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Synthesis of microsized gold nanoplates by a self-seeding method in ethanol solution

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Abstract

Single-crystalline gold nanoplates with microsized edges have been synthesized by a simple self-seeding method with the assistance of aniline in an ethanol solution. The as-synthesized gold nanoplates showed strong absorption in near infrared region (NIR). Investigation suggests the amount of aniline added to the reaction solution plays a key role in the generation of nanoplates. A possible formation mechanism for these gold nanoplates is also proposed.

Keywords: Gold nanoplates; Aniline; Seed; Synthesis

1. Introduction

Metal nanoparticles have received extensive attentions due to their unique performance in catalytic, optical, electronic, magnetic, biomedical and many other fields [1,2]. With the development of nanotechnology and material science, it is generally accepted that the physicochemical properties of nanoparticles heavily depend on the shape and size besides their inherent chemical constitutions [3]. Therefore, many recent studies have been focused on preparing non-spherical metal nanostructures such as wires, rods, ribbons, cubes, cages and so forth for their promising novel features [4,5]. Seed-growth synthesis, which was previously used to control the size of metal nanoparticles, is currently an active strategy to obtain non-spherical metal nanostructures. For example, copper nanocubes, gold nanorods and silver nanodisks have been synthesized using seeds as the growth cores of the metal precursors [6–8]. Furthermore, It was also reported that spherical silver seeds could transform into nanoplates through a photoinduced or a thermal process [9,10]. However, in most of the above publications, additional surfactants or capping agents are indispensable to producing these anisotropic metal nanoparticles.

In this letter, we demonstrate a simple self-seeding method to prepare single-crystalline, microsized gold nanoplates in an ethanol solution without the requirement of introducing capping agents or surfactants. During this approach, hydrogen tetrachloroaurate ($HAuCl_4 \cdot 4H_2O$) was reduced to form gold seeds by aniline in a boiling ethanol solution at the first stage, and then the reaction solution was refluxed sequentially and the gold seeds transformed to microsized gold nanoplates through an Ostwald ripening process. It is found that the amount of aniline in the reaction solution is crucial to the formation of these gold nanoplates.

2. Experimental section

In our experiments, all chemicals were analytical grade from Shanghai Chemical Reagent Co. Ltd. (China). Aniline was distilled twice at a reduced pressure in the presence of zinc metal powder. $HAuCl_4 \cdot 4H_2O$ and anhydrous ethanol were used as received. The water used was purified through a Millipore system.

A typical synthesis is as follows: a 50 ml ethanol was degasified by N_2 bubbling and heated to boiling at normal atmosphere in a three-necked flask equipped with a reflux condenser for 20 min, then, 1.5 ml ethanol solution (0.024 M) of $HAuCl_4 \cdot 4H_2O$ were rapidly injected to the boiling ethanol

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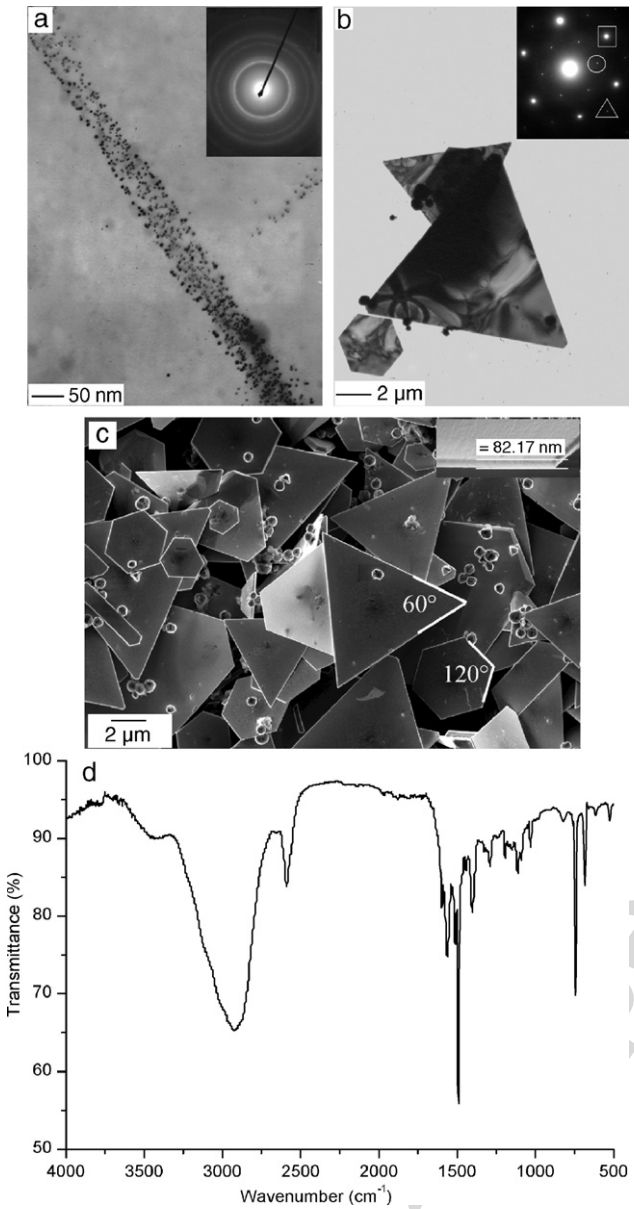


