Synthesis of Ordered Metallic Nanowires inside Ordered Mesoporous Materials through Electroless Deposition

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Recent breakthroughs[1−5] in nanomaterial synthesis have resulted in a novel methodology for preparing mesoporous inorganic materials with unprecedentedly large surface areas and highly ordered mesostructures. Both mesoporous silicon and transition-metal oxides have been synthesized. The essence of this new methodology is the use of molecular self-assemblies of surfactants or related substances as templates during the formation of oxides. The size of the oxide mesopores can be precisely tailored from 1.2 to 20 nm based on the use of various surfactant or block copolymer assemblies. The perfect periodic mesopore structures of these materials suggest that they could serve as *generic nanoscale reactors*[6] for manufacturing and replicating technologically important nanomaterials. The metallic nanowire is a key element in nanotechnology. Extensive attempts have been made recently to fabricate such nanowires inside the ordered mesoporous hosts.[7−17] All methodologies reported thus far have involved the direct impregnation of the mesoporous materials with precursor molecules or ions followed by thermal or chemical reduction. Only noble metallic nanowires (such as platinum or silver) have been synthesized through this protocol. Notably, Yang and co-workers have reported facile assembly of silver nanorods inside SBA-15 through the direct impregnation and evaporation of silver ion sources.[8] In the present study, a new synthesis methodology has been developed to generate ultra-high-density arrays of metallic nanowires inside ordered porous inorganic materials through a Pd-catalyzed electroless deposition process. The porous host used in the present application is SBA-15, which was originally developed by Stucky and co-workers.[2] The nanopore diameters of these ordered mesoporous materials are 1−2 orders of magnitude smaller than those of anodic porous alumina (d > 30 nm) prepared by an anodization process[18,19] or nanochannel glasses prepared by a draw process similar to that used in the preparation of optical fibers (d > 30 nm).[20,21] Martin and co-workers[22] have pioneered the use of electroless deposition of metallic tubes inside channels of anodic alumina disks for novel separation applications. Natan, Mallouk, and their co-workers[23] have successfully synthesized gold nanorods through electrochemical deposition using anodic alumina membranes as masks. The diameters of the nanorods synthesized by this method are between 200 and 300 nm. Metallic nanowires with diameters of 14 nm have been recently synthesized by electrochemical deposition of metals inside channels formed by the self-assembly of block copolymers.[24]

The synthetic protocol used here to prepare metallic nanowires is shown in Scheme 1. The synthesis of the SBA-15 hosts was conducted in accordance with a procedure reported in the literature.[2] The external surface of the SBA-15 was functionalized with trimethylsilyl groups.[25,26] The block copolymer templates inside the mesopores were removed by solvent extraction.[27] The dried sample was slurried in a 7.5×10^{-4} wt % H_2O−MeOH solution of $[Pd(NH_3)_4]Cl_2$ to introduce $[Pd(NH_3)_4]^{2+}$ ions into the channels of externally function-

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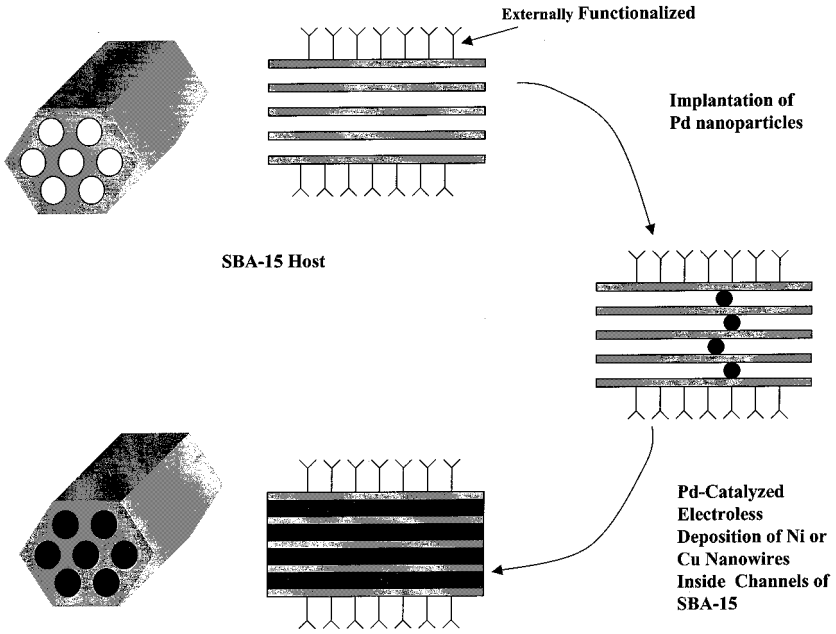
Scheme 1



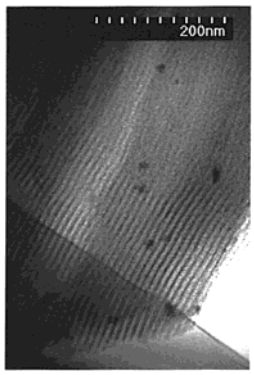


Figure 1. Bright-field TEM image of SAB-15 loaded with Pd nanoparticles.

alized SBA-15 by exploiting the weak ion-exchange capability of the silica material and hydrophobicity of the external surface caused by hydrophobic trimethylsilyl groups.[28] The sample was filtered, washed, and dried in a vacuum oven at 80 °C for 5 h. The dried sample (0.5 g) was then added to 25 mL of absolute ethanol, and the mixture was refluxed for 0.5 h. The color of the resulting solution turned to deep brown-black because of reduction of Pd(II) to the elemental palladium.[29] The sample was then separated and dried.

