

Preparation of Polystyrene- and Silica-Coated Gold Nanorods and Their Use as Templates for the Synthesis of Hollow Nanotubes

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ABSTRACT

We report the preparation of polystyrene and silica-coated Au nanorods (aspect ratio 13 with 16 nm short axis). The coating resulted in a modification of the optical properties of the Au nanorods. Dissolution of the Au core from the polystyrene- and silica-coated Au nanorods using KCN enabled the formation of hollow polystyrene and silica nanotubes.

Metal nanoparticles of different shapes and sizes, particularly gold, silver, and copper, have attracted considerable attention from the inorganic, materials, and physical community.¹ For nanoparticles made in solution, uncontrollable aggregation effects can be detrimental to many applications (e.g., electronics). Common stabilizers such as polymers, surfactants, and dendrimers have been used to increase nanoparticle stability.² Coating nanoparticles by in situ polymerization reactions provides an alternative method to increasing nanoparticle stability.³ Another potential use of coated nanoparticles is to make precursors to hollow nanoparticles. Hollow nanoparticles are an interesting and increasingly important class of materials with diverse applications, ranging from drug delivery,⁴ cell and enzyme transplantation,^{4b,5} contaminated waste removal,⁶ and gene therapy.⁷ Controlling the shape of the hollow nanoparticles is a great challenge.⁸ Most of the work done in this field makes use of spherical inorganic cores. We have recently synthesized high aspect ratio cylindrical Au nanorods.⁹ We here report a method of coating these nanorods with polystyrene and silica, followed by subsequent dissolution of the Au nanorods to form hollow nanotubes of the coating material.

A solution of Au nanorods in the presence of the surfactant cetyltrimethylammonium bromide (CTAB) was prepared as described earlier.⁹ The particle concentration in terms of Au atoms was 2.5×10^{-4} M. Polystyrene coating of the particles was accomplished by the emulsion polymerization of styrene in the presence of CTAB-coated Au nanorods. Typically, 1 μ L of styrene (Aldrich) was added to 10 mL of the Au

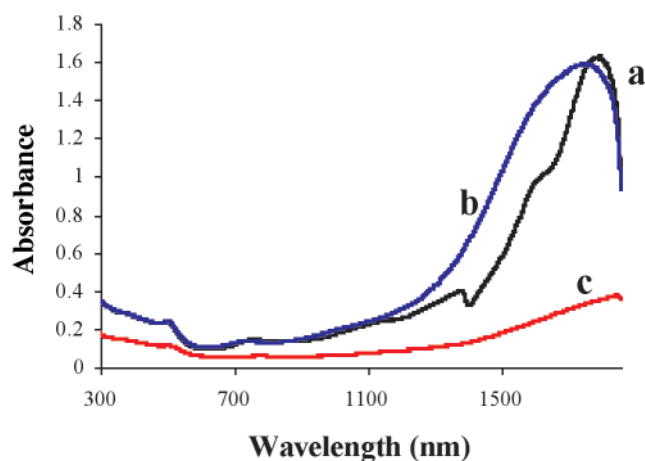


Figure 1. UV-visible absorbance spectra of (a) Au nanorods, (b) polystyrene-coated Au nanorods, (c) silica-coated Au nanorods.

nanorod solution. The solution was stirred for 5 min and 4 μ L of a 0.1 M solution of the initiator ammonium persulfate (APS) was added. The polymerization was allowed to take place, and after 15 min the stirring was stopped. The solution was allowed to sit at room temperature for about 1 h before analysis. The polystyrene-coated Au nanoparticles were separated from spheres and excess CTAB by centrifugation and resuspended in deionized water for characterization by TEM and UV-visible absorption spectroscopy.

For silica coating, Au nanorods were first separated from spheres and excess CTAB as described earlier.⁹ Next, a Au nanorod solution that was 0.01–0.1 wt % nanorod concentration was prepared. For typical silica coating, 10 μ L of a (3-mercaptopropyl)trimethoxysilane (MPTMS) solution (10

