Wet Chemical Synthesis of High Aspect Ratio Cylindrical Gold Nanorods

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Gold nanorods with aspect ratios of 4.6 ± 1.2, 13 ± 2, and 18 ± 2.5 (all with 16 ± 3 nm short axis) are prepared by a seeding growth approach in the presence of an aqueous miceller template. Citrate-capped 3.5 nm diameter gold particles, prepared by the reduction of $HAuCl_4$ with borohydride, are used as the seed. The aspect ratio of the nanorods is controlled by varying the ratio of seed to metal salt. The long rods are isolated from spherical particles by centrifugation.

Introduction

The shape of nanoparticles influences their optical, electronic, and catalytic properties.[1−4] Plate and rodlike nanoparticles are also attractive due to their liquid crystalline phase behavior.[5,6] Gold nanorods and nanowires in particular may be useful for various optoelectronic devices.[2,3] It is well-known that chemical reduction of gold salts produces spherical gold nanoparticles.[7,8] Templates are commonly used for making gold nanorods and nanowires.[9−15] Gold nanorods have been prepared using electrochemical[9] and photochemical[10] reduction methods in aqueous surfactant media, porous alumina templates,[11,12] polycarbonate membrane templates,[13] and carbon nanotube templates.[14,15]

Recently we have used a seeding growth method to make varied aspect ratio gold and silver nanorods.[16,17] The gold particle aspect ratio can be controlled from 1 to 7 by simply varying the ratio of seed to metal salt in the presence of a rodlike micellar template. We observed that the use of additives such as $AgNO_3$ and cyclohexane strongly influenced the gold nanorod formation. However, preparation of gold rods >7 aspect ratio was difficult by varying those additives. We observed that high aspect ratio gold rods could be prepared by carefully controlling the growth conditions. Herein we report a procedure for reproducibly preparing 4.6, 13, and 18 aspect ratio rods. The cylindrical shape of our gold rods is distinctly different from an earlier observed needlelike shape.[16] Our method requires no nanoporous template and therefore may be more practical for large-scale synthesis.

Experimental Section

I. Preparation of 3.5 nm Seed. 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 conical flask. Next, 0.6 mL of ice cold 0.1 M $NaBH_4$ solution was added to the solution all at once while stirring. The solution turned pink immediately after adding $NaBH_4$, indicating particle formation. The particles in this solution were used as seeds within 2−5 h after preparation. The average particle size measured from the transmission electron micrograph was 3.5 ± 0.7 nm. Some irregular and aggregated particles were also observed that were not considered for determining the size distribution. Here, citrate serves only as the capping agent since it cannot reduce gold salt at room temperature (25 °C). Experiments performed in the absence of citrate resulted in particles approximately 7−10 nm in diameter.

II. Preparation of 4.6 ± 1 Aspect Ratio Rod. In a clean test tube, 10 mL of growth solution, containing 2.5×10^{-4} M $HAuCl_4$ and 0.1 M cetyltrimethylammonium bromide (CTAB), was mixed with 0.05 mL of 0.1 M freshly prepared ascorbic acid solution. Next, 0.025 mL of the 3.5 nm seed solution was added. No further stirring or agitation was done. Within 5−10 min, the solution color changed to reddish brown. The solution contained 4.6 aspect ratio rods, spheres, and some plates. The solution was stable for more than one month.

III. Preparation of 13 ± 2 Aspect Ratio Rod. A three-step seeding method was used for this nanorod preparation. Three test tubes (labeled A, B, and C), each containing 9 mL growth solution, consisting of 2.5×10^{-4} M $HAuCl_4$ and 0.1 M CTAB, were mixed with 0.05 mL of 0.1 M ascorbic acid. Next, 1.0 mL of the 3.5 nm seed solution was mixed with sample A. The color of A turned red within 2−3 min. After 4−5 h, 1.0 mL was drawn from solution A and added to solution B, followed by thorough mixing. The color of solution B turned red within 4−5 min. After 4−5 h, 1 mL of B was mixed with C. Solution C turned red in color within 10 min. All of the solutions were stable for more than a month. Solution C contained gold nanorods with aspect ratio 13.

