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Improving the Catalytic Activity of Au_{25} 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 $Au_{25}(SCH_2CH_2Ph)_{18}$ (Au_{25} for short) nanocluster has been transformed to a rare cadmium doped gold nanocluster $[Au_{13}Cd_2(PPh_3)_6(SC_2H_4Ph)_6(NO_3)_2]_2Cd(NO_3)_4$ ($Au_{26}Cd_5$ for short) by peeling and doping. Although Au_{25} exhibits no catalytic activity toward A^3-coupling reaction under the investigated conditions, the novel cadmium doped gold nanocluster $Au_{26}Cd_5$ 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 Au_{13} 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, A^3-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 PPh_3 can peel the core-shell Au_{25} nanoclusters and assist the transformation from core-shell Au_{25} to Au_{13}, Au_{11}, and finally to biicosahedral Au_{25}.[26] We also revealed that Cd can be doped into core-shell Au_{25} via an anti-galvanic reduction (AGR).[27-29] Herein, both peeling and doping are adopted to tune the composition and structure of core-shell Au_{25} targeting the improvement of its catalysis performance. Fortunately, we successfully synthesized $[Au_{13}Cd_2(PPh_3)_6(SC_2H_4Ph)_6(NO_3)_2]_2Cd(NO_3)_4$ ($Au_{26}Cd_5$ for short) by this strategy, and found that $Au_{26}Cd_5$ exhibits high catalytic activity, as well as good recyclability and substrate tolerance for the A^3-coupling, although the precursor Au_{25} shows no catalytic activity under the same conditions.

Experimental

Materials

Cadmium nitrate tetrahydrate [$Cd(NO_3)_2 \cdot 4H_2O$, 99.0%], triphenylphosphine (PPh_3, 99.0%), dichloromethane (CH_2Cl_2, A.R.), methanol (CH_3OH, A.R.), hexane (C_6H_{12}, A.R.), petroleum ether (A.R., 30—60 ℃) 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. $[Au_{25}(SC_2H_4Ph)_{18}]^-$,[30,31] $Au_{24}Cd(SC_2H_4Ph)_{18}$[29] and $Au_{13}(PPh_3)_4(SC_2H_4Ph)_4$[32] were synthesized following the previous methods. $Cd(PPh_3)_2(NO_3)_2$ was prepared by the mixing of $Cd(NO_3)_2$ with PPh_3 in methanol. $Cd(SC_2H_4Ph)_x(NO_3)_y$ was synthesized by the mixing of $Cd(NO_3)_2$ with PhC_2H_4SH 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 μL/min. The source temperature was fixed at 70 ℃. The spray voltage was set at 2.20 kV and the cone voltage was set at 60 V. ^1H 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 Kα 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 Kα 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 Au_{25} to $Au_{26}Cd_5$

$Cd(PPh_3)_2(NO_3)_2$ (5.0 mg) was added to 10 mg of $[Au_{25}(SC_2H_4Ph)_{18}]^-$ in 2.0 mL of dichloromethane. The mixture was stirred at room temperature for 1 h, and then precipitated by hexane. $Au_{26}Cd_5$ was purified by crystallization from the mixed solvent of dichloromethane and toluene at 4 ℃. The yield of $Au_{26}Cd_5$ was 91%.

$Au_{26}Cd_5$ catalyzed A^3-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 $Au_{26}Cd_5$ (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 $Au_{26}Cd_5$ in the model reaction

A mixture of phenylacetylene (30.6 mg, 0.3 mmol), benzaldehyde (21.2 mg, 0.2 mmol), pyrolidine (17.8 mg, 0.25 mmol) and $Au_{26}Cd_5$ (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 $Au_{26}Cd_5$ 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 $Au_{26}Cd_5$), respectively. The recovered $Au_{26}Cd_5$ was reused for the next cycle.

