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A generic approach to nanocables via nanochannel-confined sequential electrodeposition

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We have exploited a generic method for nanocables, consisting of two materials that can be obtained via electrodeposition, by first electrodepositing the cable “shells” on the interior walls of nanochannels inside anodic aluminum oxide template with one planar surface side coated with a thin meshlike Au layer and then filling the cavities inside the shells by electrodeposition again to achieve the cable “cores.” The method has been demonstrated for the nanocables of Cu-Bi (Cu shell and Bi core) and Bi-Cu (Bi shell and Cu core). Nanocables of other two materials with tunable shell thickness and inner core diameter can be achieved by modulating the Au-layer thickness, and might have potential in the future nanotechnology. © 2008 American Institute of Physics.
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Coaxial nanocables, consisting of a core/shell heterojunction in radial direction, have attracted interests due to their potential applications in future nanodevices, such as transistors,^{1,2} diodes,² power sources,³ solar cells,^{3,4} and logical gates.⁴ Up to now, various methods have been exploited to synthesize nanocables, such as epitaxial growth via modulation of gaseous reactants in sequential steps to achieve nanocables of Si-Ge (Si as shell and Ge as core),¹ growing *p*-type Si core via nanocluster-catalyzed vapor-liquid-solid mechanism and then depositing *i*- and *n*-type Si shells via chemical vapor deposition to achieve *p-i-n* coaxial Si nanocables, template-assisted electroless deposition of Au as shell and then electrodepositing Te as core to achieve Au-Te nanocables,⁴ thermal reaction using silicon wafer as silicon source and substrate to grow SiO₂-SiC nanocables,⁵ one-step coelectrodeposition of Cu and Ni inside the channels of anodic aluminum oxide (AAO) template to form Ni-Cu nanocables,⁶ and carbothermal reduction of sol-gel derived silica xerogels containing carbon nanoparticles to achieve SiO_x-SiC nanocables.⁷ Although the above-mentioned methods have been developed, however, a generic method for nanocables is still a challenge.

In this letter, we show a generic nanochannel-confined sequential electrodeposition approach to synthesize coaxial nanocables via first electrodeposition of cable “shells” on the interior walls of the nanochannels inside AAO template coated with a meshlike Au layer covering the top-view surface of pore walls but still leaving the pores open, and then filling the cavities of the shells by a second electrodeposition to get the “cores” of the cables, as shown schematically in Fig. 1. Theoretically, any material that can be achieved by electrodeposition could be constructed as either core or shell of the nanocable. Herein, we take Cu (metal) and Bi (semimetal) as examples. Using this method, both nanocables of Cu-Bi (Bi as core and Cu as shell of the cable) and Bi-Cu (Cu as core and Bi as shell) have been achieved. We will only focus on Cu-Bi nanocables in the text, while Bi-Cu

nanocables can be found in supplemental material.

The AAO templates with pore diameter of about 75 nm were fabricated via a two-step anodization process.^{8,9} A meshlike thin Au layer (only covering the top-view wall surface of the pores and still leaving the pores open) was sputtered on one planar surface side of the AAO template to serve as working electrode during the electrodeposition of the cable shells. The electrolytes we used for Cu and Bi are the same as those we used in our previous work.⁹ For the Cu-Bi nanocable arrays, the Cu shells (CuNTs) were firstly electrodeposited on the walls of the nanochannels inside AAO template under a constant current density of 1.0 mA/cm² for 1 h at room temperature. After the AAO template embedded with electrodeposited CuNTs was rinsed with deionized water thoroughly, the top caps of the deposited tubes were etched with an aqueous solution of 0.5M CuCl₂ in 30% HCl and then a thick Au layer was coated on the same planar surface side again to fully cover the open mouths of the tubes at the tube root ends. Subsequently, Bi cores (BiNWs) were infiltrated inside the cavities of the CuNTs via electrodeposition at a constant current density of 0.1–0.2 mA/cm² for 3 h.

