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From aqueous to organic: A step-by-step strategy for shape evolution of gold nanoparticles

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Abstract

Uniform-sized gold nanoparticles were synthesized by a facile method, which is comprised of three steps: the first step to prepare Au colloid in aqueous, the second to transfer the particles into organic solvent and the third to reflux organic solution. The 2D/3D superlattices of as-prepared gold nanoparticles were fabricated by evaporating solvent from colloid solution at optimal concentration.

The controlled fabrication and self-assembly of very small structures at nano-scales have attracted great interest because it is one of most important technological ways toward the practical application of nanomaterials [1–4]. Nanosized gold clusters/particles have been the most popular subjects for the study of self-assembly behaviors of nanosized materials [5–8] since Brust et al. [9] developed the two-phase approach. The Brust method provides an effective way to synthesize alkanethiol-protected gold nanoparticles with a size rang from 1 to 4 nm. This method is also proven to be practicable for synthesizing other metal or alloy nanocrystals by our previous work [10–12] and other group's work [13,14]. However, the wide size distribution is not favorable for packing ordered superlattice, and thus much attention was paid to postsynthesis treatments for improving the size distribution of gold nanoparticles. Particularly, heating treatment [15,16] was reported as one of most effective postsynthesis treatment for Brust method. For examples, heating treatment could result in the size and shape evolution of thiolate-encapsulated Au nanoparticles in solution [17], while thermal annealing small Au nanoparticles in solid state could control their size by changing the heating temperature [18]. Recently, some other methods involving thermal treatment for preparing uniform-sized gold nanoparticles, such as digestive ripening procedure [19] and single-phase method [20], were also reported. For digestive ripening procedure, gold nanoparticle precursor was prepared in organic solution by reduction of 9.4 M aqueous $NaBH_4$ in the presence of didodecyldimethylammonium bromide (DDAB) and further capped by other ligands via ligand exchange reaction. In single-phase method, gold nanoparticles were prepared in toluene by reduction of tetrabutylammonium borohydride (TBAB) or its mixture with hydrazine in the presence of ammonium surfactants such as DDAB. These reports demonstrate the alternative methods for preparing thiolate-capped gold nanoparticles, which as precursors were induced to be uniform in size by heating treatment. Although there are many reports employing heating treatment to improve size distribution of Au nanoparticles, the methods used to prepare thiolate-capped Au precursor is still limited to several ones and most of them are not easy to perform due to their complex working procedures and long lists of reagents.

In this Letter, we report on a facile strategy for synthesizing uniform-sized gold nanoparticles. A simple procedure

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'from aqueous to organic' is employed here to obtain thiolate-capped Au nanoparticles, which shows a shape evolution toward very narrow size distribution via refluxing in organic solvent. Our experiment is attempting to provide an easy approach involving least reagents for fabricating uniform-sized Au nanoparticles and its superlattice.

The typical procedure for synthesis of gold nanoparticles is comprised of three steps and shown schematically in Fig. 1. At first step, a 20 ml aqueous solution containing 2.5×10^{-4} M $HAuCl_4$ and 2.5×10^{-4} M tri-sodium citrate was prepared in a clean flask. Then, 0.5 ml freshly prepared 0.1 M $NaBH_4$ was added into the solution under stirring. The solution color turned to orange immediately after adding $NaBH_4$. Second step was carried out two hours later: a 20 ml toluene solution containing 1×10^{-3} M 1-nonanethiol is added into the as-prepared gold colloid [21] under vigorous stirring. The stirring was continued for 12 h. That the aqueous phase turned to colorless and the organic phase turned to purple indicated that the gold particles were capped by 1-nonanethiol and transferred from aqueous to organic (toluene) phase. For final step, the organic phase was separated from mixture and then was refluxed in toluene solution for 6 h. The resulting solution containing uniform-sized gold nanoparticles can be directly investigated by transmission electron microscopy (TEM) without any further treatment. To fabricate 2D/3D superlattice of as-prepared gold particles, the solution is evaporated completely in a rotary evaporator and then the precipitates were redispersed in 5 ml (for 2D) or 2 ml (for 3D) toluene. This solution was dropped on copper grid and allowed to dry slowly at room temperature. TEM and HRTEM were performed on a JEOL-200CX operating at 120 kV and a Philips CM200FEG operating at 200 kV, respectively. UV–Vis absorption spectra were recorded by a Cary IE UV–Vis spectrometer. X-ray photoelectron spectroscopy (XPS) was carried out by an ESCA LAB5 spectrometer with monochromated Al Kα X-ray beam.

