

Silver Nanowires Can Be Directly Coated with Amorphous Silica To Generate Well-Controlled Coaxial Nanocables of Silver/Silica

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ABSTRACT

This paper describes a simple and convenient approach that allowed for the facial synthesis of silver/silica coaxial nanocables with well-controlled sheath thicknesses in the range of 2–100 nm. The lengths of these nanocables could be up to $\sim 50\ \mu\text{m}$. Such nanocables were prepared by *directly* coating bicrystalline silver nanowires with conformal sheaths of silica through a sol–gel process. The silver nanowires were, in turn, synthesized using a polyol method that involved the reduction of silver nitrate with ethylene glycol in the presence of poly(vinyl pyrrolidone). The thickness of silica coating could be controlled by changing the concentration of the precursor solution and/or the reaction time. Selective removal of the silver cores led to the formation of silica nanotubes having well-controlled dimensions and wall structures.

One-dimensional nanostructures (such as wires, rods, and tubes) have been the focus of extensive research in recent years due to their potential applications in fabricating nanoscale electronic, optoelectronic, and sensing devices.¹ More recently, nanocables as another type of one-dimensional nanostructures have also begun to attract interests because their functions could be further enhanced by fabricating the core and sheath from different materials. A number of methods have been developed to generate nanocables having coaxial structures: Lieber et al. and Lee et al. have employed a laser ablation method to fabricate nanocables containing Si cores (for example, Si/SiO₂ and Si/SiO₂/C).² A similar method was used by Iijima et al. to synthesize three-layered nanocables consisting of silicon carbide (SiC) cores, amorphous silica intermediate layers, and sheaths of boron nitride and carbon (BNC).³ Nanocables of SiC/SiO₂ have also been prepared by Zhang et al. through the carbothermal reduction of silica xerogels with carbon nanoparticles.⁴ In addition to these vapor-phase, high-temperature routes, several solution-based methods have also been demonstrated to generate polymer/polymer, semiconductor/polymer, and metal/polymer nanocables at relatively low temperatures. For instance, polypyrrole/poly(methyl methacrylate) coaxial nanocables have been synthesized through sequential polymerization of monomers within the channels

of mesoporous silica, followed by dissolution of the template.⁵ CdSe/poly(vinyl acetate) hybrid nanocables have been obtained by growing the semiconductor nanowires inside polymer tubules.⁶ Gold nanorods have recently been coated with polystyrene or silica to form cable-like structures.⁷ Layer-by-layer deposition of oppositely charged species on nickel nanorods has been adopted to prepare nickel/composite nanocable structures.⁸ Here we describe an approach that should be particularly useful for the synthesis of coaxial nanocables containing metallic cores and insulating sheaths that will find use as interconnects in fabricating nanoelectronic devices.

The first step of our synthesis involved the production of silver nanowires using a polyol process,^{9,10} in which platinum nanoparticles were first produced by reducing PtCl₂ with ethylene glycol at $\sim 160\ ^\circ\text{C}$. These Pt nanoparticles could serve as seeds for the heterogeneous nucleation and growth of silver that was produced in the solution via the reduction of AgNO₃ with ethylene glycol. We were able to direct the silver to grow into uniform nanowires by adding poly(vinyl pyrrolidone) (PVP) to the reaction mixture. These silver nanowires were bicrystalline, having uniform diameters that could be easily controlled in the range of 30–40 nm. The lengths of these nanowires could also be varied from ~ 2 to $\sim 50\ \mu\text{m}$ by changing the reaction conditions. The silver nanowires synthesized using this method formed well-dispersed suspensions in solvents such as water, alcohols, and acetone, without adding other surfactants.

