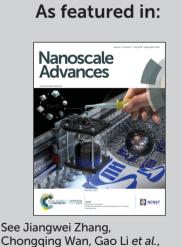


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Tailoring the stability, photocatalysis and photoluminescence properties of Au₁₁ nanoclusters *via* doping engineering

The atomically precise structure of $Au_8Ag_3(PPh_3)_7Cl_3$ alloy nanoclusters with multiple Ag doping in a C_3 axis manner is determined by SXRD for the first time. The photothermodynamic and electrochemical stability remarkably improved as compared with that of $Au_{11}(PPh_3)_7Cl_3$ nanoclusters, evidenced by UV-vis and DPV respectively. $Au_8Ag_3(PPh_3)_7Cl_3$ exhibits PL enhancement and two time activity of $Au_8Ag_3(PPh_3)_7Cl_3$ in the photooxidation of benzylamine. Controllable heteroatom doping engineering is a powerful strategy to mediate electronic properties of clusters and improve their stability for photocatalytic performances.





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Tailoring the stability, photocatalysis and photoluminescence properties of Au₁₁ nanoclusters *via* doping engineering†

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Dopants in gold nanoclusters have been proved to mediate the intrinsic electronic properties of homoclusters. In this work, we report the precise synthesis of atomically precise Au₈Ag₃(PPh₃)₇Cl₃ alloy nanoclusters with multiple Aq dopants for the first time. Their structure was resolved by single-crystal Xray crystallography. $Au_8Ag_3(PPh_3)_7Cl_3$ nanoclusters possessed a similar structure topology to the wellknown Au₁₁(PPh₃)₇Cl₃ nanoclusters. It is observed that the three Ag atoms were fixed at the cluster surface and bound selectively with the chlorine ligands in a C_3 -axis manner. The alloy nanoclusters exhibited a closed-shell electronic structure (i.e., $8(Au 6s^1) + 3(Aq 5s^1) - 3(Cl) = 8e$), as evidenced by electrospray ionization-mass spectrometry (ESI-MS). The photothermodynamic stability of alloy clusters was remarkably improved (e.g., full decomposition after 7 days under sunlight irradiation vs. 3 days for $Au_{11}(PPh_3)_7Cl_3$ clusters). DFT calculations indicated that the Aq dopants in a C_3 -axis manner could obviously delocalize the electrons of Au to the orbitals of P atoms and then mediate the electronic property of the clusters. Shrinkage of the HOMO-LUMO gap to 1.67 eV of Au₈Aq₃(PPh₃)₇Cl₃ was observed as compared with that of homo-nanoclusters of Au₁₁(PPh₃)₇Cl₃ (2.06 eV). The electrochemical gap of $Au_8Ag_3(PPh_3)_7Cl_3$ alloy nanoclusters was 1.272 V, which was higher than that of $Au_{11}(PPh_3)_7Cl_3$ nanoclusters, which indicated higher electrochemical stability, as evidenced by the differential pulse voltammetry (DPV) method. Au₈Aq₃(PPh₂)₇Cl₃ clusters exhibited three specific photoluminescence peaks at 405, 434 and 454 nm. AuAg alloy clusters exhibited twofold greater activity than homo gold clusters in the photooxidation of benzylamine, which was mainly due to the unique electronic properties of the alloy clusters. Controllable heteroatom doping engineering is a powerful method to tune the electronic properties of clusters, and then improve their photothermodynamic and electrochemical stability simultaneously for potential photocatalytic applications.

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Introduction

Gold nanoclusters with atomic precision have emerged as a novel, robust class of nanomaterials over the last decade.¹⁻³

These gold nanoclusters are usually protected by thiolate, phosphine and alkyne ligands, which are exploited widely in the areas of photosensitizers, electronics, biomedicine, and catalysis.4-10 These nanoclusters exhibit a nonmetallic nature due to electron energy quantization arising from a quantum size effect, which exerts a strong influence on their physical and chemical properties. With regard to phosphine-stabilized gold nanoclusters, $Au_{11}(PPh_3)_{7/8}X_{3/2}$ (X = SCN, Cl, or Br) nanoclusters are the most well-known and investigated nanoclusters, which were discovered in the 1980s. They are composed of an 11-atom incomplete icosahedral kernel, which is derived from the icosahedral Au13 synthon through etching and removal of two gold atoms. 11,12 The major drawback of these phosphinestabilized Au nanoclusters is very poor stability because the electron-rich phosphine groups oxidized readily and detached from the surface of gold nanoclusters. Subsequently, the phosphine-capped Au nanoclusters will decompose rapidly to Au(0) species (e.g., gold mirrors) in a few days, especially under light irradiation in air, which limits their practical applications

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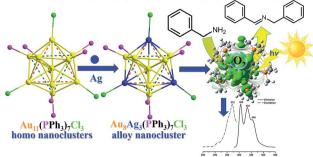
significantly. An effective strategy is urgently required to enhance the stability of these nanoclusters.

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Recently, several scholars have discovered that doping of heteroatom metal atoms in Au nanoclusters can mediate their electronic properties (e.g., optical property, stability) even though these nanoclusters with heteroatom metal dopants often exhibit similar topological frameworks. 13-16 It is well known that Pd and Pt heteroatoms in the gold nanoclusters can improve the stability of nanoclusters considerably. 17,18 For example, Negishi and colleagues synthesized mono-Pd-doped Pd₁Au₁₀(PPh₃)₈Cl₂ nanoclusters, and showed much better stability against the homo-nanocluster Au₁₁(PPh₃)₈Cl₂.¹⁷ Also, the photoluminescence (PL) property of such alloy nanoclusters was modified. Similarly, the Au₂₄Pt₁(SR)₁₈ nanoclusters improved the thermal and antioxidation stabilities considerably compared with homo Au₂₅(SR)₁₈.18 In such Pd and Pt doping modes, heteroatoms are located in the center of the metal core mode with only mono-atom.

