

## Synthesis of Au-X (X = Polypyrrole, Silica) Core-Shell Nanorods

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Since nanosized materials have their own characteristic optical, electronic, magnetic, and catalytic properties different from the bulk materials, the research on nanomaterials has been an important subject in basic science as well as in technological applications. The characteristic properties of nanomaterials often depend not only on particle size but also on particle shape.<sup>1,2</sup> Therefore, current research has been directed to develop synthetic strategies for size and shape controlled nanocrystal growth.<sup>3</sup> Especially, composite nanoparticles, organic or inorganic cores coated with shells of different chemical compositions, are of significant interest from both technological and scientific points of view, since the core-shell particles often exhibit different chemical and physical properties from those of core materials. Considerable efforts have been made on the synthesis of composite nanoparticles, since these nanostructured composites and hollow shells have many potential applications, such as drug delivery,<sup>4</sup> cell and enzyme transplantation,<sup>5</sup> gene therapy,<sup>6</sup> and heterogeneous catalysis.<sup>7</sup> Hollow polymer or silica capsules can be achieved when the core material is selectively removed from metal core-polymer or silica shell nanocomposites. For these reasons, the synthesis of composite nanoparticles has been demonstrated for many different preparation methods using spherical nanoparticles as seeds. Despite many of these studies on composite nanoparticle preparation, there have not been many reports on core-shell nanorods.<sup>3a,8,9</sup>

In this communication, we describe a simple and easy synthetic method on the shell growth of silica and conducting polymer, polypyrrole on pre-formed Au nanorods as seeds at ambient condition.

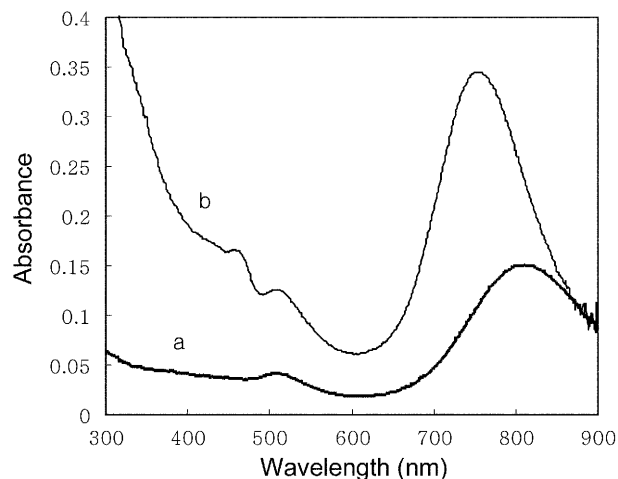
Au-polypyrrole core-shell nanorod colloids were prepared as follows. Au nanorods were used as seeds, which were prepared using a seeding method following a literature procedure.<sup>10</sup> Au nanorod colloid solution (1.0 mL) was mixed with 20  $\mu\text{L}$  of pyrrole solution, which was prepared with 10  $\mu\text{L}$  of pyrrole dissolved in 1 mL of de-ionized water. The solution was mixed slowly by hand shaking, and then was not disturbed for 6 hr. Then 8  $\mu\text{L}$  of 0.1 M  $\text{FeCl}_3$  was added under slow stirring. The polymerization reaction was allowed to take place for 24 hr.

Au-silica core-shell nanorod colloids were prepared as follows. Au nanorod colloids (1.0 mL) was mixed with 10  $\mu\text{L}$  of (3-mercaptopropyl)trimethoxysilane (MPTMS) solu-