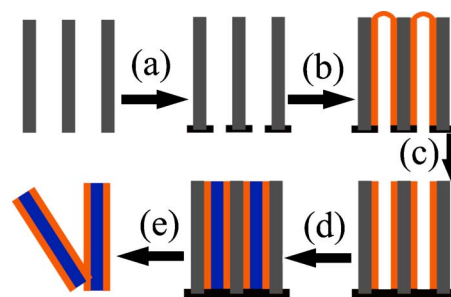


FIG. 1. (Color online) Schematic for the synthesis of nanocables consisting of two materials that can be achieved via electrodeposition. (a) Sputtering a meshlike Au layer on one planar surface side of the AAO template. (b) Electrodepositing one material as the shells (marked in orange) of the cables. (c) Etching the caps on top of the deposited shells and sputtering a thick Au layer at the bottom of the shells. (d) Electrodepositing another material as cores (marked in blue) of the cables inside the first-deposited shells. (e) Removal of the AAO template.

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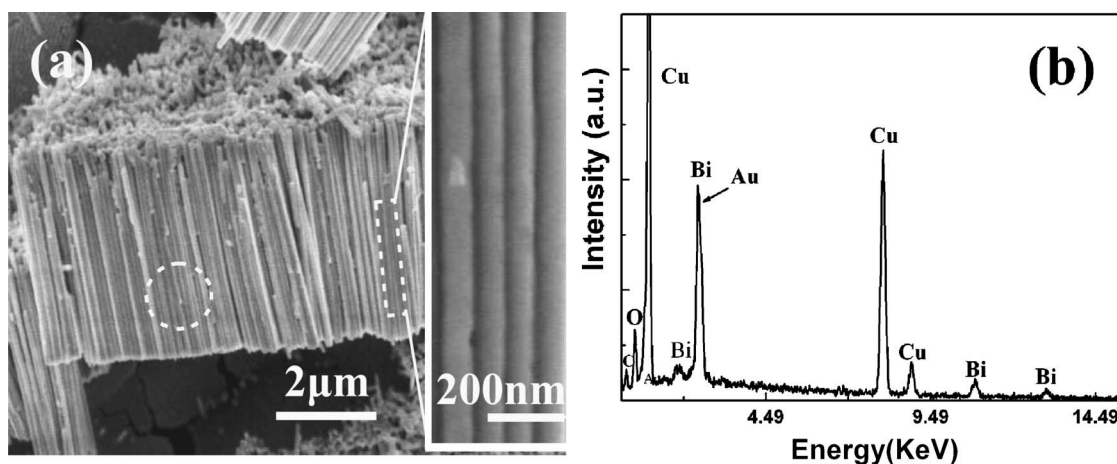


FIG. 2. (a) Scanning electron microscopy image of the Cu-Bi nanocable arrays. The inset is taken from the dashed rectangle. (b) The EDS analysis result of the dashed circle in (a), where Au is from the sputtered Au layer on AAO template.

Figure 2(a) reveals a bundle of Cu-Bi nanocables with length about 6 μm, the inset is an enlarged image, showing the nanocables with smooth surface and uniform diameters about 75 nm, in agreement with those of the nanochannels inside the AAO template. The energy dispersive spectroscopy (EDS) spectrum [Fig. 2(b)] taken from the side-view surface near bottom confirms that the nanocables consist of Cu and Bi, suggesting that Bi cores have been electrodeposited inside the Cu shells.

Our experiments demonstrate that slow-rate electrodeposition is crucial when infiltrating Bi cores into the cavities of the firstly deposited CuNTs (shell of the cable). The confinement growth of BiNW cores takes CuNTs as a second template. Firstly, the CuNTs with open mouths embedded in AAO template were filled with Bi electrolyte and then the deposition of BiNWs was carried out with a very slow rate under a constant current density of 0.1–0.2 mA/cm². It should be emphasized that the slow-rate electrodeposition is crucially important by using under potential technique.⁴ We have tried several experiments and found that if the electrodeposition rate of BiNW core is fast, the mouth of the CuNT may be blocked, no nanocable could be achieved. In our experiments, a third element was not added to slow down the deposition rate, as it was reported elsewhere previously.⁴

The Cu shell and Bi core in the Cu-Bi nanocables could be distinguished by transmission electron microscopy (TEM) observation. Figure 3(a) is a TEM image of a single Cu-Bi nanocable with the core (dark in the middle of the cable) and shell (light dark around the core) being clearly identified.

