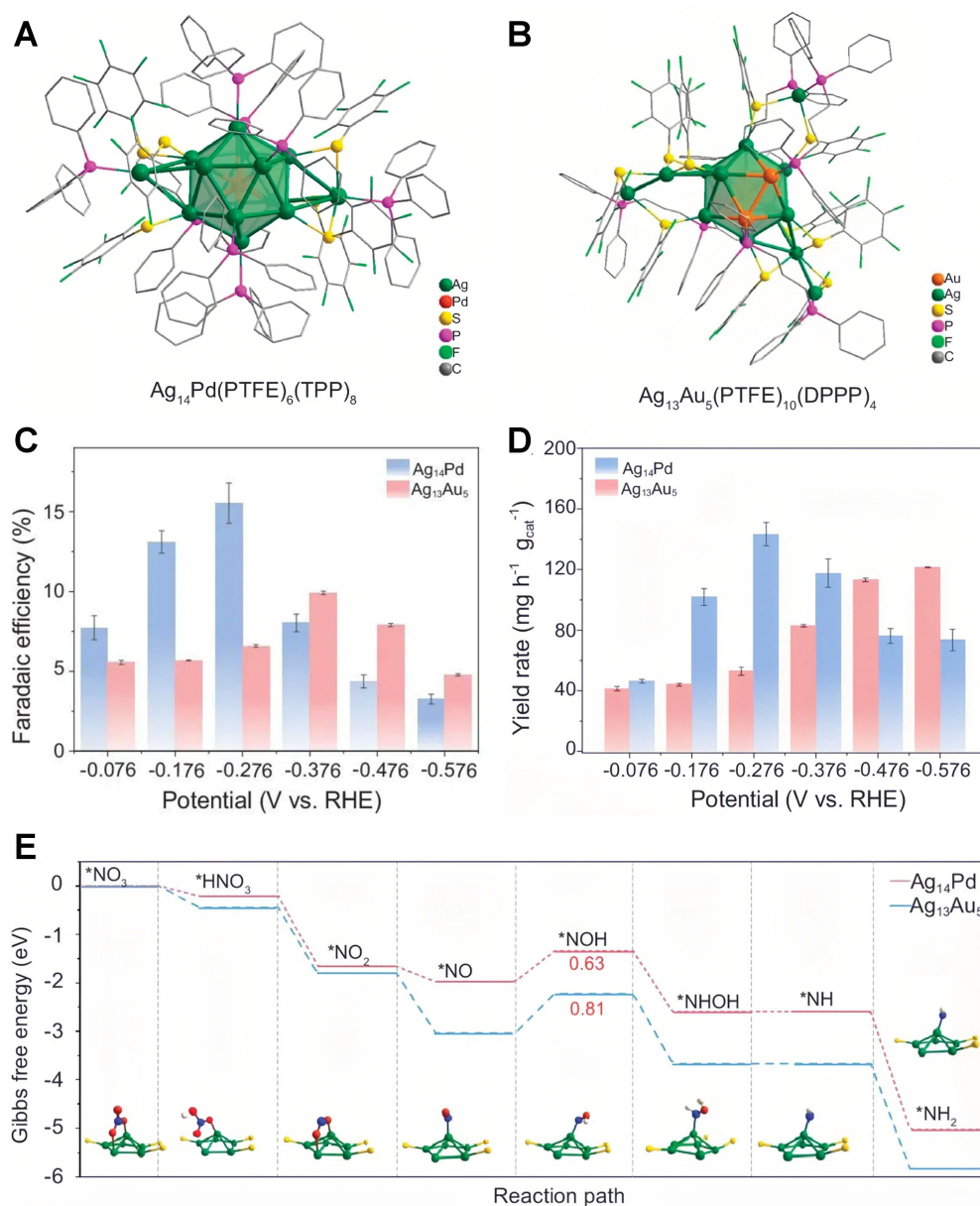


Figure 4. Overall structures of (A) Ag₁₄Pd and (B) Ag₁₃Au₅ nanoclusters; (C) Potential dependent urea FEs and (D) the urea yield rates of Ag₁₄Pd and Ag₁₃Au₅ nanoclusters; (E) Gibbs-free energy profile for urea production on Ag₁₄Pd and Ag₁₃Au₅. Reproduced with permission, 2024 Oxford Academic Press^[129]. FEs: Faradaic efficiencies; RHE: reversible hydrogen electrode.

