

Hydrogen Evolution Electrocatalyst Design: Turning Inert Gold into Active Catalyst by Atomically Precise Nanochemistry

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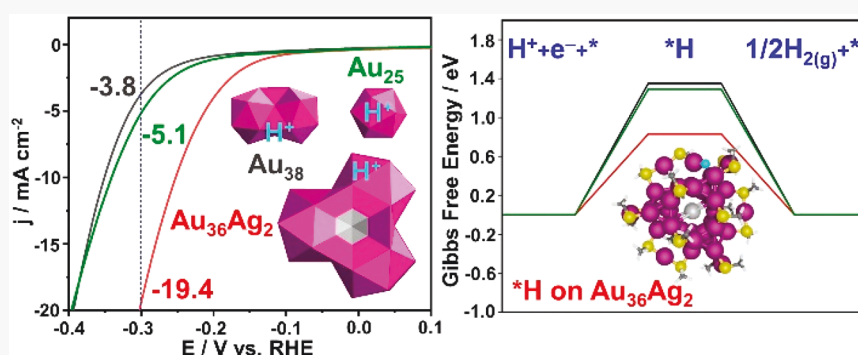
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ABSTRACT: Electrocatalytic hydrogen evolution reaction (HER) holds promise in the renewable clean energy scheme. Crystalline Au and Ag are, however, poor in catalyzing HER, and the ligands on colloidal nanoparticles are generally another disadvantage. Herein, we report a thiolate (SR)-protected $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ nanocluster with low coverage of ligands and a core composed of three icosahedral (I_h) units for catalyzing HER efficiently. This trimeric structure, together with the monomeric I_h $\text{Au}_{25}(\text{SR})_{18}^-$ and dimeric I_h $\text{Au}_{38}(\text{SR})_{24}$, constitutes a unique series, providing an opportunity for revealing the correlation between the catalytic properties and the catalyst's structure. The $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ surprisingly exhibits high catalytic activity at lower overpotentials for HER due to its low ligand-to-metal ratio, low-coordinated Au atoms and unfilled superatomic orbitals. The current density of $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ at -0.3 V vs RHE is 3.8 and 5.1 times that of $\text{Au}_{25}(\text{SR})_{18}^-$ and $\text{Au}_{38}(\text{SR})_{24}$, respectively. Density functional theory (DFT) calculations reveal lower hydrogen binding energy and higher electron affinity of $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ for an energetically feasible HER pathway. Our findings provide a new strategy for constructing highly active catalysts from inert metals by pursuing atomically precise nanoclusters and controlling their geometrical and electronic structures.

INTRODUCTION

Noble metal Pt and its alloy nanoparticles (NPs) are considered to be the most promising catalysts for hydrogen evolution reaction (HER)^{1–3} with large cathodic current densities at low overpotentials. Recently, non-noble, earth-abundant metals are also studied for electrochemical HER.^{4–7} Gold and silver are unfortunately less active in the HER process due to high free energy of hydrogen ($^*\text{H}$) adsorption and low current densities.^{8,9} The size regime between conventional Au (or Ag) NPs and organometallic complexes gives rise to nanoclusters (NCs) consisting of dozens to hundreds of metal atoms per particle. Recent progress has led to atomic precision for 1–3 nm metal NCs protected by organic ligands (e.g., thiolate (SR)).¹⁰ This emergent class of nanomaterials provides unprecedented opportunities for relating the atomic-level structures to various properties,^{11–14} as the total structures of NCs can be revealed by single crystal X-ray diffraction (SCXRD).^{15–17} Such NCs possess much higher surface-to-volume ratios than regular NPs and are thus

potentially promising catalysts for H_2 evolution, but they have not been widely applied due to the inert nature of Au and Ag from previous work with regular NPs.³ In recent work, doping Pt/Pd into $\text{Au}_{25}(\text{SR})_{18}$ was found to improve the HER performance compared to the homogold counterpart,^{18,19} but Ag doping showed an adverse effect.²⁰

To design effective HER catalysts based on Au and Ag, much effort has been put in controlling the structures of NCs, for example, fusion of 13-atom icosahedral building blocks into a linear dimer or trimer.^{21,22} Trimeric NCs often exhibit outstanding electronic and optical properties.²³ We aim at obtaining NCs with more exposed surface metal atoms for $^*\text{H}$

