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通过赝反伽伐尼反应实现金纳米粒子模块替换

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摘要 通过可控的方式精确调控纳米粒子的结构仍是一个富有挑战性和鼓舞人心的课题. 尽管单原子或两、三个金属原子的精细调控已经在金纳米粒子中实现, 涉及三个以上金属原子的取代(模块取代)还没有报道. 本工作报道了环己硫醇配体保护的 $Au_{48}(CHT)_{26}$ 的合成及其通过赝反伽伐尼过程的模块取代. 单晶结构揭示模块取代的产物与母体团簇共用一个相似的 $Au_{31}(CHT)_{12}$ 主体, 但剩余部分不同($Au_6(CHT)_{11}$ vs. $Au_{16}(CHT)_{14}$). 一个有趣的发现是模块取代抑制了 $Au_{48}(CHT)_{26}$ 的光热过程, 却增强了它的发射, 赋予了所合成团簇更好的双(多)功能应用潜力. 光热效应的减弱和发射的增强也暗示了这两种作用能够彼此至少部分转化, 对于研究这两种效应之间的相互影响也具有重要的启示.

关键词 金纳米团簇; 模块替换; 赝反伽伐尼反应; 光热效应; 荧光

Module Replacement of Gold Nanoparticles by a Pseudo-AGR Process

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Abstract Precisely modulating the structure of nanoparticles in a controlled manner is still a challenging and inspiring topic. Although the single or few-metal atom tailoring of gold nanoparticles has been reported, local structural replacement involving over three net metal atoms (module replacement, MR) has not been hitherto achieved. Herein, we report the synthesis of cyclohexanethiolated metal nanoclusters (NCs) $Au_{48}(CHT)_{26}$ and their MR by a so-called pseudo-anti-galvanic reaction (AGR) process. The MR product $Au_{37}(CHT)_{23}$ shares a similar $Au_{31}(CHT)_{12}$ unit with its predecessor $Au_{48}(CHT)_{26}$; however,

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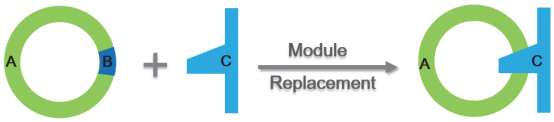
it differs from its predecessor in the remaining section ($Au_6(CHT)_{11}$ vs. $Au_{16}(CHT)_{14}$), as revealed by single-crystal X-ray crystallography (SCXC). Interestingly, the MR inhibits the photothermy but enhances the emission of $Au_{48}(CHT)_{26}$ NCs, which might endow the as-obtained NC better potential for bi(multiple)-functional application. The counter effects of the MR on the emission and photothermy indicate that photoluminescence and photothermy can be at least partly converted into each other, which has some important implications for the understanding of their interaction.

Keywords gold nanoparticles; module replacement; pseudo-anti-galvanic reaction (AGR); photothermy; photoluminescence

1 Introduction

For organic molecules, people can precisely tailor the specific substructure without altering the major carbon bones to endow them with various functions. Meanwhile, for traditional nanoparticles, it is nearly impossible to precisely tune the structure at the atomic level. With the development of wet chemistry, breakthroughs have been achieved in the synthesis of ultrasmall metal nanoparticles (often called nanoclusters (NCs)) in the past decades.[1-10] Metal NCs have the merits of mono-dispersity,[11-14] well-defined compositions and structures,[1,15-22] intriguing physicochemical properties[7, 23-28] and so on. In particular, these ultrasmall nanoparticles provide opportunities for precisely tuning the overall or even partial structure (including specific sites), which is of great significance to understand the structure-property correlation and improve the performance in a sustainable way. The overall structure transformation has been repeatedly reported; for example, Au_{25} NCs can be converted into Au_{20},[29] Au_{23},[30] Au_{24},[31] Au_{28},[32] or Au_{38}[33,34] by various methods such as ligand exchange/etching, reduction and acid-induction. Recently, the single or few metal-atom tailoring of metal nanoparticles with the remnant structure untouched has also been accomplished. For example, Jin *et al*. reported an interesting molecular "surgery"[35,36] by employing the combined anti-galvanic[37-39] and pseudo-anti-galvanic reactions.[31] Wu *et al*. successfully realized single or few metal-atom addition and replacement by employing an anti-galvanic reaction (AGR)[40-44] (notably, the same group also introduced the surface single-atom tailoring method recently).[45] However, to date, the local structural replacement involving over three net metal atoms (Scheme 1) has not been fulfilled no matter the replacement is an elementary reaction or not. For clarification, such a structure manipulation was named module replacement (MR). To explore such a concept, we conducted this study.



