

Controlling Length of Gold Nanorods and Monitoring Their Growth Mechanism Using X-ray Absorption Spectroscopy

Beamline

17C Extended X-ray Absorption Fine Structure (EXAFS) beamline

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A new approach to fabricate long length of gold nanorods by controlling the volume of growth solution will be reported. The shape evolution ranging from fusiform nanoparticles to 1-D rods was observed. Increasing the addition of growth solution can control the length of nanorods. The length of rods can be extended to 2 μm , and nanorods with aspect ratio of up to ~ 70 could be obtained. Moreover, X-ray absorption spectroscopy (XAS) is applied herein to elucidate the growth mechanism of gold nanorods. The gold ions were directly reduced to gold atoms by ascorbic acid during the reaction, and then gold atoms were deposited on the surface of gold seeds that were introduced into the reaction. Extended X-ray absorption fine structure (EXAFS) confirmed the growth of gold and the environment around Au atoms over the reaction. The XAS are expected to have wide applications in the growth of gold and other related materials.

Many characteristics of nano-materials are size- and shape-dependent, including their catalytic, optical, and physical properties. Spherical particles can be prepared easily by wet chemical methods. Recent studies of spherical metallic particles investigated include the bimetallic systems such as Au/Pd, Pd/Pt, Cu/Pd, Pt/Ru, Co/Pt, and Au/Pt. Anisotropic metal nanoparticles have been prepared by using electrochemical, photochemical reduction method in aqueous system, bubbling hydrogen with capping polymer, and polyol process. Metal nanoparticles with variable shapes, e.g. cubes, boxes, rods, prisms, multi-pod, and triangular rings can be fabricated via these methods. The studies in one dimension nanorods draw a lot of attention to these variable-shape nanoparticles. Au nanorods of short aspect ratio are especially interesting because of their optical properties. They exhibit transverse and longitudinal plasmon bands in the visible region of the spectrum, enabling their application in sensing and imaging areas. Both the electrochemical method and seed-mediated growth method used the cetyltrimethylammonium bromide (CTAB) as soft template upon which gold nanorods dispersed in aqueous solution are fabricated. A number of reports have studied the

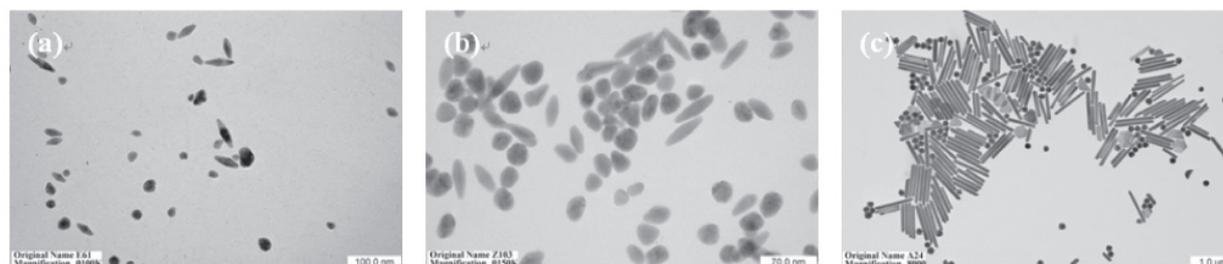


Fig. 1: TEM images of gold nanoparticles synthesized by seed-mediated growth method. The (a), (b), and (c) referred to growth conditions that used one, two, and three portions of growth solutions, respectively.

growth mechanism of 1-D gold nanoparticles in the presence of CTAB. The growth direction of gold nanorods in the presence of CTAB has been confirmed by electron diffraction pattern and HRTEM image analyses. The surface atomic defect structure and thermal reshaping of gold nanorods have been studied, and it was observed that the mean aspect ratio of the nanorods in solution decreases with increasing temperature while the average width remains constant. Thermal stability of the shape of the nanorod was examined, and the shape was found to be stable until the temperature reaches ca 600°C. Therefore, the reshaping of gold nanorods is due to the unstable nature of CTAB in high temperature solution. The pH value effect of ascorbic acid has been studied by Busbee et al. There is different amount of proton in the ascorbic acid, wherein the reductant has variable strength and results in change of aspect ratio of gold nanorods. On the other hand, the concentration of silver ion, $[Au^{3+}]/[ascorbic\ acid]$ ratio, and concentration of CTAB have been studied by Murphy et al. Therefore, the understanding of the growth mechanism of gold nanorods will be useful and important.

