

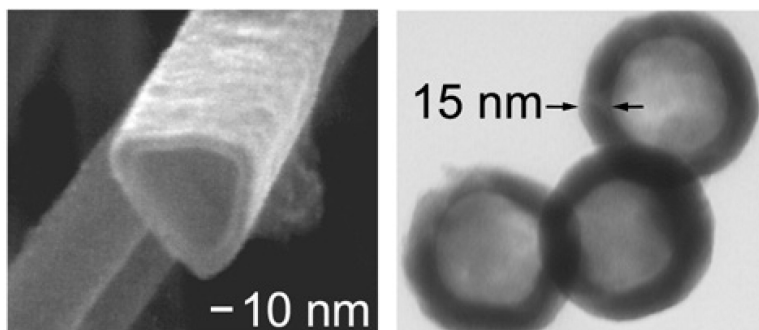
Communication

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*J. Am. Chem. Soc.*, **2003**, 125 (44), 13364-13365 • DOI: 10.1021/ja0379722 • Publication Date (Web): 09 October 2003

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## Hollow Nanostructures of Platinum with Controllable Dimensions Can Be Synthesized by Templating Against Selenium Nanowires and Colloids

Brian Mayers,<sup>†</sup> Xuchuan Jiang,<sup>†</sup> David Sunderland, Bryan Cattle, and Younan Xia\*

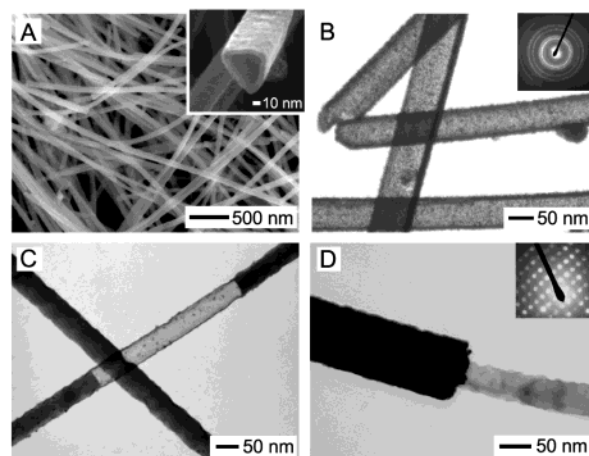
Department of Chemistry, University of Washington, Seattle, Washington 98195

Received August 16, 2003; E-mail: xia@chem.washington.edu

Metal nanostructures with hollow interiors have been shown to exhibit a range of interesting properties superior to their solid counterparts.<sup>1</sup> A number of methods have been demonstrated for generating such nanostructures,<sup>2</sup> with the most versatile one being based on template-directed synthesis. In this case, the surface of a template (e.g., the channel in a porous membrane, nanowire, and colloidal particle) can be directly coated with a conformal layer of the metal to generate a core-shell structure.<sup>3</sup> Subsequent removal of the template results in the formation of a hollow nanostructure with controllable dimensions. Surface treatment is often required to form complete and conformal coating on the template. In a modified procedure (or the template-engaged synthesis), the template (e.g., Ag nanostructures) can be converted to another metal with complementary morphology via galvanic replacement reaction.<sup>4</sup> The major drawback of this route is that the dimension and wall thickness of the resultant hollow structures cannot be independently varied. Here we report a new class of templates—trigonal selenium (*t*-Se) nanowires and amorphous selenium (*a*-Se) spherical colloids—that provide solutions to these problems. Different from our previous work where *t*-Se nanowires were used as chemical templates to form chalcogenide nanostructures<sup>5</sup> here the Se structures served as both chemical and physical templates. A unique combination of these two processes allowed for the formation of hollow nanostructures of metals with controllable shape, size, and wall thickness.