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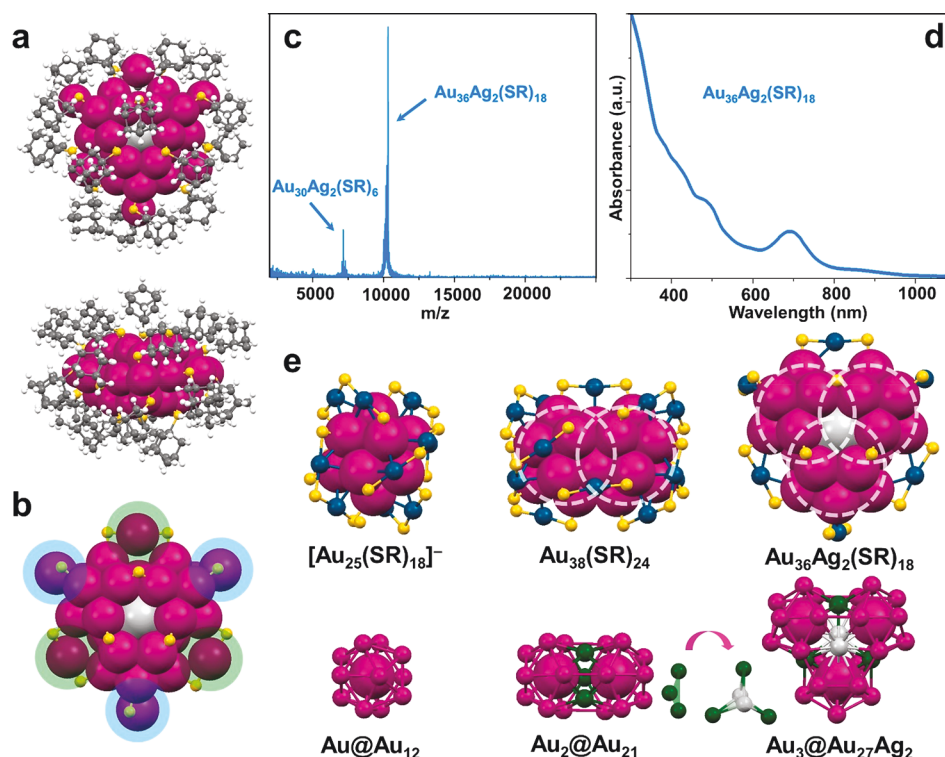


Figure 1. (a) The total structure (top and side views) of $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ NC. (b) The carbon tail-omitted $\text{Au}_{36}\text{Ag}_2\text{S}_{18}$ structure: the Au atoms of $\text{Au}(\text{SR})_2$ motifs on each I_h unit are indicated by blue circles; whereas the Au atoms of $\text{Au}(\text{SR})_2$ motifs that bridge two I_h units are indicated by green circles. (c) MALDI-MS spectrum and (d) UV-vis spectrum of $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ NCs; note that $\text{Au}_{30}\text{Ag}_2(\text{SR})_6$ in the mass spectrum is a fragment. (e) The Au–S structures (top) and kernel structures (bottom) of monomeric I_h $[\text{Au}_{25}(\text{SR})_{18}]^-$ (left), dimeric I_h $\text{Au}_{38}(\text{SR})_{24}$ (middle), and trimeric I_h $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ (right), each dashed circle indicates one I_h unit. Color codes: a and b, magenta = Au, light gray = Ag, yellow = S, gray = C, and white = H; e, magenta/green = kernel Au, navy = motif Au, light gray = Ag, and yellow = S.

adsorption via atomically precise nanochemistry to design an effective Au/Ag catalyst for HER, even though the catalyst is composed of traditionally inactive metals.

Herein, we report a success in synthesizing a trimeric $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ NC in which three icosahedral (I_h) units are face-fused together in a cyclic manner. A series of NCs, i.e., monomeric $\text{Au}_{25}(\text{SR})_{18}^-$, dimeric $\text{Au}_{38}(\text{SR})_{24}$ and trimeric $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$, are thus available for a comparative study in HER and for revealing important insight. The “face-fusion” mode makes the three I_h building blocks more closely attached to each other, resulting in unfilled supermolecular orbitals (note that the $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ supermolecule comprises three I_h superatoms), in contrast to the NCs composed of multiple vertex-shared icosahedrons (indicated by the total free-valence-electron counts to be integer multiples of 8e, i.e., 8e, 16e, 24e).^{23,24} As a result, $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ exhibits a much lower onset overpotential for HER and greatly increased current density. This is important as Au and Ag, as well as thiolate ligands are known to be adverse for HER catalysis.^{8,9,25} DFT calculations demonstrate that the trimeric NC exhibits favorable hydrogen formation thermodynamics and a higher electron affinity compared to the monomeric and dimeric NCs. Thus, tailoring the geometrical and electronic structures of atomically precise Au/Ag NCs can lead to highly active catalysts for HER.

