

Mono-Mercury Doping of Au₂₅ and the HOMO/LUMO Energies Evaluation Employing Differential Pulse Voltammetry

Lingwen Liao,^{†,§} Shiming Zhou,^{‡,§} Yafei Dai,[‡] Liren Liu,[‡] Chuanhao Yao,[†] Cenfeng Fu,[‡] Jinlong Yang,^{*,‡} and Zhikun Wu^{*,†}

[†]Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences (CAS), Hefei, 230031, China

[‡]Hefei National Laboratory for Physics Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China

Supporting Information

ABSTRACT: Controlling the bimetal nanoparticle with atomic monodispersity is still challenging. Herein, a monodisperse bimetal nanoparticle is synthesized in 25% yield (on gold atom basis) by an unusual replacement method. The formula of the nanoparticle is determined to be Au₂₄Hg₁(PET)₁₈ (PET: phenylethanethiolate) by high-resolution ESI-MS spectrometry in conjunction with multiple analyses including X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). X-ray single-crystal diffraction reveals that the structure of Au₂₄Hg₁(PET)₁₈ remains the structural framework of Au₂₅(PET)₁₈ with one of the outer-shell gold atoms replaced by one Hg atom, which is further supported by theoretical calculations and experimental results as well. Importantly, differential pulse voltammetry (DPV) is first employed to estimate the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) energies of Au₂₄Hg₁(PET)₁₈ based on previous calculations.

Bimetal nanoparticles are currently a frontier in the nanoscience and nanotechnology research.¹ Among various bimetal nanoparticles, atom-precise and atom-monodisperse ultrasmall nanoparticles doped (alloyed) by a second metal have received wide attention due to the insightful structure (composition)–properties correlation and the precise tailoring of properties of these bimetal nanoparticles.^{1a,2} Murray's group³ and Negishi's group⁴ reported the first case of such bimetal nanoparticle (Au₂₄Pd₁), following that, a number of atom-precise bimetal nanoparticles including Au₂₄Pt₁, Au_{25-x}Ag_x, Au_{38-x}Ag_x, Au_{144-x}Ag_x, etc., were successfully synthesized by reducing the mixed metal–thiolates (synchro-synthesis).^{2b–d,f,g,5} Due to the uncontrolled formation of diverse and similar products in synchro-synthesis, atomically monodisperse bimetal nanoparticles were not obtained except a few cases like Au₂₄Pd₁^{3,4} and Au₂₄Pt₁.^{5e} Even for the few exceptional cases, monodisperse doped nanoparticles were obtained in low yields (e.g., ca. 5% for Au₂₄Pt₁^{5e}) together with complex isolation (or purification), and the crystal structures of them are not solved.^{3–5} Galvanic reduction (GR) is another well-recognized way to synthesize bimetal nanoparticles,⁶ but it requires the preparation of more reactive (i.e., less noble) metal nanoparticles initially, followed by the

substitution with the less reactive metal atoms. However, no atomically monodisperse bimetal nanoparticles were obtained so far by this method, probably due to the uncontrolled GR process. Overall, the synthesis of atomically monodisperse doped nanoparticles is still challenging, which hampers the subsequent investigation on the properties and potential application of such intriguing materials. Fortunately, the recent unexpected finding^{7a,b} provides a novel strategy for the synthesis of bimetal nanoparticles that are otherwise difficult to obtain, and very recently we successfully synthesized monodisperse Au₂₅Ag₂(PET)₁₈ (PET: phenylethanethiolate) employing this unusual strategy, in which the two silver atoms do not replace two gold atoms but are simply deposited on the Au₂₅ nanoparticle.^{7c}

Herein, we have obtained atomically monodisperse Au₂₄Hg₁(PET)₁₈ and solved its single crystal structure. In remarkable contrast to the above case,^{7c} in this case one gold atom in the outer-shell of Au₂₅(PET)₁₈ was replaced by one Hg atom, which is fully characterized by high-resolution mass spectrometry, single crystal X-ray crystallography, etc. Furthermore, the Kohn–Sham (K–S) orbital energy levels of the as-prepared nanoalloy are probed by differential pulse voltammetry (DPV), together with electron spin-resonance spectroscopy (ESR). The results indicate that the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) energies of Au₂₅(PET)₁₈ are greatly decreased by mono-mercury doping. Below we present the detailed results and discussion.