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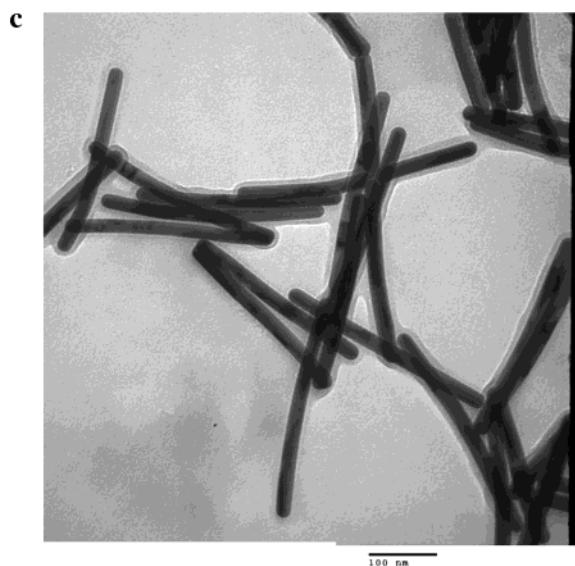
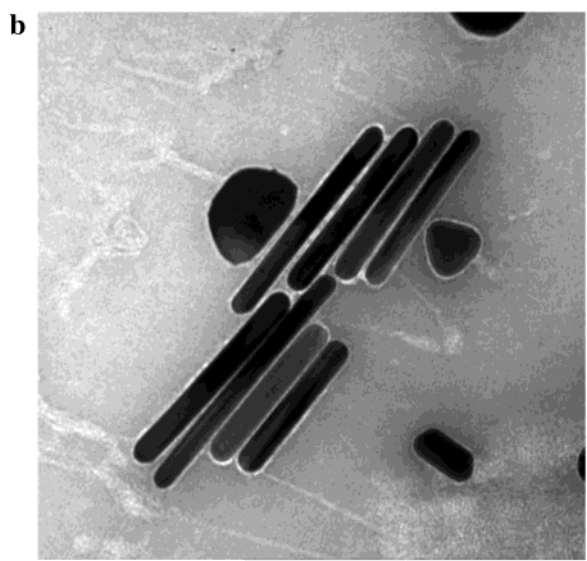
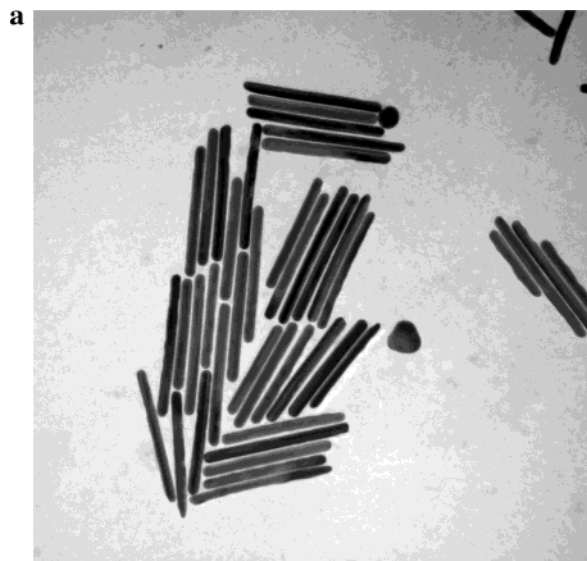


Figure 2. TEM images of (a) Au nanorods, (b) polystyrene-coated Au nanorods, and (c) silica-coated Au nanorods. Scale bars = 100 nm.

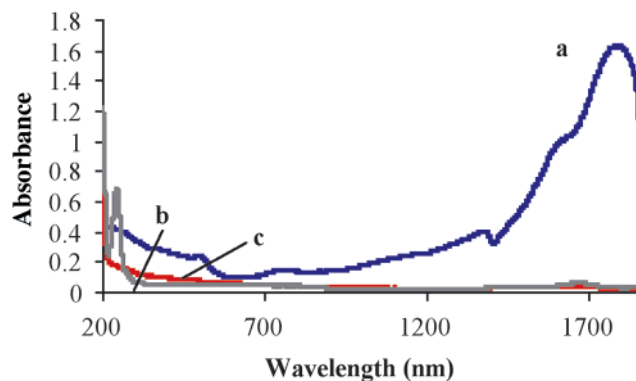


Figure 3. UV-visible absorbance spectra of (a) Au nanorods, (b) hollow polystyrene nanotubes, and (c) hollow silica nanotubes.

μL of MPTMS in 1 mL of ethanol) was added to 1 mL of the nanorod solution and stirred for 20 min. Next, 40 μL of a 2.0 M freshly prepared aqueous sodium silicate (Aldrich) solution was added and stirring continued for another 20 min. The solution was allowed to sit at room temperature overnight and was directly used for TEM and UV-visible analysis.

The UV-visible spectra (Figure 1) for Au nanorods before and after coating showed that the optical properties of the Au nanorods were changed. The 13 aspect ratio nanorods have a weak transverse plasmon band at 530 nm and a strong longitudinal plasmon band at 1700 nm. The absorbance peak at 1700 nm shifted as a function of the dielectric constant surrounding the nanoparticle. In the case of polystyrene-coated ($\epsilon = 2.4$) Au nanorods, the 1700 nm peak blue-shifted in comparison to the CTAB-coated nanorods, whereas the silica-coated ($\epsilon = 4.5$) Au nanorods exhibited a red-shifted longitudinal plasmon band. The observations are consistent with others and with the Mie theory.¹⁰