Results and Discussion

The syntehesis of $Au_{26}Cd_5$ is facile and high-yielded. Briefly, 5.0 equiv. (per mole of Au_{25}) of $Cd(PPh_3)_2(NO_3)_2$ (for the identification by ESI-MS, see Figure S1), which was obtained by mixing PPh_3 with cadmium nitrate, was added into Au_{25} 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 Au_{25} at 400, 445 and 685 nm, respectively (Figure 1), indicating that it is of different composition (structure) with that of Au_{25}. Of note, the absorption spectrum of the product is also different from that of $Au_{24}Cd(SC_2H_4Ph)_{18}$ ($Au_{24}Cd$ 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 Cd^{2+} (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 $[Cd(NO_3)_4]^{2-}$ anions (Figure 2), *i.e.* two nanocluster cations share one $[Cd(NO_3)_4]^{2-}$ anion, thus the precise molecular formula is $[Au_{13}Cd_2(PPh_3)_6(SC_2H_4Ph)_6(NO_3)_2]_2Cd(NO_3)_4$. 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 $[Au_{13}Cd_2(PPh_3)_6(SC_2H_4Ph)_6(NO_3)_2]^+$ ($Au_{13}Cd_2$ for short) contains an Au_{13} icosahedron similar to the Au_{13} core of the Au_{25} nanocluster (Figures 3A and 3B): The averaged Au—Au distance from the central gold atom to the other twelve gold atoms is 2.769 Å, a little shorter than that in the Au_{13} core of Au_{25} (2.773 Å),[33] and the averaged Au—Au distance between the outer twelve gold atoms is 2.901 Å, also close to that in the Au_{13} core of Au_{25} (2.906 Å).[33] Two cadmium atoms connect with two NO_3 units, adhering to two Au_3 facets in the contraposition on surface of Au_{13} icosahedron by six Cd-S-Au motifs, where the averaged Cd—S distance and Au—S distance are 2.553 and 2.327 Å, respectively. Six triphenylphophines coordinate to the other six unprotected gold atoms (one to one) with averaged Au—P distance of 2.294 Å. Based on our previous work,[25-29,34] it is proposed that $Au_{26}Cd_5$ is formed after the Au_{12} shell of core-shell Au_{25} is "peeled" by PPh_3[26] and then Cd^{2+} is reduced and deposited on the surface of the Au_{13} icosahedron (Figure 3C).[25,27-29,34]

The two exerted cadmium atoms and the neighbor gold atoms on the surface of Au_{13} icosohedron remind one that they could act as some active sites and cooperate in catalyzing multi-molecule reactions. Three-com-

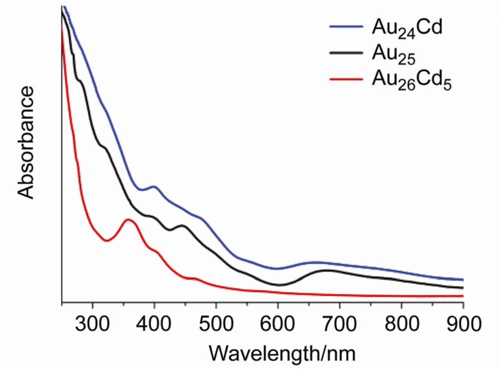


Figure 1 UV/Vis/NIR spectra of $Au_{24}Cd$, Au_{25} and $Au_{26}Cd_5$. The spectra are vertically shifted for clarity.

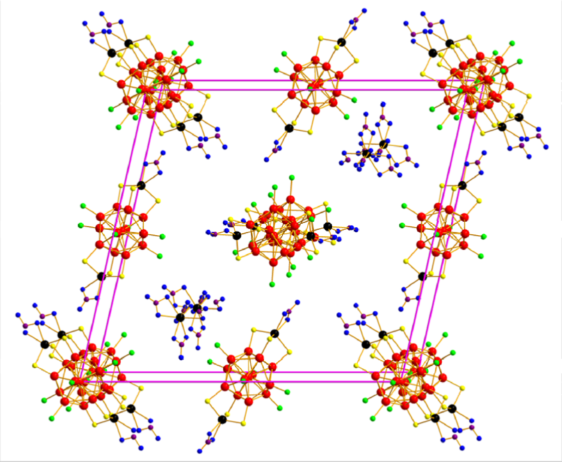


Figure 2 One unit cell of $Au_{26}Cd_5$. C and H atoms are omitted for clarity.