The synthesis of the title nanoparticle was obtained from previous work.^{7c} Briefly, 24 mg of [Au₂₅(PET)₁₈][−] nanocluster⁸ was dissolved in 8 mL of acetonitrile, and an aqueous solution of Hg(NO₃)₂ (1 equiv per mole of Au₂₅(PET)₁₈) was quickly added into the solution under vigorous stirring. Ninety minutes later, 300 μL of acetonitrile containing 10 μL of PET was slowly added to the reaction mixture under vigorous stirring (the addition of excess PET can improve the purity of product by ligand etching,⁹ but the addition of PET is not critical for the forming of the title nanoparticle). The precipitate was collected and thoroughly washed with MeOH three times and redispersed in the toluene/

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acetonitrile (1:4, V:V) mixture. Rhombic single crystals were formed after 1–2 days with a yield of 25% (on gold atom basis).

The crystals (dissolved in toluene) show two absorption bands centered at ~ 700 and ~ 405 nm (Figure 1a), distinctly different

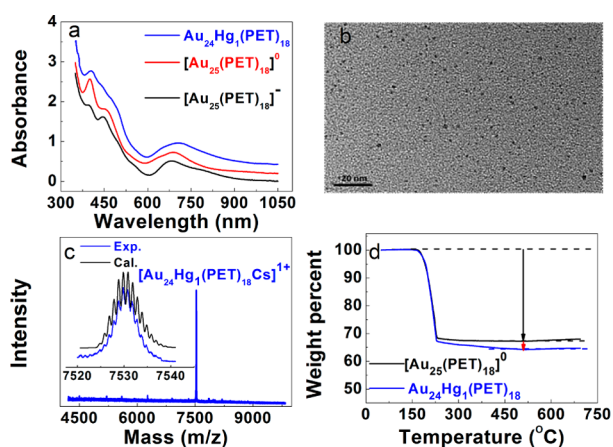


Figure 1. UV/vis/NIR absorption spectra (a), HRTEM image (b), ESI-MS spectrum (c), and TGA curves (d) of $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$.

from the absorption spectra of variously charged $\text{Au}_{25}(\text{PET})_{18}$, indicating the formation of a new product. The absence of plasma peak (at ~ 520 nm) excludes the production of large nanoparticles (typically >3 nm). High resolution transmission electron microscopy (HRTEM) confirms this and reveals that the as-prepared particles are monodisperse with a size of ~ 1.1 nm (Figure 1b). The monodispersity and the precise size were further evaluated by a very soft ionization mass spectrometry–electrospray ionization mass spectrometry (ESI-MS). The spectrum consists essentially and entirely of the 7530 ion (Figure 1c), which can be readily assigned to $[\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}\text{Cs}]^+$ (deviation: 0.03 Da; CsOAc was added to assist ionization of the nanoparticles under ESI conditions). The assignment was further supported by the excellent agreement between the simulated and experimental isotope patterns (see Figure 1c inset). Based on the assignment as well as the positive ion nature, the native cluster has a molecular formula of $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$ with neutral charge state. This molecular formula is also supported by X-ray fluorescence (XRF) analyses, X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA). The quantitative XRF and XPS analyses reveal that the Au/Hg atomic ratio is 23.8:1 (Figure S1) and that the Au/Hg/S atomic ratio is 24/0.96/18.2 (Figure S2), respectively, well consistent with the expected ratios of 24/1 and 24/1/18 for $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$. TGA reveals a weight loss of 35.8 wt %, which is in agreement with the theoretical value of $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$ (36.1 wt %). Moreover, compared to the TGA of $[\text{Au}_{25}(\text{PET})_{18}]^0$ (see Figure 1d), an additional gradual weight loss of ~ 3 wt % was found in the temperature range from 220 to 510 °C, which is ascribed to the loss of mercury. In addition, the XPS results (Figure S2a) exclude the possibility of anionic or cationic cases, i.e., $[\text{Au}_{25}(\text{PET})_{18}]^-$ or $[\text{Au}_{25}(\text{PET})_{18}]^+$, since the other elements (N, Cl, and Br) contained in potential counterions such as $\text{N}(\text{C}_8\text{H}_{17})_4^+$, Cl^- , and Br^- are below the limit of detection of the instrument used (<0.1 atom %).

