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Tailoring the stability, photocatalysis and photoluminescence properties of  $Au_{11}$  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 SXR D 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 Au<sub>11</sub> nanoclusters via doping engineering†

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Dopants in gold nanoclusters have been proved to mediate the intrinsic electronic properties of homo-clusters. In this work, we report the precise synthesis of atomically precise Au<sub>8</sub>Ag<sub>3</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> alloy nanoclusters with multiple Ag dopants for the first time. Their structure was resolved by single-crystal X-ray crystallography. Au<sub>8</sub>Ag<sub>3</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> nanoclusters possessed a similar structure topology to the well-known Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> 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<sub>3</sub>-axis manner. The alloy nanoclusters exhibited a closed-shell electronic structure (*i.e.*, 8(Au 6s<sup>1</sup>) + 3(Ag 5s<sup>1</sup>) – 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<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> clusters). DFT calculations indicated that the Ag dopants in a C<sub>3</sub>-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 Au<sub>8</sub>Ag<sub>3</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> was observed as compared with that of homo-nanoclusters of Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> (2.06 eV). The electrochemical gap of Au<sub>8</sub>Ag<sub>3</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> alloy nanoclusters was 1.272 V, which was higher than that of Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> nanoclusters, which indicated higher electrochemical stability, as evidenced by the differential pulse voltammetry (DPV) method. Au<sub>8</sub>Ag<sub>3</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> 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.<sup>1–3</sup>

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.<sup>4–10</sup> 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<sub>11</sub>(PPh<sub>3</sub>)<sub>7/8</sub>X<sub>3/2</sub> (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 Au<sub>13</sub> synthon through etching and removal of two gold atoms.<sup>11,12</sup> The major drawback of these phosphine-stabilized 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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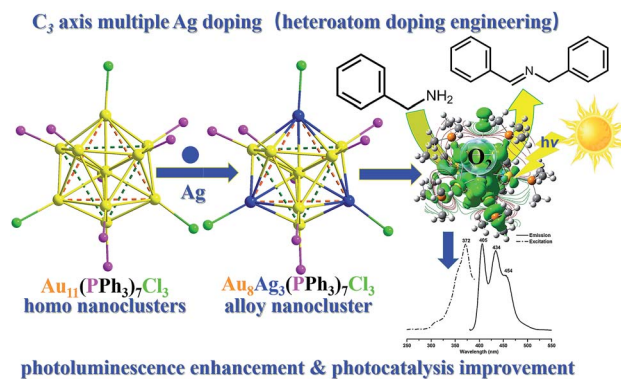


significantly. An effective strategy is urgently required to enhance the stability of these nanoclusters.

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.<sup>13–16</sup> It is well known that Pd and Pt heteroatoms in the gold nanoclusters can improve the stability of nanoclusters considerably.<sup>17,18</sup> For example, Negishi and colleagues synthesized mono-Pd-doped  $\text{Pd}_1\text{Au}_{10}(\text{PPh}_3)_8\text{Cl}_2$  nanoclusters, and showed much better stability against the homo-nanocluster  $\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2$ .<sup>17</sup> Also, the photoluminescence (PL) property of such alloy nanoclusters was modified. Similarly, the  $\text{Au}_{24}\text{Pt}_1(\text{SR})_{18}$  nanoclusters improved the thermal and antioxidation stabilities considerably compared with homo  $\text{Au}_{25}(\text{SR})_{18}$ .<sup>18</sup> 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  $\text{Au}_{25}$  nanoclusters has also been investigated intensively.<sup>3</sup> However, in all cases, gold nanoclusters with Ag dopants have been shown to decrease their stability.<sup>19–21</sup> In our previous study, the  $\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}$  (where,  $x$ : 1 to 13, and SR represents thiolate) showed very poor stability upon exposure to sunlight. The alloy clusters quickly decomposed to  $\text{Au}(\text{I}):\text{SR}$  and  $\text{Ag}(\text{I}):\text{SR}$  complexes in a  $\text{CH}_2\text{Cl}_2$  solution in a few hours.<sup>20</sup> Similar phenomena have been observed in  $\text{Ag}_x\text{Au}_{25-x}(\text{PPh}_3)_{10}(\text{SR})_5\text{Cl}_2$ ,  $\text{Ag}_x\text{Au}_{38-x}(\text{SR})_{24}$  and  $\text{Ag}_x\text{Au}_{144-x}(\text{SR})_{60}$  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  $\text{Au}_{11}$  nanoclusters in a precise manner has not been achieved yet.