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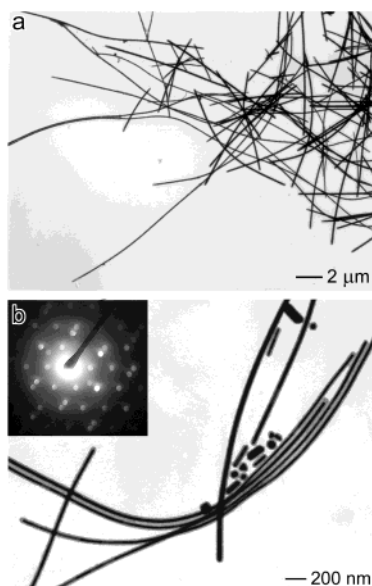


Figure 1. (a) TEM image of silver/silica coaxial nanocables synthesized by directly coating silver nanowires with amorphous silica. (b) A higher magnification TEM image of these nanocables that confirms the uniformity of silica sheath. A few silica-coated silver nanorods and nanoparticles are also included to illustrate the uniformity of coating regardless the morphologies of core structures. The inset gives an electron microdiffraction pattern obtained by focusing the beam on an individual nanocable. This diffraction pattern indicates a bicrystalline structure for the silver core.

Coating of these silver nanowires with amorphous silica was achieved using the Stöber method.¹¹ This sol–gel approach has been extensively exploited to form uniform coatings on nanoparticles of various metal oxides.¹² It has also been explored by a number of groups to coat nanoparticles and nanorods of metals with silica shells or sheaths.^{7,13} For metal surfaces such as gold or silver, it has been emphasized in previous studies that a primer (e.g., amine- or mercapto-terminated siloxane) is often required in order to generate a homogeneous, conformal coating.^{7,13} Here we demonstrate that silica coatings could be *directly* applied to the silver nanowires synthesized using the polyol process without the involvement of any primer. In a typical procedure, the silver nanowires were separated from its original ethylene glycol solution and then redispersed into a mixture of 2-propanol and water.¹⁴ The formation of silica coatings involved the base-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS) and subsequent condensation of silica onto the surfaces of silver cores. In most cases, ammonia could be added as the catalyst to speed up the deposition process. Figure 1 shows two typical transmission electron microscopy (TEM) images of some silver/silica coaxial nanocables that were synthesized using this sol–gel approach. These nanostructures remained as well-dispersed suspensions during the entire process of silica coating. Figure 1a clearly shows that there was no aggregation between the nanocables. The PVP macromolecules adsorbed on the surfaces of silver nanowires were probably retained in the silica sheaths. The silica coating had a uniform thickness over the entire surface of each nanowire, including both ends, as shown by the high magnification TEM image in Figure

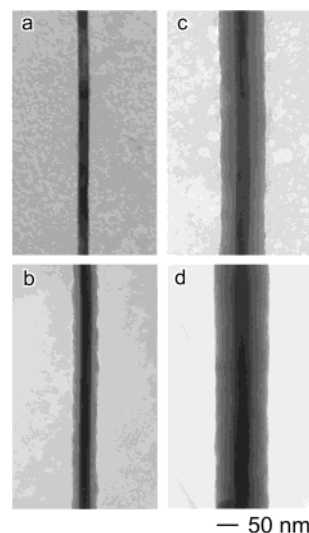
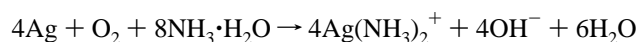


Figure 2. TEM images of silver/silica coaxial nanocables obtained after the coating reaction had proceeded for (a) 5, (b) 10, (c) 30, and (d) 45 min. The concentration of TEOS was 0.072 M. By controlling the reaction time, we could easily tune the sheath thickness from 2 to 100 nm.

1b. The lengths of these nanocables were mainly determined by the original silver nanowires and could be as long as ~ 50 μm . The sample in Figure 1b also contained some nanorods and nanoparticles of silver, and both of their surfaces were also coated with uniform, conformal layers of amorphous silica. Interestingly, the specific morphology (including sharp corners and edges) of each type of silver nanostructure was essentially preserved in this surface-coating process.

