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Synthesis of High Yield Au₂₁(SR)₁₅ Nanoclusters

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Abstract: In recent years, Au nanoclusters have attracted much attention as new nanomaterials, which contain several to two hundred Au atoms and are protected by ligands. The structures and properties of Au nanoclusters are usually sensitive to the particle size due to quantum confinement effect. Au nanoclusters have been applied to different fields, such as optical properties, catalysis, and biology. There are two common methods for the synthesis of atomically precise Au nanoclusters: “size focusing” and “ligand exchange”. Although a series of Au nanocluster have been obtained via “size focusing” and “ligand exchange”, obtaining high yield of such Au nanoclusters is a challenge. Au₂₁(S-Adam)₁₅ was previously synthesized via etching Au₁₈ nanoclusters with excess thiols, and its crystal structure was determined by X-ray diffraction crystallography; however, the yield of Au nanoclusters was low. In this study, we prepared Au₂₁(S-Adam)₁₅ in high yield via conversion of Au₂₃(S-Adam)₁₆ to Au₂₁(S-Adam)₁₅. Firstly, Au₂₃(S-Adam)₁₆ nanoclusters were synthesized using adamantanethiols(HS-Adam) as the protecting ligand and HAuCl₄ as the gold resource in ethyl acetate solvent. Au₂₃(S-Adam)₁₆ were further etched with excess thiols at room temperature. After reacting for 30 min, highly pure Au₂₁(S-Adam)₁₅, with high yield of ~20% based on HAuCl₄ precursor, were successfully prepared. Au₂₃(S-Adam)₁₆ and Au₂₁(S-Adam)₁₅ were characterized by electrospray ionization (ESI), UV-Vis absorption spectroscopy, matrix-assisted laser desorption ionization (MALDI) mass spectrometry, and thermogravimetric analysis (TGA). ESI-MS and UV-Vis spectra confirm the high purity of the Au₂₃(S-Adam)₁₆. After conversion, UV-Vis spectra show the absorption peaks of Au₂₁(S-Adam)₁₅ at 700, 540, 435 and 380 nm. The MALDI-MS of Au₂₁(S-Adam)₁₅ shows several peaks at 6502, 6471, 6106, 5411, and 5048, assigned to Au₂₁(S-Adam)₁₄S, Au₂₁(S-Adam)₁₄, Au₂₀(S-Adam)₁₃, Au₁₉(S-Adam)₁₀, and Au₁₈(S-Adam)₉, respectively. The fragments of Au nanoclusters were produced by the strong laser intensity, which easily removes carbon tails from HS-Adam. Thermogravimetric analysis (TGA) was also performed to check the purity of Au₂₁(S-Adam)₁₅ nanoclusters. The TGA curve shows a weight loss of 42% (expected value, 38%). UV-Vis absorption spectroscopy was performed to track the conversion of Au₂₃(S-Adam)₁₆ to Au₂₁(S-Adam)₁₅. It was found that Au₂₃(S-Adam)₁₆ can convert to Au₂₁(S-Adam)₁₅ with a conversion efficiency of up to 97%, using excess thiols at room temperature within 30 min. In general, we successfully synthesized highly pure Au₂₁(S-Adam)₁₅ nanoclusters, with high yield of ~20% based on HAuCl₄, by etching Au₂₃(S-Adam)₁₆ with excess thiols at room temperature.

Key Words: Gold nanocluster; Au₂₁(S-Adam)₁₅; High-yield

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合成高产率的 $\text{Au}_{21}(\text{SR})_{15}$ 纳米簇

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摘要: 近年来, 精确原子个数的金纳米簇因其在催化、生物医药、传感等领域具有潜在应用而备受关注。本研究中使用金刚烷硫醇(HS-Adam)作为配体制备了 $\text{Au}_{23}(\text{S-Adam})_{16}$ 纳米簇。在室温条件下, 通过HS-Adam刻蚀 $\text{Au}_{23}(\text{S-Adam})_{16}$ 纳米簇, 得到了纯度较高的 $\text{Au}_{21}(\text{S-Adam})_{15}$, 其转换率可达20% (根据金原子计算)。并通过紫外可见吸收光谱(UV-Vis), 电喷雾(ESI)和基质辅助激光解析飞行时间(MALDI)质谱以及热重分析(TGA)对合成的金纳米簇进行表征。