An Ag doping strategy in Au_{25} nanoclusters has also been investigated intensively.³ However, in all cases, gold nanoclusters with Ag dopants have been shown to decrease their stability.¹⁹⁻²¹ In our previous study, the $Ag_xAu_{25-x}(SR)_{18}$ (where, x: 1 to 13, and SR represents thiolate) showed very poor stability upon exposure to sunlight. The alloy clusters quickly decomposed to Au(i):SR and Ag(i):SR complexes in a CH_2Cl_2 solution in a few hours.²⁰ Similar phenomena have been observed in $Ag_x-Au_{25-x}(PPh_3)_{10}(SR)_5Cl_2$, $Ag_xAu_{38-x}(SR)_{24}$ and $Ag_xAu_{144-x}(SR)_{60}$ systems. Thus, multiple doping of Ag atoms into Au nanoclusters in a precise manner and maintaining/improving their stability (e.g., under sunlight irradiation) are big challenges. Doping multiple Ag dopants into Au_{11} nanoclusters in a precise manner has not been achieved yet.

Herein, we developed a novel synthetic protocol to afford Au₈Ag₃(PPh₃)₇Cl₃ (abbreviated as Au₈Ag₃) alloy nanoclusters with multiple Ag dopants. Its precise crystal frameworks were determined fully by single crystal X-ray crystallography. We found the surface gold (7) and silver (3) atoms to be bound selectively with the seven phosphine and three chlorine ligands, respectively. The three AgCl motifs located in the C3 axis in the Au₈Ag₃ alloy nanoclusters. Experimental evaluation showed that Au₈Ag₃ alloy nanoclusters were more stable than the corresponding homo-Au₁₁(PPh₃)₇Cl₃ nanoclusters under sunlight irradiation. Density functional theory (DFT) calculations indicated that the AgCl motifs in the C3 axis could obviously delocalize the electrons of Au to the orbitals of P atoms in PPh3 ligands and mediate the electronic property of Au₈Ag₃. A decrease in the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap would ensure easier excitation of the electrons of Au₈Ag₃(PMe₃)₇Cl₃ at a lower energy, resulting in PL enhancement. Au₈Ag₃ clusters exhibited specific three PL peaks at 405, 434 and 454 nm. The electrochemical gap of the Au₈Ag₃(PPh₃)₇Cl₃ alloy nanoclusters was 1.272 V, which was higher than that of $Au_{11}(PPh_3)_7Cl_3$, which suggested higher electrochemical stability as evidenced by differential pulse voltammetry (DPV). Besides, these Au₈-Ag₃(PPh₃)₇Cl₃ alloy nanoclusters exhibited twofold greater activity of the HOMO gold clusters in the photooxidation of C₃ axis multiple Ag doping (heteroatom doping engineering)



photoluminescence enhancement & photocatalysis improvement

Scheme 1 $Au_8Ag_3(PPh_3)_7Cl_3$ alloy nanoclusters synthesis through controllable multiple Ag doping of C_3 axes with photoluminescence enhancement and photocatalysis improvement.

benzylamine, which was due mainly to the unique electronic properties of the alloy nanoclusters (Scheme 1).

Experimental

Chemicals

All chemicals were commercially available in reagent grade and used as received without further purification. Hydrogen tetrachloroaurate(III) tetrahydrate (HAuCl₄·4H₂O, 99.95%) was purchased from HWG. AgSbF₆ (99.95%), dimethyl sulfide (Me₂S, 99%), sodium borohydride (NaBH₄, 98%), triphenylphosphine (98%), benzylamine (98%), P25, ethyl ether (99.5%), ethanol (99.5%), methanol (99.5%), acetonitrile (99%), and dichloromethane (99.5%) were purchased from Adamas-beta. Ultrapure water (resistance, 18.2 M Ω cm) was purified with a Barnstead Nanopure Di-waterTM system. All glassware was cleaned thoroughly with aqua regia (3 : 1 mix of hydrochloric acid and nitric acid), rinsed with copious amounts of ultrapure water, and then stored in an oven at 100 °C before use.

Synthesis of Au₈Ag₃ nanoclusters

All procedures were carried out in the dark under an air atmosphere. Ph $_3$ PAuCl was synthesized νia the reaction of HAuCl $_4$ and two equivalent PPh $_3$ in an ethanolic solution. Then, 25 mg of Ph $_3$ PAuCl (0.05 mmol) was dissolved in 1 mL of CH $_2$ Cl $_2$ solution, followed by addition of AgSbF $_6$ (17.2 mg in 1 mL of CH $_2$ Cl $_2$). The mixture was stirred for 10 min at room temperature. Then, the white AgCl solid obtained was filtrated and removed. The filtrate was reduced by NaBH $_4$ (0.5 mg in 1 mL of methanol) in an ice bath. After 36 h of stirring, the red-brown solution was filtered and concentrated to 1 mL. Diethyl ether was added and the solution volatilized for 1 week. The Au $_8$ Ag $_3$ clusters (\sim 5 mg) were collected as a red plate crystal. The cluster yield was \sim 24% based on Ph $_3$ PAuCl consumption.