IV. Preparation of 18 ± 2.5 Aspect Ratio Rod. This procedure was similar to the method for preparing 13 aspect ratio rods. The only difference was the timing of seed addition in successive steps. For 13 aspect ratio rods, the seed or solutions A and B were added to the growth solution after the growth occurring in the previous reaction was complete. But to make 18 aspect ratio rods, particles from A and B were transferred to the growth solution while the particles in these solution were still growing. Typically, solution A was transferred to B after 15 s of adding 3.5 nm seed to A, and solution B was transferred to C after 30 s of adding solution A to B.

V. Procedure for Shape Separation. Long rods were concentrated and separated from spheres and surfactant by centrifugation. 10 mL of the particle solution was centrifuged at 2000 rpm for 6 min. The supernatant, containing mostly spheres, was removed and the solid part containing rods and some plates was redispersed in 0.1 mL water.

Absorption spectra of the particle dispersions were measured using a CARY 500 Scan UV−vis NIR spectrophotometer.

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Transmission electron microscopy (TEM) images were acquired with a JEOL JEM-100CXII electron microscope. TEM grids were prepared by placing 1 μL of the particle solution on a carbon-coated copper grid and evaporating the solution at room temperature. At least 200−300 particles were counted and measured per grid.

Results and Discussion

Ascorbic acid is too weak to reduce gold salt in the presence of CTAB and in the absence of seed, as judged by the absence of a gold plasmon band under these conditions. However, gold salt reduction occurs very fast in the presence of 3.5 nm seed particles, indicated by the solution turning red-brown in color. It is possible to grow the 3.5 nm seeds into larger nanospheres, depending on the ratio of seed to metal salt (unpublished data). However, when this method was used to make particles > 20 nm (in the presence of a relatively low concentration of 3.5 nm seed), rodlike particles were also observed. This observation suggested that gold nanorods could be prepared by carefully controlling the growth conditions.

Following the procedures outline in the Experimental Section, 4.6 ± 1.2, 13 ± 2, and 18 ± 2.5 aspect ratio gold nanorods have been prepared. For making 4.6 aspect ratio rods, a one-step seeding growth method was used. The 13 and 18 aspect ratio rods were separated from spheres by centrifugation. The 4.6 aspect ratio rods were too close in size to the spheres to allow for sufficient separation. We found that rod yield decreased substantially when the micellar template (CTAB) was absent.

Figure 1 shows the TEM images corresponding to the three samples of nanorods. The 4.6 aspect ratio rods were mixed with spheres and plates (Figure 1a), and the longer rods (13 and 18 aspect ratio) were imaged after their separation from spherical products (Figures 1b and 1c). The short axes of the nanorods were all 16 ± 3 nm.

Solutions of the shape-separated 13 and 18 aspect ratio rods were faint blue in color, and solutions of the 4.6 aspect ratio rods were pink. The electronic absorption spectra of the 4.6 aspect ratio rod solutions show the conventional plasmon band at ∼525 nm, along with an additional long wavelength plasmon band at 885 nm (Figure 1Sa). As the aspect ratio increases, the short wavelength plasmon band blue shifts to ∼500 nm and becomes very weak, but the long wavelength plasmon band red shifts to ∼1750 nm for the 13 aspect ratio rods (Figure 1Sb). We did not observe a longitudinal plasmon band for the 18 aspect ratio rods within the confines of our scan (Figure 1Sc), but a band may occur beyond 1800 nm. An additional broad band appears at 800−900 nm region for the 18 aspect ratio rods, attributed to the nonseparable platelets (Figure 1Sc). Platelets of this shape should have another band around 350−425 nm; however, we did not observe a significant band in this region compared to the longer wavelength band (800−900 nm).[18] The presence of these plates consequently produces a bluish color of the shape-separated rod dispersions. Though platelets are also observed in solutions of 13 aspect ratio rods, the overall observation from the entire TEM grid indicates that they are relatively small and less concentrated than in the 18 aspect ratio rod solutions; thus we do not observe the 800−900 nm "platelet" band in the absorption spectra of the 13 nm aspect ratio solution unless the solution is very concentrated. The prominent red shift of the longitudinal plasmon band in the absorption and the slight blue shift in the transverse plasmon band in the optical spectra of noble metal particles with increasing aspect ratio is a well-known phenomenon.[1,3,9,12−14]

