

Improving the Catalytic Activity of Au₂₅ Nanocluster by Peeling and Doping

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Tuning the nanoclusters' compositions and structures is critical for the performance improvement of nanoclusters. Herein, a well-known Au₂₅(SCH₂CH₂Ph)₁₈ (Au₂₅ for short) nanocluster has been transformed to a rare cadmium doped gold nanocluster [Au₁₃Cd₂(PPh₃)₆(SC₂H₄Ph)₆(NO₃)₂]₂Cd(NO₃)₄ (Au₂₆Cd₅ for short) by peeling and doping. Although Au₂₅ exhibits no catalytic activity toward A³-coupling reaction under the investigated conditions, the novel cadmium doped gold nanocluster Au₂₆Cd₅ shows high catalytic activity, as well as good recyclability and substrate tolerance for the same reaction. The high catalytic activity is attributed to the cooperation between the exerted cadmium atoms and the neighbor gold atoms on the surface of Au₁₃ icosahedron. This work has important implication for the tuning of nanoclusters' compositions and structures targeting the improvement of catalytic performance by some unusual but effective strategies.

Keywords peeling, doping, gold nanocluster, A³-coupling reaction, catalysis

Introduction

Owing to their ultra-small size, well-defined composition/structure and unusual chemico-physical properties, gold nanoclusters have attracted wide attention as a new kind of metal materials.^[1-16] However, the potential of gold nanoclusters as a new type of nanocatalysts has not been fully realized,^[9,17-23] especially the high-performance gold nanoclusters in catalyzing the reactions other than oxidation and reduction are rarely reported. The introducing of foreign atoms (doping) is verified to be an effective strategy to improve the catalytic performance of gold nanoclusters,^[24,25] however, the combined use of doping with some other treatments targeting the improvement of the catalytic performance of gold nanoclusters has not been reported so far to the best of our knowledge. Previously, we found that PPh₃ can peel the core-shell Au₂₅ nanoclusters and assist the transformation from core-shell Au₂₅ to Au₁₃, Au₁₁, and finally to biicosahedral Au₂₅.^[26] We also revealed that Cd can be doped into core-shell Au₂₅ via an anti-galvanic reduction (AGR).^[27-29] Herein, both peeling and doping are adopted to tune the composition and structure of core-shell Au₂₅ targeting the improvement of its catalysis performance. Fortunately, we successfully

synthesized [Au₁₃Cd₂(PPh₃)₆(SC₂H₄Ph)₆(NO₃)₂]₂Cd(NO₃)₄ (Au₂₆Cd₅ for short) by this strategy, and found that Au₂₆Cd₅ exhibits high catalytic activity, as well as good recyclability and substrate tolerance for the A³-coupling, although the precursor Au₂₅ shows no catalytic activity under the same conditions.

Experimental

Materials

Cadmium nitrate tetrahydrate [Cd(NO₃)₂•4H₂O, 99.0%], triphenylphosphine (PPh₃, 99.0%), dichloromethane (CH₂Cl₂, A.R.), methanol (CH₃OH, A.R.), hexane (C₆H₁₂, A.R.), petroleum ether (A.R., 30–60 °C) and ethyl acetate (A.R.) were purchased from Sinopharm Chemical Reagent Co. Ltd. All alkynes, aldehydes and amines were purchased from Aladdin Chemical Reagent Co. Ltd. All reagents were used as received without further purification. [Au₂₅(SC₂H₄Ph)₁₈]⁻,^[30,31] Au₂₄Cd(SC₂H₄Ph)₁₈^[29] and Au₁₃(PPh₃)₄(SC₂H₄Ph)₄^[32] were synthesized following the previous methods. Cd(PPh₃)₂(NO₃)₂ was prepared by the mixing of Cd(NO₃)₂ with PPh₃ in methanol. Cd(SC₂H₄Ph)_x(NO₃)_y was synthesized by the mixing of Cd(NO₃)₂ with PhC₂H₄SH in methanol.

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In Memory of Professor Enze Min.