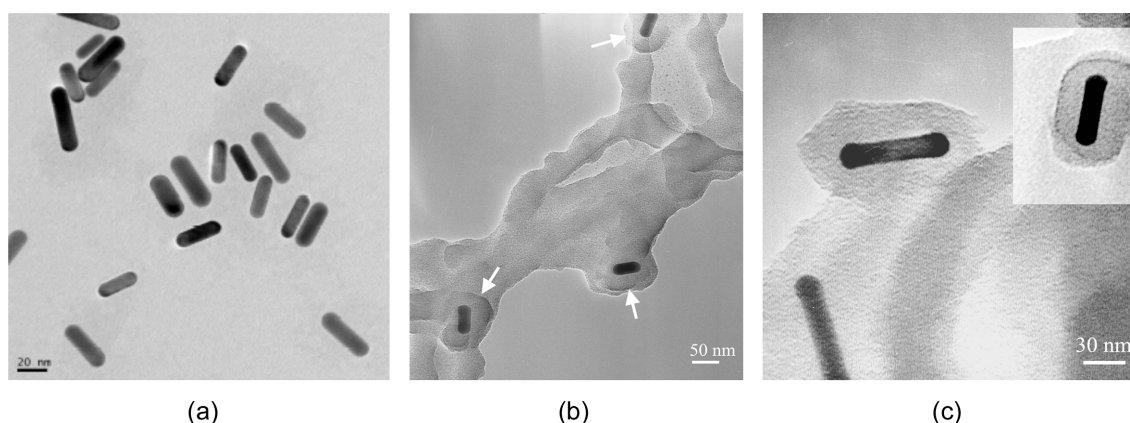
tion, which was prepared by dissolving 10  $\mu\text{L}$  of MPTMS in 10 mL ethanol. The solution mixture was stirred for 20 min, and then 40  $\mu\text{L}$  of sodium silicate solution, (0.173 mL of sodium silicate dissolved in 5 mL of deionized water) was added. This solution was slowly stirred for 20 min and was allowed to sit on bench-top overnight.

UV-Vis spectra were measured using a Cary 3 spectrophotometer. TEM images of  $\text{Au}_{\text{core}}\text{polypyrrole}_{\text{shell}}$  and  $\text{Au}_{\text{core}}\text{silica}_{\text{shell}}$  nanorod colloids were obtained without any further purification like centrifugation.

The UV-Vis absorbance spectrum of as-made Au nanorod colloids is shown in Figure 1a. The solution appeared light brown and displayed two surface plasmon absorption peaks at 510 and 811 nm. Gold nanorods have characteristic surface plasmon bands, transverse and longitudinal, arising from a collective oscillation of conduction band electrons by applied optical and electric field.<sup>11</sup> The position and shape of these two surface plasmon absorption depend not only on the aspect ratio of Au nanorods, but also on the medium dielectric constant. The aspect ratio (length to diameter) of as prepared Au nanorods was between 3-4. As the polymerization of monomer, pyrrole proceeded, the color of the solution changed from light brown to dark green. After polypyrrole coating on the surface of Au nanorods, it was observed that a weak transverse surface plasmon band appeared at 509 nm (Figure 1b), which was essentially the



**Figure 1.** UV-Vis absorbance spectra of (a) as-made Au nanorods, and (b) polypyrrole-coated Au nanorods.



**Figure 2.** TEM images of (a) as-made Au nanorods, (b) polypyrrole-coated gold nanorods, and (c) silica-coated gold nanorods.

same wavelength as that of unmodified Au nanorods, while a strong longitudinal surface plasmon peak underwent a blue shift to 760 nm, which is probably due to different medium dielectric constant due to the polypyrrole shell on the surface of Au nanorods.<sup>12</sup> The broad peak at ~460 nm confirms the presence of polypyrrole.<sup>13</sup>

Transmission electron microscopy (TEM) image of the as-made Au nanorods before shell coating is shown in Figure 2a. Figure 2b shows TEM image of Au-polypyrrole core-shell nanorods. We note that pyrrole polymerization occurred not only on the surface of Au seeds but also in the solution as the form of continuous matrix, which can be avoided by adjusting experimental conditions, such as the use of additives. Polymer stabilizers including polyvinylpyrrolidone (PVP) have been used to effectively avoid undesired homogeneous polymerization.<sup>14</sup> Our preliminary results show that the polymer shell thickness was uniform throughout the surface of Au nanorod, as indicated by arrows in Figure 2b. It can be clearly seen that polypyrrole shell formed around the edges of Au nanorods. If the unmodified Au nanorods were simply embedded in the bulk polypyrrole, the optical changes of Au nanorods can not be expected as seen in Figure 1. It is clearly seen that Au nanorod seed is coated with polymers, since organic materials such as polypyrrole shell have less electron density compared to Au.

Figure 2c shows TEM image of Au<sub>core</sub>-silica<sub>shell</sub> nanorods. We observed a thick silica shell around the surface of Au nanorod. Inset shows a better silica shell coating.

In conclusion, we have successfully prepared Au-X (X=polypyrrole, silica) core-shell nanorods. Au nanorod colloids prepared via seed-mediated process were used as seeds for the growth of shell of polymer and silica at ambient condition.

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