Scheme 1 The illustration of the module replacement process.

Unlike the common ligands such as 4-*tert*-butylbenzenethiolate (TBBT), 2,4-dimethylbenzenethiolate (CHT) (2,4-DMBT), and *p*-methylbenzenethiolate (*p*-MBT), cyclohexanethiolate is short and flexible, making it suitable for this study as a protecting ligand of metal NCs. Actually, cyclohexanethiolated gold NCs have gained extensive interest recently, and several cyclohexanethiolated gold NCs including $Au_{18}(CHT)_{14}$,[46] $[Au_{23}(CHT)_{16}]^-$,[47] $Au_{28}(CHT)_{20}$,[48] $Au_{34}(CHT)_{22}$,[49] $Au_{42}(CHT)_{26}$,[49] and $Au_{43}(CHT)_{25}$[50] have been reported and structurally resolved until now. However, it remains unknown whether the cyclohexanethiolated gold NCs larger than $Au_{43}(CHT)_{25}$[50] can be structurally resolved. To address this issue as well, we investigated the synthesis of cyclohexanethiolated gold NCs and obtained a slightly larger NC $Au_{48}(CHT)_{26}$.

2 Results and discussion

2.1 ESI-MS

Electrospray ionization mass spectrometry (ESI-MS) was applied to determine the exact molecular formulas of the as-obtained gold NCs. To assist in the ionization, cesium acetate (CsOAC) was added to the NC solution to form positively charged adducts. Notably, the NCs are charge neutral since the charge number is equal to the number of adducted Cs ions, which is further supported by the fact that there were no sound signals in the mass spectra acquired in both the positive and negative ionization modes without the addition of the assistant reagent. As shown in Figure 1a, one dominant peak centered at *m*/*z* 6358.95 was shown in the mass spectrum, which can be readily assigned to $[Au_{48}(CHT)_{26}Cs_2]^{2+}$ species (calculated: 6358.37 Da, deviation: 0.58 Da). Therefore, the NC formula was determined to be $Au_{48}(CHT)_{26}$.

2.2 SCXC

Single-crystal X-ray crystallography (SCXC) confirms the composition and reveals that the NCs crystallize in the axisymmetric space group $P2_1/c$ with the unit cell comprised of a pair of enantiomers (Figure S1). As shown in Figure 2, the overall structure of $Au_{48}(CHT)_{26}$ is distinctly different from the previously reported $Au_{48}(TBBT)_{28}$ NC, which is protected by 28 4-*tert*-butylbenzenethiolates with a Au_{31} kernel consisting of face-fused bi-icosahedral Au_{23} and a special Au_8 bottom cap.[51] Meanwhile, the structure of $Au_{48}(CHT)_{26}$ contains a Au_{35} kernel (Figure 2c) composed of one quasi-fcc Au_{21} unit (Figure 2a) and one non-fcc Au_{14} unit (Figure 2b). This quasi-dual-packed-kerneled structure resembles that of Au_{49}(2,4-DMBT)$_{27}$, which contains a Au_{34} kernel consisting of one quasi-fcc Au_{21} unit and one non-fcc Au_{13} unit,[52] and it has not been previously reported in cyclohexanethiolated metal NCs. The Au_{35} kernel of $Au_{48}(CHT)_{26}$ is capped by an exterior shell including four $Au_2(SR)_3$ dimers, five $Au(SR)_2$ monomers and four bridging SR thiolates (Figure 2d-2f).

A pseudo-anti-galvanic reaction (AGR) was employed for the MR of the as-obtained $Au_{48}(CHT)_{26}$ due to that pseudo-AGR has shown great potential to modulate the

