



Synthesis, characterization and mechanism of cetyltrimethylammonium bromide bilayer-encapsulated gold nanosheets and nanocrystals

Zhijuan Wang^{a,b,c}, Junhua Yuan^{a,b}, Min Zhou^{a,b}, Li Niu^{a,b,c,*}, Ari Ivaska^c

^a State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

^b Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Changchun 130022, PR China

^c Laboratory of Analytical Chemistry, Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500 Åbo-Turku, Finland

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ABSTRACT

Single-crystal Au nanosheets and fcc gold nanocrystals of uniform size were synthesized by a novel and simple route. The results of field-emission scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) indicated the formation of the single-crystal structure of gold nanosheets and fcc nanocrystals. Energy-dispersive analysis of X-ray (EDAX) showed absorbance of cetyltrimethylammonium bromide (CTAB) molecules onto the surface of gold nanostructures. Moreover, zeta potential measurements showed that CTAB-coated nanostructures were positively charged and the zeta potential remained almost the same upon centrifugation and redispersion of the resulting nanostructures in methanol, confirming the high stability of the surfactant-protected nanocomposites. Evolution of the nanostructures during the reaction was monitored by TEM observations. The results indicated that the formation of the gold nanostructures followed a two-step mechanism with a bilayer CTAB structure on the surface of the gold nanostructures.

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1. Introduction

A variety of methods have been developed to prepare gold nanoparticles in all kinds of shapes, including stars [1], rods [2], cubes [3], wires [4] and dendrimer-like particles [5]. Recently, there has been intense effort focused on preparation of gold nanosheets and fcc nanostructures due to their unique properties and promising applications [6–11]. For example, the size-dependent surface plasmon absorption of gold nanosheets in the visible–near-infrared (vis–NIR) region [12] enables their promising use in biomedical diagnostics, biosensors and heat absorption in special equipment [10]. Moreover, the sharp corners and edges make the gold nanosheets be active for surface-enhanced Raman scattering (SERS) (where the local electromagnetic field could be enhanced more than 500 times) [13].

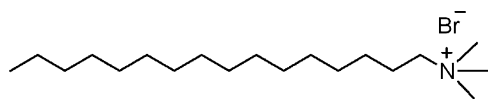
Among several synthetic approaches in preparation of Au nanosheets and plates, two approaches have been widely used. One is the template-directed method, by using various templates, such as mesoporous inorganic materials [14], organic surfactants [15], or polymers [16], to control the shapes of the metal

nanostructures. The other one is the crystal growth method controlled by appropriate capping reagents, such as polymeric or small molecules, where certain interactions between the molecules and the facets of metal nanocrystals induce anisotropic growth of different planes [17]. Among these capping reagents, the surfactant CTAB (Scheme 1) is widely introduced as a stabilizer to prevent aggregation of the products during the synthesis of noble metal (Au, Ag, etc.) nanostructures. Furthermore, CTAB can also influence the growth rate of different crystallographic planes by interacting with these planes *via* adsorption and desorption. On the basis of this role of CTAB, recently, many metallic nanostructures with well-controlled morphologies, such as Au nanorods [18], Au nanopods [19] and Ag nanowires [20], have been successfully synthesized. Consequently, in this work, CTAB was chosen as a capping reagent to synthesize Au nanosheets and fcc nanocrystals by directly mixing H₂AuCl₄ and aniline acetic acid solutions at room temperature.

Moreover, additional effort has been devoted to understanding of the formation mechanism of those gold nanostructures. Currently, there are different opinions on the mechanism of morphological synthesis of inorganic nanoparticles. In solutions containing polymer, a soft templating mechanism has been proposed for generation of gold nanowires [7]. On the other hand, it is argued that the adsorption of the inorganic ions on different crystal planes of the particles should be the main cause for anisotropic growth of the particles [10]. Based on our results,

* Corresponding author at: State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China. Fax: +86 431 526 2800.

E-mail address: lniu@ciac.jl.cn (L. Niu).



Scheme 1. Molecular structure of CTAB.

strong adsorption of CTAB on the (1 1 1) plane of Au nuclei account for the anisotropic growth of Au nanosheets and fcc nanocrystals.

2. Experimental

2.1. Synthesis of Au nanosheets and Au nanocrystal

In a typical experiment, an aqueous solution of 1 mM HAuCl₄ (1 ml) was added dropwise into the acetic acid solution of aniline (appropriate concentration) and CTAB (0.171 M) under vigorous stirring. A quick color change, from green, via yellow to ruby red, was observed upon addition of HAuCl₄. At the same time, some precipitates were observed and collected by centrifugation, washed several times with pure water and methanol, and then suspended in ethanol. The resulting suspension was used for further characterizations.