The thickness of the silica sheath could be readily controlled by changing the reaction time and/or the concentration of the precursor solution. Figure 2 shows a set of TEM images of silver nanowires that had been immersed in the sol–gel solution for different periods of time. At ~ 5 min, only ~ 2 nm silica coating was formed on the silver nanowire. This thin layer of silica was relatively rough but seemed to be continuous along this nanowire. As coating proceeded, the silica sheath became thicker, smoother, and more uniform (Figures 2b–d). Figure 3a shows the dependence of coating thickness (as measured from TEM images) on the reaction time. This curve suggests that the deposition of silica increased linearly within the first 30 min and reached a maximum thickness (~ 50 nm in this case) after ~ 45 min. We could also tune the thickness of the silica coating by controlling the concentration of the precursor solution. Figure 3b gives the relationship between the silica thickness and the concentration of TEOS. Similar to the previous work that involved coating nanoparticles, the thickness of the silica sheath increased linearly with the concentration of the sol–gel precursor.¹⁵

In this sol–gel process, the ammonia mainly served as a catalyst for the hydrolysis of the TEOS precursor. It might also attack the silver nanowires through the following reaction:



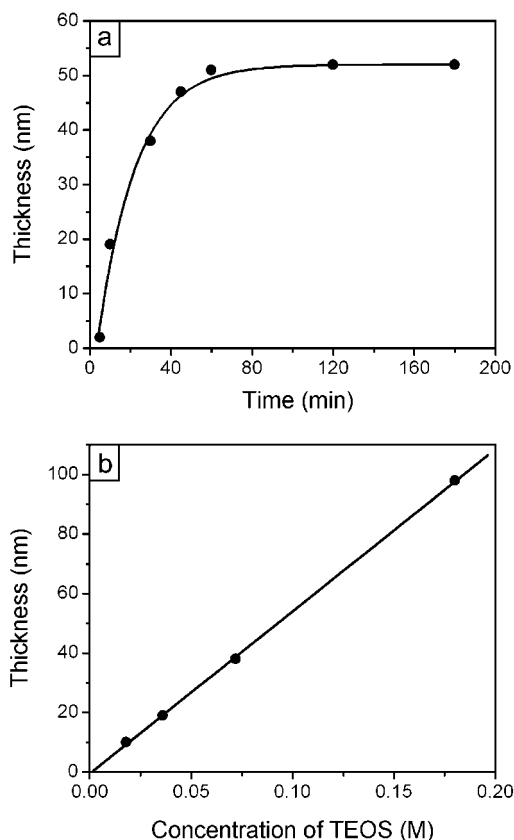


Figure 3. Graphs showing that control over the thickness of silica sheath could be conveniently achieved by changing either (a) the reaction time or (b) the concentration of TEOS. The concentration of TEOS was 0.072 M in (a). All the samples in (b) were collected after the coating reactions had proceeded for ~ 45 min.

The etching of silver was not significant enough to be observed until the coating reaction had processed for ~ 45 min. The silver/silica nanocables separated from the reaction medium before this time always had complete silver cores, as shown in Figure 1. The silver could be slowly etched away if the nanocables were kept in the coating solution for longer than 45 min. The dissolution of silver usually started from the ends of each silver nanowire and then moved toward the middle portion. Figure 4a shows the TEM image of some silver/silica nanocables, where several portions of the silver cores had been etched away during the silica coating process. If these nanocables were immersed in an aqueous solution of ammonia with a pH around 10.5–11, the silver cores could be completely removed from the interiors in ~ 1 day to leave behind silica nanotubes with well-controlled dimensions and wall structures (Figure 4b). The solution changed from turbid gray to colorless and appeared essentially transparent. We noted that nanotubes of metal oxides have also been prepared by templating against polymer fiber and carbon nanotubes,¹⁶ albeit the length, width, and sheath thickness of these tubes could not be easily controlled. In addition, these tubular nanostructures often had relatively rough surfaces and sometimes could be easily broken because most of these methods did not involve a good condensation step. In the present method, the condensation of silica on the surfaces of nanowires was relatively slow but complete. As shown in Figure 4b, the silica nanotubes obtained using

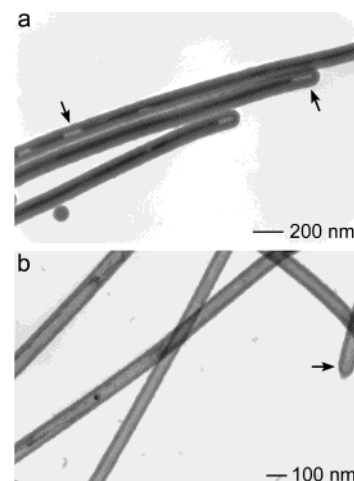


Figure 4. (a) TEM image of several silver/silica nanocables where the silver cores have been partially attacked by the ammonia (as marked by arrows) in the sol–gel solution during the coating process. (b) TEM image of several silica nanotubes obtained by selectively dissolving their silver cores in an ammonia solution (with pH around 10.5–11). Note that the end (as indicated by an arrow) of the nanotube essentially kept the original shape.

