Preparation of Noble Metal Nanowires Using Hexagonal Mesoporous Silica SBA-15

Yong-Jin Han, Ji Man Kim, and Galen D. Stucky*

Department of Chemistry and Biochemistry, University of California at Santa Barbara, Santa Barbara, California 93106

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With increasing miniaturization of electronic and mechanical materials, the field of nanostructured materials has received much attention.[1] Due to their size, nanomaterials exhibit optical, electrical, and mechanical properties which differ from the properties of the bulk materials. Various nanostructured materials[1,2] have been synthesized using conductive polymers, metals, and semiconductors. Metal nanowires in particular have been the focus of many researchers due to their potential applications in fields such as nanoelectronic circuits and nanorobotics.

Heretofore nanowires have been prepared via laser ablation,[3] template assisted electrochemical[4] and chemical deposition,[5] within single walled carbon nanotubes,[6] and self-assembly[7] of colloidal metal particles. Recently, Ryoo and co-workers have reported the preparation of Pt nanowires inside the channels of mesoporous silicate materials to image the channel structures.[5] This suggested the possibility of obtaining various metal nanowires using mesoporous silicate materials. Stucky and co-workers have reported the synthesis of mesoporous silica SBA-15[8] with a well-ordered hexagonal array of one-dimensional channels and different pore diameters in the range of 4−30 nm. Large surface area, variable pore diameter and long-range order make SBA-15 an ideal template for fabrication of metal nanowires with different diameters. Herein, we report a simple approach for the preparation of Au, Ag, and Pt nanowires using SBA-15 as a template and the isolation of unsupported metal nanowires by removal of the silica framework.

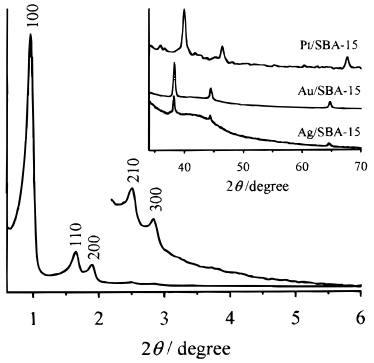

Figure 1. XRD patterns for the mesoporous silica SBA-15. Inset: XRD patterns at high angle after reduction of metal precursors. XRD patterns were collected with Scintag PADX diffractometer using Cu Kα radiation detected by a Si(Li) solid-state detector cooled by a Peltier cell.

SBA-15 was obtained using Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, $M_{AV} = 5800$, Aldrich) and tetraethyl orthosilicate (98%, Aldrich) under acidic conditions following the method reported in the literature.[8] To incorporate metal precursors inside the mesoporous channels, calcined SBA-15 materials (10 mg) were immersed in aqueous solutions (20 mL) of $HAuCl_4 \cdot 3H_2O$ (5 mg/50 mL, Aldrich), $Pt(NH_3)_4(NO_3)_2$ (5 mg/50 mL, Aldrich), and $AgNO_3$ (5 mg/50 mL, Aldrich), respectively. The solvent was evaporated in a rotary evaporator, and subsequently, 20 mL of CH_2Cl_2 was added to induce the outer surface bound metal precursors to move into the channels of SBA-15. CH_2Cl_2 was also removed by evaporation, and the obtained solids were dried in a vacuum oven at room temperature. The samples were placed in a tube furnace, and the metal precursors were reduced under a constant H_2 flow. The reduction temperatures for Au, Ag, and Pt precursors were 393, 623, and 593 K, respectively. The temperature was increased from room temperature to the desired temperature by 1.25 K/min and maintained for 1 h. The resultant samples are designated Au/SBA-15, Ag/SBA-15, and Pt/SBA-15. To obtain unsupported metal nanowires, silica frameworks were dissolved using a solution of HF/H_2O/EtOH.

Metal/SBA-15 samples were characterized with powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). Figure 1 shows XRD patterns for SBA-15 material after calcination. XRD patterns exhibit one very intense diffraction peak and four weak peaks, which are characteristic of a 2-d hexagonal (*p6mm*) structure. Existence of the (210) and (300) peaks indicates excellent textural uniformity of the material. Pore size was determined to be 7 nm by BdB−FHH pore size analysis[9] utilizing the data obtained from the N_2 sorption isotherm.[10] There are no significant changes

* To whom correspondence should be addressed. Telephone: 1-805-893-4872. Fax: 1-805-893-4120. E-mail: stucky@chem.ucsb.edu.