关键词: 金纳米簇; $\text{Au}_{21}(\text{S-Adam})_{15}$; 高产率
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1 Introduction

Gold nanoclusters with size smaller than 2 nm as new nanomaterials have received wide interest in nanoscience and nanotechnology¹⁻⁵. Gold nanoclusters are usually composed of exact Au atom number ranging from several to a few hundred atoms and exact protecting ligands. Gold nanoclusters are very different from plasma gold nanoparticles (NPs), usually exhibit very remarkable quantum confinement effect⁶ and are very sensitive to their sizes². In past decade, a number of gold nanoclusters with precise atom number have been achieved, and the crystal structures have already been determined as well, such as Au_{25} ^{7,8}, Au_{38} ^{9,10}, Au_{60} ¹¹ and Au_{130} ¹². Due to the quantum effect, gold nanoclusters possess unique chemical and physical properties^{13,14}, which endow gold nanoclusters with the great application potential in many fields, such as optic^{7,15}, biology¹⁶, catalysis¹⁷⁻²⁴ and magnetism^{25,26}.

There are two main methods to synthesize gold nanoclusters: “size focusing”²⁷ and “ligand exchange”²⁸⁻³⁰. In term of “size focusing” process, the important point is to obtain proper size distribution of polydispersed gold nanoclusters. During this process, the polydispersed gold nanoclusters were further etched under harsh environment (high temperature or excess thiols). Finally, the unstable gold nanoclusters convert to stable ones. On the other hand, “ligand exchange” means the protecting ligands on gold nanoclusters were replaced with other ligands. New methodology has been developed to control the size and structure of nanoclusters, which is usually hard to achieve *via* simple one-step method. Liu *et al.* prepared high-yield $\text{Au}_{99}(\text{SPh})_{42}$ *via* ligand exchange of polydispersed gold nanoclusters³¹. This method also provides idea to synthesize new size gold nanoclusters *via* conversion from one stable gold nanoclusters to another stable one. Murry *et al.* synthesized $\text{Au}_{75}(\text{SR})_{40}$ *via* replacing PPh_3 with thiols³². In recent, Zeng *et al.* obtained a series of gold nanoclusters *via* “ligand exchange-induced transformation”³³.

In previous work, $\text{Au}_{21}(\text{S-Adam})_{15}$ (HS-Adam: 1-adamantane-thiolate) was synthesized by “ligand exchange-induced transformation”, that is, $\text{Au}_{18}(\text{SR})_{15}$ reacted with excess HS-Adam at high temperature³⁴. In this work, we report the synthesis of highly pure $\text{Au}_{21}(\text{S-Adam})_{15}$ with high yield *via* etching $\text{Au}_{23}(\text{S-Adam})_{16}$ with excess thiols at room temperature. The high yield of $\text{Au}_{21}(\text{S-Adam})_{15}$ was greatly improved and reached up to 20% (based on HAuCl_4 precursor).

2 Experimental

2.1 Chemicals

All the chemicals were used without further purification. Tetrachloroauric(III) acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 99.99%, Acros), tetrabutylammonium bromide (TOAB, 99%, TIC), adamantanethiols (HS-Adam, 95%, Sinopharm), sodium borohydride (NaBH_4 , 99.99%, Sinopharm), methanol (99%, Sinopharm), ethyl acetate (99%, Sinopharm), acetone (99%, Sinopharm), dichloromethane (CH_2Cl_2 , 99%, Sinopharm). Nanopure water (resistivity 18.2 $\text{M}\Omega \cdot \text{cm}$) was purified with a Barnstead NANOpure DiwaterTM system. All glassware was thoroughly cleaned with aqua regia ($V(\text{HCl}) : V(\text{HNO}_3) = 3 : 1$), rinsed with copious nanopure water, and then dried in an oven prior to use.