Transmission electron microscopy (TEM) images for polystyrene- and silica-coated and uncoated Au nanorods are shown in Figure 2. Visualization of the polystyrene-coated nanorods was achieved through negative staining with phosphotungstic acid, which was necessary because the polymer has insufficient electron density to be directly observed by TEM. The polymer appears as a uniform white layer surrounding the nanorods. The silica coating around the Au nanorods was visible without staining and appeared as a thick layer around each nanorod. We propose that the hydrophobic styrene monomer partitions into the CTAB surfactant on the nanorods; thus, the thickness of the polymer coating is controlled by the chain length of the surfactant. For the silica coating, the MPTMS adsorbs on the particle surface via complexation of the thiol group and allowing its silane group to be exposed to the incoming added silica, thus helping silica deposition surrounding the particle surface.^{8g} The thickness of the silica layer is dependent on the ratio of Au nanorod to silica concentration.

Dissolution of Au from the core of the polystyrene and silica encapsulated particles was achieved by cyanide treatment. For hollow polystyrene nanotubes formation, 0.25 mL of a 10^{-2} M KCN solution was added to 1 mL of polystyrene-coated Au nanorods. For hollow silica nanotube formation,

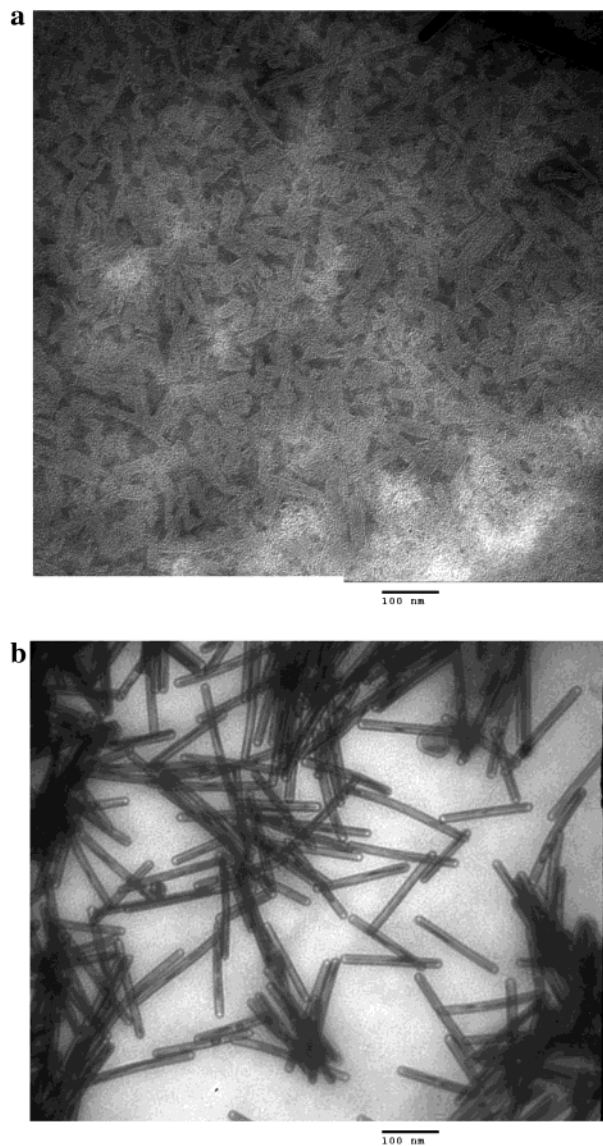


Figure 4. TEM images of (a) hollow polystyrene nanorods and (b) hollow silica nanotubes. Scale bars = 100 nm.

we added 1 mL of the 10^{-2} M KCN solution to 100 μ L of silica-coated Au nanorods. In each case, the solution color changed from faint brown to colorless. The solution was left to sit overnight, after which it was centrifuged to isolate the precipitate that contained the hollow nanotubes. The precipitates were redispersed in deionized water and used for TEM and spectroscopic analysis.

The absorption spectrum for the resulting hollow nanotubes did not show the peaks at 530 and 1700 nm, characteristic for Au nanorods (Figure 3). The dissolution of Au was further supported by elemental analysis performed

by E-SEM (environmental scanning electron microscopy), which showed the absence of elemental Au. Infrared spectra of the hollow polystyrene nanotubes were taken, and the resulting peaks at 1151, 1603.5, 1943, 2857, and 3063 cm^{-1} characteristic of polystyrene were evident.¹¹ TEM images following dissolution of Au from the polystyrene-coated and silica-coated Au nanorods are shown in Figure 4. Besides nanotubes, we also observed hollow spheres that may be a result of partial collapsing of hollow nanotubes. The polystyrene hollow nanotubes are not electron-dense compared to the hollow silica nanotubes.

In conclusion, we have successfully developed a method for coating Au nanorods with coating thicknesses ranging from 5 to 10 nm, and dissolution of the Au core leads to hollow nanotubes.

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