TEM study shows that the gold colloid prepared in step 1 is 3–4 nm in diameter (see Fig. 1). After capped by 1-nonanethiol and transferred into toluene, the gold particles have a change in its size and become 5–8 nm in diameter. The size increase and broader size distribution at this step are probably due to the slight aggregation of gold nanoparticles during the phase transfer. It is similar to the observation of significantly broader size distribution of Au nanoparticles (size >3 nm) after thiol in place of other weak ligands [20]. The gold nanoparticles are yet not uniform in size until the second step. After refluxing, 1-nonanethiol capped gold particles in uniform size are formed. Step 3 plays an important role in formation of uniform size gold particles. It provides a heat treatment on the solution of thiolate-capped gold nanoparticles similar to the usual high temperature annealing. The thermodynamic processes involving coalescence, phase transitions, and reactivities such as thiolate desorption and readsorption lead to the size and shape evolution of gold particles [16,17]. It was reported that the average size of thiol-protected Au nanoparticles via two-phase method was very sensitive to the initial ratio of thiol to Au [22]. In our experiment, however, there is no obvious difference in final particles' average sizes when using different adding amount. It is probably because the initial size of Au colloid has been specified around 4 nm and it is difficult to change it remarkably.

Because the surface plasmon (SP) resonance bands of nanoparticles are strongly dependent on size [23], UV–Vis measurement is also carried out to assess the size evolution of gold nanoparticles in solution. Fig. 2 shows the UV–Vis absorption spectra of gold particles at different stages. The gold colloid prepared in aqueous solution (step 1) displays a SP band at ~512 nm, which corresponds to its small size 3–4 nm. As capped by thiol and transferred into toluene, the colloid takes a red shift in its absorption spectra because the thiolate absorption increases the free-electron density of the particle [24]. The SP band of gold colloid

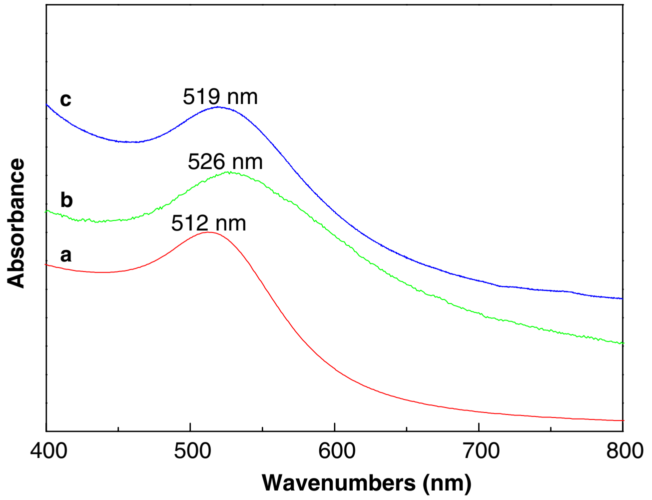

Fig. 2. Typical UV–Vis spectra of Au colloid (a), thiolate-capped Au colloid before (b) and after (c) refluxing.