RESULTS AND DISCUSSION

Characterization of Trimeric $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$. The $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ (where, SR = adamantanethiolate, $\text{SC}_{10}\text{H}_{15}$, Figure 1) NC was synthesized through a coreduction of Au^{I} –

$\text{SC}_{10}\text{H}_{15}$ and Ag^{I} – $\text{SC}_{10}\text{H}_{15}$ (molar ratio = 10:1) by NaBH_4 , and the product was purified by crystallization (see Supporting Information for details). The crystal structure of $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ was solved by SCXRD (Figure 1a/Table S1), which possesses a face-fused tri-icosahedral $\text{Au}_{30}\text{Ag}_2$ kernel on which three bridging thiolates connect the three I_h building blocks on the top and another three thiolates at the bottom. Each I_h unit is further protected by one $\text{Au}(\text{SR})_2$ motif (Figure 1b, marked in blue shadows, three total), and another $\text{Au}(\text{SR})_2$ motif bridges two I_h as well (Figure 1b, marked in green shadows, three total). The entire $\text{Au}_{36}\text{Ag}_2\text{S}_{18}$ structure without the organic tails possesses a quasi- D_{3h} symmetry. The two Ag atoms reside at the C_3 axial positions of the NC, i.e., they are shared by all three I_h units.

The UV-vis spectrum of $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ (in toluene) shows a prominent peak at ~ 690 nm, with other less pronounced ones at ~ 380 , ~ 430 , ~ 490 , and ~ 860 nm (Figure 1d), indicating a molecular state of the NC (as opposed to metallic-state NPs). MALDI mass spectrometry (MS) shows an intense peak corresponding to $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ (Figure 1c) as well as a weak peak for the $\text{Au}_{30}\text{Ag}_2(\text{SR})_6$ fragment, and the difference between these two peaks is the mass loss of $\text{Au}_6(\text{SR})_{12}$ fragment, which is consistent with the six $\text{Au}(\text{SR})_2$ motifs on the surface of the kernel; note that in the MS spectrum (Figure S1), a weaker peak representing $\text{Au}_{35}\text{Ag}_3(\text{SR})_{18}$ was also detected; however, the crystal data does not show any third Ag atom in the structure. Thus, the $\text{Au}_{35}\text{Ag}_3(\text{SR})_{18}$ byproduct should be decomposed during the crystallization, leaving pure $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$.