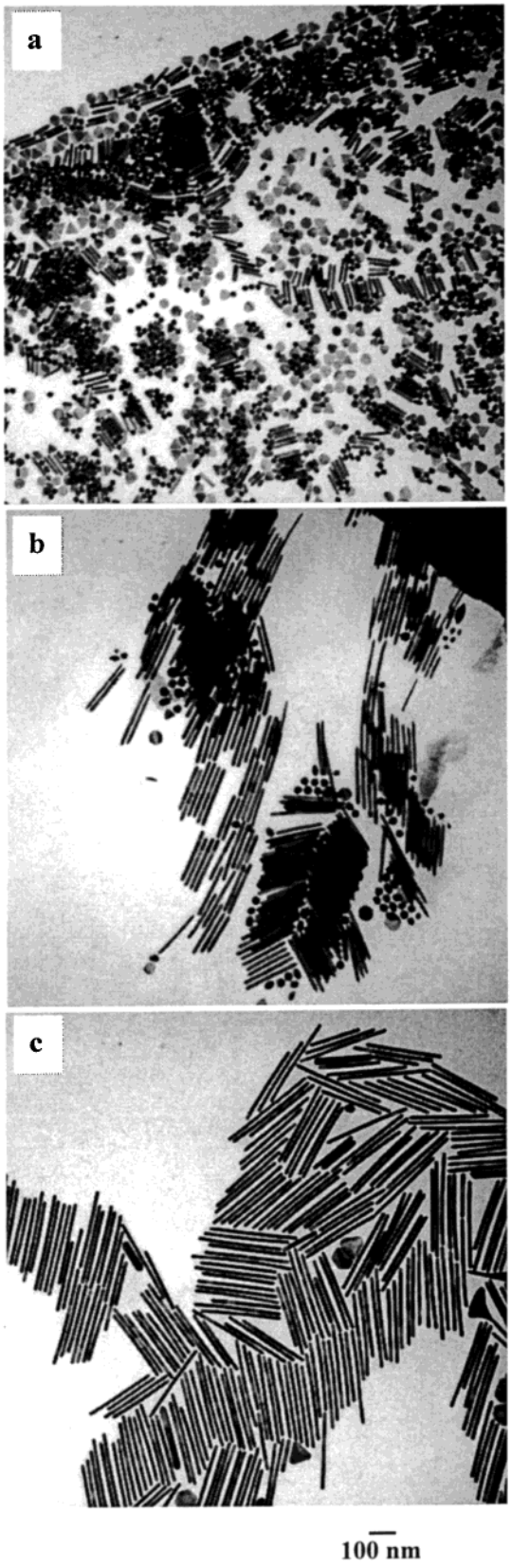

Figure 1. (a) TEM images of 4.6 aspect ratio gold nanorods, (b) shape-separated 13 aspect ratio gold nanorods, and (c) shape-separated 18 aspect ratio gold nanorods. The scale bar (100 nm) applies to all three images.

It is possible to make metallic nanorods using spherical seeds without a micellar template; however, the yield is low, and the aspect ratio is difficult to control.[19,20] We have observed that

using concentrated CTAB solution enhances the rod yield. Concentrated CTAB has a tendency to form elongated rodlike micellar structures[21] that possibly assist in rod formation, as well as stabilizing the rods. This template was used earlier for the electrochemical synthesis of gold nanorods, and the aspect ratio was controlled by introducing Ag^+ ions or a more hydrophobic cosurfactant (compared to CTAB).[9] The enhanced growth rate in the presence of seed (possibly diffusional growth) and the rodlike micellar template contribute to the rod formation.

Until this paper, the synthesis of high aspect ratio rods (>11) in the absence of a mesoporous template has not been reported. We have prepared high aspect ratio gold nanorods by a seeding growth method in an aqueous micellar template and have controlled the nanoparticle aspect ratio by properly adjusting the growth conditions. With this method, uniformly shaped rods with high aspect ratio can be prepared. This method is simple and can be achieved with common laboratory reagents.

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Supporting Information Available: Absorption spectra of 4.6, 13, and 18 aspect ratio gold nanorods. This material is available free of charge via the Internet at http://pubs.acs.org.

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