2.2 Synthesis of $\text{Au}_{23}(\text{S-Adam})_{16}$ nanoclusters

61.8 mg $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (0.15 mmol) was dissolved in 15 mL ethyl acetate. Then, 95.2 mg TOAB was added into ethyl acetate and stirred for 30 min. 126 mg HS-Adam was further added to react with Au(III) to Au(I)-SR. At last, 57 mg NaBH_4 dissolved in 4 mL cold water (4 °C) was used to reduce the Au(I)-SR to Au(0). The reaction lasts 7 days. After reaction, the product was washed with methanol for four times. Then, the crude product was extracted with acetone for twice.

2.3 Transformation of $\text{Au}_{23}(\text{S-Adam})_{16}$ to

$\text{Au}_{21}(\text{S-Adam})_{15}$

5.0 mg $\text{Au}_{23}(\text{S-Adam})_{16}$ was dissolved in 10 mL CH_2Cl_2 .

Then, 50 mg HS-Adam was added to CH_2Cl_2 . After reaction at room temperature for 60 min, the color of solution turned from purple into brown, which meant $\text{Au}_{23}(\text{S-Adam})_{16}$ converted to $\text{Au}_{21}(\text{S-Adam})_{15}$.

2.4 Characterization

UV-Vis spectra of Au nanoclusters (dissolved in CH_2Cl_2) were performed on a UV-8000s spectrophotometer at room temperature. Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) was carried out on a PerSeptive Biosystems Voyager DE super-STR time-of-flight (TOF) mass spectrometer, and trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as the matrix³⁵. Typically, 0.1 mg matrix and 10 mL analytic stock solution were mixed in 10 mL CH_2Cl_2 . Electro spray ionization mass spectrometry (ESI-MS) were recorded on a Bruker microTOF-Q system in positive ion mode. The product was dissolved in mixture of methanol and CH_2Cl_2 (Volume ratio of 5 : 7) *via* adding cesium acetate into sample. Thermo-gravimetric analysis was carried out on a TG/DTA 6300 analyzer (Seiko Instruments Inc.).

3 Result and discussion

$\text{Au}_{21}(\text{S-Adam})_{15}$ nanoclusters were synthesized *via* etching $\text{Au}_{23}(\text{S-Adam})_{16}$ with excess thiols at room temperature. In Fig. 1a, the UV-Vis absorption spectrum of $\text{Au}_{23}(\text{S-Adam})_{16}$ shows one strong optical peak at ~ 580 nm and a weak shoulder peak at ~ 450 nm, consistent with previous report³⁶. In order to further confirm the exact molecular mass of this nanocluster, ESI-MS was used to characterize its mass *via* adding cesium acetate (CsOAc) into it. ESI-MS spectrum in Fig. 1b shows four m/z peaks 7206.4, 6778.1, 6645.4 and 3323.1, which are attributed to $\text{Au}_{23}(\text{S-Adam})_{16}$, $\text{Au}_{21}(\text{S-Adam})_{15}\text{Cs}$, $\text{Au}_{21}(\text{S-Adam})_{15}$ and $[\text{Au}_{21}(\text{S-Adam})_{15}\text{H}]^{2+}$. Basis on UV-Vis absorption and ESI-MS, it can be confirmed that $\text{Au}_{21}(\text{S-Adam})_{15}$ is a fragment of $\text{Au}_{23}(\text{S-Adam})_{16}$ by losing Au_2SR .