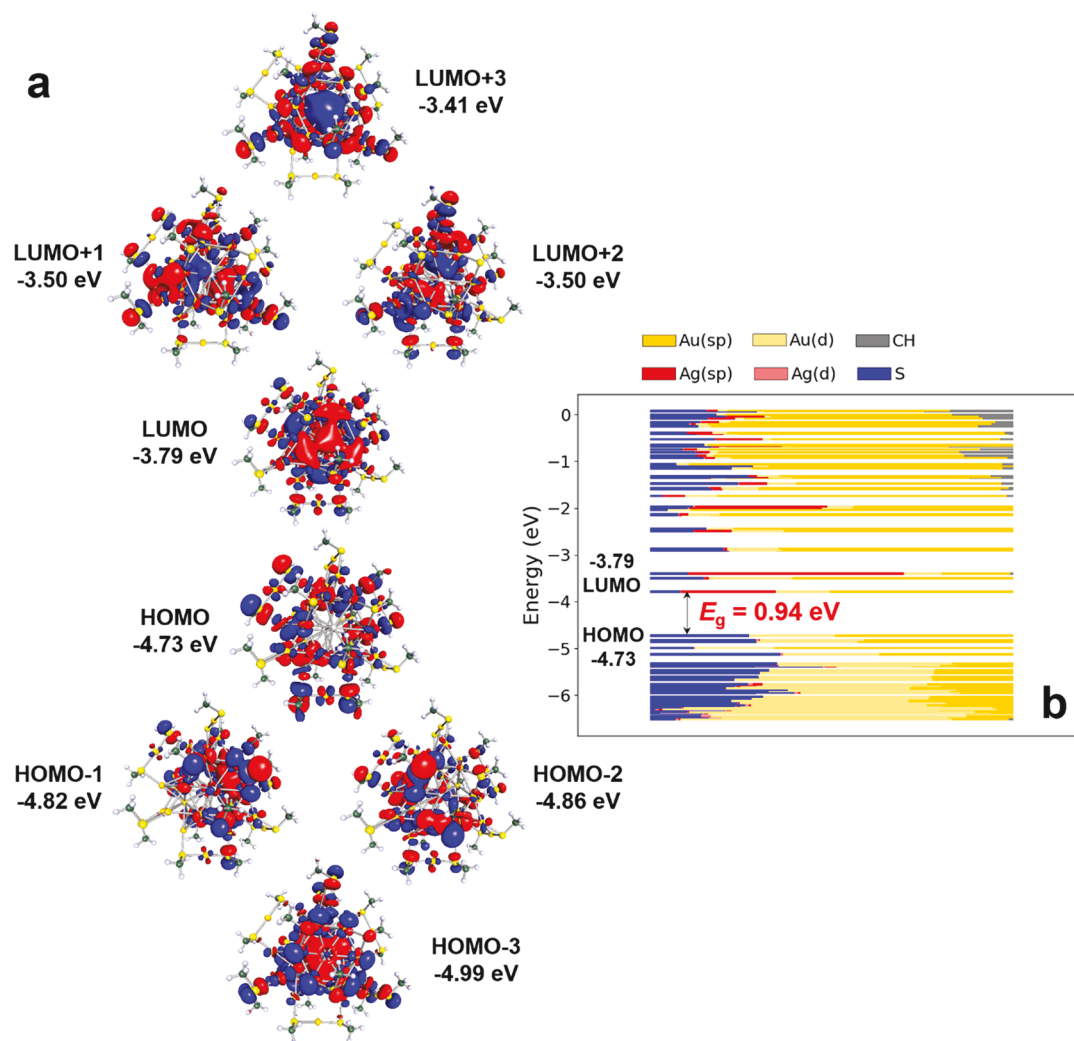


Figure 2. (a) Visualized frontier molecular orbitals of $\text{Au}_{36}\text{Ag}_2(\text{SCH}_3)_{18}$ and their corresponding energy levels. (b) KS orbital energy level diagram for $\text{Au}_{36}\text{Ag}_2(\text{SCH}_3)_{18}$ with contributions from various atomic-orbitals of Au, Ag, S, C and H.

The obtained $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ NC fulfills an interesting series of face-fusion NCs, including the mono- I_h $[\text{Au}_{25}(\text{SR})_{18}]^-$,²⁶ bi- I_h $\text{Au}_{38}(\text{SR})_{24}$,²⁷ and tri- I_h $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$ (Figure 1e). In the bi- I_h $\text{Au}_2@_{\text{Au}_{21}}$ kernel of $\text{Au}_{38}(\text{SR})_{24}$, the two Au_{13} units are face-fused at the middle Au_3 triangle (Figure 1e, middle, marked in green); in the tri- I_h $\text{Au}_3@_{\text{Au}_{27}}\text{Ag}_2$ kernel of $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$, three $\text{Au}_{11}\text{Ag}_2$ units are face-fused at the central Au_3Ag_2 three-pointed star (Figure 1e, right, marked in green/light gray).

DFT Calculations on Electronic Structures. Mulliken contribution is an effective means to illustrate the Kohn–Sham (KS) molecular orbitals at the atomic level.²⁸ Herein, similar behavior is found for the series of NCs, that is, the highest occupied molecular orbitals (HOMO) of the mono- I_h $[\text{Au}_{25}(\text{SCH}_3)_{18}]^-$, bi- I_h $\text{Au}_{38}(\text{SCH}_3)_{24}$, and tri- I_h $\text{Au}_{36}\text{Ag}_2(\text{SCH}_3)_{18}$ NCs are mainly localized on the central atom(s) in each I_h (Figure S2/S3, darker red). In contrast, the lowest unoccupied molecular orbitals (LUMO) are mainly distributed on the mono- I_h Au_{12} and bi- I_h Au_{21} shells (Figure S2, darker blue). As for the $\text{Au}_{36}\text{Ag}_2(\text{SCH}_3)_{18}$, although its LUMO is also on the tri- I_h $\text{Au}_{27}\text{Ag}_2$ shell, the orbital density is more localized on the two doping Ag atoms (Figure S3a, darker blue). This observation indicates that for the NC series, the HOMO states are primarily decided by the I_h central

atom(s), whereas the LUMO states depend more on the I_h shell atoms. In the newly obtained trimeric $\text{Au}_{36}\text{Ag}_2(\text{SR})_{18}$, we tried to dope as few heteroatoms as possible, and the controlled doping amount of Ag was proved to be critical in tailoring the structures of atomically precise NCs.²⁹ The two Ag atoms are thus important to achieve the trimeric structure in the synthesis, and according to DFT (Figure 2), LUMO and especially LUMO+3 orbitals are localized³⁰ on the two Ag atoms (Figure 2b) which are shared by the three I_h units, compared to the remaining 27 Au atoms in the tri- I_h shell. We rationalize that the I_h central atom (Au) would take more electron density than the I_h shell atoms as indicated by Bader charge analysis.²⁸ As a result, the three I_h centers in the tri- I_h structure would attract more charges and the two axial positions shared by three units should contribute more electron density to the I_h centers. Thus, the much less electronegative Ag atoms (electronegativity $\chi_{\text{Ag}} = 1.93$ vs $\chi_{\text{Au}} = 2.54$) are preferred at these C_3 axial positions.

