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Atomically precise $\text{Au}_x\text{Ag}_{25-x}$ nanoclusters with a modulated interstitial Au–Ag microenvironment for enhanced visible-light-driven photocatalytic hydrogen evolution†

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Herein, we report the study of atomically precise $\text{Au}_x\text{Ag}_{25-x}$ nanoclusters (NCs) toward photocatalytic hydrogen evolution. The incorporation of Au atoms into Ag_{25} NCs not only narrowed the HOMO–LUMO gaps but also created an interstitial Au–Ag microenvironment, which promoted the photogenerated charge carrier utilization and optimized the reaction dynamics.

Metal doping or alloying in heterogeneous catalysis provides opportunities to tailor the properties of catalysts, enhance their activity, selectivity and stability, and enable new catalytic reactions.^{1–3} In the nanoparticle regime, bimetallic nanocrystals exhibit superior performance over individual metal nanocrystals due to the synergistic effect. By varying the ratio of the two metals, it is possible to control the surface composition and electronic structure of the nanocrystals, thus allowing for fine-tuning of the catalytic activity, selectivity, and reaction kinetics.^{4–6} However, achieving precise atomic-level control over the composition of bimetallic nanocrystals is challenging due to synthetic limitations.

Metal nanoclusters (NCs), with atomic precision, represent a class of materials with tunable geometric structures at the atomic level.^{7,8} This unique characteristic makes them ideal models for studying the relationship between defined NC structures and their physicochemical properties.^{9–12} Furthermore, the broad light absorption within the UV-visible region and excellent stability in corrosive redox environments make metal NCs promising for solar energy conversion devices.^{13–15} For instance, using a glutathione-protected Au_{18} NC as a sensitizer, a solar cell achieved a power conversion efficiency of 3.79%. Incorporating Ag into Au_{18} increased the efficiency to 4.22%.¹⁶ Although the impact of hetero metal doping on the

New concepts

As one of the emerging light absorbing materials, metal nanoclusters with distinctive electronic structures have stimulated intensive research in solar energy conversion. In the past decade, efforts have been made towards the synthesis and structure determination of nanoclusters, while studies on the relationship between their structures and physicochemical properties are rare. Studying nanoclusters from the perspective of structure–activity relationships is of great significance to push nanoclusters into practical applications. In this work, we synthesized Au_{25} , Ag_{25} and alloy $(\text{AuAg})_{25}$ nanoclusters protected by 2,4-dimethylbenzenethiol, which were subsequently utilized as photosensitizers for photocatalytic hydrogen evolution. Physicochemical characterizations and DFT calculations allowed us to gain insight into the enhanced photocatalytic activities at the molecular level: a unique Au–Ag microenvironment was created by the simultaneous functioning of Au and Ag sites in the nanoclusters, which not only contributed to the separation of photogenerated charge carriers, but also balanced the hydrogen adsorption/desorption on the surface of the nanoclusters. Besides, alloying Au into Ag_{25} nanoclusters strengthened the light adsorption capabilities, which could also contribute to the photocatalytic activities. As a result, the reactivities of the alloy $(\text{AuAg})_{25}$ nanoclusters outperformed their single metal nanocluster counterparts (up to ~5 times higher).

performance of pristine metal NCs has been extensively investigated, systematic studies on bimetallic NCs and their individual metal counterparts have been hindered by synthesis challenges.^{17–23}

Due to the small size of metal NCs, they possess a high surface-to-volume ratio, with most of the metal atoms located on the surface and bound to ligands.^{24,25} Since ligand affinities to different metals vary, the coordination modes and NC structures may differ.^{10,26} As an example, the well-known Au_{25} NCs with a solved structure are protected by aliphatic 2-phenylethanethiol (PET), while the Ag_{25} NCs with a solved structure are protected with aromatic thiol. Doping Ag into $\text{Au}_{25}(\text{PET})_{18}$ successfully yields $(\text{AuAg})_{25}(\text{PET})_{18}$.²⁷ However, Ag_{25} NCs protected by PET remain unavailable.²⁸ Recently, Wang *et al.* reported a universal synthesis approach for preparing Au_{25} NCs protected by various aromatic thiols, enabling a comparison between the properties of bimetallic NCs and their

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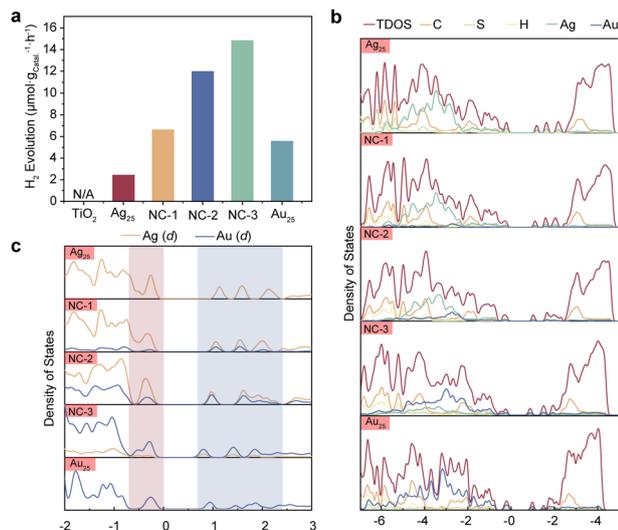