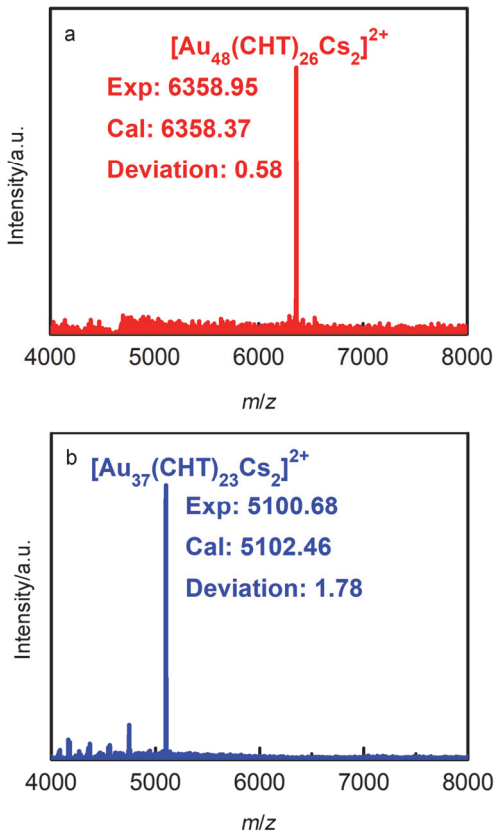


Figure 1 ESI-MS spectra of $Au_{48}(CHT)_{26}$ (a) and $Au_{37}(CHT)_{23}$ (b) NCs.

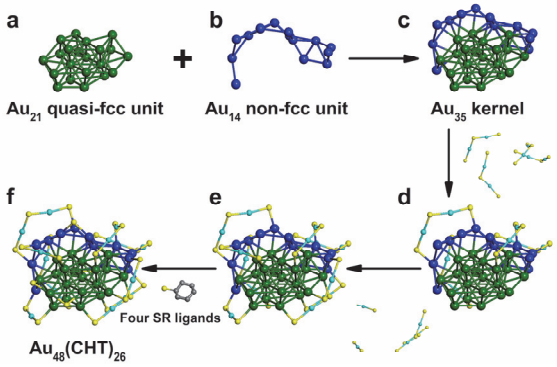


Figure 2 Anatomy of the structure of the $Au_{48}(CHT)_{26}$ NC: (a) Au_{21} quasi-fcc unit; (b) Au_{14} non-fcc unit; (c) Au_{35} kernel; (d) $Au_{43}(CHT)_{12}$ framework; (e) $Au_{48}(CHT)_{22}$ framework; and (f) total structure of $Au_{48}(CHT)_{26}$. For clarity, C and H are omitted. Color labels: yellow=S; others=Au.

structure of gold NCs in a controlled way.[31,35,44] Luckily, we successfully achieved the MR manipulation and obtained a novel NC, whose composition was determined to be $Au_{37}(CHT)_{23}$ (Figure 1b). SCXC further confirms this composition and reveals that $Au_{37}(CHT)_{23}$ crystallizes in the axisymmetric space group *P*-1, with the unit cell comprised of a pair of enantiomers (Figure S2). The overall structure of $Au_{37}(CHT)_{23}$ is composed of an Au_{25} kernel capped by an outer shell containing one $Au_3(SR)_4$ trimer, three $Au_2(SR)_3$ dimers, three $Au(SR)_2$ monomers and four bridging SR thiolates (Figure S3). It can be readily found that the Au_{35} kernel of $Au_{48}(CHT)_{26}$ can be regarded as the net addition of one Au_{10} unit to the Au_{25} kernel of $Au_{37}(CHT)_{23}$ (Figure 3a-3f). In the Au_{10} unit, four Au atoms belong to the part of the quasi-fcc structure, and the other six Au atoms belong to the part of the non-fcc structure. Of note is that the proportion of fcc structure in the kernel of $Au_{37}(CHT)_{23}$ increases compared to that in the kernel of $Au_{48}(CHT)_{26}$. However, the Au_{25} kernel connected staples in $Au_{37}(CHT)_{23}$ are the same as those in $Au_{48}(CHT)_{26}$, *i.e.*, $Au_{37}(CHT)_{23}$ and $Au_{48}(CHT)_{26}$ share the same $Au_{31}(CHT)_{12}$ section with the other section different ($Au_6(CHT)_{11}$ vs. $Au_{17}(CHT)_{14}$). Therefore, the transformation from $Au_{48}(CHT)_{26}$ to $Au_{37}(CHT)_{23}$ can be regarded as a MR process (Figure 4), and the net reaction can be described in Table 1. DFT calculations (see Supporting Information for the details) reveal the formation energy (ΔE) is −22.0 eV, indicating that the reaction is energy-favorable. It should be noted that $Au_{48}(CHT)_{26}$ and $Au_{37}(CHT)_{23}$ can also be regarded as kernel homologues previously proposed by Zhuang *et al.*[51] The local internal structural change also leads to the remarkable alternation of the external structure (crystallographic arrangement). As shown in Figure S4, the $Au_{48}(CHT)_{26}$ adopts the "ABCD" arrangement, which is essentially different from the "ABAB" arrangement in $Au_{37}(CHT)_{23}$ crystals.