our procedure are smooth on both inner and outer surfaces. Due to the uniformity in the size of our silver nanowires, the outer diameter and thickness of these silica nanotubes also had a homogeneous structure along the longitudinal direction. Hollow spheres of silica were also observed in the final products when samples containing silver nanoparticles were kept in the ammonia solution for a sufficiently long period of time.

In summary, we have demonstrated a convenient approach to the large-scale synthesis of silver/silica nanocables with uniform and controllable sheath thickness. Dissolution of the silver cores led to the formation of silica nanotubes with well-defined dimensions and wall structures. We believe that this approach could be extended to prepare silver nanocables coated with other metal oxides by employing different sol–gel precursors.¹⁷ Because a rich variety of other functional materials have also been processed into nanowires, the sol–gel process described here may be extended to these systems to fabricate metal/dielectric coaxial nanocables with various properties for different applications. These nanocables could also be used as the building blocks to generate two-dimensional or three-dimensional arrays of ordered lattices, in which the spacing between the metal wires could be easily varied by controlling the sheath thickness.

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References

- (1) See, for example: (a) Iijima, S. *Nature* **1991**, *354*, 56. (b) Hu, J.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435. (c) Feldman, Y.; Wasserman, E.; Srolovitz, D. J.; Tenne, R. *Science* **1995**, *267*, 222. (d) Kong, J.; Soh, H. T.; Cassell, A. M.; Quate, C. F.; Dai,