Fig. 2 (a) Hydrogen evolution under visible light irradiation. (b) Density of states projected to each atom. (c) Density of states projected to the d states of Ag and Au atoms.

facilitate the flow of photoinduced electrons from the LUMO+X states to the CB (Fig. S7, ESI†). However, there are other competitive pathways for these electrons. In the case of photo-excited dye systems, electrons on the LUMO can return to their ground state or participate in reduction reactions.³⁸ Since most dyes are catalytically inactive, hydrogen evolution only occurs when these electrons flow to the semiconductor. In contrast, metal NCs exhibit both photoactivity and catalytic activity.^{39–41} Therefore, enhancing the composite's performance under visible light is achievable if the photoinduced electrons remain at the metal NCs and reduce the hydrogen ions adsorbed onto them. This proposed mechanism is illustrated in Fig. S8 (ESI†). In order to gain these molecular-level insights, we performed a series of DFT calculations, including the electronic structures and the charge dynamics when hydrogen was adsorbed on the NC surface. Firstly, we started with the electronic structures of the NCs by comparing the projected density of states of the NCs. As it is shown in Fig. 2b, the HOMO and LUMO states were greatly contributed by the metallic d states from Ag and Au. Different from the case of pristine Ag₂₅ NCs, the PDOS of Au atoms in the Au₂₅ NCs exhibited broad distribution rather than isolated peaks within a wide range of energies of HOMO states (Fig. 2c). This indicates that the d states in the Au₂₅ NCs are more delocalized than that in the pristine Ag₂₅ NCs. Similar phenomena were also observed in the bimetallic clusters, indicating that alloying has a great impact on the electronic structures. It can also be observed that both the bonding and antibonding d states of Au have been strongly overlapped with the Ag counterparts in the bimetallic NCs. This overlapping PDOS of the d orbitals of the Ag and Au atoms suggests the formation of diffuse superatomic d-type orbitals, which could facilitate the transfer of hot electrons in space.^{42,43}

Besides, the Bader charge and charge density difference analysis provided direct evidence for this electron transfer behavior. The net charges on each atom with a negative sign

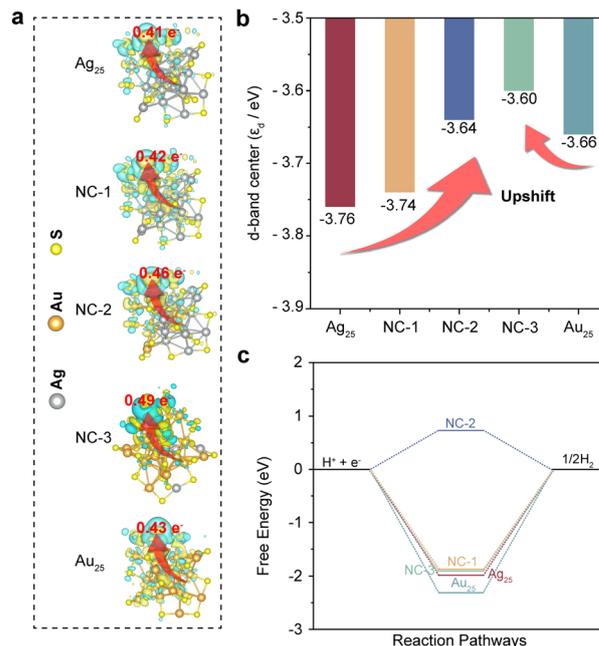


Fig. 3 (a) The isosurfaces of charge density difference of H* adsorbed NCs; (b) the relationships of d-band center of the NCs; (c) the calculated free energy diagram of the HER on the motif scaffolds at the equilibrium potential, respectively.