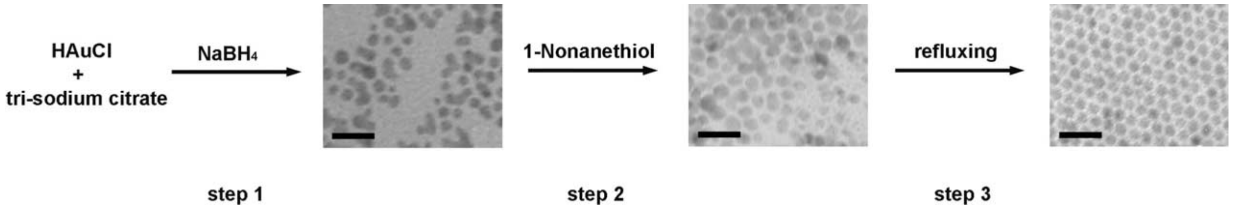

Fig. 1. A schematic diagram showing the steps for the synthesis of uniform-sized Au nanoparticles. Scale bar is 10 nm.

blue shifting to 519 nm after step 3 indicates that the size of particles decreased during the heat treatment. The optical absorption spectra are consisted well with the result of TEM investigation.

The resulting gold nanoparticles in uniform size can be spontaneously assembled into 2D/3D superlattices at optimal concentration. Fig. 3a shows the TEM image of 2D superlattice formed by as-prepared gold nanoparticles. The inset is the Fourier transform power spectrum, which identifies a hexagonal close-packed (hcp) structure. The corresponding histogram of size distribution (Fig. 3b) indicates the gold particles are uniform in size and have an average diameter 4 nm. HRTEM image of a single gold particle, as shown in Fig. 3c, reveals complicated interference patterns, which are consisted with multiple crystal orientations contained within a single nanoparticles [25].

Fig. 4 shows the TEM images of two typical regions of two-layer 3D superlattices fabricated by dropping a solution of particles in high concentration. The superlattice shown in Fig. 4a is formed by ring-like arrays of particles. This structure was previously reported by Zanchet et al. [7] and corresponds to a packing in which the second layer on top occupies saddle positions of the first layer, i.e., the second layer is rotated 30° respect to the first one. Another packing way shown in Fig. 4b is regular close packing, in which the second layer occupies two-fold saddle positions (the hollow sites of first one) [8]. The two typical packing models are illustrated in Fig. 4c.

XPS was used to determine the valence state of gold in the nanoparticles. The spectra are shown in Fig. 5. The characteristic binding energies (Fig. 5a) of Au^0 at 83.5 and 87.1 eV correspond to the double peaks of Au $4f_{7/2}$ and Au $4f_{5/2}$. There are the typical valence states are consistent with standard spectra of element Au^0. From Fig. 5b, the binding energy of S element is observed at 162.8 eV ($2p_{3/2}$) and 164.2 eV (tiny shoulder $2p_{1/2}$), indicating 1-nonanethiol molecule is adsorbed on the surface of Au nanoparticles by the binding between Au and S atoms.

In summary, we have synthesized uniform-sized Au nanoparticles via a step-by-step strategy. A simple procedure 'from aqueous to organic' is employed to prepare thiolate-capped Au colloid. Further refluxing at boiling point

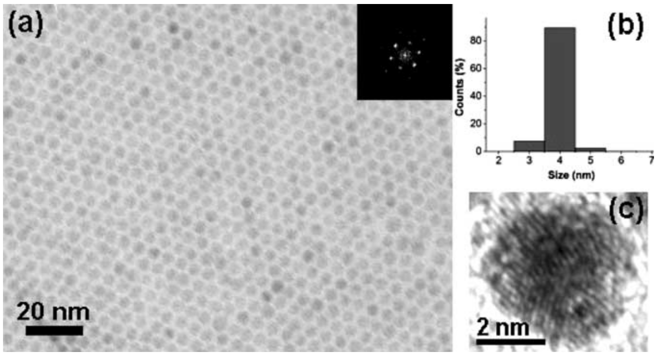

Fig. 3. TEM image of a 2D superlattice of as-prepared gold nanoparticles (a) and the histogram of size distribution (b). The 2D Fourier transform power spectrum of image is inset in (a). (c) HRTEM image of a single particle with multiple crystal orientations.