The molecule formula and neutral charge state of the as-prepared nanoparticle are further confirmed by single crystal X-ray analysis. The solved structure shows that the Hg-doped nanoparticle remains the structure framework of $\text{Au}_{25}(\text{PET})_{18}$

but with one outer-shell gold atom replaced by a Hg atom (every gold atom in the outer-shell can be replaced by mercury and the replacement probability is almost the same based on the X-ray data), see Figure 2. In other words, it is composed of an Au_{13}

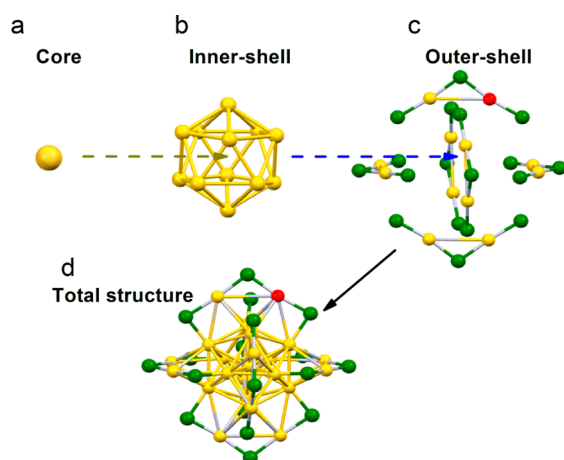


Figure 2. Structure of $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$: core (a), inner-shell (b), outer-shell (c), and total structure of $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$ (d). Au, yellow; Hg, red; S, green; C and H atoms are omitted for clarity.

icosahedron and five surrounding “-SR-Au-SR-Au-SR-” staples and one “-SR-Hg-SR-Au-SR-” staple (R: phenylethanethiolate) (the fact that no counterion was found confirms the neutral state of $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$). Such a doping mode is quite different from the previous cases where the inner-shell (core) gold atoms were usually replaced by the heteroatoms^{2b,f,3,4,5b,f,10} and may be due to the differences in the synthesis methods. Theoretical simulations of UV/vis/NIR spectra also reveal that the replacement of outer-shell gold atoms is more likely than the replacement of inner-shell (core) gold atom of $\text{Au}_{25}(\text{PET})_{18}$ in our case, see Figure 3. Furthermore, the fragmentation mode of $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$ in MALDI-TOF MS spectrum provides additional support for the replacement of outer-shell gold atom (Figure S3). Besides, the successive loss of ligands and Hg in TGA of $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$ (see Figure 1d) may also implicate that the outer-shell gold atom (rather than the inner-shell or the

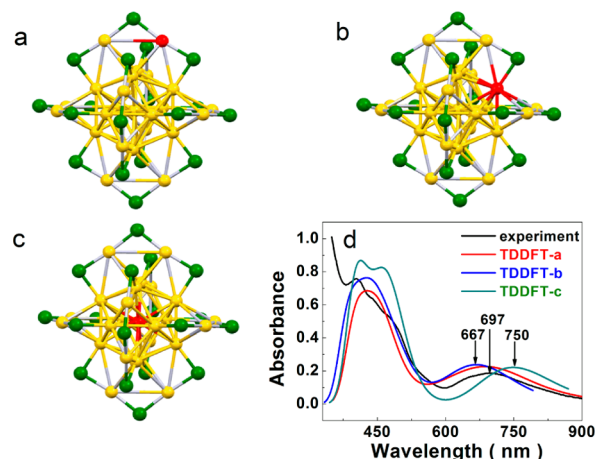


Figure 3. Structure illustration of $\text{Au}_{24}\text{Hg}_1(\text{SH})_{18}$ with various Hg positions (a, outer-shell; b, inner-shell; c, core), and experimental and TDDFT results of UV/vis/NIR adsorption spectra (d). Au, yellow; Hg, red; S, green; H atoms are omitted for clarity.

central gold atom) of $\text{Au}_{25}(\text{PET})_{18}$ is replaced by one mercury atom. To be noted, such a result is also totally different from our recent report of $\text{Au}_{25}\text{Ag}_2(\text{PET})_{18}$.^{7c} In that case, two silver atoms do not replace the two gold atoms in $\text{Au}_{25}\text{Ag}_2(\text{PET})_{18}$ but are deposited on the surface of the $\text{Au}_{25}(\text{PET})_{18}$ nanoparticle. Metal mercury is less noble than gold; thus, such a replacement is not suggested by the galvanic series for bulk metals and unit activities, but it does not violate thermodynamics and indicates that these interesting metal clusters and their surface chemistry differ from the bulk materials.