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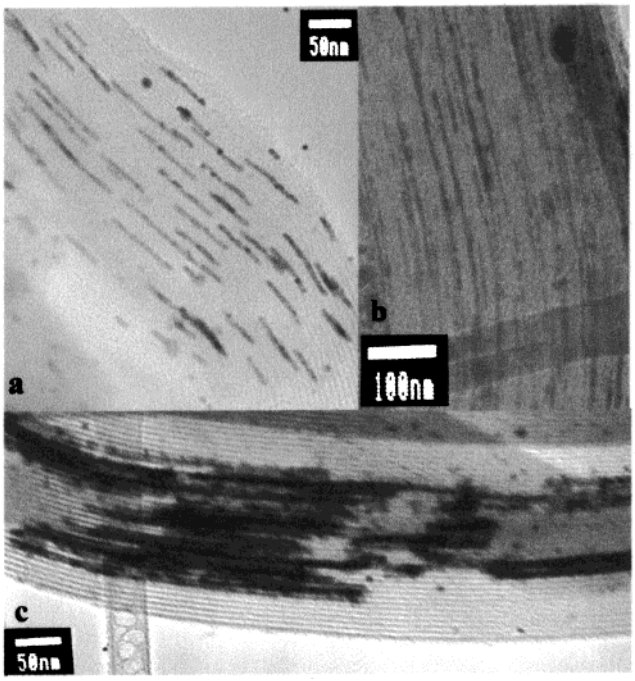

Figure 2. TEM micrographs of nanowires within the framework of SBA-15: (a) Au/SBA-15; (b) Ag/SBA-15; (c) Pt/SBA-15. TEM micrographs were taken with a 2000 FX JEOL instrument operating at 200 kV.

to the mesoporous materials upon metal loading, except for the expected decrease in the XRD peak intensity at low angle. Inset shows the XRD patterns for Au/SBA-15, Ag/SBA-15, and Pt/SBA-15, respectively. These show the formation of the reduced metals.

Figure 2 shows TEM images of the wires within the channels of SBA-15. The nanowires appear as dark rodlike objects between the walls of SBA-15. The uniform diameter of the nanowires is 7 nm, which is consistent with the diameter of the SBA-15. Using SBA-15 as the template, we are able to control the size of the wire thickness and growth direction and prevent bulk aggregation of the metal. The lengths of the wires range from 50 nm to 1 μm. This can be controlled with the loading percentage and annealing temperature and time. Metal-loading the mesoporous materials in conjunction with TEM provides good images of the channels of mesoporous materials.[5b] We are able to detect defects and other structural variables within the channels. This technique is currently being utilized in our laboratory to image other families of mesoporous materials. Spectra obtained from EDAX confirm the presence of the metals loaded along with a strong Si band. EDAX also provided the weight percent loading of each metal, ca. 5, 5, and 14% for Au, Pt, and Ag, respectively.[11]

(10) Nitrogen sorption was carried out on a Micromeritic ASAP 2000 system at 77 K with samples outgassed at 180 °C under vacuum for at least 8 h.

(11) Higher loading is possible, but not shown in the interest of obtaining clear TEM images.

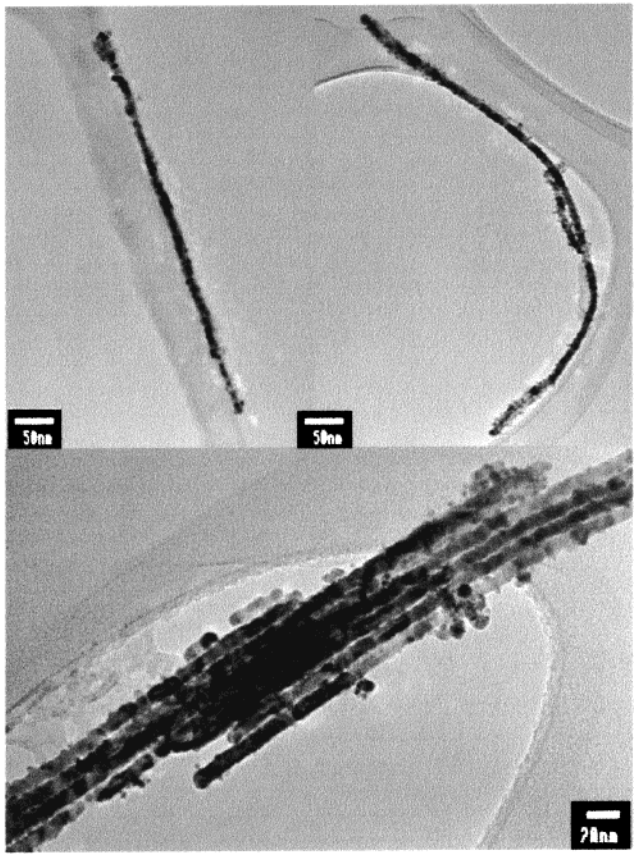

Figure 3. TEM micrographs of the unsupported Pt nanowires obtained by removal of silica framework with aqueous HF solution.

Figure 3 shows the unsupported Pt wires after removal of the silica framework by addition of HF. From the TEM image we can observe the flexible single nanowires which conform to the shape of the lacey carbon grid. The average length of the single wires obtained is 0.5 μm.

In conclusion, we have demonstrated a simple procedure for the formation of nanowires using mesoporous SBA-15 as the template. Highly ordered SBA-15 has a distribution of pore sizes which can control the growth direction and the diameters of the nanowires. Isolated nanowires can be easily obtained by treating the mesoporous silicates with HF. Systematic studies of the transport and optical properties of these wires and related conducting inclusion nanostructures are currently in progress.

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