X-ray crystallography

Suitable single crystals were selected and data from synchrotron radiation X-ray diffraction were collected at the BL17B beamline of the National Facility for Protein Science and Shanghai Paper Nanoscale Advances

Synchrotron Radiation Facility, China, using a constant wavelength of $\lambda = 0.65248$ Å and a large Debye-Scherrer camera. Data reduction, cell refinement and experimental correction of absorption were undertaken with software packages (HKL-3000 and Bruker APEX3). The cluster structure was solved by intrinsic phasing and refined against F^2 by the full-matrix least-squares method. Non-hydrogen atoms were refined anisotropically. All calculations were carried out by SHELX22 and Olex2 v1.2.10.23

Characterization

The UV-vis spectra of Au₈Ag₃ clusters (dissolved in CH₂Cl₂) were analyzed on a diode array spectrophotometer (8453) from Agilent Technologies. Electrospray ionization (ESI) mass spectra were obtained using a Waters quadrupole time-of-flight (Q-TOF) mass spectrometer equipped with a Z-spray source. The alloy clusters were dissolved in ethanol with CsOAc adducts. PL spectra were recorded on a spectrofluorometer (Fluorolog 3; Horiba) between 800 nm and 1500 nm using a liquid N2-cooled InGaAs detector, an excitation wavelength of 350 nm, slits of 14.7 nm, and a longpass optical filter at 550 nm between the sample and detector to block overtones from the excitation source. DPV measurements were made on a CHI 760E electrochemical station at room temperature under a N2 atmosphere with TBABF4 as the electrolyte and methanol as the solvent. A Pt wire (counter electrode), Pt working electrode, and Ag/AgCl quasi-reference electrode were used for DPV. Thermal gravimetric analysis (TGA) was undertaken on a Mettler Toledo TGA/SDTA851 in air flow of 50.0 mL min⁻¹ with heating rate of 20 °C min⁻¹.

Computational details

All DFT calculations were carried out with a Gaussian 09 program. Au₈Ag₃(PPh₃)₇Cl₃ and Au₁₁(PPh₃)₇Cl₃ clusters were simplified using Au₈Ag₃(PMe₃)₇Cl₃ and Au₁₁(PMe₃)₇Cl₃ molecular models, respectively. The geometries of Au₈Ag₃(PMe₃)₇Cl₃ and Au₁₁(PMe₃)₇Cl₃ were optimized fully via the DFT method with the Lee-Yang-Parr gradient-corrected correction function (B3LYP)²⁴⁻²⁶ in combination with two basis sets: the SDD basis set for Au and Ag atoms and the 6-31G(d) basis set for other elements. Calculated absorption spectra were obtained using the time-dependent density functional theory (TDDFT) method with the same functional and basis sets as mentioned above. To be consistent in experiments, the solvent (dichloromethane) was represented based on the polarizable continuum model using the integral equation formalism variant (IEF-PCM). 27-30

Photocatalysis of benzylamine

A 5 mg cluster was dissolved in 12 mL of dichloromethane, and then 1 g of P25 was added. After stirring for 1 h, the obtained solids were collected by centrifugation and washed thrice by dichloromethane. The solids were dried in a vacuum at 60 °C overnight to prepare the 0.5 wt% Au₈Ag₃/P25 and Au₁₁/P25 photocatalysts. Typically, 5 mg of photocatalysts, 20 mg of benzylamine, 0.1 mmol of p-xylene and 1 mL of CH₃CN was added in a 5 mL quartz tube with a magnetic stirrer. The system was fully furnished with O2. The tube was sealed and irradiated with a LED light (455 nm; Ceaulight) for 1 h. After the reaction,

the catalysts were separated by a membrane filter. The product solution was quantified by gas chromatography-mass spectrometry (GC-MS; 7890B GC system with 5977A MSD; Agilent Technologies). The conversion of benzylamine and selectivity for amine products were determined using internal standards. The photocatalysts were recovered by filtration and reused in the recyclability test with fresh solvent and reactants under identical conditions.

Results and discussion

Synthesis and structure determination of Au₈Ag₃ alloy nanoclusters

The Au₈Ag₃ alloy clusters were obtained by simultaneous NaBH₄ reduction of the mixture of Ph₃PAuCl and AgSbF₆ in a CH₂Cl₂ solution at 0 °C. A block-like crimson crystal was obtained via evaporation and resolved by X-ray crystallography.31 The Au₈Ag₃ clusters crystallized in the monoclinic group of $P2_1/n$, and the full framework is shown in Fig. 1a. The cluster exhibited a similar structure of the reported Au₁₁(PPh₃)₇Cl₃ (hereafter referred to as Au11) clusters12 and a C3 axis along the Ag3 plane (Fig. 1b). The three chlorine and seven phosphine ligands were coordinated selectively with the three Ag and seven Au atoms, leaving only one central Au atom in the M₁₁ kernel (Fig. 1). Such coordination selectivity arose because gold is substantially more electronegative than silver. The more electron-donating phosphine ligands prefer the more electronegative Au atoms, whereas the more electron-withdrawing halide ligands prefer the more electropositive Ag atoms.

A fixed number of three Ag atoms were doped controllably and precisely into the Au₁₁ framework in a C₃-axis manner in specific positions instead of a statistical distribution resembling Ag_xAu_{25-x} nanoclusters reported previously. 14a This phenomenon could be attributed to specific coordination selectivity in which the three "origin" Au atoms coordinated with three Cl atoms in the Au₁₁(PPh₃)₇Cl₃ framework are more prone to substitution by three Ag atoms to form Au₈Ag₃ alloy nanoclusters. Besides doping along the C3 axis, Ag could also

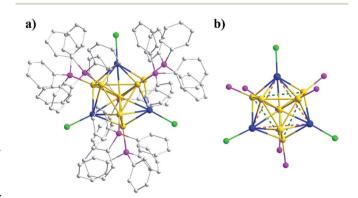


Fig. 1 (a) Complete structure of Au₈Ag₃(PPh₃)₇Cl₃ clusters. (b) Atomic arrangement of the Au₈Ag₃ kernel seen along the C₃ axis. Au: orange; Ag: blue; P: purple; Cl: green; C: gray. All the H atoms have been omitted for clarity. The chlorine and phosphine ligands bond the silver and gold atoms selectively, respectively.

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maximally delocalize the electrons of Au in the Au₈Ag₃ framework to enhance its stability, as supported by related DFT calculations (see below).