Herein, we developed a novel synthetic protocol to afford  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  (abbreviated as  $\text{Au}_8\text{Ag}_3$ ) 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  $C_3$  axis in the  $\text{Au}_8\text{Ag}_3$  alloy nanoclusters. Experimental evaluation showed that  $\text{Au}_8\text{Ag}_3$  alloy nanoclusters were more stable than the corresponding homo- $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$  nanoclusters under sunlight irradiation. Density functional theory (DFT) calculations indicated that the AgCl motifs in the  $C_3$  axis could obviously delocalize the electrons of Au to the orbitals of P atoms in  $\text{PPh}_3$  ligands and mediate the electronic property of  $\text{Au}_8\text{Ag}_3$ . A decrease in the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap would ensure easier excitation of the electrons of  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  at a lower energy, resulting in PL enhancement.  $\text{Au}_8\text{Ag}_3$  clusters exhibited specific three PL peaks at 405, 434 and 454 nm. The electrochemical gap of the  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  alloy nanoclusters was 1.272 V, which was higher than that of  $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$ , which suggested higher electrochemical stability as evidenced by differential pulse voltammetry (DPV). Besides, these  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  alloy nanoclusters exhibited twofold greater activity of the HOMO gold clusters in the photooxidation of



Scheme 1  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  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 ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ , 99.95%) was purchased from HWG.  $\text{AgSbF}_6$  (99.95%), dimethyl sulfide ( $\text{Me}_2\text{S}$ , 99%), sodium borohydride ( $\text{NaBH}_4$ , 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  $\text{M}\Omega$  cm) was purified with a Barnstead Nanopure Di-water™ 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 $\text{Au}_8\text{Ag}_3$ nanoclusters

All procedures were carried out in the dark under an air atmosphere.  $\text{Ph}_3\text{PAuCl}$  was synthesized *via* the reaction of  $\text{HAuCl}_4$  and two equivalent  $\text{PPh}_3$  in an ethanolic solution. Then, 25 mg of  $\text{Ph}_3\text{PAuCl}$  (0.05 mmol) was dissolved in 1 mL of  $\text{CH}_2\text{Cl}_2$  solution, followed by addition of  $\text{AgSbF}_6$  (17.2 mg in 1 mL of  $\text{CH}_2\text{Cl}_2$ ). The mixture was stirred for 10 min at room temperature. Then, the white  $\text{AgCl}$  solid obtained was filtrated and removed. The filtrate was reduced by  $\text{NaBH}_4$  (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  $\text{Au}_8\text{Ag}_3$  clusters (~5 mg) were collected as a red plate crystal. The cluster yield was ~24% based on  $\text{Ph}_3\text{PAuCl}$  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



Synchrotron Radiation Facility, China, using a constant wavelength of  $\lambda = 0.65248 \text{ \AA}$  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 SHELX<sup>22</sup> and Olex2 v1.2.10.<sup>23</sup>

### Characterization

The UV-vis spectra of  $\text{Au}_8\text{Ag}_3$  clusters (dissolved in  $\text{CH}_2\text{Cl}_2$ ) 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  $\text{N}_2$ -cooled InGaAs detector, an excitation wavelength of 350 nm, slits of 14.7 nm, and a long-pass 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  $\text{N}_2$  atmosphere with TBABF<sub>4</sub> 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  $\text{min}^{-1}$  with heating rate of 20 °C  $\text{min}^{-1}$ .

### Computational details

All DFT calculations were carried out with a Gaussian 09 program.  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  and  $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$  clusters were simplified using  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  and  $\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$  molecular models, respectively. The geometries of  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  and  $\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$  were optimized fully *via* the DFT method with the Lee–Yang–Parr gradient-corrected correction function (B3LYP)<sup>24–26</sup> 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).<sup>27–30</sup>

### 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%  $\text{Au}_8\text{Ag}_3/\text{P25}$  and  $\text{Au}_{11}/\text{P25}$  photocatalysts. Typically, 5 mg of photocatalysts, 20 mg of benzylamine, 0.1 mmol of *p*-xylene and 1 mL of  $\text{CH}_3\text{CN}$  was added in a 5 mL quartz tube with a magnetic stirrer. The system was fully furnished with  $\text{O}_2$ . 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 $\text{Au}_8\text{Ag}_3$ alloy nanoclusters