According to Gole and Murphys' results, the length and width both increase at the increasing size of seed particles. The diameter of seed particles dominated the width of resulting rod. Therefore, it is crucial to know the factors which are in controlling the length of the nanorods. In present study we investigated the changing of gold valence during the reaction under ambient conditions by using the X-ray absorption spectroscopy. The X-ray absorption spectrum is sensitive to the valence of transition metal, and we therefore can monitor the electronic state of gold during the reaction.

Figure 1 shows the TEM images of gold nanoparticles synthesized by the seed-mediated growth method. The (a), (b), and (c) represent growth solution with one, two, and three portions of growth solution, respectively. We observed that there were some elliptic nanoparticles in Fig. 1(a) while there were a lot of spherical nanoparticles. For the growth from using two portions of added solution, the length of gold nanorods increased and the amount of spherical nanoparticles decreased. The shape of gold nanorods was Φ shape and looked like leaf [Fig. 1(b)]. The resulting nanoparticles were almost one dimension nanorods after adding third addition. Therefore, increasing the number of addition times of growth solution gives rise to increasing aspect ratio of nanorods and increasing the yield of 1-D nanorods.

To confirm the oxidation state of gold nanoparticles during the reaction, X-ray absorption spectroscopic experiments were performed. Figure 2 shows the X-ray absorption spectra of Au L_3 edge during the experiment. This result reveals that the oxidation state of gold ions did not change in the surfactant aqueous solution [Fig. 2(b)], and the valence of gold ions were the same as the aqueous solution of gold ions without surfactant. The color of gold ion solution was slight yellow, and the color of the CTAB solution was colorless. However, the solution of gold ions in the presence of CTAB was yellow-brown. This phenomenon was due to the formation of $AuBr_4^-$ complex in the solution. After adding ascorbic acid, the position of absorption edge moved [Fig. 2(c)] and was the same as the position of Au foil [Fig. 2(a)]. Moreover, the intensity of white line decreased. This result confirmed that gold ions were reduced to atoms with zero valence by ascorbic acid. By monitoring the color of solution, we observed that color changed from yellow-brown to colorless on the instant after the addition of ascorbic acid. This phenomenon proved the reduction of $AuBr_4^-$ by ascorbic acid into Au atoms and Br^- ions. Generally gold nanoparticles give rise to absorption in the visible region, but we could not observe any absorption in our sample. Because the gold atoms did not aggregate and form nanoclusters at that time, they existed in the solution as atom form and surrounded by surfactants. The CTAB as capping agent on the surface of gold atoms prevented aggregation of gold atoms, this situation was stable for one or two hours. After several hours, the gold atoms aggregated and then displayed the metallic shine of gold. These atoms cannot be used for fabrication gold nanorods.

The spectra with the energy above 11.97 KeV exhibited fine oscillations called extended X-ray atomic fine structure (EXAFS) as shown in Fig. 2, the basic origin of EXAFS can thus be ascribed to the modulation of the final-state wave function of outgoing photoelectrons due to the presence of neighboring atoms which scatter the photoelectrons. The oscillations in the region was a smooth curve before adding seed particles, confirming that there were not any scattering atoms near absorption atoms. This result is consistent with the observation of experiment during the reaction. The Br^- ions are too light and few in number to cause observable oscillation in the absorption spectrum. After addition of seed particles, we observed the colour of solution gradually turned red. However, the position of absorption edge in the spectrum did not change; it reveals that there was no oxidation or reduction reaction as the seed