Fig. 1. (a) TEM image of the gold seeds before refluxing for 8 h, the inset shows their SAED pattern. (b) TEM and (c) SEM image of the final gold products after refluxing for 8 h, indicating the formation of gold plates. The inset in (b) shows a typical SAED pattern of a single gold plate and the inset in (c) reveals the thickness of a single plate is about 82.17 nm. (d) The FTIR spectrum of the purified gold nanoplates in a KBr pellet.

solution using a micropipette under vigorously stirring. Then, 0.1 M ethanol solution of aniline was introduced to the reaction solution at one portion to obtain a 3:1 molar ratio of aniline to gold. This process was kept for 40 min and the color of the reaction mixture changed gradually from pale yellow to claret-red. Then, the stirring stopped and a small amount of the reaction solution was taken out for characterization. The reaction solution was refluxed continuously for 8 h without any stirring. As a result, it was found plenty of particles with metallic gold color dispersed in the resulting solution. These particles were collected by centrifugation at 2500 rpm for 20 min and the supernatant was removed. After then, the precipitates were dispersed in de-ionized water for further measurements.

The images of transmission electron microscopy (TEM) were obtained by a JEM-2000EX microscope using an accelerating voltage of 120.0 kV and the samples were prepared by placing a drop of gold products aqueous dispersion on carbon-coated copper grid. The Scanning electron microscopy (SEM) images were recorded using a LEO-1530 VP field-emission scanning electron microscope with an accelerating voltage of 5.0 kV and the samples were deposited on silicon substrate. For the infrared spectrum analysis, the vacuum-dried samples were made in a KBr pellet and the spectrum was recorded with a Nicolet Magna FTIR-750 spectrometer. The optical properties of these gold plates were measured by a Shimadzu UV–Vis–NIR spectrophotometer (UV-3150).

3. Results and discussion

A typical TEM image (Fig. 1a) shows these gold seeds are in spherical-like shapes with an average diameter of about 5 nm. The selected-area-electron–diffraction (SAED) pattern (inset of Fig. 1a) indicates these nanoparticles are crystallized in the face-centered cubic structure. The SEM image (Fig. 1c) confirms these final gold products after refluxing for 8 h are dominated by triangular and hexangular planar plates of several micrometers in edge size (up to 10 μm) and a few small spherical and rod-like particles as byproducts are also observed. It is noticed that these triangular or hexagonal plates possess regular edges with 60° or 120° between the adjacent sides. The inset in Fig. 1c gives the thickness between the