The  $\text{Au}_8\text{Ag}_3$  alloy clusters were obtained by simultaneous  $\text{NaBH}_4$  reduction of the mixture of  $\text{Ph}_3\text{PAuCl}$  and  $\text{AgSbF}_6$  in a  $\text{CH}_2\text{Cl}_2$  solution at 0 °C. A block-like crimson crystal was obtained *via* evaporation and resolved by X-ray crystallography.<sup>31</sup> The  $\text{Au}_8\text{Ag}_3$  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  $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$  (hereafter referred to as  $\text{Au}_{11}$ ) clusters<sup>12</sup> and a  $\text{C}_3$  axis along the  $\text{Ag}_3$  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  $\text{M}_{11}$  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  $\text{Au}_{11}$  framework in a  $\text{C}_3$ -axis manner in specific positions instead of a statistical distribution resembling  $\text{Ag}_x\text{Au}_{25-x}$  nanoclusters reported previously.<sup>14a</sup> This phenomenon could be attributed to specific coordination selectivity in which the three “origin” Au atoms coordinated with three Cl atoms in the  $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$  framework are more prone to substitution by three Ag atoms to form  $\text{Au}_8\text{Ag}_3$  alloy nanoclusters. Besides doping along the  $\text{C}_3$  axis, Ag could also

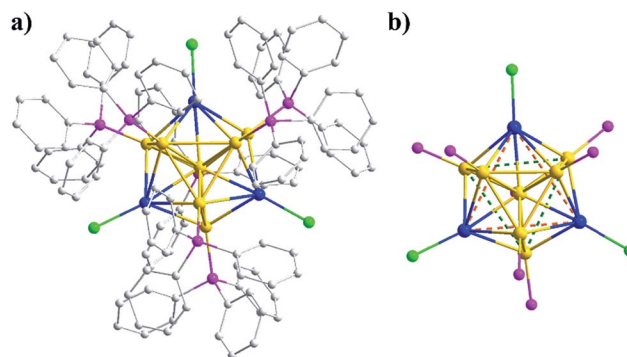


Fig. 1 (a) Complete structure of  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  clusters. (b) Atomic arrangement of the  $\text{Au}_8\text{Ag}_3$  kernel seen along the  $\text{C}_3$  axis. Au: orange; Ag: blue; P: purple; Cl: green; C: gray. All the H atoms have been omitted for clarity. The chlorine and phosphine ligands bond the silver and gold atoms selectively, respectively.



maximally delocalize the electrons of Au in the  $\text{Au}_8\text{Ag}_3$  framework to enhance its stability, as supported by related DFT calculations (see below).

The selected bond lengths of  $\text{Au}_8\text{Ag}_3$  are compiled in Table 1. Compared with  $\text{Au}_{11}$ , the average bond length of  $\text{Au}_{(\text{staple})}-\text{Au}_{(\text{center})}$  in  $\text{Au}_8\text{Ag}_3$  clusters was shorter than that in  $\text{Au}_{11}$  clusters (2.647 vs. 2.672 Å, Table 1, entry 1). However, the average of  $\text{Ag}_{(\text{Cl})}-\text{Au}_{(\text{center})}$  bonds in the  $\text{Au}_8\text{Ag}_3$  cluster was much longer than the  $\text{Au}_{(\text{Cl})}-\text{Au}_{(\text{center})}$  of the  $\text{Au}_{11}$  (2.754 vs. 2.701 Å, Table 1, entry 2). These data suggested that the Au sphere in  $\text{Au}_8\text{Ag}_3$  was reduced slightly (−0.49%) compared with  $\text{Au}_{11}$  clusters. However, the Ag segment was stretched considerably (+1.96%). The kernel of  $\text{M}_{11}$  was mainly responsible for the HOMO–LUMO electronic transition of the clusters.<sup>32</sup> The average Ag–Cl and Au–P bonds in  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  were also much longer than these bonds in  $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$  (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  $\text{Au}_{11}$  clusters.