In previous report, $\text{Au}_{21}(\text{S-Adam})_{15}$ was prepared *via* etching Au_{18} in excess HS-Adam at high temperature³⁴. To realize the conversion of $\text{Au}_{23}(\text{S-Adam})_{16}$ to $\text{Au}_{21}(\text{S-Adam})_{15}$, excess HS-Adam was used to react with $\text{Au}_{23}(\text{S-Adam})_{16}$ at the room temperature. In this process, it was found that $\text{Au}_{23}(\text{S-Adam})_{16}$ was not stable under harsh condition (excess thiols). As shown in Fig. 2, after reaction for 15 min, the peak at 580 nm decreased and one weak peak at 700 nm appeared. After reaction for 25 min, the peak at 580 nm obviously weakened and the peak at 700 nm gradually strengthened, meanwhile, new peaks at 540, 435 and 380 nm appeared, indicating $\text{Au}_{23}(\text{S-Adam})_{16}$ almost turned into $\text{Au}_{21}(\text{S-Adam})_{15}$. Furthermore, after reaction for 30 min, the purple solution of gold nanoclusters totally changed to brown, and UV-Vis spectrum shows multiple absorption bands at 700, 540, 435 and 380 nm, respectively, indicating the conversion process of $\text{Au}_{23}(\text{S-Adam})_{16}$ to $\text{Au}_{21}(\text{S-Adam})_{15}$ completed. The conversion efficiency of $\text{Au}_{23}(\text{S-Adam})_{16}$ to $\text{Au}_{21}(\text{S-Adam})_{15}$ reached up to

97% (Au atom basis), and the yield of $\text{Au}_{21}(\text{SR})_{15}$ reached up to $\sim 20\%$ (based on HAuCl_4 precursor). However, it has been reported that the conversion efficiency of Au_{18} to Au_{21} is 20% (Au atom basis)³⁴.

To obtain highly pure $\text{Au}_{21}(\text{S-Adam})_{15}$, the crude product was purified by washing with methanol and extracted with CH_2Cl_2 . The purified $\text{Au}_{21}(\text{S-Adam})_{15}$ shows multiple absorption bands in UV-Vis spectrum at 700, 540, 435 and 380 nm, respectively (Fig. 3a). The MALDI-MS of purified $\text{Au}_{21}(\text{S-Adam})_{15}$ in Fig. 3b shows several peaks at 6502, 6471, 6106, 5411 and 5048, which are assigned to $\text{Au}_{21}(\text{S-Adam})_{14}\text{S}$, $\text{Au}_{21}(\text{S-Adam})_{14}$, $\text{Au}_{20}(\text{S-Adam})_{13}$, $\text{Au}_{19}(\text{S-Adam})_{10}$ and $\text{Au}_{18}(\text{S-Adam})_9$, respectively. However, it is hard to obtain the complete molecular mass of $\text{Au}_{21}(\text{S-Adam})_{15}$ *via* MALDI-MS spectrometry, because thiol of HS-Adam is easy to loss carbon

Fig. 1 UV-Vis absorption (a) and ESI-MS spectra (b) of $[\text{Au}_{23}(\text{S-Adam})_{16}]^+$ nanoclusters.

Fig. 2 Time-dependent UV-Vis spectra of the conversion process of $\text{Au}_{23}(\text{S-Adam})_{16}$ to $\text{Au}_{21}(\text{S-Adam})_{15}$.

Fig. 3 UV-Vis absorption (a) and MALDI-MS spectra (b) of purified $[\text{Au}_{21}(\text{S-Adam})_{15}]$ nanoclusters.

Fig. 4 Thermogravimetric analysis of purified $\text{Au}_{21}(\text{S-Adam})_{15}$ nanoclusters.

tail under strong laser environment.

Furthermore, we performed thermogravimetric analysis (TGA) to check the purity of $\text{Au}_{21}(\text{S-Adam})_{15}$ nanoclusters. TGA curve in Fig. 4 shows a weight loss of 42%, corresponding to the loss of the surface thiolate ligands, consistent with the expected value (38%) according to the formula of $\text{Au}_{21}(\text{S-Adam})_{15}$ and the previous work³⁴.

In summary, we successfully synthesized highly pure $\text{Au}_{21}(\text{S-Adam})_{15}$ nanoclusters with high yield of ~20% based on HAuCl_4 via converting $\text{Au}_{23}(\text{S-Adam})_{16}$ with excess thiols at room temperature. The optical absorption and molecular mass of $\text{Au}_{21}(\text{S-Adam})_{15}$ were checked with UV-Vis spectroscopy and matrix-assisted laser desorption ionization mass spectroscopy. Thermogravimetric analysis were further carried out to confirm the purity of $\text{Au}_{21}(\text{S-Adam})_{15}$.

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