2.2. Instruments and measurements

The samples for scanning electron microscopy (SEM) and XRD characterizations were prepared by placing 100 μl of the suspension on a silicon wafer sputtered with Pt, and allowing the solvent to slowly evaporate at room temperature. The samples for the TEM measurements were similarly prepared by placing a drop of the suspension on a carbon-coated copper grid. The SEM images were obtained on a XL30 ESEM FEG scanning electron microscopy operating at 20 kV. The TEM images were recorded on a JEOL 2000 transmission electron microscopy operating at 200 kV. The XRD pattern was collected on a D/Max 2500 V/PC X-ray diffractometer using Cu Kα (40 kV, 200 mA) radiation. Zeta potentials (effective surface charge) of the CTAB-coated nanocrystals were measured with a ZETASIZER 3000 HAS, MALERRN, UK.

3. Results and discussion

3.1. Characteristics of structure and morphology

The morphology of the precipitate was characterized by SEM and the result is shown in Fig. 1. The lower magnification image

(Fig. 1A) shows that the precipitate consists of a large amount of particles, and the higher magnification images (Fig. 1B–D) clearly reveal that these particles constitute of two different structures. One of the structures is a sheet (Fig. 1B and C). The other one is fcc nanocrystal (Fig. 1D). Moreover, the thickness of the nanosheets was estimated to tens of nanometers by SEM measurement in Fig. 1B.

The product was further analyzed by TEM and XRD. Fig. 2 shows the TEM images of the Au nanostructures (a single Au nanosheet is shown in Fig. 2B and C) as well as the related selected area electron diffraction pattern (shown as inset in Fig. 2B and C) obtained by focusing the electron beam on a nanosheet lying flat on the TEM grid, confirming that these nanosheets are single crystals bounded mainly by (1 1 1) facets [21]. We believe that the prepared gold nanosheets with a large flat area can be used in wide applications as thin gold films [22]. The immobilization of the resulted gold nanosheets on the glass surface and the silicon wafer is still under our investigation. The band-like patterns on the surface of the nanosheet in Fig. 2 obviously originate from the differences in electron density [7]. Similar band-like patterns have also been reported early in the preparation of nanosheets [7,8,22,23].

In addition, the crystalline structure of the product was also confirmed by XRD measurement. The XRD pattern recorded from the batch sample is displayed in Fig. 3, and the preferred orientation at 38.3° plane parallel to the surface and a second orientation at 44.48°, and other orientations at 64.66°, 77.64°, 81.80°. These XRD peaks can be assigned to the diffractions from the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes of an fcc gold, respectively. It is worth noting that the ratio of the intensities of the (2 0 0) to (1 1 1) diffraction peaks is much lower than that in previous report (0.05 versus 0.53 JCPDS 04-0784). The ratio of the (2 2 0) to (1 1 1) peaks is also much lower than earlier report (0.024 versus 0.33). These observations confirm that our product is mainly dominated by (1 1 1) facet, and thus the (1 1 1) plane tends to be preferentially oriented in parallel to the surface of the supporting substrate.

3.2. Surface analysis

As reported early, it was considered that a monolayer of CTAB molecules should adsorb predominantly on the (1 1 1) basal plane [24,25]. To further ascertain this assumption, energy-dispersive analysis of X-ray (EDAX) line analysis was conducted with individual nanosheets and a typical result is shown in Fig. 4. A

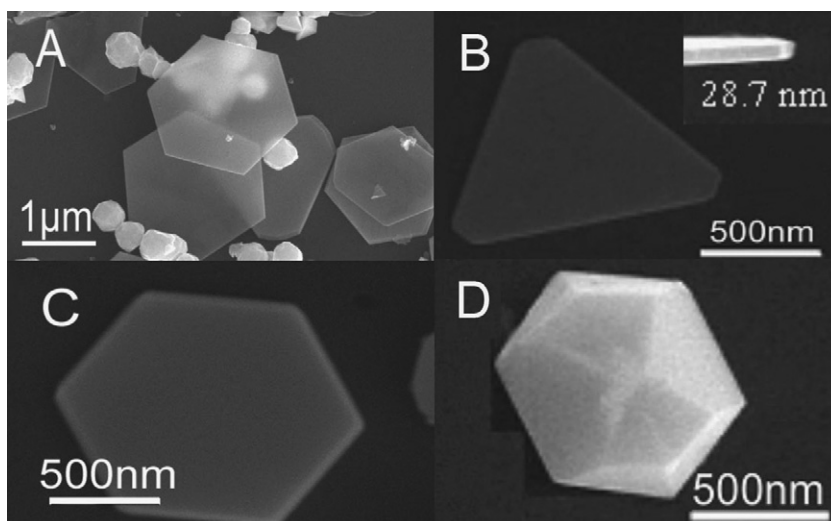


Fig. 1. SEM images of the precipitate at low magnification (A) and at high magnifications (B–D).

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