### Characterization of $\text{Au}_8\text{Ag}_3$ nanoclusters

The final product of  $\text{Au}_8\text{Ag}_3$  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  $\text{Au}_8\text{Ag}_3$  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  $\text{Au}_{11}$  clusters (black profile vs. red profile). The optical energy gap (derived from UV-vis spectroscopy) was 1.69 and 2.05 eV for  $\text{Au}_8\text{Ag}_3$  and  $\text{Au}_{11}$ , respectively (Fig. S1†).

Next, the as-obtained nanoclusters were characterized by ESI-MS (Fig. 2b). No counter ion (e.g.,  $\text{Na}^+$  and  $\text{Cl}^-$ ) 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)  $\text{Cs}_z$ ]<sup>z+</sup> ( $z = 1, 2, 3$ , 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  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  ( $\text{Au}_8\text{Ag}_3\text{P}_7\text{C}_{126}\text{H}_{105}\text{Cl}_3$ , theoretical  $m/z$ : 3841.69 Da, deviation: +0.03 Da). Of note, the singly charged adduct (*i.e.*,  $[\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3]\text{Cs}^+$ ,  $m/z$ : 3974.64 Da) was beyond the limit of detection. The experimental isotope pattern matched well with the simulated one. Thus, the  $\text{Au}_8\text{Ag}_3$  nanocluster had a closed-shell electronic structure (*i.e.*,  $8(\text{Au } 6s^1) + 3(\text{Ag } 5s^1) -$

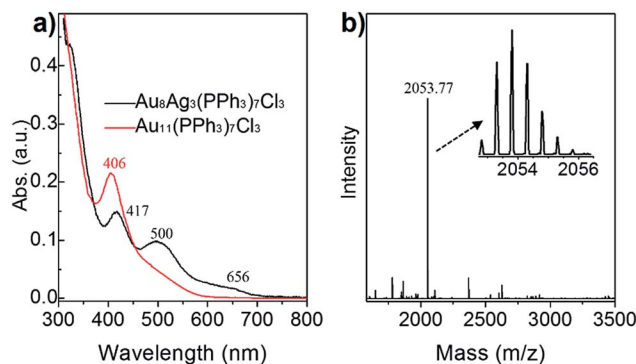


Fig. 2 (a) Comparison of the optical spectra of  $\text{Au}_{11}$  and  $\text{Au}_8\text{Ag}_3$  clusters. (b) Positive-mode ESI-MS of  $\text{Au}_8\text{Ag}_3$ ; inset shows a close-up of the intense mass peak.

$3(\text{Cl}) = 8e$ ), implying that the alloy nanoclusters should exhibit good stability.

### Thermal and photothermodynamic stability of the $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$ nanoclusters

To compare the thermal stability between  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  alloy nanoclusters and  $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$  nanoclusters, TGA was conducted from 30 °C to 600 °C, respectively.  $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$  nanoclusters remained intact up to 250 °C. Complete desorption of ligands from nanocluster surfaces began from 250 °C to 600 °C with ~50% weight loss, which was highly consistent with the theoretical value (51.5 wt%). We found that  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  remained intact up to 200 °C, and complete desorption of ligands from nanocluster surfaces began from 200 °C to 600 °C with ~55% weight loss, which was highly consistent with the theoretical value (53.7 wt%) (Fig. S3†). The thermal stability of  $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$  was slightly better than that of  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$ . 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  $\text{Au}_{11}$  clusters were not stable in  $\text{CH}_2\text{Cl}_2$  solution in the presence of air; the clusters decomposed in a few hours.<sup>33</sup> Recently, we found that the stability of  $\text{Au}_{11}$  nanoclusters was improved when using diphenyl-2-pyridylphosphine ( $\text{PPh}_2\text{Py}$ ) as capping ligands.<sup>34</sup> Here, we evaluated and compared the photothermodynamic stability of  $\text{Au}_8\text{Ag}_3$  and  $\text{Au}_{11}$  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  $\text{CH}_2\text{Cl}_2$  solution became colorless, which was also evidenced by

Table 1 Comparison of the average bond lengths and angles in  $\text{Au}_{11}$  and  $\text{Au}_8\text{Ag}_3$  clusters

Entry	Lengths (Å)	$\text{Au}_{11}$	$\text{Au}_8\text{Ag}_3$	Ref. (%)
1	$\text{Au}_{(\text{PPh}_3)}-\text{Au}_{(\text{center})}$	2.660 (2.608–2.678)	2.647 (2.605–2.669)	–0.49
2	$\text{M}_{(\text{Cl})}-\text{Au}_{(\text{center})}$	2.701 (2.700–2.704)	2.754 (2.749–2.757)	1.96
3	$\text{M}(\text{Au}/\text{Ag})-\text{Cl}$	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