- H. *Nature* **1998**, 385, 878. (e) Chung, S.-W.; Yu, J.-Y.; Heath, J. R. *Appl. Phys. Lett.* **2000**, 76, 2068. (f) Dekker, C. *Phys. Today* **1999**, May, 22. (g) Frank, S.; Poncharal, P.; Wang, Z. L.; de Heer, W. A. *Science* **1998**, 280, 1744. (h) Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, 292, 1897.
- (2) (a) Morales, A. M.; Lieber, C. M. *Science* **1998**, 279, 208. (b) Shi, W. S.; Peng, H. Y.; Xu, L.; Wang, N.; Tang, Y. H. H.; Lee, S. T. *Adv. Mater.* **2000**, 12, 1927.
- (3) (a) Zhang, Y.; Suenaga, K.; Colliex, C.; Iijima, S. *Science* **1998**, 281, 973. (b) Zhang, Y.; Gu, H.; Suenaga, K.; Iijima, S. *Chem. Phys. Lett.* **1997**, 179, 264.
- (4) (a) Meng, G. W.; Zhang, L. D.; Mo, C. M.; Zhang, S. Y.; Qin, Y.; Feng, S. P.; Li, H. J. *J. Mater. Res.* **1998**, 13, 2533. (b) Zhang, L. D.; Meng, G. W.; Philipp, F. *Mater. Sci. Eng.* **2000**, A286, 34.
- (5) Jang, J.; Lim, B.; Lee, J.; Hycon, T. *Chem. Commun.* **2001**, 83.
- (6) Xie, Y.; Qiao, Z.; Chen, M.; Liu, X.; Qian, Y. *Adv. Mater.* **1999**, 11, 1512.
- (7) Obare, S. O.; Jana, N. R.; Murphy, C. J. *Nano Lett.* **2001**, 1, 601.
- (8) Mayya, K. S.; Gittins, D. I.; Dibaj, A. M.; Caruso, F. *Nano Lett.* **2001**, 1, 727.
- (9) Sun, Y.; Gates, B.; Mayers, B.; Xia, Y. *Nano Lett.* **2002**, in press.
- (10) In a typical synthesis, 2×10^{-5} g of PtCl_2 (Aldrich, 99.99%) was dissolved in 0.5 mL ethylene glycol (Aldrich, 99.8%) and then added to 5 mL ethylene glycol (heated to 160 °C) under continuous magnetic stirring. The PtCl_2 was immediately reduced by ethylene glycol to form suspended nanoparticles (with diameter <5 nm) of Pt. After ~4 min, 2.5 mL ethylene glycol solution of AgNO_3 (0.050 g, Aldrich, 99+%) and 5 mL ethylene glycol solution of poly(vinyl pyrrolidone) (PVP, 0.200 g, Aldrich, MW \approx 40,000) were added together to the ethylene glycol containing platinum seeds. This reaction mixture was then constantly heated at 160 °C for another 60 min. The final solution exhibited a turbid, gray color. This mixture was centrifuged at ~4000 rpm to separate the silver nanowires from colloidal particles. The solid portion was rinsed with acetone three times and characterized using XRD, SEM, TEM, HRTEM, and electron diffraction. The products obtained using this approach were uniform nanowires of bicrystalline silver with diameter of 30–40 nm and length up to ~50 μm .
- (11) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, 26, 62.
- (12) (a) Ocana, M.; Hsu, W. P.; Matijevic, E. *Langmuir* **1991**, 7, 2911. (b) Hsu, W. P.; Yu, R.; Matijevic, E. *J. Colloid Interface Sci.* **1993**, 156, 56. (c) Partch, R. E.; Xie, Y.; Oyama, S. T.; Matijevic, E. *J. Mater. Res.* **1993**, 8, 2014. (d) Lu, Y.; Yin, Y.; Mayers, B. T.; Xia, Y. *Nano Lett.* **2002**, in press.
- (13) (a) Ohmori, M.; Matuevic, E. *J. Colloid Interface Sci.* **1992**, 150, 594. (b) Liz-Marzán, L. M.; Giersig, M.; Mulvaney, P. *Chem. Commun.* **1996**, 731. (c) Liz-Marzán, L. M.; Giersig, M.; Mulvaney, P. *Langmuir* **1996**, 12, 4329.
- (14) Approximately 2.44×10^{-3} g of the silver nanowires were dispersed into a mixture of 20 mL 2-propanol and 4 mL deionized (DI) water. Under continuous magnetic stirring, 0.4 mL of 30% ammonia solution and various amounts of TEOS (Aldrich) were consecutively added to this system. After the reaction had proceeded for various periods of time, the solution was centrifuged at ~4000 rpm to isolate the precipitate, which was then redispersed into DI water. The silica formed through the hydrolysis of TEOS could either form coatings on the surfaces of silver nanowires via a heterogeneous nucleation process or form core-free silica spheres via a homogeneous nucleation process. We found that the relative ratio between heterogeneous and homogeneous events was mainly determined by the ratios between the concentrations of silver nanowires and TEOS. By increasing the concentration of silver nanowires or decreasing the concentration of TEOS, the homogeneous nucleation events could be essentially eliminated. Based on our observations, the concentration of TEOS had to be kept below 0.2 M and the number density of silver nanowires (~40 nm in diameter, ~25 μm in length) had to be maintained above $3 \times 10^{11}/\text{L}$ to eliminate homogeneous nucleation events. The formation of silica nanotubes was achieved by keeping the nanocables in an ammonia solution with pH around 10.5~11 for 1 day. The resultant nanocables could be separated by centrifugation and redispersion into DI water. TEM measurements were carried out on a JEM-1200 EX II electron microscope (JEOL) with an accelerating voltage of 80 kV. TEM samples were prepared by placing a drop of the solution on a carbon-coated copper grid.
- (15) Klotz, M.; Ayrat, A.; Guizard, C.; Menager, C.; Cabuil, V. *J. Colloid Interface Sci.* **1999**, 220, 375.
- (16) (a) Nakamura, H.; Matsui, Y. *J. Am. Chem. Soc.* **1995**, 117, 2651. (b) Nakamura, H.; Matsui, Y. *Adv. Mater.* **1995**, 7, 871. (c) Rao, C. N. R.; Satishkumar, B. C.; Govindaraj, A. *Chem. Commun.* **1997**, 1581. (d) Caruso, R. A.; Schattka, J. H.; Greiner, A. *Adv. Mater.* **2001**, 13, 1577.
- (17) Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, 90, 33–72.

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