Previously several groups have theoretically predicted the ligand effect of K–S energy levels.¹¹ An interesting issue pertains to the K–S energy level change of $\text{Au}_{25}(\text{PET})_{18}$ caused by the doping of mono-mercury. Herein, differential pulse voltammetry was employed to probe the energy level change of $\text{Au}_{25}(\text{PET})_{18}$ after doping by mercury, inspired by Murray's work¹² and some theory works.¹¹ We conducted the DPV measurements of three Au_{25} species protected by various ligand (SR: R = $-\text{C}_6\text{H}_{13}$, $-\text{C}_2\text{H}_4\text{Ph}$, and $-\text{Ph}$, respectively), see Figure 4. It was found that

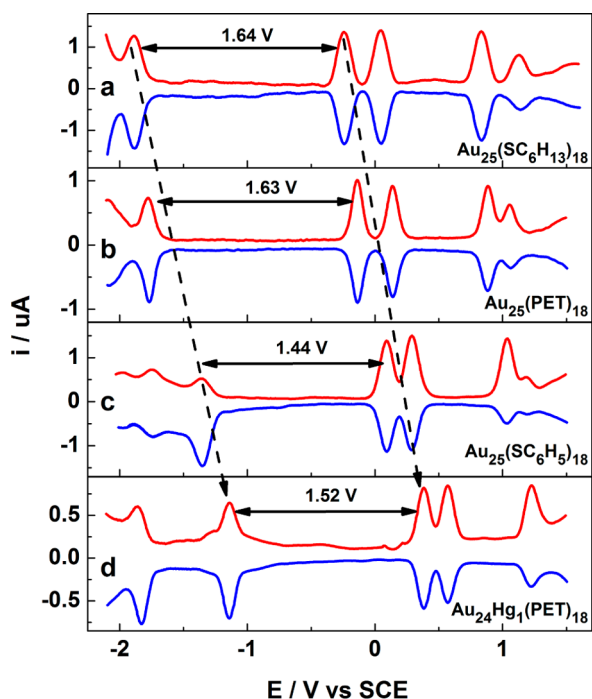


Figure 4. Differential pulse voltammetry (DPV) of $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$ (a), $\text{Au}_{25}(\text{PET})_{18}$ (b), $\text{Au}_{25}(\text{SC}_6\text{H}_5)_{18}$ (c), and $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$ (d) at 0.01 V/s in degassed CH_2Cl_2 containing 0.1 M Bu_4NPF_6 with 1 mm diameter Pt working, SCE reference, and carbon rod counter electrodes.

DPV results have some good correlation to the theoretical results,^{11d} for instance, the gaps between the first oxidation and the first reduction after subtracting the charging energy (0.29 V)¹² for the three Au_{25} species are 1.35, 1.34, and 1.16 V, respectively, which fit the calculated HOMO–LUMO gap values 1.25, 1.23, and 1.16 eV, respectively;¹² the first oxidation/reduction potential values in DPV, together with the HOMO/LUMO energy values for the three Au_{25} species are linearly related with the polarity of the ligand, see Figures 4 and 5. The theory–experiment consistence indicates that the HOMO/LUMO energies can be rationally correlated with the DPV results, and based on this good linear relation the HOMO and LUMO energies of $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$ are readily deduced to be -3.8 and -2.6 eV (Figure 5), respectively, which is in good

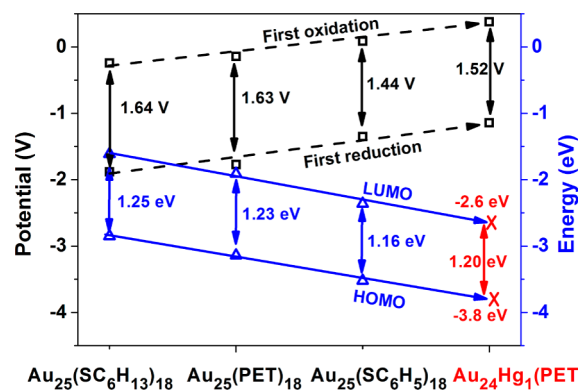


Figure 5. Summary of the first oxidation/reduction potentials and the HOMO/LUMO energies of $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$, $\text{Au}_{25}(\text{PET})_{18}$, $\text{Au}_{25}(\text{SC}_6\text{H}_5)_{18}$, and $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$.