Characterizations

The UV/Vis/NIR absorption was measured on a UV-3600 spectrophotometer at room temperature. Electrospray ionization mass spectra (ESI-MS) were acquired on a Waters Q-TOF mass spectrometer equipped with a Z-spray source. The sample was dissolved in dichloromethane (*ca.* 1 mg/mL) and diluted 1 : 1 in dry ethanol, then directly infused at 5 μ L/min. The source temperature was fixed at 70 $^{\circ}$ C. The spray voltage was set at 2.20 kV and the cone voltage was set at 60 V. 1 H NMR and 13 C NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz) using tetramethylsilane as the internal reference. The diffraction data of single crystal were collected on an Agilent Gemini S Ultradiffractometer using Cu K α radiation and the crystal structure was unraveled by direct methods and refined by full-matrix least-squares methods with SHELXL-2013 program (Sheldrick, 2013). X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB 250Xi XPS spectrometer (Thermo Scientific, America), using a monochromatized Al K α source and equipped with an Ar $^+$ ion sputtering gun. All binding energies were calibrated using the C(1s) carbon peak (284.8 eV).

Peeling and doping Au₂₅ to Au₂₆Cd₅

Cd(PPh₃)₂(NO₃)₂ (5.0 mg) was added to 10 mg of [Au₂₅(SC₂H₄Ph)₁₈] $^-$ in 2.0 mL of dichloromethane. The mixture was stirred at room temperature for 1 h, and then precipitated by hexane. Au₂₆Cd₅ was purified by crystallization from the mixed solvent of dichloromethane and toluene at 4 $^{\circ}$ C. The yield of Au₂₆Cd₅ was 91%.

Au₂₆Cd₅ catalyzed A³-coupling reaction

Alkyne (0.3 mmol), aldehyde (0.2 mmol) and amine (0.25 mmol) were mixed in 0.5 mL of dichloromethane, and then Au₂₆Cd₅ (5.31 mg, 0.5 mol%) was added to the mixture. The reaction mixture was stirred at room temperature under nitrogen atmosphere for 10 h, and purified by column chromatography on silica gel (ethyl acetate/petroleum ether, *V* : *V* = 1 : 15) to give propargylamine.

Cyclic test of Au₂₆Cd₅ in the model reaction

A mixture of phenylacetylene (30.6 mg, 0.3 mmol), benzaldehyde (21.2 mg, 0.2 mmol), pyrrolidine (17.8 mg, 0.25 mmol) and Au₂₆Cd₅ (5.31 mg, 0.5 mol%) in 0.5 mL of dichloromethane was stirred at room temperature under nitrogen for 10 h. Propargylamine (**1a**) and Au₂₆Cd₅ were separated by gradient elution on silica gel with eluent of ethyl acetate/petroleum ether (*V* : *V* = 1 : 15) (for propargylamine **1a**) and methanol/dichloromethane (*V* : *V* = 1 : 20) (for Au₂₆Cd₅), respectively. The recovered Au₂₆Cd₅ was reused for the next cycle.

Results and Discussion

The synthesis of Au₂₆Cd₅ is facile and high-yielded.

Briefly, 5.0 equiv. (per mole of Au₂₅) of Cd(PPh₃)₂(NO₃)₂ (for the identification by ESI-MS, see Figure S1), which was obtained by mixing PPh₃ with cadmium nitrate, was added into Au₂₅ solution (dichloromethane as solvent), and the resulting mixture was continuously stirred at room temperature for 1 h, then stopped by the addition of adequate hexane. The precipitate was collected by centrifuging, washed by excessive hexane and recrystallized from the mixed dichloromethane and toluene solvents in over 90% yield.