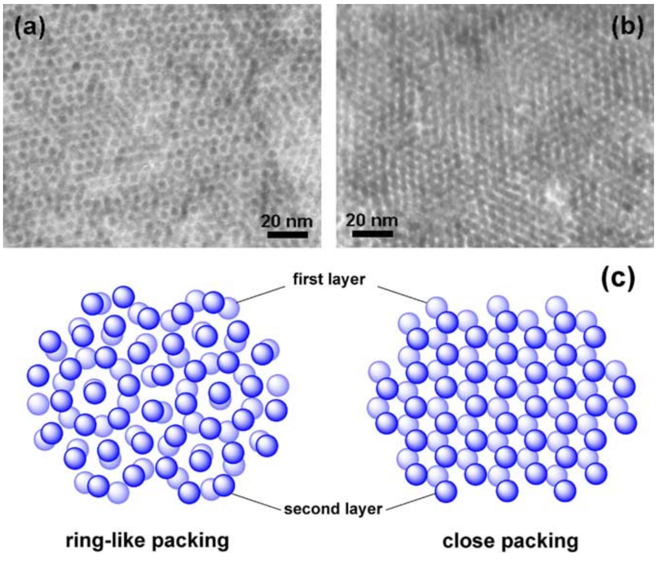

Fig. 4. TEM images of two typical bilayer regions of 3D superlattice of as-prepared gold nanoparticles: ring-like packing (a) and regular close packing (b). (c) The models of two typical packing.

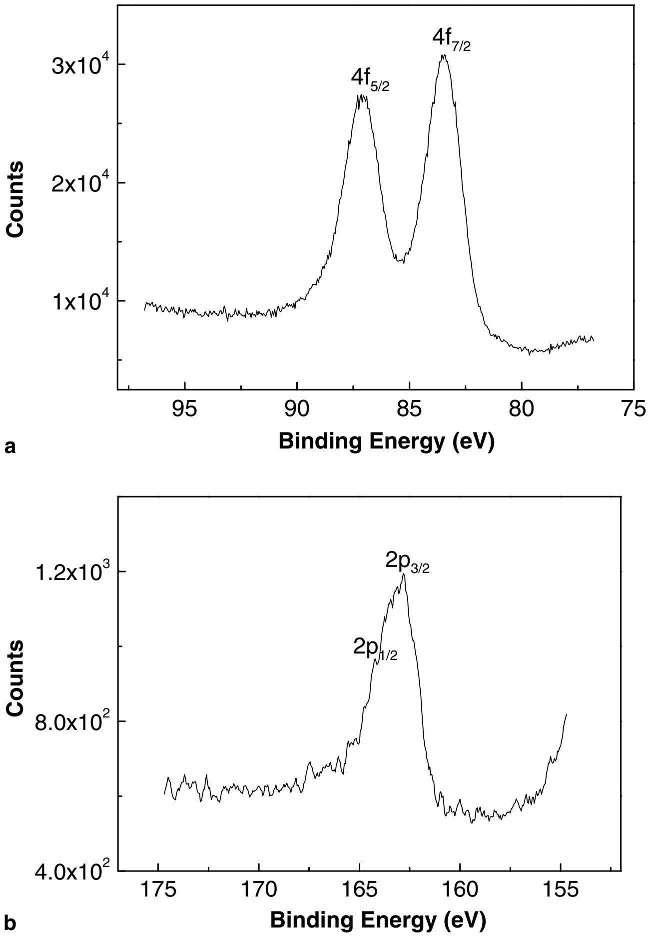

Fig. 5. XPS spectra of Au 4f (a) and S 2p (b) of as-prepared Au nanoparticles.

of organic solvent leads to an improvement of size distribution. The average size of thiol-capped Au nanoparticles is insensitive to the molar ratio of thiol to Au. As-prepared Au nanoparticles can be manipulated to form ordered 2D/3D superlattice by self-assembly technique without any size-selective precipitation. The monolayer 2D superlattice is packed as a hexagonal close-packed structure. The bilayer 3D superlattice prefers to packing with two models, ring-like and regular close packing.

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