agreement with the results calculated by the same method for $\text{Au}_{25}(\text{SR})_{18}$ (R = $-\text{C}_6\text{H}_{13}$, $-\text{C}_2\text{H}_4\text{Ph}$, or $-\text{Ph}$).^{11d} As a result, the simplified energy level diagram of $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$ can be represented as in Figure 6.¹¹

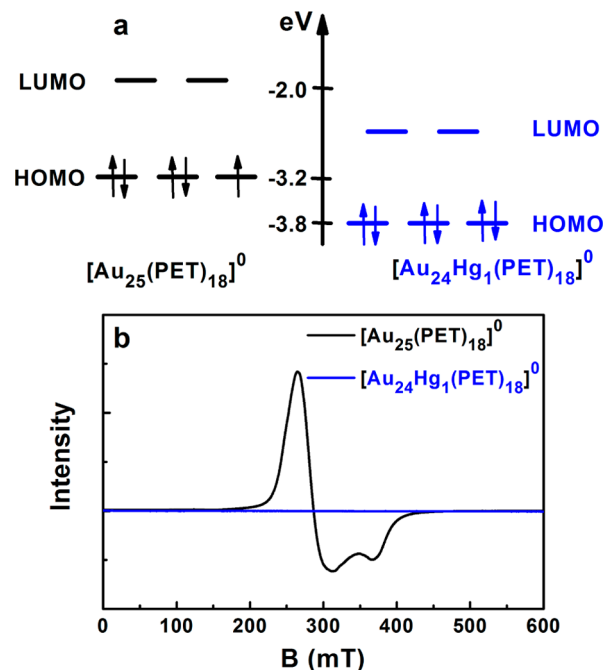


Figure 6. Simplified energy level diagrams (a) and ESR signals (b) of $[\text{Au}_{25}(\text{PET})_{18}]^0$ and $[\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}]^0$ (the differentiation of HOMO and LUMO is not considered for simplification).

Theoretically, $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$ should be of the 8-electron shell closing electronic structure ($n^* = N\nu_A - M - Z = 24 \times 1 + 1 \times 2 - 18 + 0 = 8$).¹³ If the proposed energy level diagram is correct, the HOMO should be fully occupied by the valence electrons of $\text{Au}_{24}\text{Hg}_1(\text{PET})_{18}$, which was indeed confirmed by the absence of ESR signals (Figure 6). Taken together, these theory–experiment consistencies demonstrate the rationality of the introduced method in this work, which could provide a facile way to estimate the HOMO/LUMO energy change of $\text{Au}_{25}(\text{PET})_{18}$ after tuning its composition (may be applicable to other materials, too). Further studies are underway in our lab.

In summary, an atomically monodisperse bimetal nanoparticle was synthesized in medium yield (25%) through an unusual

replacement process. The composition of the as-prepared bimetal nanoparticle was precisely determined to be Au₂₄Hg₁(PET)₁₈ by high-resolution mass spectrometry together with other analyses such as XPS and TGA. X-ray single-crystal diffraction, together with theoretical calculation, MALDI-TOF MS spectrum, and TGA reveal that Au₂₄Hg₁(PET)₁₈ remains the structural framework of Au₂₅(PET)₁₈ with one of the outer-shell gold atoms replaced by one Hg atom. The doping of mono-mercury results in a large decrease of HOMO/LUMO energies of Au₂₅(PET)₁₈. Importantly, for the first time, an experimental method was introduced to evaluate the HOMO/LUMO energies of Au₂₄Hg₁(PET)₁₈ based on previous calculation, and this method may be extended to other systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03483.

Experimental details; X-ray fluorescence spectra of Au₂₄Hg₁(PET)₁₈; XPS spectra of Au₂₄Hg₁(PET)₁₈; MALDI-TOF MS spectrum of Au₂₄Hg₁(PET)₁₈ (PDF)
Detailed structural data (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*zkwu@issp.ac.cn

*jlyang@ustc.edu.cn

Author Contributions

§L.L. and S.Z. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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