In DFT calculations, we further replaced the two Ag atoms with Au to obtain a hypothetical trimeric $\text{Au}_{38}(\text{SCH}_3)_{18}$ NC (Figure S3b) to highlight the specific Au atoms at the Ag positions (i.e., Au substitution for Ag) in the KS diagram. One can observe that the two Au atoms still contribute significantly to LUMO and LUMO+1. Accordingly, the KS diagrams of

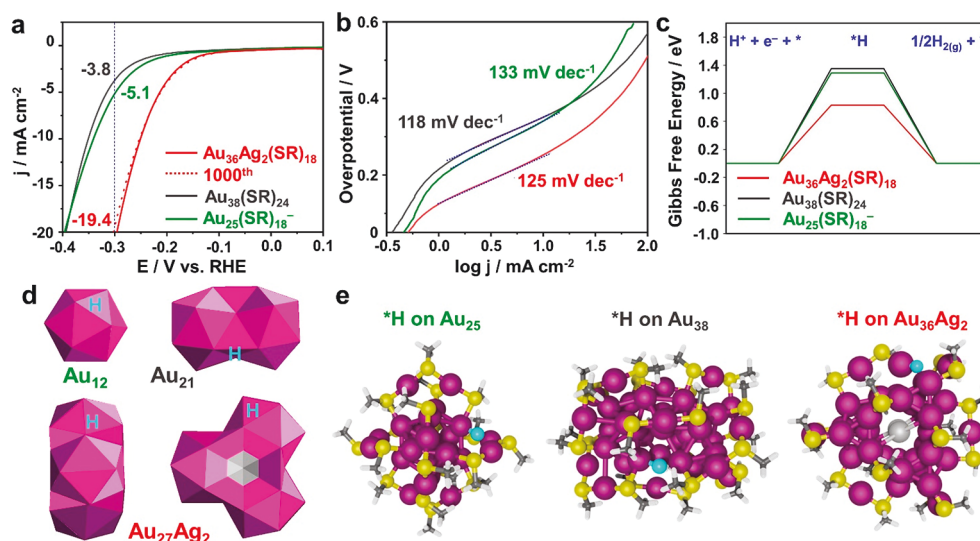


Figure 3. (a) HER voltammograms of NC catalysts. (b) Tafel plots of NC catalysts. (c) Calculated Gibbs free energy of $H_2(g)$ formation (HER pathway) on the NC catalysts. (d) Illustrated kernel surfaces of NC catalysts for hydrogen adsorption. (e) Relaxed structures of the NCs upon hydrogen adsorption on Au active site. Color codes: magenta = Au, light gray = Ag, yellow = S, cyan = adsorbed H, gray = C, and white = H.

$Au_{36}Ag_2(SCH_3)_{18}$ and $Au_{38}(SCH_3)_{18}$ demonstrate a similar energy for the HOMO, while the replacing Au atoms result in a more negative energy for the LUMO and hence, a 0.15 eV smaller energy gap in $Au_{38}(SR)_{18}$ (Figure S4). The smaller gap might be related to a less stable electronic configuration of homogold trimeric $Au_{38}(SR)_{18}$ which is yet to be synthesized.

The free valence electron number is important for the electronic configuration of superatomic NCs.³¹ The number increases from 8e ($25-18+1=8$) for the monomeric $[Au_{25}(SR)_{18}]^-$ to 14e ($38-24=14$) for the dimeric $Au_{38}(SR)_{24}$ (resembling a diatomic supermolecule), then to 20e ($36+2-18=20$) for the trimeric $Au_{36}Ag_2(SR)_{18}$ (a triatomic supermolecule), with a 6e interval, indicating that face-fusion in the kernel makes the supermolecular orbitals electronically nonclosing, i.e., there are unfilled supermolecular orbitals in Au_{38} and $Au_{36}Ag_2$ NCs.

DFT calculations are further performed to reveal the electronic structure of $Au_{36}Ag_2(SCH_3)_{18}$ near the HOMO–LUMO gap. The KS diagrams clearly demonstrate the trimeric electronic structure of the molecular orbitals (Figure 2a). The LUMO+1 and LUMO+2 orbitals are degenerate, and the energy levels of HOMO–1 and HOMO–2 are also very close to each other. As no existing triatomic molecule has a cyclic structure, we cannot find an isoelectronic analogue. Nevertheless, the lobes of the molecular orbitals of $Au_{36}Ag_2(SCH_3)_{18}$ remind us of BF_3 (Figure S5); the D_{3h} symmetric BF_3 molecule (24e) is not isoelectronic to $Au_{36}Ag_2(SCH_3)_{18}$ (20e). However, it is interesting to note that the HOMO–3 to LUMO+3 frontier orbitals of $Au_{36}Ag_2(SCH_3)_{18}$ are comparable to those of BF_3 , except the order of LUMO+1/+2 and LUMO+3 energy levels. The order shift is similar to that in the comparison between $Au_{38}(SR)_{24}$ and its isoelectronic F_2 molecule.³²