The UV/vis/NIR spectrum of the as-obtained product exhibits featured absorption peaks at 360, 400 and 470 nm, remarkably different from those of the mother nanocluster Au₂₅ at 400, 445 and 685 nm, respectively (Figure 1), indicating that it is of different composition (structure) with that of Au₂₅. Of note, the absorption spectrum of the product is also different from that of Au₂₄Cd(SC₂H₄Ph)₁₈ (Au₂₄Cd for short), which exhibits featured absorption at 400, 477 and 658 nm, respectively.^[29] X-ray photoelectron spectroscopy (XPS) reveals the co-existence of Au, Cd, S, P and N and the reduction of Cd²⁺ (Figure S2), indicating that it is another Cd-doped gold nanocluster. Single crystal X-ray crystallography reveals its composition and structure. One unit cell in the single crystals of the product contains four nanocluster cations and two [Cd(NO₃)₄]²⁻ anions (Figure 2), *i.e.* two nanocluster cations share one [Cd(NO₃)₄]²⁻ anion, thus the precise molecular formula is [Au₁₃Cd₂(PPh₃)₆(SC₂H₄Ph)₆(NO₃)₂]₂Cd(NO₃)₄. Quantitative XPS measurement supports this: the Au/Cd/S/P/N atomic ratio is 6.21/1.22/2.96/2.88/1.99, which is consistent very well with the Au/Cd/S/P/N ratio of 26/5/12/12/8 determined by X-ray crystallography. Further anatomy reveals that the inclusive nanocluster ion [Au₁₃Cd₂(PPh₃)₆(SC₂H₄Ph)₆(NO₃)₂] $^+$ (Au₁₃Cd₂ for short) contains an Au₁₃ icosahedron similar to the Au₁₃ core of the Au₂₅ nanocluster (Figures 3A and 3B): The averaged Au—Au distance from the central gold atom to the other twelve gold atoms is 2.769 \AA , a little shorter than that in the Au₁₃ core of Au₂₅ (2.773 \AA),^[33] and the averaged Au—Au distance between the outer twelve gold atoms is 2.901 \AA , also close to that in the Au₁₃ core of Au₂₅ (2.906 \AA).^[33] Two cadmium atoms connect with two NO₃ units, adhering to two Au₃ facets in the contraposition on surface of Au₁₃ icosahedron by six Cd—S—Au motifs, where the averaged Cd—S distance and Au—S distance are 2.553 and 2.327 \AA , respectively. Six triphenylphosphines coordinate to the other six unprotected gold atoms (one to one) with averaged Au—P distance of 2.294 \AA . Based on our previous work,^[25-29,34] it is proposed that Au₂₆Cd₅ is formed after the Au₁₂ shell of core-shell Au₂₅ is “peeled” by PPh₃^[26] and then Cd²⁺ is reduced and deposited on the surface of the Au₁₃ icosahedron (Figure 3C).^[25,27-29,34]

The two exerted cadmium atoms and the neighbor gold atoms on the surface of Au₁₃ icosahedron remind one that they could act as some active sites and cooperate in catalyzing multi-molecule reactions. Three-com-

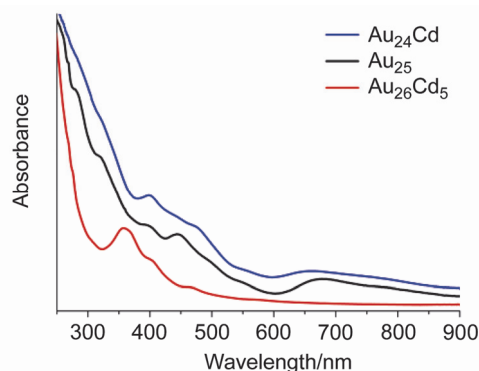


Figure 1 UV/Vis/NIR spectra of Au₂₄Cd, Au₂₅ and Au₂₆Cd₅. The spectra are vertically shifted for clarity.

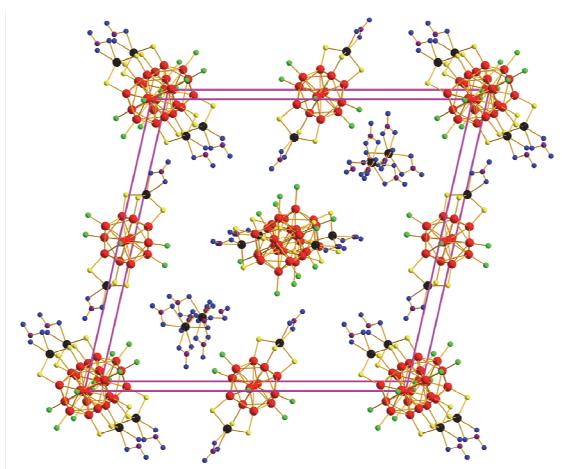


Figure 2 One unit cell of Au₂₆Cd₅. C and H atoms are omitted for clarity.