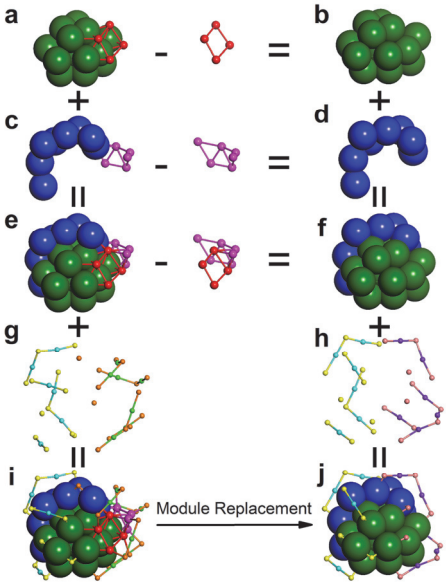


Figure 3 Anatomy of structures of $Au_{37}(CHT)_{23}$ and $Au_{48}(CHT)_{26}$ NCs: (a) Au_{21} quasi-fcc unit of $Au_{48}(CHT)_{26}$; (b) Au_{17} quasi-fcc unit of $Au_{37}(CHT)_{23}$; (c) Au_{14} non-fcc unit of $Au_{48}(CHT)_{26}$; (d) Au_8 non-fcc unit of $Au_{37}(CHT)_{23}$; (e) Au_{35} kernel of $Au_{48}(CHT)_{26}$; (f) Au_{25} kernel of $Au_{37}(CHT)_{23}$; (g) total staple motifs of $Au_{48}(CHT)_{26}$; (h) total staple motifs of $Au_{37}(CHT)_{23}$; (i) total structure of $Au_{48}(CHT)_{26}$; and (j) total structure of $Au_{37}(CHT)_{23}$. For clarity, C and H are omitted. Color labels: yellow, orange and pink=S; others=Au.

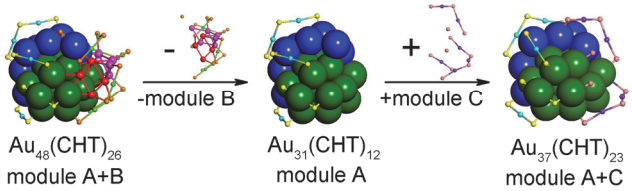
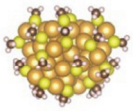
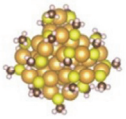


Figure 4 The illustration of module replacement process from $Au_{48}(CHT)_{26}$ to $Au_{37}(CHT)_{23}$.

Table 1 The net reaction and the formation energy estimation

$Au_{48}(CHT)_{26}+11Au(CHT)=Au_{37}(CHT)_{23}+Au_{17}(CHT)_{14}+5Au^{+}$

$Au_{48}(SCH_3)_{26}$	$Au(SCH_3)$	$Au_{37}(SCH_3)_{23}$	$Au_{17}(SCH_3)_{14}$	Au^+
				
-781.4 eV	-25.4 eV	-674.6 eV	-391.7 eV	-3.3 eV

$\Delta E=[(-674.6)+(-391.7)+(-3.3\times5)-(-781.4)+(-25.4\times11)]$ eV $=-22.0$ eV <0

E denotes formation energy, herein the *E* approximates the free energy.

2.3 Photothermy and photoluminescence

More interest pertains to the property tuning of the MR. Photoluminescence is an intriguing property that has been extensively studied,[53-61] while photothermy is rarely studied for well-defined NCs despite its potential in a large range of fields such as energy conversion[62,63] and biomedicine.[64-68] To the best of our knowledge, the combination study of photoluminescence and photothermy for well-defined metal NCs has not yet been examined. Herein, we investigated and compared their photoluminescence and photothermy. As shown in Figure 5 and Figures S5 and S6, both NCs exhibit obvious photothermal effects. Specifically, the temperatures of $Au_{48}(CHT)_{26}$ and $Au_{37}(CHT)_{23}$ solutions with a concentration of 0.1 mmol/L increased by 17.2 ℃ and 12.0 ℃ under the investigated conditions with photothermal conversion efficiencies of 42.9% and 30.3%, respectively (see Figure 5a and Supporting Information), indicating that $Au_{48}(CHT)_{26}$ had a stronger photothermal effect than $Au_{37}(CHT)_{23}$, which is also supported by their infrared thermal imaging results (Figure S5). However, the emission intensity of $Au_{37}(CHT)_{23}$ is about three-fold the intensity of $Au_{48}(CHT)_{26}$ (Figure 5b), indicating that emission and photothermy are in a balance[69-71] and they can be at least partly converted into each other, which was not previously reported for well-defined NCs. These facts also indicate that MR can efficiently tune the properties of metal NCs. It should be noted that such bi(multiple)-functional NCs are particularly promising for practical applications. For example, such materials might be applied for both imaging and curing cancer since they have both NIR photoluminescence and photothermy properties. Nevertheless, this is beyond the scope of the current study and should be pursued in the future.