The selected bond lengths of Au₈Ag₃ are compiled in Table 1. Compared with Au₁₁, the average bond length of Au_(staple)-Au_(central) in Au₈Ag₃ clusters was shorter than that in Au₁₁ clusters (2.647 vs. 2.672 Å, Table 1, entry 1). However, the average of Ag_(Cl)-Au_(central) bonds in the Au₈Ag₃ cluster was much longer than the $Au_{(Cl)}$ - $Au_{(central)}$ of the Au_{11} (2.754 vs. 2.701 Å, Table 1, entry 2). These data suggested that the Au sphere in Au₈Ag₃ was reduced slightly (-0.49%) compared with Au₁₁ clusters. However, the Ag segment was stretched considerably (+1.96%). The kernel of M_{11} was mainly responsible for the HOMO-LUMO electronic transition of the clusters.³² The average Ag-Cl and Au-P bonds in Au₈Ag₃(PPh₃)₇Cl₃ were also much longer than these bonds in Au₁₁(PPh₃)₇Cl₃ (2.418 vs. 2.374 Å and 2.290 vs. 2.275 Å, Table 1, entries 3 and 4). Overall, the Ag dopants modified the topological framework of Au₁₁ clusters.

Characterization of Au₈Ag₃ nanoclusters

The final product of Au₈Ag₃ at a large scale (e.g., 10 mg) was analyzed further by UV-vis spectroscopy, and its purity was determined by ESI-MS. As seen in the Fig. 2a, the Au₈Ag₃ clusters exhibited three main UV-vis peaks at 417, 500 and 656 nm in the range 300-800 nm, which was remarkably different to the optical property of Au₁₁ clusters (black profile vs. red profile). The optical energy gap (derived from UV-vis spectroscopy) was 1.69 and 2.05 eV for Au₈Ag₃ and Au₁₁, respectively (Fig. S1†).

Next, the as-obtained nanoclusters were characterized by ESI-MS (Fig. 2b). No counter ion (e.g., Na⁺ and Cl⁻) was found in the single-crystal analysis, thereby implying the electrical neutrality of the nanocluster (vide supra). Therefore, cesium acetate was added to impart charges to the metal clusters to form [(cluster) $Cs_z|^{z+}$ (z=1, 2, 3, etc.) adducts before ESI-MS. Only one expected intense peak at m/z = 2053.77 Da was found in the positive-mode spectrum in the range of 1500 Da to 3500 Da (Fig. 2b). The spacing of the isotope patterns was 0.5 Da (Fig. 2b, inset), confirming that the adducts were double charged (i.e., z = 2). After detailed calculations, the molecular mass of the adducts was determined to be 3841.72 Da (i.e., $[2053.77 \times 2] - [132.91 \times 2]$ = 3841.72 Da) and, accordingly its chemical formula was determined to be Au₈Ag₃(PPh₃)₇Cl₃ (Au₈Ag₃P₇C₁₂₆H₁₀₅Cl₃, theoretical m/z: 3841.69 Da, deviation: +0.03 Da). Of note, the singly charged adduct (i.e., $[Au_8Ag_3(PPh_3)_7Cl_3]Cs^+$, m/z: 3974.64 Da) was beyond the limit of detection. The experimental isotope pattern matched well with the simulated one. Thus, the Au₈Ag₃ nanocluster had a closed-shell electronic structure (i.e., 8(Au 6s¹) + 3(Ag 5s¹) –

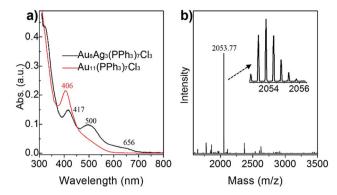


Fig. 2 (a) Comparison of the optical spectra of Au₁₁ and Au₈Ag₃ clusters. (b) Positive-mode ESI-MS of Au₈Ag₃; inset shows a close-up of the intense mass peak.

3(Cl) = 8e), implying that the alloy nanoclusters should exhibit good stability.

Thermal and photothermodynamic stability of the Au₈Ag₃(PPh₃)₇Cl₃ nanoclusters

To compare the thermal stability between Au₈Ag₃(PPh₃)₇Cl₃ alloy nanoclusters and Au₁₁(PPh₃)₇Cl₃ nanoclusters, TGA was conducted from 30 °C to 600 °C, respectively. Au₁₁(PPh₃)₇Cl₃ nanoclusters remained intact up to 250 °C. Complete desorption of ligands from nanocluster surfaces began from 250 °C to 600 °C with \sim 50% weight loss, which was highly consistent with the theoretical value (51.5 wt%). We found that Au₈Ag₃(-PPh₃)₇Cl₃ remained intact up to 200 °C, and complete desorption of ligands from nanocluster surfaces began from 200 °C to 600 °C with \sim 55% weight loss, which was highly consistent with the theoretical value (53.7 wt%) (Fig. S3†). The thermal stability of Au₁₁(PPh₃)₇Cl₃ was slightly better than that of Au₈Ag₃(-PPh₃)₇Cl₃. Thus, they should be thermally stable at room temperature with sunlight exposure. Under sunlight irradiation, their photothermodynamic stability is important.

Hutchison et al. reported that Au₁₁ clusters were not stable in CH₂Cl₂ solution in the presence of air; the clusters decomposed in a few hours.33 Recently, we found that the stability of Au11 nanoclusters was improved when using diphenyl-2pyridylphosphine (PPh₂Py) as capping ligands.³⁴ Here, we evaluated and compared the photothermodynamic stability of Au₈Ag₃ and Au₁₁ clusters under atmospheric condition with sunlight irradiation at room temperature for 1 week, which was monitored by UV-vis spectroscopy. Interestingly, an obvious gold mirror was seen on the wall of the glass beaker. Also, the CH₂Cl₂ solution became colorless, which was also evidenced by

Table 1 Comparison of the average bond lengths and angles in Au_{11} and Au_8Ag_3 clusters

Entry	Lengths (Å)	Au ₁₁	Au_8Ag_3	Ref. (%)
1	$Au_{(PPh3)}$ - $Au_{(center)}$	2.660 (2.608–2.678)	2.647 (2.605–2.669)	-0.49
2	$M_{(Cl)}$ -Au _(center)	2.701 (2.700-2.704)	2.754 (2.749-2.757)	1.96
3	M(Au/Ag)–Cl	2.374 (2.372–2.377)	2.418 (2.412-2.422)	1.85
4	Au-P	2.275 (2.269–2.285)	2.290 (2.273–3.295)	0.66