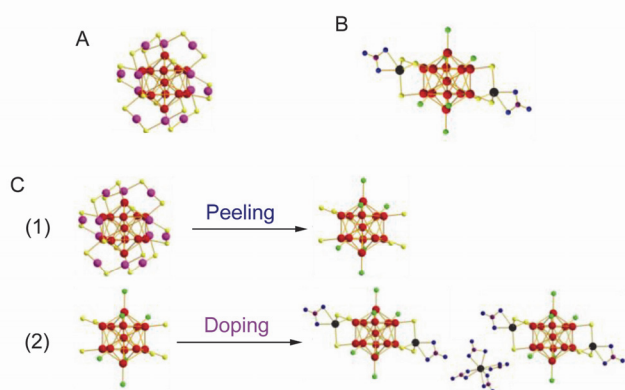


Figure 3 Structure of Au₂₅ (A) and Au₁₃Cd₂ unit of Au₂₆Cd₅ (B); Structural evolution from Au₂₅ to Au₂₆Cd₅ (C). Color labels: red=Au; black=Cd; yellow=S; green=P; purple=N; blue=O; C and H atoms are omitted for clarity.

ponent coupling of alkynes, aldehydes, and amines (A³-coupling) is an important reaction in organic chemistry to prepare propargylamines and their derivatives, which is often catalyzed by copper, gold or other metal salts/complexes but suffers from the harsh reaction con-

ditions (e.g. high temperature), low substrate tolerance or the unrecoverability of the catalysts.^[35-37] It's known that gold nanocluster can activate the C_{sp}-H bond of terminal alkynes to give R-≡-[Au]H intermediates.^[38-40] We also note that cadmium can coordinate with nitrogen atom effectively to catalyze the reaction of phosphonates with aldehydes and amines to produce aminophosphonates.^[41] Thus, we speculate that Au₂₆Cd₅ might be fit for catalyzing the A³-coupling on the basis of the above reasoning.

For simplification, the coupling of phenylacetylene, benzaldehyde and pyrrolidine was chosen as the model reaction to test the catalytic activity of Au₂₆Cd₅. Prior to its use in the catalytic reaction, Au₂₆Cd₅ was neither calcinated nor loaded on any supporters, excluding the possible influence from the supporter or structure change after calcination. To our delight, Au₂₆Cd₅ indeed exhibits high activity in catalyzing the model reaction even at room temperature: the yield of propargylic amine **1a** is 80% (Table 1, Entry 1), and it can be further improved to 92% after the optimization of reaction parameters (Table 1, Entry 8). The conversion vs. time data is shown in Figure S3. To verify that the excellent catalytic activity originates from the corporation of the Cd and the neighbor gold atoms on the surface of Au₁₃ icosahedron of Au₂₆Cd₅, a series of catalysts were tested. Both Au₂₅ and Au₁₃(PPh₃)₄(SC₂H₄Ph)₄ do not show any catalytic activity in the model reaction (Table 1, Entries 2 and 3), neither does Cd(NO₃)₂ or Cd(SC₂H₄Ph)_x(NO₃)_y (Table 1, Entries 4 and 5), indicating that the sole Au₁₃ icosahedron structure or Cd species does not work. Even the mixture of Au₁₃(PPh₃)₄(SC₂H₄Ph)₄ and Cd(SC₂H₄Ph)_x(NO₃)_y exhibits no catalytic activity under the same conditions (Table 1, Entry 6), which excludes the possibility that the catalytic activity comes from the simple cooperation between the Au₁₃ icosahedron and

Table 1 Comparison of catalytic activities of various catalysts and optimization of reaction conditions^a

Entry	Catalyst	Yield ^b /%
1	Au ₂₆ Cd ₅	80
2	Au ₂₅	0
3	Au ₁₃ (PPh ₃) ₄ (SC ₂ H ₄ Ph) ₄	0
4	Cd(NO ₃) ₂	0
5	Cd(SC ₂ H ₄ Ph) _x (NO ₃) _y	0
6	Au ₁₃ (PPh ₃) ₄ (SC ₂ H ₄ Ph) ₄ + Cd(SC ₂ H ₄ Ph) _x (NO ₃) _y	0
7	Au ₂₄ Cd	0
8 ^c	Au ₂₆ Cd ₅	92