Hydrogen Evolution Reaction. Although Au and Ag are generally poor in HER catalysis, the $Au_{36}Ag_2(SR)_{18}$ NC with low ligand coverage (*vide infra*) motivated us to test its HER performance. Indeed, $Au_{36}Ag_2(SR)_{18}$ gives rise to a much-enhanced activity in the HER (Figure 3a), manifested in (1) the onset overpotential of $Au_{36}Ag_2(SR)_{18}$ to generate H_2 is ~ 0.1 V smaller than that of $Au_{25}(SR)_{18}^-$ and $Au_{38}(SR)_{24}$ and

(2) the mass activity of the trimetric NC at an applied voltage of -0.3 V vs RHE is -19.4 mA cm^{-2} , which is 3.8 times that of $Au_{25}(SR)_{18}$ (-5.1 mA cm^{-2}) and 5.1 times that of $Au_{38}(SR)_{24}$ (-3.8 mA cm^{-2}). The Tafel slopes (Figure 3b) of the NC series are determined to be 125, 118, and 133 mV dec^{-1} for $Au_{36}Ag_2(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{25}(SR)_{18}^-$, respectively. These similar values indicate similar surface chemistry and the same rate-limiting (Volmer) step for all these three catalysts.

The catalytic activity of the NC series toward HER was further evaluated by DFT (Figure 3c). Fully ligand-protected Au NCs are typically poor catalysts as they exhibit highly endergonic binding energies (>1.2 eV) for hydrogen (H) adsorption.³³ However, it is evident that fully ligated $Au_{36}Ag_2(SCH_3)_{18}$ has a significantly lower binding energy of hydrogen ($\Delta G = 0.83$ eV, Figure 3c) to form the $*H$ intermediate than $Au_{25}(SCH_3)_{18}^-$ (1.29 eV) or $Au_{38}(SCH_3)_{24}$ (1.35 eV).

The electrochemically active surface areas (ECSA) of the NC series were also measured (Figure S7). The results show that $Au_{25}(SR)_{18}^-$ (2.15 mF cm^{-2}) and $Au_{38}(SR)_{24}$ (2.27 mF cm^{-2}) have similar active surface areas, which is consistent with our HER voltammograms and DFT calculations (Figure 3a/c, green/black lines). By contrast, $Au_{36}Ag_2(SR)_{18}$ shows a much larger ECSA (3.86 mF cm^{-2}) than those of the monomeric- I_h and dimeric- I_h counterparts (Figure S7d), hence, providing a direct evidence that the much improved HER of $Au_{36}Ag_2(SR)_{18}$ is related to its trimeric- I_h structure with a larger active surface area or lower ligand coverage (*vide infra*).

The stability test was performed by cycling the catalyst 1000 times within 0.1 V to -0.6 V (Figure 3a, red dot line). The voltammetry curves before and after the stability test prove the high stability of our catalyst.

The most feasible active sites for H adsorption are found to be the kernel's shell Au atoms, i.e., Au_{12} shell for $Au_{25}(SR)_{18}^-$, Au_{21} shell for $Au_{38}(SR)_{24}$,^{19,34} and $Au_{27}Ag_2$ shell for $Au_{36}Ag_2(SR)_{18}$ (Figure 3d). The optimized structures of the three NCs with one H adsorbed on the kernel's shell are shown in Figure 3e, where the H attaches to an atom of the I_h

Au₁₂ shell in Au₂₅(SCH₃)₁₈[−] (Figure 3e, left);^{19,34} for Au₃₈(SCH₃)₂₄, the hydrogen binds at the bridging site of two fused icosahedrons (Figure 3e, middle),¹⁹ whereas the HER active site on Au₃₆Ag₂(SCH₃)₁₈ is any of the exposed Au on each I_h (Figure 3e, right). Note that due to the high symmetry of these NCs, beside the selected positions shown in Figure 3e, other sites can also form *H with similar energies and thus constitute active sites. Typically, the number of surface atoms required to adsorb hydrogen³⁴ is similar for most Au_n(SR)_m NCs from small to large size.²⁰ With the same mass (0.5 mg) of NCs, the surface atoms ($N_{\text{surf.}} = 8.46 \times 10^{17}$) for the tri-I_h Au₂₇Ag₂ shell of Au₃₆Ag₂(SR)₁₈ is much higher than 5.87×10^{17} for the bi-I_h Au₂₁ shell of Au₃₈(SR)₂₄ and 4.89×10^{17} for the mono-I_h Au₁₂ shell of Au₂₅(SR)₁₈ (Figure S8).