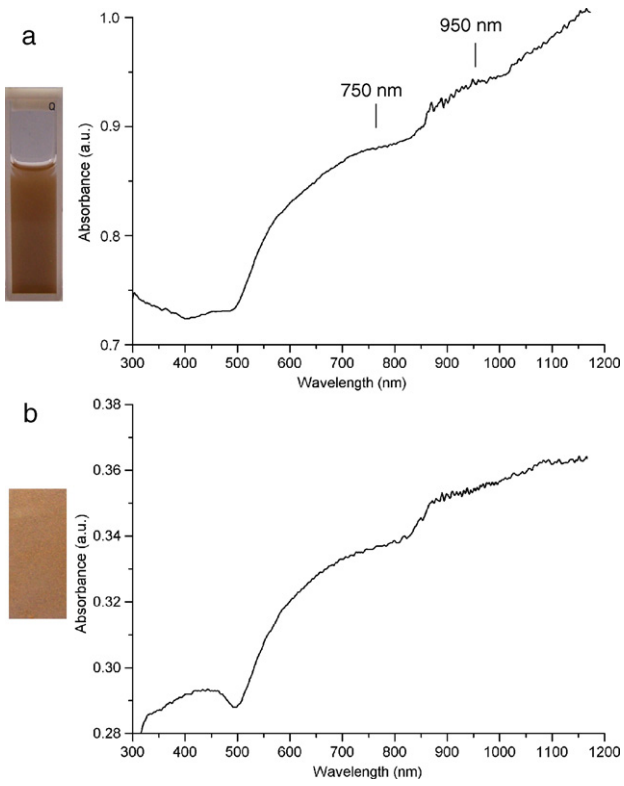


Fig. 2. (a) Photograph (left) and UV–vis–NIR spectrum of the as-prepared gold nanoplates dispersed in water. (b) Photograph (left) and UV–vis–NIR spectrum of the same batch gold plates forming thin coatings on a glass slide.

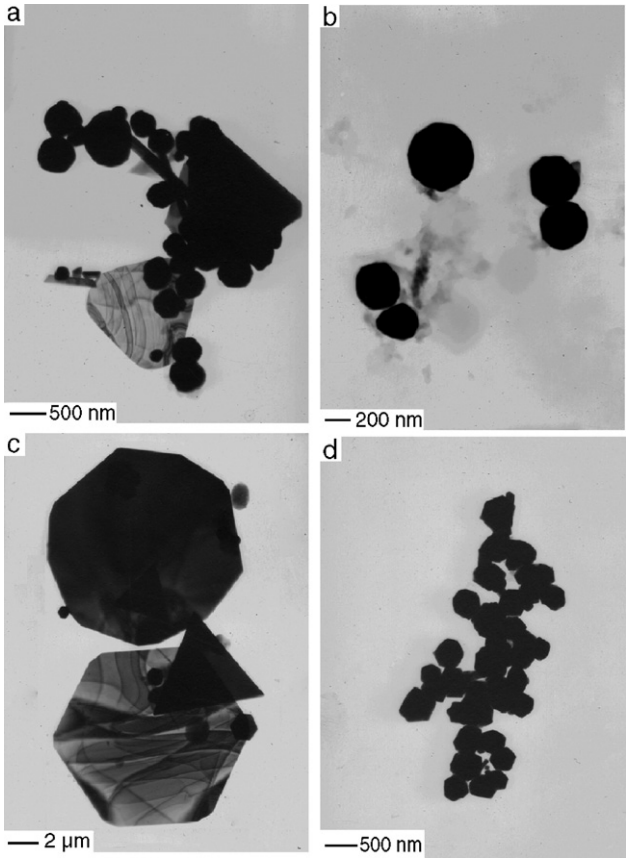


Fig. 3. (a) Typical TEM images of gold nanoparticles obtained with an initial molar ratio (aniline to gold) of (a) 6:1. (b) 9:1. (c) 2:1 and (d) without aniline.

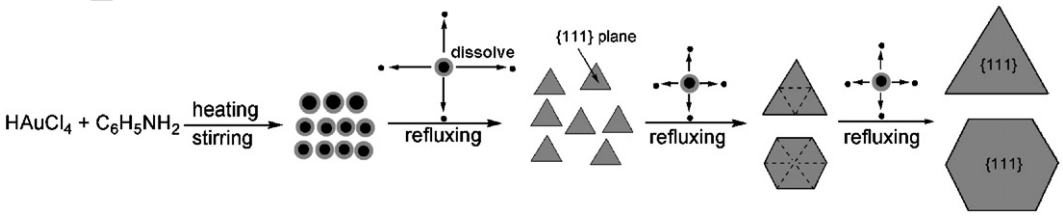
two parallel basal planes of one plate protruding from the substrate, which provides the evidence that these plates are several tens of nanometers in thickness. Fig. 1b gives the corresponding TEM image of these gold nanoplates. The bending patterns across the gold nanoplates indicate the existence of the internal stress within these thin plates [11]. By focusing the electron beams perpendicular to the basal planes of a single gold nanoplate, hexagonal symmetrical spots of the SAED pattern are obtained, which clearly indicates that these gold nanoplates are single crystals bound mainly by {111} planes. The spots with the strongest intensity (squared) could be indexed to the {220} planes of gold. The outer spots (triangled) are ascribed to the {422} planes reflection and the inner spots (circled) correspond to the formally forbidden (1/3) {422} reflection. These results accord with previously reported on planar gold or silver nanostructures bounded by atomically flat basal planes [10,12,13]. EDX analysis of these purified gold nanoplates confirms very strong peaks of gold elemental and the weaker peaks of carbon and nitrogen are also observed. Fig. 1d shows the FTIR spectrum of these gold nanoplates. The clear bands located at 1482 and 1557 cm^{-1} are the characteristics of bezenoid and quinoid ring deformation of the polyaniline respectively [14,15]. The above analysis suggests that these gold nanoplates are covered with the polymerized aniline.