^a Reaction conditions: phenylacetylene (0.3 mmol), benzaldehyde (0.2 mmol), pyrrolidine (0.25 mmol), catalyst (0.5 mol%), solvent (1.0 mL), 5 h. ^b Isolated yield. ^c Run for 10 h in 0.5 mL of DCM.

phenylethathiolated cadmium. Au_{24}Cd cannot catalyze the reaction at room temperature, either, indicating the importance of the specific structure in catalyzing the A^3 -coupling reaction (Table 1, Entry 7). Taken together, these facts demonstrate that the cooperation between the exerted Cd and the neighbor gold atoms plays vital role in the catalysis of the A^3 -coupling. Based on the above experimental results and some previous works,^[35-37] it is proposed that the exerted cadmium atom in $\text{Au}_{26}\text{Cd}_5$ grabs and activates the imine generated in situ from the aldehyde and the amine, and the neighbor gold atom traps and activates the $\text{C}_{\text{sp}}-\text{H}$ bond of the alkyne, after that, the activated alkyne attacks the activated imine to yield the propargylic amine (the illustration is shown in Figure S4).

The catalyst can be readily recovered by column chromatography for reuse after a minimum of 5 cycles without obvious loss of catalytic activity (see Figure 4), indicating that the structure of $\text{Au}_{26}\text{Cd}_5$ is rather stable during the reaction. The stability of $\text{Au}_{26}\text{Cd}_5$ in the catalysis process is also demonstrated by the UV/vis/NIR monitoring, see Figure S5.

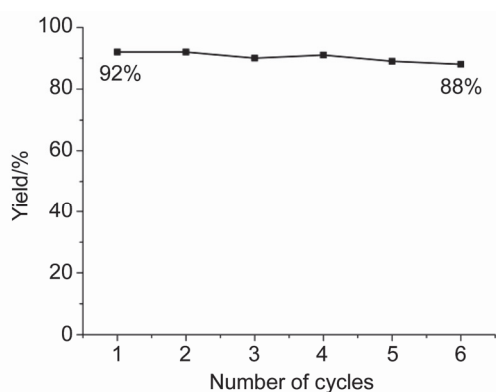
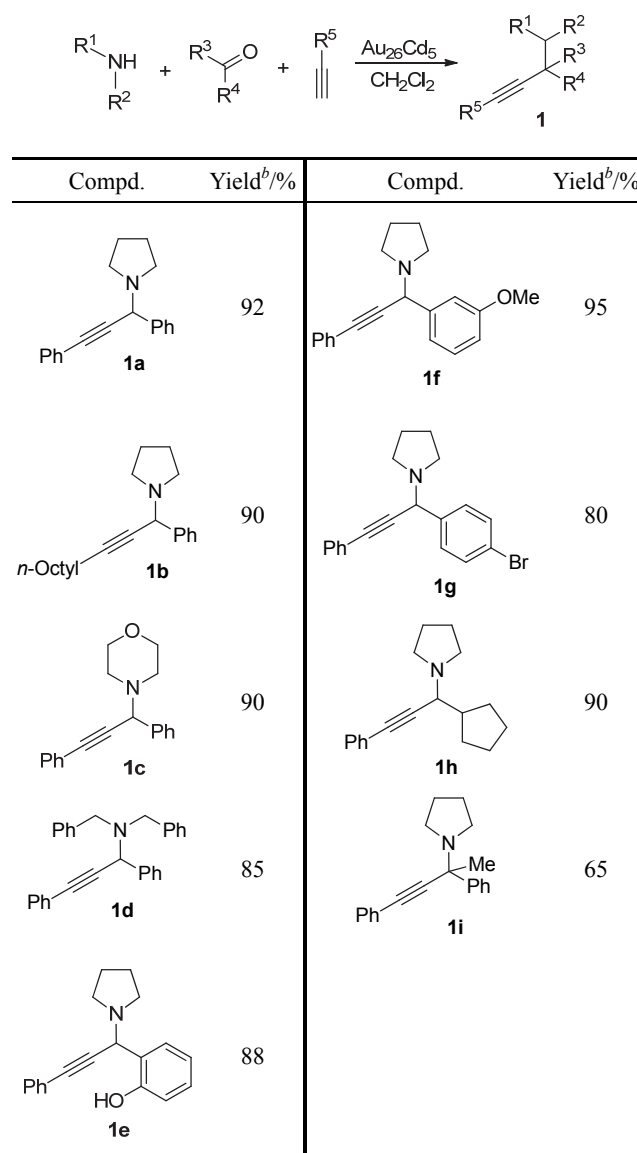