Besides the above electrocatalytic reactions, AuAg nanoclusters have also demonstrated great potential in other catalytic reactions such as multiple-component coupling reactions^[135] and photoelectrochemical reactions^[136]. Yet, from the structural view, the (electro)catalytic performance of the AuAg nanoclusters for various reactions, especially the complicated CO₂RR and electrochemical urea synthesis, is mainly governed by the following factors: size, composition, charge state, metal core configuration, ligand type and spatial structure, as well as the metal-ligand bonding structure. These factors can significantly tune the catalytic active site, induce charge redistribution/polarization, optimize the adsorption capability of the reaction intermediates, and alter the energy barrier of the rate-determining step. These cross-reaction mechanistic principles must be considered in future AuAg nanocluster design for catalytic applications.

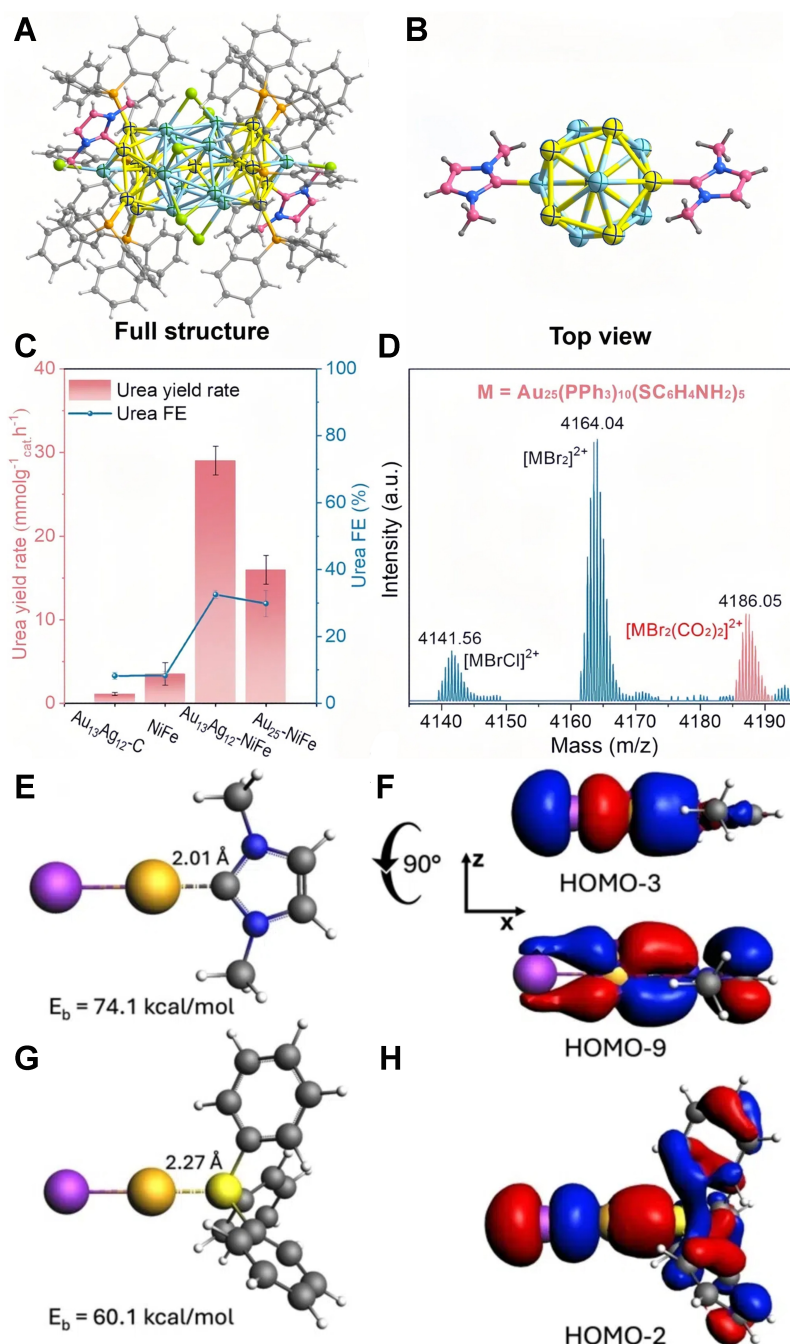


Figure 5. Crystal structure of Au₁₃Ag₁₂-BMIIm: (A) full, (B) top view. Color code: Au, yellow; Ag, slate; P, orange; I, green; N, blue; C, gray and pink; (C) Urea FEs and the yield rates of a series of samples at -0.5 V (vs. RHE); (D) ESI-MS analysis of [Au₂₅(PPh₃)₁₀(SC₆H₄NH₂)X₂]²⁺ (X: Cl/Br) nanocluster in CO₂ saturated solution; (E) DFT structure of I-Au-BMIIm and bond properties; (F) Two frontier MOs exhibit constructive overlap between Au orbitals and the carbene ligand; (G) DFT structure of I-Au-PPh₃ and bond properties; (H) The HOMO-2 orbital possesses s character identical with that of the HOMO-3 orbital in I-Au-BMIIm. Color code: Au (gold), P (yellow), Cl (green), C (gray), N (blue). Reprinted with permission, 2024 Wiley-VCH^[70]. BMIIm: 1, 3-Bimethylimidazole; FEs: Faradaic efficiencies; RHE: reversible hydrogen electrode; ESI-MS: electrospray ionization mass spectrometry; DFT: density functional theory; MOs: molecular orbitals; HOMO: highest occupied molecular orbital.

CONCLUSION AND OUTLOOK