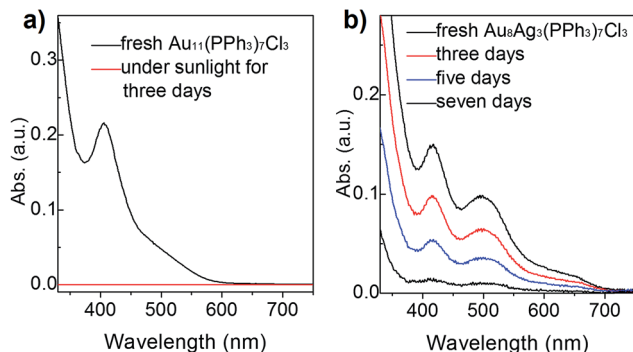


Fig. 3 Stability of (a)  $\text{Au}_{11}$  and (b)  $\text{Au}_8\text{Ag}_3$  clusters (dissolved in  $\text{CH}_2\text{Cl}_2$  solution) under sunlight at room temperature for 1 week according to UV-vis spectroscopy.

UV-vis spectroscopy (the spectrum became straight, Fig. 3a, red line). These results indicated clearly that the  $\text{Au}_{11}$  clusters were not stable and decomposed to  $\text{Au}(0)$  species under sunlight irradiation, data that are consistent with the literature.<sup>33</sup>  $\text{Au}_8\text{Ag}_3$  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  $\text{Au}_{11}$  clusters improved the photothermodynamic stability considerably.

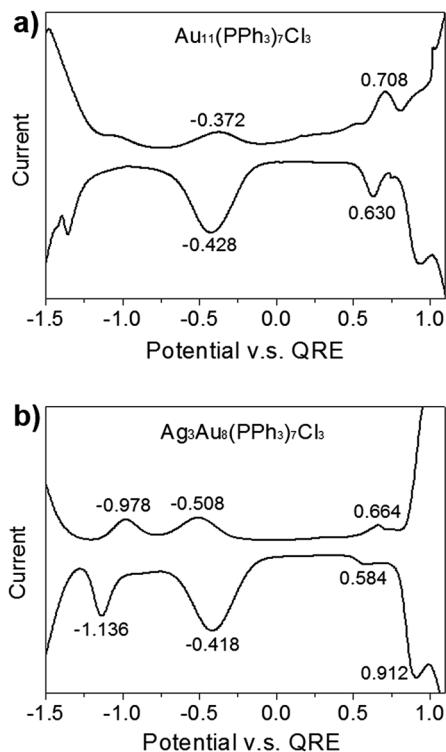


Fig. 4 DPV behaviour of (a)  $\text{Au}_{11}$  and (b)  $\text{Au}_8\text{Ag}_3$  nanoclusters (dissolved in methanol/0.1 M TBABF<sub>4</sub>) on a Pt electrode at room temperature (measurement conditions: pulse cycle, 0.2 s; scan rate in either direction, 0.05 V s<sup>-1</sup>).

## Computational simulation

The absorption spectra of  $\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$  and  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  have been calculated based on ground-state geometries using the TDDFT method. The calculated results are compiled in Fig. 5.  $\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$  gave maximum absorption at 343.9 nm, and  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  showed two absorption bands at 261.4 and 382.5 nm, implying that more shells of electrons of  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  were excited in a shorter wavelength range. The delocalization effect of clusters induced decreasing energy. In addition, it would be easier for  $\pi$  electrons to be excited. For further analyses of the stability of  $\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$  and  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$ , the energies and frequencies of  $\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$ ,  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  and  $\beta\text{-Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  were calculated. Three  $\text{PMe}_3$  ligands were grafted on Ag atoms whereas three Cl ligands were grafted on Au atoms in  $\beta\text{-Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  (Fig. S2†).