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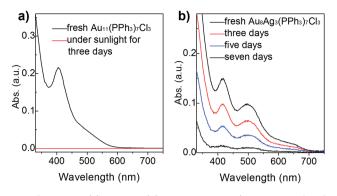
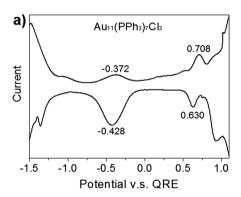


Fig. 3 Stability of (a) Au₁₁ and (b) Au₈Ag₃ clusters (dissolved in CH₂Cl₂ solution) under sunlight at room temperature for 1 week according to **UV-vis spectroscopy**

UV-vis spectroscopy (the spectrum became straight, Fig. 3a, red line). These results indicated clearly that the Au₁₁ clusters were not stable and decomposed to Au(0) species under sunlight irradiation, data that are consistent with the literature. 33 Au $_8$ Ag $_3$ alloy nanoclusters showed much greater stability under identical conditions. The intensity of the optical peaks decreased after 3 days (~66% clusters survived), and disappeared after 7 days under sunlight irradiation (Fig. 3b). These data strongly demonstrated that the Ag dopants in the Au₁₁ clusters improved the photothermodynamic stability considerably.



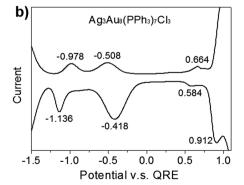


Fig. 4 DPV behaviour of (a) Au₁₁ and (b) Au₈Ag₃ nanoclusters (dissolved in methanol/0.1 M TBABF₄) on a Pt electrode at room temperature (measurement conditions: pulse cycle, 0.2 s; scan rate in either direction, 0.05 V s⁻¹).

Computational simulation

The absorption spectra of Au₁₁(PMe₃)₇Cl₃ and Au₈Ag₃(PMe₃)₇Cl₃ have been calculated based on ground-state geometries using the TDDFT method. The calculated results are compiled in Fig. 5. Au₁₁(PMe₃)₇Cl₃ gave maximum absorption at 343.9 nm, and Au₈Ag₃(PMe₃)₇Cl₃ showed two absorption bands at 261.4 and 382.5 nm, implying that more shells of electrons of Au₈Ag₃(-PMe₃)₇Cl₃ were excited in a shorter wavelength range. The delocalization effect of clusters induced decreasing energy. In addition, it would be easier for π electrons to be excited. For further analyses of the stability of Au₁₁(PMe₃)₇Cl₃ and Au₈Ag₃(-PMe₃)₇Cl₃, the energies and frequencies of Au₁₁(PMe₃)₇Cl₃, Au₈- $Ag_3(PMe_3)_7Cl_3$ and β - $Au_8Ag_3(PMe_3)_7Cl_3$ were calculated. Three PMe₃ ligands were grafted on Ag atoms whereas three Cl ligands was grafted on Au atoms in β-Au₈Ag₃(PMe₃)₇Cl₃ (Fig. S2†).

As shown in Table 2, the energies of Au₈Ag₃(PMe₃)₇Cl₃ and β- $Au_8Ag_3(PMe_3)_7Cl_3$ were lower than that of $Au_{11}(PMe_3)_7Cl_3$, implying that the former were more stable. The frequencies of β-Au₈Ag₃(PMe₃)₇Cl₃ were negative, indicating that β-Au₈Ag₃(-PMe₃)₇Cl₃ was not stable. As stated above, the electronegative nature of metals contributes to such coordination selectivity.

We wished to further illustrate the mediation of electronic property and HOMO-LUMO gap with regard to Ag dopants in a C₃-axis manner in Au₈Ag₃(PMe₃)₇Cl₃ alloy nanoclusters. Hence, the electron density map isocontours of fully optimized Au₈Ag₃(PMe₃)₇Cl₃ and Au₁₁(PMe₃)₇Cl₃ were calculated (Fig. 6). With Ag dopants, the electrons of Au were obviously delocalized to the orbitals of P atoms in PPh₃ ligands, whereas the electrons of Au assembled in the kernels of Au₁₁(PMe₃)₇Cl₃. Therefore, $Au_8Ag_3(PMe_3)_7Cl_3$ possessed higher stability. The

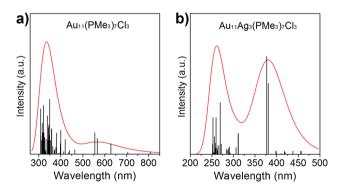


Fig. 5 Calculated UV-vis spectra of (a) Au₈Ag₃(PMe₃)₇Cl₃ and (b) Au₁₁(PMe₃)₇Cl₃ nanoclusters in CH₂Cl₂ solution.

Table 2 DFT results for the Gibbs (G) free energy, Hartree–Fock (HF) energy and frequencies of Au₈Ag₃(PMe₃)₇Cl₃, Au₁₁(PMe₃)₇Cl₃ and β-Au₈Cl₃Ag₃(PMe₃) models in gas phases

G (a.u.)	HF (a.u.)	Frequency (cm^{-1})
-6135.69	-6136.35	8.21
-6101.81 -6135.65	-6102.47 -6136.31	3.46 -9.93
	-6135.69 -6101.81	-6135.69 -6136.35 -6101.81 -6102.47

corresponding HOMO–LUMO gap of $Au_8Ag_3(PMe_3)_7Cl_3$ alloy nanoclusters was reduced to 1.67 eV, compared with that of $Au_{11}(PMe_3)_7Cl_3$ of 2.06 eV (Fig. 6), data that were consistent with the optical gaps (Fig. S1†). The shrinkage of the HOMO–LUMO gap would make excitation of the electrons in $Au_8Ag_3(PMe_3)_7Cl_3$ alloy nanoclusters easier at a lower energy, which may result in

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PL enhancement.8

We wished to further investigate mediation of electrochemical redox properties and electrochemical gap (EG) with regard to Ag dopants in a C_3 -axis manner in $Au_8Ag_3(PPh_3)_7Cl_3$ alloy nanoclusters. Hence, we compared the DPV data of Au_{11} and Au_8Ag_3 nanoclusters (Fig. 4).