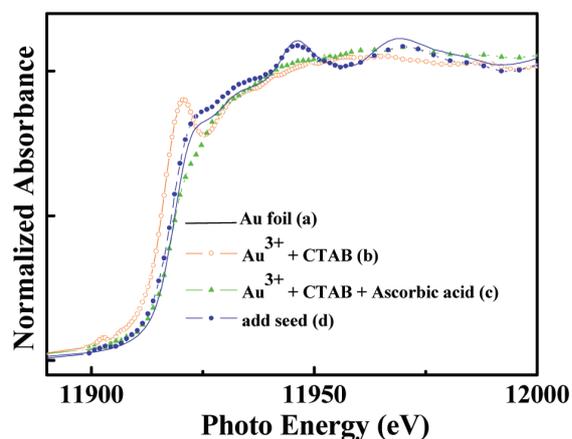


Fig. 2: X-ray absorption spectra of Au L_3 edge during the experiment in the presence of (a) Au foil, (b) prior to adding ascorbic acid, (c) adding ascorbic acid, and (d) adding seed particles, respectively.

was added. Based on this observation, it is concluded that the seed particles provide active sites for the crystal to grow and then the gold atoms suspended in the solution deposited and grow on the surfaces of the seed particles during seed addition. The spectrum as shown in Fig. 2(d) exhibited the observable oscillation in the EXAFS region and its oscillation was similar to that of Au foil [Fig. 2(a)]. As more gold atoms were deposited on the seed particles, the interference of photoelectrons between emitters and scatterers becomes more pronounced, leading to a noticeable oscillation. This observation confirmed that the gold atoms grew and formed nanoclusters, and eventually became nanowires.

We have monitored the growth mechanism of seed-mediated method by using TEM and X-ray absorption spectroscopy at room temperature. The TEM images show the change of gold rod morphology during the reaction, wherein the shape of gold nanoparticles evolved from sphere into one dimension rod as increasing the addition amount of gold growth solution. Measuring the absorption spectra for Au L_3 edge has proved the change of gold valence. After addition of ascorbic acid, the valence of gold changes from $3+$ to 0 directly. This result confirms that ascorbic acid can reduce the gold ions to atoms at room temperature. Besides, the EXAFS oscillation proved that gold atoms deposited and grown on the surface of seed particles as adding seed particles. We conclude that: first, gold ions suspend in the aqueous solution and surfactant acts as capping agent. Next the gold ions are reduced to atoms with zero valence as adding ascorbic acid and then the gold atoms deposit at the seed particles, grow along one direction restricted by CTAB. Thus, we have demonstrated the growth mechanism of gold nanorods fabricated by seed-mediated method.

Experimental Technique

Preparation of growth solution. First, a 100 mL of 250 μ M HAuCl₄ aqueous solution was prepared in a conical flask and then 3.0 g of solid CTAB was added to the gold salt solution. The solution was heated to 60°C while stirring to dissolve the CTAB. The solution was used as the growth solution after cooling to room temperature.

Preparation of gold seeds. First, a 20 mL aqueous solution containing 0.25 mM HAuCl₄ and 0.25 mM trisodium citrate was prepared. Next, 0.6 mL of a 0.01 M NaBH₄ solution was added at once into the gold solution under constant stirring. Stirring was continued for another 30 s. The solution turned a wine red color, indicating particle formation.

Growth of Rods. First, 0.02 mL of gold seeds was placed in a beaker. Then 0.2, 20, and 200 mL of growth solution were prepared. 0.1, 1, and 10 mL of freshly prepared ascorbic acid (10 mM) was mixed with each set of growth solution, respectively. Next, three colorless growth solutions were added to gold seeds solution. The color of the solutions turned pink to violet within 10 min. Transmission electron microscope (TEM) images were acquired with a JEOL JEM- 2000EX electron microscope. The TEM pictures were taken after separating the surfactant from the metal particles by centrifugation. Typically 1 mL of the sample was centrifuged for 5 min at a speed of 4000 rpm. The upper part of the colorless solution was removed and the solid portion was redispersed in 1 mL of water.

Experimental Station

X-ray Absorption Spectroscopy end station

References

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