As shown in Table 2, the energies of  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  and  $\beta\text{-Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  were lower than that of  $\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$ , implying that the former were more stable. The frequencies of  $\beta\text{-Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  were negative, indicating that  $\beta\text{-Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  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 C<sub>3</sub>-axis manner in  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  alloy nanoclusters. Hence, the electron density map isocontours of fully optimized  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  and  $\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$  were calculated (Fig. 6). With Ag dopants, the electrons of Au were obviously delocalized to the orbitals of P atoms in  $\text{PPh}_3$  ligands, whereas the electrons of Au assembled in the kernels of  $\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$ . Therefore,  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  possessed higher stability. The

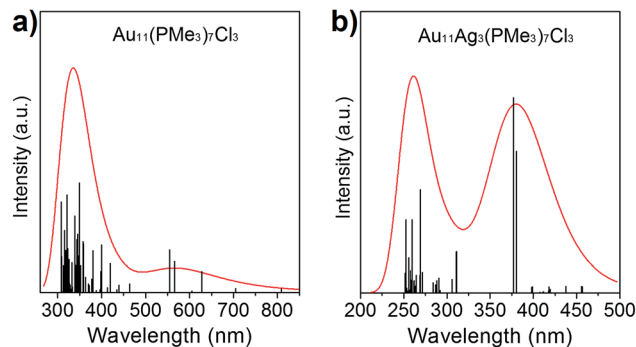


Fig. 5 Calculated UV-vis spectra of (a)  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  and (b)  $\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$  nanoclusters in  $\text{CH}_2\text{Cl}_2$  solution.

Table 2 DFT results for the Gibbs (G) free energy, Hartree–Fock (HF) energy and frequencies of  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$ ,  $\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$  and  $\beta\text{-Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  models in gas phases

Clusters	G (a.u.)	HF (a.u.)	Frequency (cm <sup>-1</sup> )
$\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$	-6135.69	-6136.35	8.21
$\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$	-6101.81	-6102.47	3.46
$\beta\text{-Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$	-6135.65	-6136.31	-9.93



corresponding HOMO–LUMO gap of  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  alloy nanoclusters was reduced to 1.67 eV, compared with that of  $\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$  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  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  alloy nanoclusters easier at a lower energy, which may result in PL enhancement.<sup>8</sup>

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  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  alloy nanoclusters. Hence, we compared the DPV data of  $\text{Au}_{11}$  and  $\text{Au}_8\text{Ag}_3$  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.<sup>35</sup> The first oxidation wave (O1) and first reduction wave (R1) of  $\text{Au}_{11}$  nanoclusters were at +0.708 and  $-0.372$  V (*versus* the quasi-reference Ag electrode), respectively (Fig. 4a). Hence, the EG of  $\text{Au}_{11}$  was 1.180 V. The O1, R1 and R2 of  $\text{Au}_8\text{Ag}_3$  nanoclusters were at +0.664,  $-0.508$  and  $-0.978$  V, respectively (Fig. 4b). The EG of  $\text{Au}_8\text{Ag}_3$  was 1.272 V (*i.e.*, (+0.664 V) – ( $-0.508$  V)), which was larger than that for  $\text{Au}_{11}$ . These data indicated that Ag dopants in a  $C_3$ -axis manner in  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  alloy nanoclusters dramatically mediated its corresponding electrochemical redox property compared with homo-nanocluster  $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$  with a similar structure. The lower EG of  $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$  nanoclusters indicated that  $\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3$  nanoclusters were more prone to undergo redox processes, whereas the higher EG of  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  alloy nanoclusters suggested that they had higher electrochemical stability. Heteroatom dopants could obviously mediate the corresponding electrochemical redox property.

### PL properties of $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$

In recent years, the luminescence properties of gold clusters have motivated researchers due to their potential utility as new types of quantum dots.<sup>36–38</sup> It has been reported that the PL of gold nanoclusters can be mediated by protecting ligands and other heteroatom metal dopants.<sup>17,39</sup> For example, Negishi *et al.* demonstrated that  $\text{PdAu}_{10}(\text{PPh}_3)_8\text{Cl}_2$  clusters exhibit strong PL

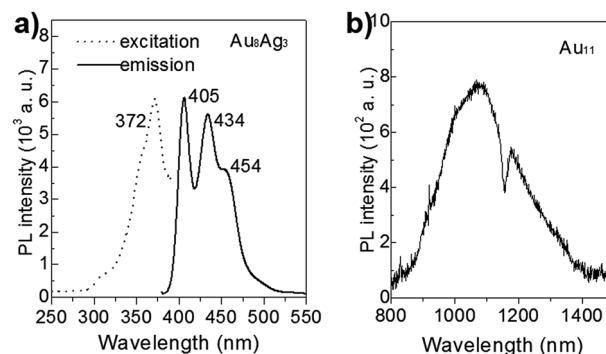


Fig. 7 PL spectra of (a)  $\text{Au}_8\text{Ag}_3$  (excited at 372 nm) and (b)  $\text{Au}_{11}$  clusters (excited at 350 nm), dissolved in  $\text{CH}_2\text{Cl}_2$  solution.