The EG is defined as the gap between the first oxidation potential and the first reduction potential, which correlates to some fundamental physicochemical properties of materials, including electrochemical stability.35 The first oxidation wave (O1) and first reduction wave (R1) of Au₁₁ nanoclusters were at +0.708 and -0.372 V (versus the quasi-reference Ag electrode), respectively (Fig. 4a). Hence, the EG of Au₁₁ was 1.180 V. The O1, R1 and R2 of Au₈Ag₃ nanoclusters were at +0.664, -0.508 and -0.978 V, respectively (Fig. 4b). The EG of Au₈Ag₃ was 1.272 V (i.e., (+0.664 V) - (-0.508 V)), which was larger than that for Au₁₁. These data indicated that Ag dopants in a C₃-axis manner in Au₈Ag₃(PPh₃)₇Cl₃ alloy nanoclusters dramatically mediated its corresponding electrochemical redox property compared with homo-nanocluster Au₁₁(PPh₃)₇Cl₃ with a similar structure. The lower EG of Au₁₁(PPh₃)₇Cl₃ nanoclusters indicated that Au₁₁(PPh₃)₇Cl₃ nanoclusters were more prone to undergo redox processes, whereas the higher EG of Au₈Ag₃(PPh₃)₇Cl₃ alloy nanoclusters suggested that they had higher electrochemical stability. Heteroatom dopants could obviously mediate the corresponding electrochemical redox property.

PL properties of Au₈Ag₃(PPh₃)₇Cl₃

In recent years, the luminescence properties of gold clusters have motivated researchers due to their potential utility as new types of quantum dots.³⁶⁻³⁸ It has been reported that the PL of gold nanoclusters can be mediated by protecting ligands and other heteroatom metal dopants.^{17,39} For example, Negishi *et al.* demonstrated that PdAu₁₀(PPh₃)₈Cl₂ clusters exhibit strong PL

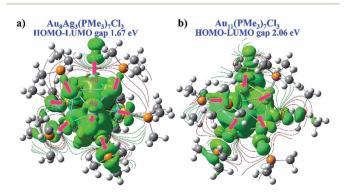
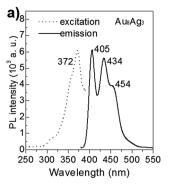


Fig. 6 DFT electron density map isocontours and HOMO–LUMO gap of (a) $Au_8Ag_3(PMe_3)_7Cl_3$ and (b) $Au_{11}(PMe_3)_7Cl_3$ from the same perspective.



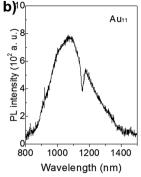


Fig. 7 PL spectra of (a) Au_8Ag_3 (excited at 372 nm) and (b) Au_{11} clusters (excited at 350 nm), dissolved in CH_2Cl_2 solution.

at 950 nm and that $Au_{11}(PPh_3)_8Cl_2$ clusters do not show luminescence. The unique PL properties of Au_8Ag_3 clusters are presented in Fig. 7. The Au_{11} clusters gave near-infrared PL, centered at ~ 1074 nm (1.16 eV), consistent with the reported result. The PL spectrum of Au_8Ag_3 clusters contained three main emission peaks centered at ca. 405 (~ 3.06 eV), 434 (2.86 eV), and 454 nm (2.73 eV), respectively, which were distinctly different compared with Au_{11} . Overall, these results suggested that Ag dopants definitely mediated the electronic structure of Au_8Ag_3 alloy clusters, thereby leading to PL enhancement.

Catalytic activity in the photocatalytic oxidation of amines

Very recently, free and TiO2-supported Au nanocluster catalysts have been applied in the photocatalytic oxidation of amines to imines, which are applied widely in dye industries. 40-43 Such photocatalytic oxidation involved activation of oxygen molecules.8,40 Imines are important versatile intermediates for fine chemicals and pharmaceuticals. The nature of the photothermodynamic stability (especially under light irradiation) and electrochemical stability of Au₈Ag₃(PPh₃)₇Cl₃ nanoclusters with a suitable lower HOMO-LUMO gap (1.67 eV) located in the sunlight range (1.55-2.06 eV) makes them promising material for amine photocatalysis. Thus, we explored and compared the photocatalytic properties of Au₈Ag₃ and Au₁₁ nanoclusters (supported on P25) via a one-step chemical transformation of benzylamine to N-(phenylmethylene)benzenemethanamine under LED light ($\lambda \sim 455$ nm) in the presence of molecular oxygen at room temperature.

The results of the photocatalysis are compiled in Table 3. The $Au_8Ag_3/P25$ catalysts gave 72.5% benzylamine conversion under irradiation for 1 h (Table 3, entry 2). Low conversion (37.8%) was found when using $Au_{11}/P25$ as catalysts under identical reaction conditions (Table 3, entry 3). The selectivity towards the N-(phenylmethylene)benzenemethanamine product was >99%. In a control experiment, the P25 support gave only 13.8% conversion with >99% selectivity (Table 3, entry 6). The turnover frequency of the $Au_8Ag_3/P25$ photocatalyst (turnover frequency = (reacted mol of amine)/[(mol of cluster) \times (reaction time in second)]) was calculated to be 2.92 s⁻¹. This value was \sim 2 times that for $Au_{11}/P25$ (1.51 s⁻¹), which was caused mainly by the unique electronic property of Au_8Ag_3 alloy

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Table 3 Photocatalysis of benzylamine over P25-supported Au₈Ag₃ nanoclusters in the presence of O_2^a