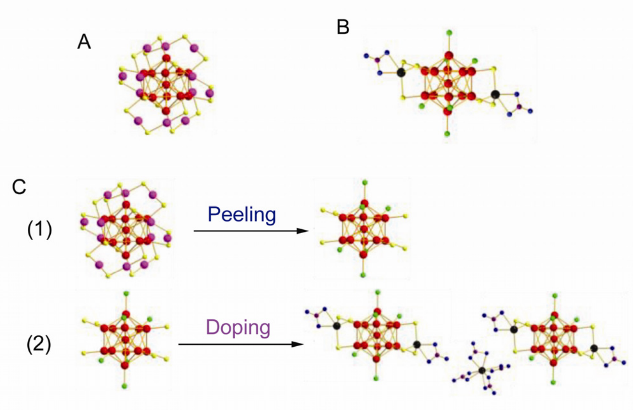
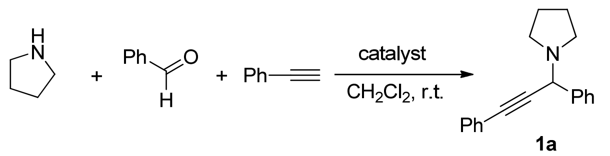


Figure 3 Structure of Au_{25} (A) and $Au_{13}Cd_2$ unit of $Au_{26}Cd_5$ (B); Structural evolution from Au_{25} to $Au_{26}Cd_5$ (C). Color labels: red=Au; black=Cd; yellow=S; green=P; purple=N; blue=O; C and H atoms are omitted for clarity.

ponent coupling of alkynes, aldehydes, and amines (A^3-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 conditions (*e.g.* high temperature), low substrate tolerance or the unrecyclability of the catalysts.[35-37] It's known that gold nanocluster can active 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 $Au_{26}Cd_5$ might be fit for catalyzing the A^3-coupling on the basis of the above reasoning.

For simplification, the coupling of phenylacetylene, benzaldehyde and pyrolidine was chosen as the model reaction to test the catalytic activity of $Au_{26}Cd_5$. Prior to its use in the catalytic reaction, $Au_{26}Cd_5$ was neither calcinated nor loaded on any supporters, excluding the possible influence from the supporter or structure change after calcination. To our delight, $Au_{26}Cd_5$ 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 Au_{13} icosahedron of $Au_{26}Cd_5$, a series of catalysts were tested. Both Au_{25} and $Au_{13}(PPh_3)_4(SC_2H_4Ph)_4$ do not show any catalytic activity in the model reaction (Table 1, Entries 2 and 3), neither does $Cd(NO_3)_2$ or $Cd(SC_2H_4Ph)_x(NO_3)_y$ (Table 1, Entries 4 and 5), indicating that the sole Au_{13} icosahedron structure or Cd species does not work. Even the mixture of $Au_{13}(PPh_3)_4(SC_2H_4Ph)_4$ and $Cd(SC_2H_4Ph)_x(NO_3)_y$ 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 Au_{13} 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	$Au_{13}(PPh_3)_4(SC_2H_4Ph)_4$	0
4	$Cd(NO_3)_2$	0
5	$Cd(SC_2H_4Ph)_x(NO_3)_y$	0
6	$Au_{13}(PPh_3)_4(SC_2H_4Ph)_4+Cd(SC_2H_4Ph)_x(NO_3)_y$	0
7	$Au_{24}Cd$	0
8[c]	$Au_{26}Cd_5$	92

[a] Reaction conditions: phenylacetylene (0.3 mmol), benzaldehyde (0.2 mmol), pyrolidine (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 Au$_{26}$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 C$_{sp}$—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 Au$_{26}$Cd$_5$ is rather stable during the reaction. The stability of Au$_{26}$Cd$_5$ in the catalysis process is also demonstrated by the UV/vis/NIR monitoring, see Figure S5.