It has documented that aqueous solution of small spherical gold nanoparticles is in red color owing to surface plasmon resonance and exhibits a single absorption band at around 520 nm or longer wavelengths when increasing size [16]. However, the solution of the as-synthesized gold nanoplates is in orange color and exhibits two asymmetric absorption bands centering at around 750 and 950 nm (Fig. 2a), which could be ascribed to the transverse and longitudinal plasmon resonances respectively arising from the anisotropy of these large gold nanoplates [17,18]. Similar optical absorption spectrum was also obtained from the thin films of the same batch gold nanoplates covered on a glass slide (Fig. 2b). The strong near-infrared absorption feature could make these gold nanoplates potential candidate for applications in thermotherapy and architectural fields [19].

The effects of the amount of aniline used on the formation of gold nanostructures were studied by fixing other parameters of reaction. As revealed in Fig. 3a, when the synthesis was conducted at a 6:1 molar ratio of aniline to gold, the final gold products were dominated by quasi-spherical gold nanoparticles and a small portion of sub-micro-sized gold nanoplates with less sharp edges. When increasing the mole ratio to 9:1, the obtained gold products were mainly spherical-like gold particles (Fig. 3b). However, microsized gold nanoplates with less sharp edges were produced when decreasing the molar ratio to 2:1, (Fig. 3c). Furthermore, the synthesis without aniline only resulted in the aggregated irregular gold particles (Fig. 3d). Therefore it can be suggested that the amount of aniline is critical to the formation of gold nanoplates.

On the basis of the above studies, a possible mechanism for the formation of gold nanoplates via our route can be proposed (Scheme 1). At the first stage, the gold seeds were generated from $AuCl_4^-$ by the reduction of aniline and subsequently parts of the polyaniline acted as a stabilizer by covering on the surfaces of these seeds [20,21].

Because of the different surface energy between the large and small gold seeds, some small seeds were dissolved to atoms and then the larger ones grew at the expense of the smaller ones through an Ostwald ripening process promoted by the continuous refluxing [10,22,23]. At the mean time, the polyaniline in solution served as capping agent and preferentially adsorbed the {111} planes of these growing particles and decreased the surface energy of these planes. Thereby other crystal planes grew more quickly than that of {111} planes leading to planar structures bound primarily by {111} planes. Considering the large edge size while very thin thickness feature of the final gold nanoplates, it is believed that many small nanoplates were formed firstly: some of them grew into larger ones through the adsorption of the gold atoms dissolved from the seeds. On the other



Scheme 1. Possible formation mechanism of gold nanoplates transformed by gold seeds.

hand, parts of these small nanoplates fused them each other along the lateral sides due to the higher surface energy compared with the {111} basal planes [24], which resulted in larger triangular or hexagonal nanoplates. These triangular or hexagonal ones continuously grew by the adsorption of the dispersive gold atoms. Finally, microsized gold nanoplates with regular triangular or hexagonal shapes stable in thermodynamics were developed. During the synthesis procedure, excessive addition of aniline brings on a heavy polymeric coverage on the surface of gold nanoparticles and results in the products dominated by spherical-like gold products because of an isotropic growth of all the planes. Moreover, a short amount of aniline leads to an insufficient coverage and gold plates with irregular edges are produced due to the similar reason.

4. Conclusions

In summary, single-crystalline, microsized gold nanoplates with {111} planes as the basal planes have been synthesized by a simple self-seeding method without additional surfactants or capping agents. In this synthesis, aniline served as reducing agents to produce gold seeds at first stage and then its polymeric resultant worked as capping agent to preferentially adsorb the {111} planes of the growing gold particles during an Ostwald ripening process. Preliminary investigation shows that the amount of aniline added to the reaction solution plays a key role in the formation of these gold nanoplates. These large sizes, single-crystalline gold nanoplates with strong adsorption in near-infrared region could find their usage in both fundamental researches and practical applications.

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