2 Ph
$$\sim$$
 NH₂ $\xrightarrow{O_2$, λ = 455 nm Ph \sim N \sim Ph

Entry	Catalyst	Conversion ^b (%)	Selectivity ^b (%)
1	Au ₈ Ag ₃ /P25	72.5	>99
2	Au ₁₁ /P25	37.8	>99
3	P25	13.8	>99
4^c	$Au_8Ag_3/P25$	_	_
5^c	$Au_{11}/P25$	_	_
6^d	$Au_8Ag_3/P25$	<1	_
7^d	$Au_{11}/P25$	<1	_
8	_	_	_
9^e	$Au_8Ag_3/P25$	70.8	>99
10^f	Au ₈ Ag ₃ /P25	71.7	>99

^a Reaction conditions: 20 mg of benzylamine, 0.1 mmol of p-xylene, 1 mL of acetonitrile, 10 mg of Au₈Ag₃/P25 or Au₁₁/P25 or P25 in the presence of O_2 at 30 °C under LED light centered at $\lambda \sim 455$ nm for 1 h. ^b The conversion of benzylamine and selectivity for imine were determined by GC-MS. ^c In absence of light. ^d Under a N₂ atmosphere. Second reuse of the Au₈Ag₃/P25 photocatalysts recovered from entry 1. Third reuse of the Au₈Ag₃/P25 photocatalysts recovered from entry 1.

clusters. Furthermore, Au₈Ag₃/P25 and Au₁₁/P25 photocatalysts showed no activity in the absence of light irradiation, and gave <1% conversion under a N₂ atmosphere (Table 3, entries 4-7). Meanwhile, conversion was not observed in the blank experiment without TiO2 and gold clusters (Table 3, entry 8). Next, we investigated the reusability of Au₈Ag₃/P25 photocatalysts under identical reaction conditions. During the second and third cycles, appreciable loss of catalytic activity or product selectivity were not observed (Table 1, entries 9 and 10). Overall, these catalysis results clearly demonstrated that photocatalytic oxidation was promoted by oxygen and was associated with the specific electronic property through heteroatom Ag dopants in gold nanoclusters as Au₈Ag₃(PPh₃)₇Cl₃ alloy nanoclusters. Actually, shrinkage of the HOMO-LUMO gap to 1.67 eV of Au₈Ag₃(PPh₃)₇Cl₃, as compared with 2.06 eV for homonanoclusters of Au₁₁(PPh₃)₇Cl₃, through Ag doping, was the reason for the higher photocatalytic activity of Au₈Ag₃. Metal nanoclusters with a suitably low HOMO-LUMO gap located at the sunlight range (1.55-2.06 eV) are more prone to generating ¹O₂ molecules via photoexcitation of metal nanoclusters, 8,40 which involves Dexter-type electron-exchange coupling between the metal nanocluster (serving as an excited photosensitizer) and ground-state 3O2 molecules. This would greatly enhance their corresponding photocatalytic-oxidation activity. For such metal nanoclusters with a HOMO-LUMO gap >2.06 eV that are out of the sunlight range, generation of ¹O₂ molecules is not possible, so they would not show photocatalytic oxidation.

Conclusions

In summary, a novel synthetic protocol to afford Au₈Ag₃(-PPh₃)₇Cl₃ alloy nanoclusters with precise Ag dopants in a controllable manner was developed. The precise atomic framework was determined by single-crystal X-ray diffraction. Au₈Ag₃(PPh₃)₇Cl₃ nanoclusters possessed a closed-shell electronic structure and a similar framework to Au₁₁(PPh₃)₇Cl₃ nanoclusters. The alloy clusters exhibited significant photothermodynamic stability (e.g., under sunlight irradiation) and electrochemical stability as evidenced by UV-vis spectroscopy and DPV, respectively, by comparison with homo-nanocluster Au₁₁(PPh₃)₇Cl₃ with a similar structure. DFT calculations indicated that the Ag dopants in a C3-axis manner obviously delocalized the electrons of Au to the orbitals of P atoms, and induced shrinkage of the HOMO-LUMO gap to 1.67 eV. These actions made excitation of the electrons of alloy clusters easier at a lower energy, resulting in PL enhancement. The EG of Au₈Ag₃(PPh₃)₇Cl₃ alloy nanoclusters was 1.272 V, which is higher than that of Au₁₁(PPh₃)₇Cl₃ nanoclusters, which indicated higher electrochemical stability. Finally, the Au₈Ag₃(-PPh₃)₇Cl₃ clusters exhibited twofold greater values for turnover frequency for Au₁₁(PPh₃)₇Cl₃ nanoclusters in the photocatalysis of benzylamine. Heteroatom doping could obviously mediate the intrinsic electronic properties and frontier molecular orbitals of alloy nanoclusters, leading to shrinkage of the HOMO-LUMO gap, EG modification and the corresponding PL enhancement and photocatalytic activity improvement. This study provides a new strategy to synthesize alloy clusters with both high photothermodynamic and electrochemical stability simultaneously for potential photocatalysis applications through heteroatom doping engineering.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

- 1 R. Jin, C. Zeng, M. Zhou and Y. Chen, Chem. Rev., 2016, 116, 10346.
- 2 J. Fang, B. Zhang, Q. Yao, Y. Yang, J. Xie and N. Yan, Coord. Chem. Rev., 2016, 322, 1.
- 3 I. Chakraborty and T. Pradeep, Chem. Rev., 2017, 117, 8208.
- 4 G. Li and R. Jin, Acc. Chem. Res., 2013, 46, 1749.
- 5 S. Yamazoe, K. Koyasu and T. Tsukuda, Acc. Chem. Res., 2014, 47, 816.