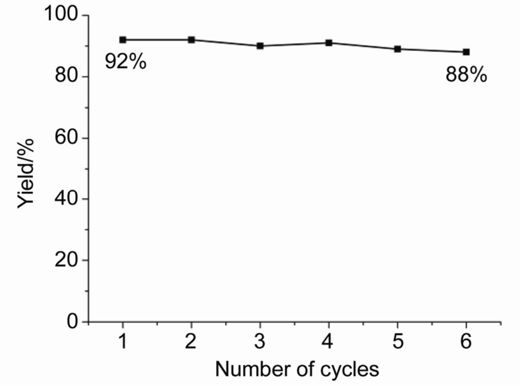
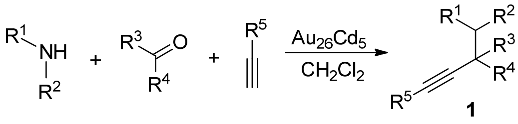
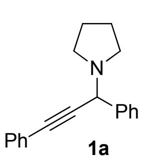
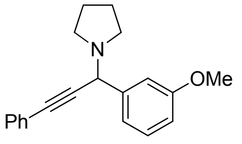
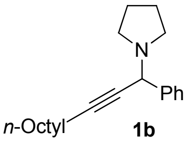
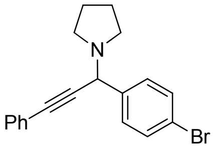
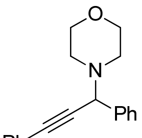
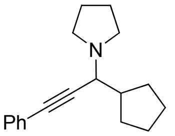
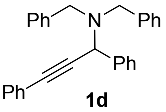
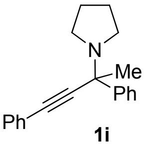
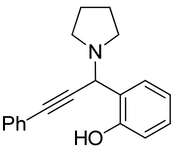


Figure 4 Cyclic test of Au$_{26}$Cd$_5$ in the model reaction.

Another merit of Au$_{26}$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 Au$_{26}$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 (⩾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 Au$_{26}$Cd$_5$. With combined merits such as high activity, good recyclability and high substrate tolerance, Au$_{26}$Cd$_5$ is very promising as a catalyst for the A^3-coupling reaction.

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



Compd.	Yield[b]/%	Compd.	Yield[b]/%
 **1a**	92	 **1f**	95
 **1b**	90	 **1g**	80
 **1c**	90	 **1h**	90
 **1d**	85	 **1i**	65
 **1e**	88		

[a] Reaction conditions: alkyne (0.3 mmol), aldehyde or ketone (0.2 mmol), amine (0.25 mmol), Au$_{26}$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 Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$ to a novel cadmium doped gold nanocluster Au$_{26}$Cd$_5$ in high yield (>90%) targeting the improvement of its catalytic performance. The atomic structure of Au$_{26}$Cd$_5$ was resolved by single crystal X-ray crystallography, which demonstrates that it is composed of two Au$_{13}$Cd$_2$(PPh$_3$)$_6$(SC$_2$H$_4$Ph)$_6$(NO$_3$)$_2$ cations and one shared [Cd(NO$_3$)$_4$]$^{2-}$, and every Au$_{13}$Cd$_2$ contains one Au$_{13}$ icosahedron with two [CdNO$_3$] units capping two contrapositioned Au^3 faces on surface of the Au_{13} icosahedron. Importantly, it is found that $Au_{26}Cd_5$ is promising as a catalyst for the A^3-coupling reaction due to its high activity and substrate tolerance as well as good recyclability, although Au_{25} 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 $Au_{26}Cd_5$ 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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