Platinum has been selected as a typical example to demonstrate the concept. Panels A and B of Figure 1 show the SEM and TEM images, respectively, of a sample that was obtained by coating the surfaces of *t*-Se nanowires with Pt at 50 °C for 18 h. The *t*-Se nanowires could be synthesized using a sonochemical<sup>6</sup> or chemical<sup>7</sup> method. The *t*-Se cores were removed by soaking the sample in pure hydrazine monohydrate liquid for 5 h. Note that the triangular cross-section (Figure S1) of the *t*-Se template was faithfully duplicated by the Pt nanotube. Each Pt nanotube was characterized by a uniform wall, with a mean thickness of  $9 \pm 2$  nm. The TEM image implies that a complete sheath of Pt could be formed on each *t*-Se template, including the formation of closed ends. The inset of Figure 1B shows an electron diffraction pattern, indicating that the walls of these tubes were made of nanocrystallites of Pt. The concentric rings could be assigned as diffraction from {111}, {200}, {220}, {311}, and {331} planes starting from the centermost ring. As clearly resolved from samples obtained at shorter coating times (Figure S2), the individual Pt nanocrystallites within each nanotube were only measured 2–4 nm across.

The wall thickness of Pt nanotubes could be readily controlled by varying the concentration of PtCl<sub>2</sub> solution and/or the coating time. Figure 1C shows the TEM image of a second sample that was obtained by coating the surfaces of *t*-Se nanowires with Pt at 50 °C for 30 min. For this sample, a short segment of the Se



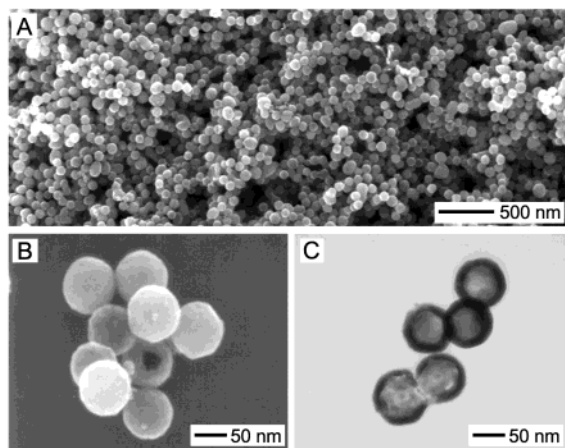
**Figure 1.** (A) SEM images of Pt nanotubes that were prepared by coating for 18 h, followed by dissolution of Se wires in hydrazine monohydrate. (B) TEM image and electron diffraction pattern of the same sample. (C) TEM image of another sample where the coating only proceeded for 30 min. A segment of the Se core had been removed in situ via continuous exposure to the electron beam. (D) TEM image of a third sample where the coating lasted for 3 days. The sample was briefly sonicated to expose the Se core by partially removing the Pt sheath. The inset shows an electron diffraction pattern taken from the exposed Se core, indicating that no structural change was involved for the template during Pt coating.

template had been selectively removed in situ by focusing the electron beam on this portion of the wire for a few seconds. This study also demonstrates the stability and robustness associated with these Pt nanotubes since their walls were only ~4 nm thick. Figure 1D shows the TEM image of a third sample where the Pt coating lasted for 3 days under conditions similar to those used for the first two samples. In this case, the wall thickness of Pt nanotubes was increased to ~19 nm. When the thick Pt sheath was removed via sonication, it became apparent that the single crystalline Se nanowire had not been consumed in the coating process. Aside from some roughening on their surfaces, the *t*-Se template was essentially unchanged. This notion was also supported by the focused electron diffraction pattern shown in the inset of Figure 1D.

After Pt coating, the Se template could be effectively removed using both chemical and thermal methods. The template could be selectively dissolved in pure hydrazine monohydrate.<sup>8</sup> The only requirement was that all excessive PtCl<sub>2</sub> should be removed before this process to avoid additional formation of Pt nanoparticles in the solution. It was also possible to evaporate the Se template by heating the dried sample on a hotplate at 200–250 °C for a few minutes. The low melting point (220.5 °C) and high vapor pressure (1 Pa at 227 °C) of selenium solid ensures quick and complete removal of the template cores. Both chemical and thermal methods gave pure Pt nanotubes (Figure S3).

In addition to nanowires of *t*-Se, the Pt templating process was also demonstrated for use with spherical colloids of amorphous

<sup>†</sup> These authors contributed equally to this project.



