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 ~50 μm. 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 polyl 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 nanocables.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 polyl method,9,10 in which platinum nanoparticles were first produced by reducing PtCl2 with ethylene glycol at ~160 °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 ~50 μm 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.
Coating of these silver nanowires with amorphous silica was achieved using the Sto¨ber method. This sol-gel approach has been extensively exploited to form uniform coatings on nanoparticles of various metal oxides. It has also been explored by a number of groups to coat nanoparticles and nanorods of metals with silica shells or sheaths. 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. 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. 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. Figures 1 and 2 show 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. 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.

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:

\[ 4Ag + O_2 + 8NH\textsubscript{3}H_2O \rightarrow 4Ag(NH\textsubscript{3})_2^+ + 4OH^- + 6H_2O \]

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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, 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 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. 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

A typical synthesis involved dissolving 2 mL of PtCl₂ in 0.5 mL of ethylene glycol (Aldrich, 99.8%) and then adding the solution to 5 mL of ethylene glycol (heated to 160 °C) under continuous magnetic stirring. The PtCl₂ was immediately reduced by ethylene glycol to form suspended nanoparticles (with diameter < 5 nm) of Pt. After ~4 min, 2.5 mL of ethylene glycol solution of AgNO₃ (0.050 g, Aldrich, 99.9%) and 5 mL of ethylene glycol solution of poly(vinyl pyrrolidone) (PVP, 0.200 g, Aldrich, MW = 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 product was precipitated, which was then redispersed 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.


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