at 950 nm and that  $\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2$  clusters do not show luminescence.<sup>17</sup> The unique PL properties of  $\text{Au}_8\text{Ag}_3$  clusters are presented in Fig. 7. The  $\text{Au}_{11}$  clusters gave near-infrared PL, centered at  $\sim 1074$  nm (1.16 eV), consistent with the reported result.<sup>8</sup> The PL spectrum of  $\text{Au}_8\text{Ag}_3$  clusters contained three main emission peaks centered at *ca.* 405 ( $\sim 3.06$  eV), 434 (2.86 eV), and 454 nm (2.73 eV), respectively, which were distinctly different compared with  $\text{Au}_{11}$ . Overall, these results suggested that Ag dopants definitely mediated the electronic structure of  $\text{Au}_8\text{Ag}_3$  alloy clusters, thereby leading to PL enhancement.

### Catalytic activity in the photocatalytic oxidation of amines

Very recently, free and  $\text{TiO}_2$ -supported Au nanocluster catalysts have been applied in the photocatalytic oxidation of amines to imines, which are applied widely in dye industries.<sup>40–43</sup> Such photocatalytic oxidation involved activation of oxygen molecules.<sup>8,40</sup> Imines are important versatile intermediates for fine chemicals and pharmaceuticals. The nature of the photo-thermodynamic stability (especially under light irradiation) and electrochemical stability of  $\text{Au}_8\text{Ag}_3(\text{PPh}_3)_7\text{Cl}_3$  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  $\text{Au}_8\text{Ag}_3$  and  $\text{Au}_{11}$  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  $\text{Au}_8\text{Ag}_3/\text{P25}$  catalysts gave 72.5% benzylamine conversion under irradiation for 1 h (Table 3, entry 2). Low conversion (37.8%) was found when using  $\text{Au}_{11}/\text{P25}$  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  $\text{Au}_8\text{Ag}_3/\text{P25}$  photocatalyst (turnover frequency = (reacted mol of amine)/[(mol of cluster)  $\times$  (reaction time in second)]) was calculated to be  $2.92 \text{ s}^{-1}$ . This value was  $\sim 2$  times that for  $\text{Au}_{11}/\text{P25}$  ( $1.51 \text{ s}^{-1}$ ), which was caused mainly by the unique electronic property of  $\text{Au}_8\text{Ag}_3$  alloy

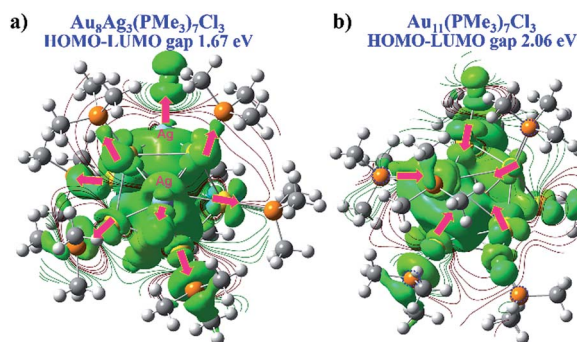


Fig. 6 DFT electron density map isocontours and HOMO–LUMO gap of (a)  $\text{Au}_8\text{Ag}_3(\text{PMe}_3)_7\text{Cl}_3$  and (b)  $\text{Au}_{11}(\text{PMe}_3)_7\text{Cl}_3$  from the same perspective.