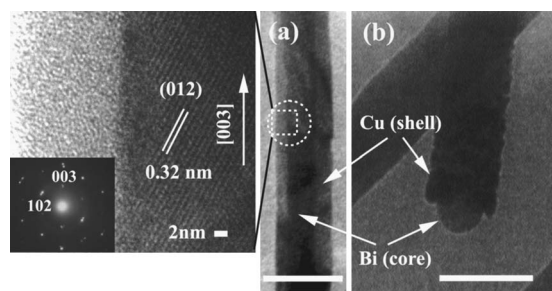


FIG. 3. TEM images of the Cu-Bi nanocables. (a) The middle segment of a cable. (b) The end segment of one cable. The scale bars are both 100 nm. The SAED pattern and high resolution TEM image are taken from the dashed circle and rectangle marked in (a), respectively.

Furthermore, the core and shell can also be distinguished from the cable end [Fig. 3(b)], revealing that the core (BiNW) is sticking out of the cable shell (CuNT). Lattice-resolved image in Fig. 3 displays a lattice spacing of about 0.32 nm, corresponding to the (012) planes of rhombohedral Bi. From the selected area electron diffraction (SAED) pattern [taken from dashed circle marked in Fig. 3(a)], it can be concluded that the preferred growth direction of the BiNW core is along the [003] orientation.

Furthermore, the diameter of the cable core and the shell thickness of the cable can be tuned by modulating the thickness of sputtered Au layer. For example, under the same current density of 1 mA/cm², if the Au layer thickness on the AAO template with channel diameter of 75 nm is about 15, 25, and 35 nm, respectively, then Bi-Cu nanocables with wall thickness and core diameter of 15 and 45 nm [Fig. 4(a)], 20 and 35 nm [Fig. 4(b)], and 25 and 25 nm [Fig. 4(c)] could be achieved, respectively. Based on the above experimental results, it can be concluded that thinner Au layer coated on one planar surface side of AAO template can lead to nanocables of Bi-Cu with thinner shells and thicker cores.

In summary, a generic method has been exploited to synthesize nanocables of two materials that can be achieved via sequential electrodeposition and the method has been demonstrated for the nanocables of Cu-Bi and Bi-Cu by electrodepositing the cable shells on the interior walls of the nanochannels inside AAO template coated with a mesh-like

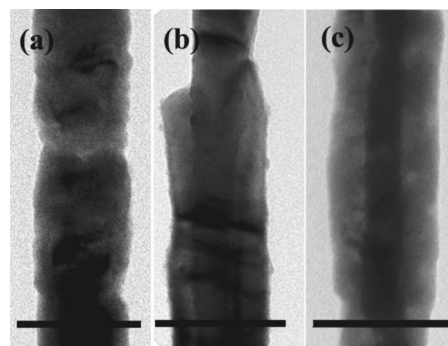


FIG. 4. Bi-Cu nanocables with the same outer diameter of 75 nm but different shell thicknesses and core diameters. The Bi shell thicknesses and Cu core diameters are 15 and 45 nm (a), 20 and 35 nm (b), and 25 and 25 nm (c), respectively. The scale bars are all 100 nm.

Au layer on one planar surface side, and then filling the cavities of the shells by electrodeposition again to achieve the cores of the cables. The core diameter and the shell thickness of the cable can be tuned by modulating the thickness of the sputtered Au layer. This method might be used to synthesize nanocables of other materials that can be obtained by electrodeposition and might have potentials in the future nanodevices and nanosystems.

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