For the electroless deposition of copper and nickel, the following copper- and nickel-plating baths were used:[30]

(a) Copper-plating bath composition: 100 mL of H_2O, 3 g of $Cu(NO_3)_2$, 14 g of Rochelle salt, 2 g of NaOH, and 5 mL of MeOH.

(b) Nickel-plating bath composition: 2 g of $Ni(NO_3)_2$, 1.5 g of EDTA, 4 g of $(NH_4)_2SO_4$, 0.8 g of NaOH, and 5 mL of MeOH.

The electroless deposition of copper nanowires inside SBA-15 was achieved by immersion of 0.1 g of Pd-loaded SBA-15 in 10 mL of the copper-bath solution for 1 h followed by reaction with 1 mL of fomaldehyde solution (37 wt %) for 5 min. The resulting product was filtered, washed immediately, and dried in a vacuum system overnight. A similar procedure was used to synthesize nickel nanowires inside the channels of SBA-15.

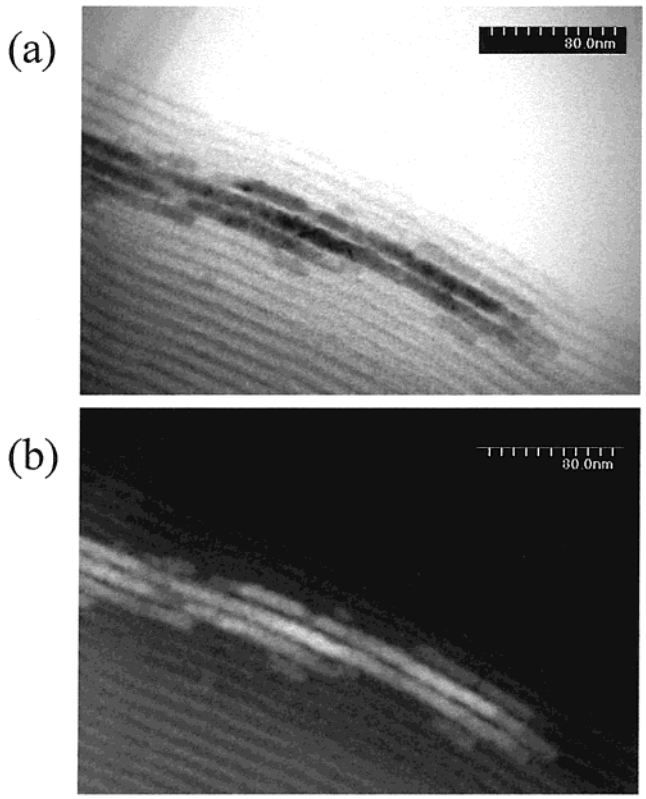


Figure 2. (a) Bright-field and (b) dark-field TEM images of nickel nanowires inside channels of SAB-15 after 20 min of electroless deposition.

Investigations of metallic nanowires using scanning transmission electron microscopy (STEM) were performed using a HD-2000 scanning transmission electron microscope (probe size ≈ 0.3 nm) operating at 200 kV.

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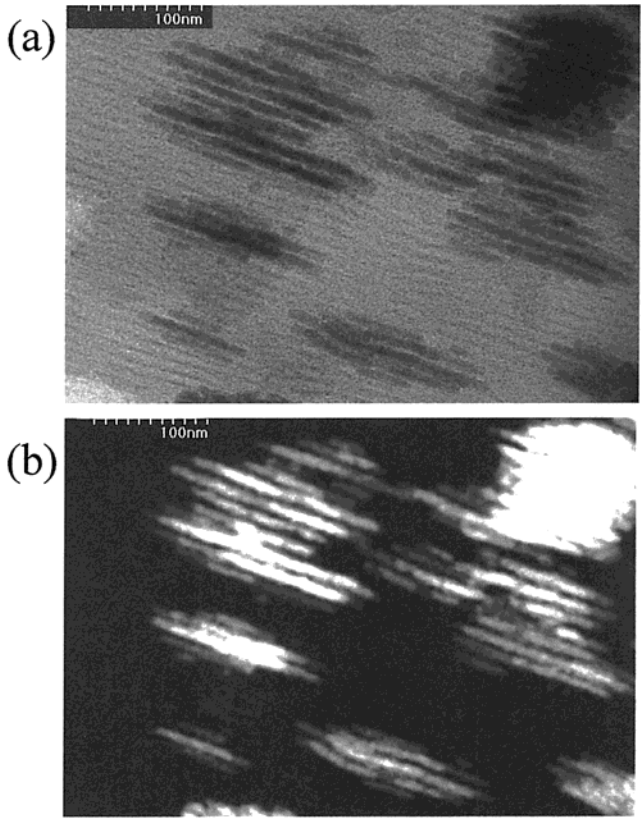

Figure 3. (a) Bright-field and (b) dark-field TEM images of nickel nanowires inside channels of SAB-15 in the same location after 60 min of electroless deposition.