Overall, the last decade has witnessed great success in the fundamental study of atomically precise AuAg nanoclusters, particularly in the development of synthetic methods and electrocatalytic applications. Despite the above progress, a series of critical challenges have gradually emerged, and addressing them with

Table 3. Comparison of the electrocatalytic urea synthesis activity between the Au₁₃Ag₁₂, Ag₁₄Pd and other Au/Ag-based nanostructure electrocatalysts

Electrocatalyst	Electrolyte	Cell type	FE _{urea} (%)	Yield rate (mmol·g _{cat} ⁻¹ ·h ⁻¹)	Ref.
Au ₁₃ Ag ₁₂	0.1 M KHCO ₃ + 0.1 M KNO ₃	H-cell	34	29.5	[70]
Ag ₁₄ Pd	1 M KOH	Flow-cell	15.8	-2.39	[129]
Ag-CuNi(OH) ₂	0.1 M KHCO ₃ + 0.1 M KNO ₃	H-cell	46.1	25.6	[130]
AuCu SANFs	0.5 M KHCO ₃ + 0.01 M KNO ₂	H-cell	24.7	64.83	[131]
PdAuHene	0.1 M KNO ₃	H-cell	33.88	6.68	[132]
Ag@BiVO ₄ /BiFeO ₃	0.2 M KHCO ₃	H-cell	24.4	1.2	[133]
AuPd@SnO _x	0.075 M KHCO ₃ + 0.025 M KNO ₃	H-cell	21.3	-21.34	[134]

FE: Faradaic efficiency; SANFs: single atom nano frameworks.

innovative solutions could bring new vitality to this field. Next, we will discuss the current main challenges and the potential opportunities for future developments.

1. Efficient synthetic methods with broad applicability are still lacking. For synthesizing atomically precise AuAg and other alloy metal nanoclusters with hierarchical structures, current methods face challenges such as complicated procedures, low yields, and poor product selectivity. More critically, most existing methods are only applicable to specific systems and lack general universality. In addition, these approaches heavily rely on “trial-and-error” strategies, which are labor-intensive, costly, tedious, and inefficient. Recently, machine learning (ML) has begun to make a significant impact on chemical sciences, including the study of metal nanoclusters^[17,137,138]. ML has demonstrated great promise in the customized synthesis of metal nanoclusters^[139], and it will likely revolutionize the future design of synthetic strategies for atomically precise AuAg nanoclusters.