Figure 4 Cyclic test of $\text{Au}_{26}\text{Cd}_5$ in the model reaction.

Another merit of $\text{Au}_{26}\text{Cd}_5$ as a catalyst is its high substrate tolerance: a broad range of alkynes, aldehydes (or ketones) and amines can be smoothly catalyzed by $\text{Au}_{26}\text{Cd}_5$ to give the as-expected propargylic amines under mild conditions (Table 2). Terminal alkynes with aryl (**1a**, **1c–1i**) and alkyl (**1b**) substituents, aromatic (**1a–1g**) and aliphatic (**1h**) aldehydes, cyclic (**1a–1c**, **1e–1i**) and acyclic (**1d**) secondary amines are all viable substrates. Even a ketone is viable to yield a propargylic amine with a quaternary carbon center (**1i**), which is challenging in the three-component coupling due to low reaction activity.^[42] Benzaldehyde derivatives bearing electron-withdrawing groups or electron-donating groups at any positions of the benzene ring also give satisfactory yields ($\geq 80\%$, see Figure 5, **1e**, **1f** and **1g**). In addition, the reaction well tolerates a variety of functional groups, such as benzyl (**1d**), hydroxyl (**1e**), alkoxy (**1f**) and halo (**1g**). These results indicate the high substrate tolerance of $\text{Au}_{26}\text{Cd}_5$. With combined

merits such as high activity, good recyclability and high substrate tolerance, $\text{Au}_{26}\text{Cd}_5$ is very promising as a catalyst for the A^3 -coupling reaction.

Figure 5 Substrate scope of $\text{Au}_{26}\text{Cd}_5$ -catalyzed A^3 -coupling reaction^a



^a Reaction conditions: alkyne (0.3 mmol), aldehyde or ketone (0.2 mmol), amine (0.25 mmol), $\text{Au}_{26}\text{Cd}_5$ (0.5 mol%), dichloromethane (0.5 mL), 10 h. ^b Isolated yield.

Conclusions

In summary, both doping and peeling were adopted to transform $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ to a novel cadmium doped gold nanocluster $\text{Au}_{26}\text{Cd}_5$ in high yield ($>90\%$) targeting the improvement of its catalytic performance. The atomic structure of $\text{Au}_{26}\text{Cd}_5$ was resolved by single crystal X-ray crystallography, which demonstrates that it is composed of two $\text{Au}_{13}\text{Cd}_2(\text{PPh}_3)_6(\text{SC}_2\text{H}_4\text{Ph})_6(\text{NO}_3)_2$ cations and one shared $[\text{Cd}(\text{NO}_3)_4]^{2-}$, and every $\text{Au}_{13}\text{Cd}_2$ contains one Au_{13} icosahedron with two $[\text{CdNO}_3]$ units

capping two contrapositioned Au³ faces on surface of the Au₁₃ icosahedron. Importantly, it is found that Au₂₆Cd₅ is promising as a catalyst for the A³-coupling reaction due to its high activity and substrate tolerance as well as good recyclability, although Au₂₅ exhibits no catalytic activity under the investigated conditions. The cooperation of the exerted cadmium atoms and the neighbor gold atoms may be responsible for the unusual high catalytic activity of Au₂₆Cd₅ at room temperature. It is expected that our work will trigger more research on the subtle tuning of nanoclusters' compositions and structures to improve their performances by some unusual and effective strategies.

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