The higher HER activity of Au₃₆Ag₂(SR)₁₈ is also related to its greater negative electron affinity (Au₃₆Ag₂(SCH₃)₁₈, EA = −2.65 eV, compared to Au₂₅(SCH₃)₁₈[−] with EA = 0.41 eV, and Au₃₈(SCH₃)₂₄ with EA = −2.31 eV), implying more favorable electron acceptance, which in turn can be crucial for the first reaction step involving proton coupled electron transfer (Volmer step, H⁺ + e[−] + * → *H). The electron affinity trend of the three NCs is consistent with their corresponding LUMO state energies (Figures S4a and S6). We correlate the favorable electron affinity of Au₃₆Ag₂(SR)₁₈ to its unfilled supermolecular orbitals, i.e., the electronic shell closing trimeric supermolecule would have 24e distributed in 12 MOs (which originate from 1S1P (4 AOs) of each I_h unit), but Au₃₆Ag₂(SR)₁₈ has only 20e, leaving two supermolecular orbitals being empty to accept electron(s) upon applied voltage, hence enhancing the catalytic activity. Note that Au₃₈(SR)₂₄, resembling a disuperatomic supermolecule, also has an empty supermolecular orbital³⁵ and EA slightly lower than Au₃₆Ag₂(SR)₁₈; however, the energy for *H adsorption on Au₃₈(SCH₃)₂₄, i.e., the energy difference between the catalyst with and without a *H, is very positive and offsets such an advantage, resulting in high ΔG (Figure 3c). DFT calculations also indicate that the hypothetical trimeric Au₃₈(SCH₃)₁₈ (replacing the central Ag₂ with Au₂) would be even better as HER catalyst due to its even lower *H bonding energy of 0.63 eV and even higher EA of −2.77 eV. We further probe the HOMO and LUMO of the two NCs to understand the *H bonding. Although there is no significant hybridization of the *H atomic orbitals in the HOMO of both hypothetical Au₃₈(SCH₃)₁₈ and experimental Au₃₆Ag₂(SCH₃)₁₈ (Figure S9, bottom row, denoted by the black arrow), a considerable hybridization is observed in the LUMO of Au₃₈(SCH₃)₁₈ (Figure S9, top left), but hybridization is absent in that of Au₃₆Ag₂(SCH₃)₁₈ (Figure S9, top right, indicated by red circle). Such hybridization differences result in the lower *H bonding energy on Au₃₈(SR)₁₈ compared to Au₃₆Ag₂(SCH₃)₁₈. However, there is no success yet in the synthesis of Au₃₈(SR)₁₈.

One may argue that, compared to Au₂₅(SC₂H₄Ph)₁₈ and Au₃₈(SC₂H₄Ph)₂₄, the different ligand on Au₃₆Ag₂(SC₁₀H₁₅)₁₈ might also be responsible for the high HER performance. This is not the case, because the adamantanethiolate ligand on Au₃₆Ag₂ is actually much bulkier at the Au–S interface than the SC₂H₄Ph ligand on Au₂₅ and Au₃₈ and thus would decrease the catalytic activity, but Au₃₆Ag₂(SR)₁₈ instead shows the best activity in the series. Overall, even with the adverse effects of the adamantanethiolate, Au₃₆Ag₂(SR)₁₈ still shows much higher catalytic activity than the other two NCs in the series,

indicating the dominant roles of geometrical and electronic effects of the metal core.

Low Ligand Coverage and Low-Coordinated Au Atoms. Although the number of kernel atoms increases from bi-I_h Au₂@Au₂₁ in Au₃₈(SR)₂₄ to tri-I_h Au₃@Au₂₇Ag₂ in Au₃₆Ag₂(SR)₁₈, the total metal number in Au₃₆Ag₂(SR)₁₈ does not change compared to Au₃₈(SR)₂₄. Interestingly, Au₃₆Ag₂(SR)₁₈ has a much smaller number of ligands (18 only), being the same as that of Au₂₅(SR)₁₈ (Figure 4, inset).

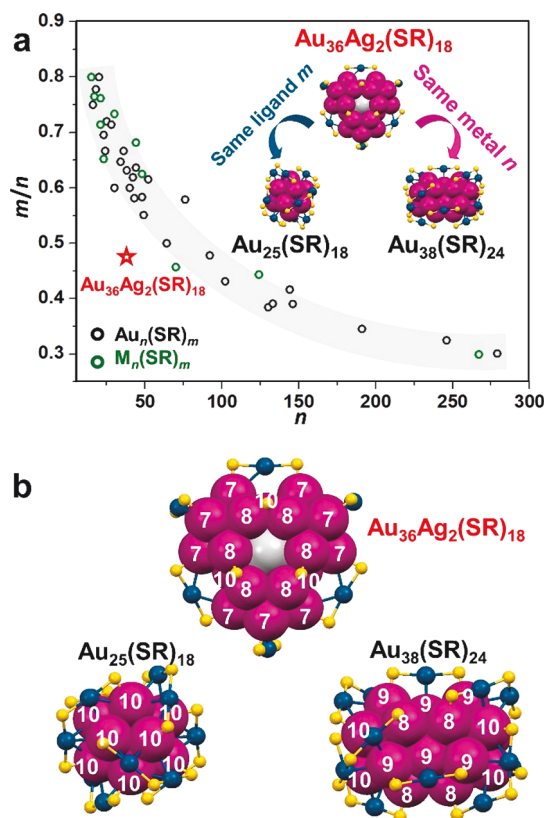


Figure 4. (a) The plot of ligand/metal number ratio (m/n) versus metal number (n). (b) The coordination numbers of Au atoms on the kernel's surface of Au₃₆Ag₂(SR)₁₈, Au₂₅(SR)₁₈[−], and Au₃₈(SR)₂₄.