**Figure 2.** (A) SEM of Se@Pt core-shell colloids formed by reacting *a*-Se colloids with PtCl<sub>2</sub> in ethanol. (B) SEM of the same sample after the *a*-Se cores had been removed by dissolving in hydrazine, followed by a brief sonication. (C) TEM of the same sample further confirming that these structures are hollow, with uniform shells.

selenium (*a*-Se). Figure 2A displays the initial product of this reaction, in which *a*-Se colloids of ~50 nm in diameter had been coated with Pt at 70 °C for 5 h. Such core-shell colloids (Se@Pt) were quite uniform and could be obtained in copious quantities. Again, the Se cores could be selectively removed via chemical or thermal means. Panels B and C of Figure 2 show the SEM and TEM images of this sample after it had been soaked in hydrazine liquid for ~3 h. Brief sonication was also applied to intentionally break some of the shells (Figure 2B). The SEM image implies the smoothness and uniformity of these hollow spheres. The TEM image further confirms that uniform Pt shells were formed. Since *a*-Se colloids can be synthesized in copious quantities with diameters ranging from a few nanometers to several micrometers,<sup>9</sup> it is believed that the procedure described here should provide an effective route to hollow spheres of Pt with controllable size and wall thickness.

The conformal coating of Se templates with Pt was believed to occur via two distinct reduction reactions: (i) the initial reduction of the Pt(II) salt by a Se template itself at the interface<sup>8</sup> and (ii) the reduction of the Pt(II) salt by the alcohol solvent.<sup>10</sup> The galvanic reduction of the Pt(II) by a Se template could continue until its surface was completely covered. Subsequent deposition of the Pt coating was dominated by the alcohol reduction. The Pt layer would continue to grow until the reaction was quenched or all of the Pt(II) salt had been consumed. Since the thickness of Pt coating was not dependent on the dimensions of the Se template, the Pt nanotubes and nanoshells could potentially be grown to any thickness by controlling reaction time and/or the concentration of the Pt(II) salt. The engagement of template in the nucleation step facilitates the formation of homogeneous, conformal coating on the template. This is also the major reason Se was such a good template for the coating of metals when compared with inert structures such as polystyrene beads or silica spheres. We note that it was hard to form continuous shells on these two types of templates without pretreating their surfaces with an appropriate functional group.<sup>11</sup>

In summary, we have demonstrated (with Pt as an example) the use of *t*-Se nanowires and *a*-Se colloids as templates in forming metal hollow nanostructures. This templating process has also been extended to other metals (such as Rh and Ir) that could be synthesized as nanoparticles through a similar, alcohol reduction

scheme.<sup>10</sup> Since the bulk of the metal coating is formed via the redox reaction with the alcohol (rather than the Se template), the wall thickness of the metal hollow structure can be independently tuned regardless of the size and morphology of the Se template. It is also worth mentioning that the Se templates are not limited to the randomly dispersed nanostructures shown in this work. It has been recently demonstrated the Se nanowires and colloids could be organized into ordered structures such as networks (or meshes) and crystalline lattices.<sup>6</sup> These templates are expected to play an increasingly important role in fabricating metal nanostructures with complex (yet controllable) morphologies. The Pt nanotubes can serve as catalysts for various organic reactions, and the use of relatively long tubes rather than particles should allow them to be easily recovered from a reaction medium via centrifugation or filtration. These nanotubes with well-defined cross-sections and dimensions may also find use as a platform to study various issues associated with nanofluidics. In addition, the monodisperse shells of Pt will be suitable for use as a new class of building blocks to fabricate colloidal crystals that are expected to exhibit improved photonic band gap properties.<sup>12</sup>

**Acknowledgment.** This work has been supported in part by a DARPA-DURINT subcontract from Harvard University, and a Fellowship from the David and Lucile Packard Foundation. Y.X. is a Camille Dreyfus Teacher Scholar. B.M. thanks the Center for Nanotechnology at the UW for the IGERT Fellowship supported by the NSF (DGE-9987620).

**Supporting Information Available:** Experimental procedures, SEM and TEM images of the *t*-Se nanowires, and XRD patterns and TEM images at different stages of the coating process (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0379722