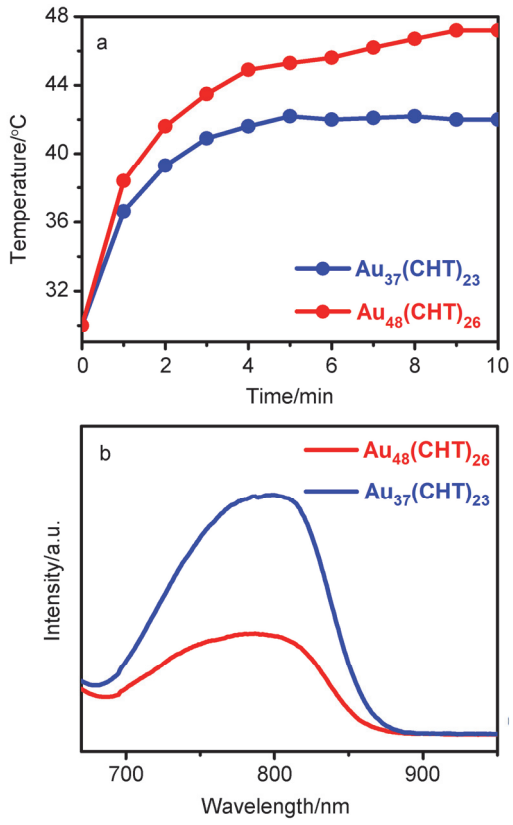


Figure 5 (a) The photothermal effects of $Au_{48}(CHT)_{26}$ and $Au_{37}(CHT)_{23}$ with a concentration of 0.1 mmol/L under 0.25 W/cm^2 650 nm laser irradiation (laser beam size: 1 cm^2). (b) The photoluminescence spectra of $Au_{48}(CHT)_{26}$ and $Au_{37}(CHT)_{23}$ (the excitation wavelength λ_{ex}=650 nm).

3 Conclusion

In summary, we have succeeded in synthesizing the largest cyclohexanethiolated metal NCs structurally resolved by ESI-MS and SCXC, revealing that one NC is composed of 48 gold atoms and 26 cyclohexanethiolates with a quasi-dual-packed-kerneled structure not reported in cyclohexanethiolated metal NCs. For the first time, we fulfill the MR manipulation of metal NCs by a pseudo-AGR process and obtain another novel NC $Au_{37}(CHT)_{23}$, which can also be regarded as the kernel homologue of $Au_{48}(CHT)_{26}$. DFT calculations also support the transformation from $Au_{48}(CHT)_{26}$ to $Au_{37}(CHT)_{23}$ is energy-favorable. The MR weakens the photoluminescence but strengthens the photothermy in this work, indicating that photoluminescence and photothermy are in a balance and they can be at least partly converted into each other for NCs. The property tuning by MR might endow NCs better potential for bi(multiple)-functional applications, which need to be pursued in the future. Overall, our work not only provides novel insights into the structures of metal NCs but also has important implications for future tuning of the compositions, structures and properties of metal nanoparticles and understanding of the interactions between various properties as well.

4 Experiment

The synthesis is facile. Briefly, the precursors of the polydisperse $Au_x(CHT)_y$ clusters were first synthesized by reducing the Au(I)-(CHT) complexes with $NaBH_4$. Then, the $Au_x(CHT)_y$ was treated with excess cyclohexanethiol at 80 ℃ for 15 h. The crude products were washed with excess methanol and then purified by preparative thin-layer chromatography (PTLC) (see Supporting Information for the experimental details). The as-purified NCs were recrystallized from the solution of toluene/methanol (V∶V=4∶3) at 0 ℃ over one week.

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