(depletion) indicating the loss of charge (positively charged) and a positive sign (accumulation) indicating the excess of charge (negatively charged). The calculated Bader charges of H* for hydrogen-adsorbing metal sites on each NC are shown in Fig. 3a, where the values were calculated to be 0.41 e⁻, 0.42 e⁻, 0.46 e⁻, 0.49 e⁻ and 0.43 e⁻ for Ag₂₅, NC-1, NC-2, NC-3 and Au₂₅, respectively. Therefore, electrons are more likely to be transferred to the adsorbed proton to catalyze the hydrogen evolution in bimetallic NCs, especially NC-3. Moreover, after the absorption of a hydrogen atom, all the bimetallic NCs displayed increased charge density area around both the Ag and Au site, which was clearly shown in the isosurfaces of charge density difference in Fig. 3a. Hence, the Au–Ag sites would be electron acceptor centers for catalyzing the hydrogen evolution, which is in accordance with the results obtained from Bader charge analysis.²⁴ Moreover, the d-band features (ϵ_d) of the clusters were also investigated. The ϵ_d of Au and Ag atoms in the bimetallic NCs showed upward shifts compared to the pristine Ag₂₅ and Au₂₅ NCs (Fig. 3b). The upward shift of ϵ_d would result in a decrease in the electron filling of the anti-bonding states, which could contribute to the adsorption of the reaction intermediate on the catalyst surface. In contrast, the downward shift of ϵ_d would facilitate the desorption of the reaction intermediate on the catalyst surface.^{44–46} Based on the results obtained above, the impact of the dual metal sites on charge dynamics in the bimetallic NCs can be proposed. The introduction of Au sites into Ag₂₅ NCs leads to the delocalization and hybridization of metallic d orbitals, forming diffuse superatomic d-type orbitals. As verified by Bader charge and charge density difference analysis, the diffuse superatomic d-type



orbitals can facilitate the transfer of photoinduced electrons to the adsorbed proton for photocatalytic reactions, which hinders the electrons from bulk recombination or migration to the CB of TiO₂. However, with the increase of the amount of Au sites in NC-3 the Ag₂₅ NCs, the positive impact on the charge dynamics for HER reactions would decrease, as confirmed by the downward shifted ϵ_d and Bader charge values of Au₂₅ compared to NC-2 and NC-3. Therefore, the unique microenvironment created by the Au–Ag dual metal sites also plays a vital role in optimizing the photocatalytic activities.

Moreover, further calculations from the perspective of reaction dynamics were performed to investigate the reaction pathways on the surfaces of the NCs. H⁺ + e⁻, adsorbed hydrogen (H*) and 1/2H₂ were considered as the initial, intermediate and final states of the reaction, respectively. The calculated free energy diagrams of the HER process on the Ag atoms of each NC were presented in Fig. 3c. Ag₂₅, NC-1, NC-3 and Au₂₅ NCs showed large upslopes with negative values of -1.95 eV, -1.94 eV, -1.86 eV and -2.31 eV, respectively, while NC-2 showed the smallest upslope with a positive value of 0.73 eV. However, the hydrogen adsorption/desorption was balanced by the Au–Ag sites because of orbital modulation, giving rise to the smallest upslope of 0.73 eV. Therefore, hydrogen desorption could be considered as the rate-determining step in the HER process for Ag₂₅, NC-1, NC-3 and Au₂₅ NCs. Compared with Au₂₅, who had the largest upslope with a negative value of -2.31 eV, the other three clusters showed more positive free energy changes, especially in the case of NC-2. The interaction energy made them more energetically favored for hydrogen adsorption compared to Au₂₅ NCs. It is reported that the reaction rate of the HER depends on the upslope process in the HER free energy diagram. With a much smaller positive upslope value, the interaction between hydrogen and the NC-2 surface would reach a more balanced hydrogen adsorption/desorption process involved in the HER process.^{47–49} Combining the results obtained from ϵ_d and reaction free energy analysis, it is proved that the unique microenvironment created by the dual Au–Ag sites not only optimizes the charge dynamics, but also the adsorption/desorption of intermediates. As a result, the HER sites on the NCs were readily modulated, making the HER rates of the bimetallic NCs much faster than the pristine Ag₂₅ and Au₂₅ counterparts.

Conclusions

In summary, we have studied the sensitizing capabilities and reaction dynamics of bimetallic Au_xAg_{25-x} NCs toward visible-light-driven photocatalytic hydrogen evolution. The incorporation of Au atoms into Ag₂₅ NCs narrowed the HOMO–LUMO gaps and modified the electronic configurations of the NCs. The unique microenvironment created by the dual Au–Ag sites in the bimetallic NCs helped to form electron-acceptor sites and upshifted the d-band centers, which hinders the electrons from bulk recombination and promotes the H₂ evolution process. On the other hand, the simultaneous role of the dual metal sites offered moderate hydrogen adsorption/desorption dynamics,

which further optimized the overall photocatalytic process. As a result, the photocatalytic activities of the NCs followed an order of NC-3 > NC-2 > NC-1 > Au₂₅ > Ag₂₅. These results provide molecular insights into the origin of the photocatalytic activities of NC-based materials.

Author contributions

Y. W. and N. P.: conceptualization. Y. L. synthesized all the NCs, and performed all the physiochemical characterizations and DFT calculations. X. H. L. and Z. L. conducted the photocatalysis experiments. Data plotting and analysis were performed by Y. L. The manuscript was drafted by Y. L. and Y. W. and then revised by all the co-authors.

Conflicts of interest

There are no conflicts to declare.

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