Figure 4. Dark-field TEM image of copper nanowires inside channels of SBA-15.

STEM imaging with a high-angle annular dark-field (HA-ADF) detector provides higher contrast for small clusters of heavy elements in a low atomic number matrix as compared to conventional transmission electron microscopy. The nature of the nanowires deposited inside the channels of SBA-15 make these samples well-suited to HA-ADF (also known as Z-contrast) STEM imaging. Figure 1 shows the bright-field STEM image of the Pd-loaded SBA-15. As shown in the figure, palladium exists inside the channels of SBA-15 in the form of nanoparticles. These nanoparticles were subsequently used as nanocatalysts for electroless deposition of copper or nickel.[29] The functionalization of the external surfaces of SBA-15 by a trimethylsilyl group plays an important role in enhancing the loading of Pd(II) only on the internal surfaces of SBA-15. Figure 2 shows both bright-field and dark-field STEM images

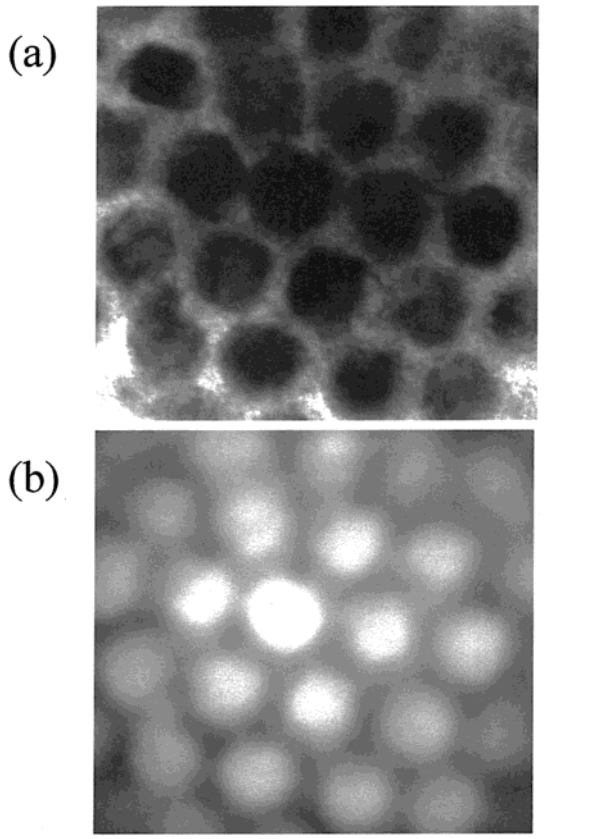

Figure 5. (a) Bright-field and (b) dark-field TEM images of hexagonal nanopores filled with copper nanowires in the same location.

recorded in the same area of the functionalized SBA-15 after electroless deposition of nickel for 20 min. The HA-ADF detector in the HD-2000 subtends between 80 and 240 mrad. The bright-field image clearly illustrates that the pore structure is regular, and the pore diameter is estimated to be 60 Å. Z-contrast imaging provides direct proof of the presence of the metallic nanowires within the channels of SAB-15. The key point with high-angle annular dark-field imaging is that the collection of the image is an incoherent process yielding atomic resolution images with strong Z (atomic number) contrast.[31] Thus, heavy atoms (such as platinum) stand out very clearly on a light background of silicon and oxygen. As seen in Figure 2b, it is apparent that part of the image shows highly bright contrast, indicating the presence of heavy elements inside the silica channels. The presence of nickel was confirmed by energy-dispersive X-ray spectroscopy (EDS) measurement. Figure 3b shows the dark-field STEM image of the metallic nickel nanowires after longer periods of electroless deposition (60 min). It is clear from the figure that the density of the nanowires is much higher than that achieved after 20 min of deposition. The color of sample was dark brown.

The same electroless methodology was applied to synthesize copper nanowires. Figure 4 shows the dark-field STEM image of copper nanowires synthesized using the same electroless deposition. The regular structures of the nanowires further demonstrate the

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superior performance of our new synthesis methodology as compared with the impregnation methods. The plan-view images of the same sample are shown in Figure 5. The dark-field images for the centers of the copper nanowires are much brighter than those of the silica walls, which indicates that the nanowires exist in the form of solid rods instead of tubular structures. This solid nanorod structure is in contrast to the tubular structure prepared by electroless deposition of copper on anodized alumina membranes.

In conclusion, we have developed a synthesis methodology for metal nanowires based on electroless deposition of the corresponding precursors inside mesoporous materials. Although this study has focused on the synthesis of arrays of copper and nickel nanowires, the potential impact of the methodology used is much broader. By means of an identical procedure, other conducting or magnetic nanowires can also be generated in the same fashion. The diameters of the nanowires can be tailored according to the sizes of the nanopores.

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