As a result, the thiolate coverage becomes much lower on Au₃₆Ag₂(SR)₁₈ ($18/38 = 0.47$). The plot summarizes the ligand coverages for the reported homogold Au_n(SR)_m and Au-based alloy Au_{n-x}M_x(SR)_m (M = Ag/Cu/Cd) NCs of atomic precision (Figure 4/Table S2). One can see that all of the previous Au_n(SR)_m and Au_{n-x}M_x(SR)_m are located within the gray belt, indicating common ligand coverages based on the metal atom numbers.³⁶ However, the new Au₃₆Ag₂(SR)₁₈ deviates significantly from the common ratios at the same metal number (n). The bulky adamantanethiolate ligand is crucial in the formation of the unique trimeric-I_h kernel of Au₃₆Ag₂(SR)₁₈. It is worth noting that other bulky ligands were also used previously to reduce the ligand coverage on Au NCs.^{37,38} Our current work demonstrates the promise of the ligand strategy for designing effective HER catalysts.

This feature of low ligand coverage is important for the high HER activity of Au₃₆Ag₂(SR)₁₈, as it relates to the lower coordination number of the metal atoms on the active site, which is critical for enhancing HER on Au nanocatalysts.³⁹ For example, laser-generated high density of stacking faults make

Ag NPs more active in HER catalysis due to the metal site's lower coordination.⁴⁰ Our approach of atomically precise nanochemistry further controls the distribution of low-coordination sites even when the sizes (number of metal atoms) of catalysts are the same. As to Au NCs, doping Ag into the Au₁₂ shell in Au_{25-x}Ag_x(SR)₁₈⁻ ($x \sim 4.5$), however, resulted in deteriorated HER performance compared to homogold counterpart.²⁰ Although the central Ag atoms in Au₃₆Ag₂(SR)₁₈ have high coordination numbers (adverse for *H adsorption), most of the Au atoms on the Au₂₇Ag₂ shell are only 7 or 8 coordinated (both neighboring metal and S atoms counted) as indicated by SCXRD (Figure 4b, top), hence, favoring H adsorption. By contrast, the coordination number for each of the 12 Au shell atoms in Au₂₅(SR)₁₈⁻ is 10, and that of the Au₂₁ shell atoms in Au₃₈(SR)₂₄ is 8 to 10 (Figure 4b, bottom). Thus, low coordinated Au atoms on Au₃₆Ag₂(SR)₁₈ also explain its much-improved H₂ generation by lowering the adsorption energy barrier.

CONCLUSIONS

Although Au and Ag have long been known as poor electrocatalysts for HER, our work demonstrates that tailoring of the geometrical and electronic structures can turn the particles into highly active HER catalysts. Specifically, a trimeric Au₃₆Ag₂(SR)₁₈ NC is obtained, and its structure exhibits three I_h units face-fused together in the kernel. This NC can be regarded as a trimeric supermolecule with 20e (rather than the commonly observed 3 × 8e = 24e) and thus exhibits two empty supermolecular orbitals. DFT calculations reveal that the binding energy of H on the active site of Au₃₆Ag₂(SR)₁₈ is >0.45 eV lower than those of Au₂₅(SR)₁₈ and Au₃₈(SR)₂₄ in the series, and its electron affinity is also higher. The high activity of Au₃₆Ag₂(SR)₁₈ originates from several distinct factors: (1) more active sites on the NC surface for H adsorption; (2) the extraordinarily low ligand-to-metal ratio leads to exposure of low-coordinated surface Au atoms for H coordination; (3) the unfilled supramolecular orbital for easier electron acceptance from the electrode and thus faster electron transfer; (4) compared to other Au NCs, the lower H binding energy (related to the lower coordination number of Au atoms) and higher electron affinity (related to more negative LUMO) for an energetically feasible HER pathway. Overall, this work opens a new strategy for nanocatalyst design by tailoring the geometrical and electronic structures of metal NCs at the atomically precise level for customized applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c04606>.

Details of synthesis, characterizations, including MS, X-ray crystallography, electrochemical measurements details, computational details, and KS orbital analysis (PDF)

Accession Codes

CCDC 2081877 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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