2. Enhance the capability of precise structural design and structure extension of AuAg nanoclusters^[29]. Improving the nanocluster catalytic performance heavily relies on precise structural design. However, technical bottlenecks persist in atomically precise control of size, composition, surface ligands, and spatial configuration. For example, designing nanocluster catalysts for electrocatalytic urea synthesis requires exact modulation of active site distribution and synergy to achieve efficient co-activation of N₂ (NO₃⁻, NO₂⁻) and CO₂ (HCO₃⁻) - a demand unmet by the current methods^[140]. In addition, extending the structures of AuAg nanoclusters can broaden the scope of research. For instance, introducing a heterometal atom into AuAg nanoclusters can tailor the catalytic performance. In 2022, our group reported the CO₂RR performance of Au₇Ag₈ and Au₂Ag₈Cu₅ clusters, where Au₇Ag₈ produces only CO, while Au₂Ag₈Cu₅ yields HCO₂H with a FE of 28.3%^[141]. Encapsulating AuAg nanoclusters into a well-defined porous structure offers another way to tailor the functionality. A good example is the study conducted by Wang *et al.*, in which the AuAg₂₄ nanocluster was encapsulated into a metal-organic framework to form AuAg₂₄@UiO-66-NH₂ (UiO: University of Oslo) composite materials^[142]. Such composite materials showed significantly enhanced activity in photocatalytic hydrogen production^[142].

3. More in-depth reaction mechanism study in electrocatalytic applications. For electrocatalytic reactions involving complex processes with multiple electron/proton transfers, understanding the reaction mechanism - especially under working conditions - is extremely challenging. Atomically precise AuAg and other alloy nanoclusters have been employed as model catalysts for urea electrosynthesis, and will be expanded to other complicated electro-synthetic systems. The *in-situ* spectroscopic techniques - including *in-situ* attenuated total reflection surface-enhanced infrared spectroscopy (ATR-SEIRS), *in-situ* Raman spectroscopy, and the *in-situ/operando* synchrotron radiation techniques such as extended X-ray absorption fine structure

(EXAFS), X-ray absorption near edge structure (XANES), and high-energy X-ray diffraction (HE-XRD) - can provide valuable information on key intermediates, helping to elucidate the reaction pathway and ultimately establish the structure-performance relationship^[3,143,144]. For instance, in a recent study, our group reported an alkynyl-protected Ag₁₆Cu₁₈ cluster with intramolecular strain for oxime electrosynthesis, where ATR-SEIRS played a critical role in elucidating the reaction mechanism^[145].

DECLARATIONS

Authors' contributions

Literature search, original manuscript writing: Yang, J.
Literature search, format analysis: Qiao, L.
Format adjustment: Wu T.; Yang, C.; Liu, Z.
Supervision, manuscript editing: Chi, K.
Supervision, manuscript editing, funding acquisition: Tang, Z.

Availability of data and materials

Not applicable.

AI and AI-assisted tools statement

Not applicable.

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Conflicts of interest

Qiao, L.; Yang, C. and Chi, K. are affiliated with the Petrochemical Research Institute, PetroChina Company Limited, China. The other authors declare that they have no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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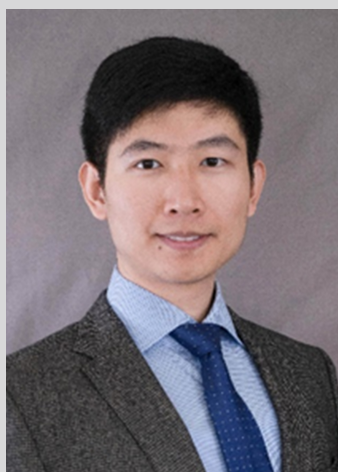


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