**Table 3** Photocatalysis of benzylamine over P25-supported Au<sub>8</sub>Ag<sub>3</sub> nanoclusters in the presence of O<sub>2</sub><sup>a</sup>

$$2 \text{ Ph-CH}_2\text{-NH}_2 \xrightarrow[\text{CH}_3\text{CN, 30 }^\circ\text{C}]{\text{O}_2, \lambda = 455 \text{ nm}} \text{Ph-CH=N-CH}_2\text{-Ph}$$

Entry	Catalyst	Conversion <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)
1	Au <sub>8</sub> Ag <sub>3</sub> /P25	72.5	>99
2	Au <sub>11</sub> /P25	37.8	>99
3	P25	13.8	>99
4 <sup>c</sup>	Au <sub>8</sub> Ag <sub>3</sub> /P25	—	—
5 <sup>c</sup>	Au <sub>11</sub> /P25	—	—
6 <sup>d</sup>	Au <sub>8</sub> Ag <sub>3</sub> /P25	<1	—
7 <sup>d</sup>	Au <sub>11</sub> /P25	<1	—
8	—	—	—
9 <sup>e</sup>	Au <sub>8</sub> Ag <sub>3</sub> /P25	70.8	>99
10 <sup>f</sup>	Au <sub>8</sub> Ag <sub>3</sub> /P25	71.7	>99

<sup>a</sup> Reaction conditions: 20 mg of benzylamine, 0.1 mmol of *p*-xylene, 1 mL of acetonitrile, 10 mg of Au<sub>8</sub>Ag<sub>3</sub>/P25 or Au<sub>11</sub>/P25 or P25 in the presence of O<sub>2</sub> at 30 °C under LED light centered at λ ~ 455 nm for 1 h. <sup>b</sup> The conversion of benzylamine and selectivity for imine were determined by GC-MS. <sup>c</sup> In absence of light. <sup>d</sup> Under a N<sub>2</sub> atmosphere. <sup>e</sup> Second reuse of the Au<sub>8</sub>Ag<sub>3</sub>/P25 photocatalysts recovered from entry 1. <sup>f</sup> Third reuse of the Au<sub>8</sub>Ag<sub>3</sub>/P25 photocatalysts recovered from entry 1.

clusters. Furthermore, Au<sub>8</sub>Ag<sub>3</sub>/P25 and Au<sub>11</sub>/P25 photocatalysts showed no activity in the absence of light irradiation, and gave <1% conversion under a N<sub>2</sub> atmosphere (Table 3, entries 4–7). Meanwhile, conversion was not observed in the blank experiment without TiO<sub>2</sub> and gold clusters (Table 3, entry 8). Next, we investigated the reusability of Au<sub>8</sub>Ag<sub>3</sub>/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 Au<sub>8</sub>Ag<sub>3</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> alloy nanoclusters. Actually, shrinkage of the HOMO–LUMO gap to 1.67 eV of Au<sub>8</sub>Ag<sub>3</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub>, as compared with 2.06 eV for homo-nanoclusters of Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub>, through Ag doping, was the reason for the higher photocatalytic activity of Au<sub>8</sub>Ag<sub>3</sub>. Metal nanoclusters with a suitably low HOMO–LUMO gap located at the sunlight range (1.55–2.06 eV) are more prone to generating <sup>1</sup>O<sub>2</sub> molecules *via* photoexcitation of metal nanoclusters,<sup>8,40</sup> which involves Dexter-type electron-exchange coupling between the metal nanocluster (serving as an excited photosensitizer) and ground-state <sup>3</sup>O<sub>2</sub> 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 <sup>1</sup>O<sub>2</sub> molecules is not possible, so they would not show photocatalytic oxidation.

## Conclusions

In summary, a novel synthetic protocol to afford Au<sub>8</sub>Ag<sub>3</sub>(-PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> alloy nanoclusters with precise Ag dopants in a controllable manner was developed. The precise atomic

framework was determined by single-crystal X-ray diffraction. Au<sub>8</sub>Ag<sub>3</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> nanoclusters possessed a closed-shell electronic structure and a similar framework to Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> nanoclusters. The alloy clusters exhibited significant photo-thermodynamic stability (*e.g.*, under sunlight irradiation) and electrochemical stability as evidenced by UV-vis spectroscopy and DPV, respectively, by comparison with homo-nanocluster Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> with a similar structure. DFT calculations indicated that the Ag dopants in a C<sub>3</sub>-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 Au<sub>8</sub>Ag<sub>3</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> alloy nanoclusters was 1.272 V, which is higher than that of Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> nanoclusters, which indicated higher electrochemical stability. Finally, the Au<sub>8</sub>Ag<sub>3</sub>(-PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> clusters exhibited twofold greater values for turnover frequency for Au<sub>11</sub>(PPh<sub>3</sub>)<sub>7</sub>Cl<sub>3</sub> 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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