6 K. Zheng, J. Zhang, D. Zhao, Y. Yang, Z. Li and G. Li, *Nano Res.*, 2019, 12, 501.

Nanoscale Advances

- 7 Q. Li, Y. Pan, T. Chen, Y. Du, H. Ge, B. Zhang, J. Xie, H. Yu and M. Zhu, *Nanoscale*, 2018, **10**, 10166–10172.
- 8 J. Zhang, Y. Zhou, K. Zheng, H. Abroshan, D. R. Kauffman, J. Sun and G. Li, *Nano Res.*, 2018, **11**, 5787.
- 9 W. Zhou, Y. Cao, D. Sui, W. Guan, C. Lu and J. Xie, *Nanoscale*, 2016, 8, 9614–9620.
- 10 Z. Li, W. Li, H. Abroshan, Q. Ge, Y. Zhou, C. Zhang, G. Li and R. Jin, *Nanoscale*, 2018, **10**, 6558–6565.
- 11 M. McPartlin, R. Mason and L. Malatesta, *Chem. Commun.*, 1969, 334.
- 12 L. C. McKenzie, T. O. Zaikova and J. E. Hutchison, *J. Am. Chem. Soc.*, 2014, **136**, 13.
- (a) R. Jin, S. Zhao, C. Liu, M. Zhou, G. Panapitiya, Y. Xing, N. L. Rosi, J. P. Lewis and R. Jin, *Nanoscale*, 2017, 9, 19183;
 (b) S. Wang, H. Abroshan, C. Liu, T.-Y. Luo, M. Zhu, H. J. Kim, N. L. Rosi and R. Jin, *Nat. Commun.*, 2017, 8, 848.
- 14 (a) S. Wang, Q. Li, X. Kang and M. Zhu, Acc. Chem. Res., 2018,
 51, 2784; (b) Z. Li, X. Yang, C. Liu, J. Wang and G. Li, Prog. Nat. Sci.: Mater. Int., 2016, 26, 477.
- 15 (a) S. Takano, S. Hasegawa, M. Suyama and T. Tsukuda, Acc. Chem. Res., 2018, 51, 3074; (b) M. Kim, Q. Tang,
 A. V. N. Kumar, K. Kwak, W. Choi, D. Jiang and D. Lee, J. Phys. Chem. Lett., 2018, 9, 982.
- 16 J. Koivisto, S. Malola, C. Kumara, A. Dass, H. Hakkinen and M. Pettersson, *J. Phys. Chem. Lett.*, 2018, 3, 3076.
- 17 W. Kurashige and Y. Negishi, J. Cluster Sci., 2012, 23, 365.
- 18 H. Qian, D. Jiang, G. Li, C. Gayathri, A. Das, R. R. Gil and R. Jin, *J. Am. Chem. Soc.*, 2012, **134**, 16159.
- 19 C. Kumara, C. M. Aikens and A. Dass, J. Phys. Chem. Lett., 2014, 5, 461.
- 20 W. Li, C. Liu, H. Abroshan, Q. Ge, X. Yang, H. Xu and G. Li, J. Phys. Chem. C, 2016, 120, 10261.
- 21 S. Yamazoe, W. Kurashige, K. Nobusada, Y. Negishi and T. Tsukuda, *J. Phys. Chem. C*, 2014, **118**, 25284.
- 22 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Adv., 2008,
- 23 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

- 24 D. Becke, J. Chem. Phys., 1993, 98, 5648.
- 25 C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, 37, 785.
- 26 B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, 157, 200.
- 27 B. Mennucci, E. Cances and J. Tomasi, J. Phys. Chem. B, 1997, 101, 10506.
- 28 E. Cances, B. Mennucci and J. Tomasi, J. Chem. Phys., 1997, 107, 3032.
- 29 R. Cammi and J. Tomasi, J. Comput. Chem., 1995, 16, 1449.
- 30 S. Miertus, E. Scrocco and J. Tomasi, *J. Chem. Phys.*, 1981, 55, 117.
- 31 Crystal data: monoclinic, $P2_1/n$, a=17.93 Å, b=26.24 Å, c=227.00 Å, $\beta=91.6646^\circ$, V=12701 Å³, Z=4, T=173 K, 21589 reflections measured, $R_1=0.0454$, $wR_2=0.1232$. CCDC-1873307 contains the supplementary crystallographic data.†
- 32 K. Spivey, J. I. Williams and L. Wang, *Chem. Phys. Lett.*, 2006, **432**, 163.
- 33 L. C. McKenzie, T. O. Zaikova and J. E. Hutchison, *J. Am. Chem. Soc.*, 2014, **136**, 13426.
- 34 C. Liu, H. Abroshan, C. Y. Yan, G. Li and M. Haruta, ACS Catal., 2016, 6, 92.
- 35 L. Liao, S. Zhuang, P. Wang, Y. Xu, N. Yan, H. Dong, C. Wang, Y. Zhao, N. Xia, J. Li, H. Deng, Y. Pei, S.-K. Tian and Z. Wu, *Angew. Chem.*, *Int. Ed.*, 2017, 56, 12644.
- 36 Y. Shichibu and K. Konishi, Small, 2010, 6, 1216-1220.
- 37 Z. Wu and R. Jin, Nano Lett., 2010, 10, 2568-2573.
- 38 S. Wang, X. Zhu, T. Cao and M. Zhu, *Nanoscale*, 2014, 6, 5777–5781.
- 39 Z. Wang, L. Wu, W. Cai and Z. Jiang, J. Mater. Chem., 2012, 22, 3632–3636.
- 40 G. Zhang, R. Wang and G. Li, *Chin. Chem. Lett.*, 2018, 29, 687-693.
- 41 S. Naya, K. Kimura and H. Tada, ACS Catal., 2013, 3, 10-13.
- 42 H. Chen, C. Liu, M. Wang, C. Zhang, N. Luo, Y. Wang, H. Abroshan, G. Li and F. Wang, *ACS Catal.*, 2017, 7, 3632–3638.
- 43 Z. Li, C. Liu, H. Abroshan, D. R. Kauffman and G. Li, *ACS Catal.*, 2017, 7, 3368–3374.