Ag nanowire formation within mesoporous silica

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Received (in Oxford, UK) 27th March 2000, Accepted 9th May 2000

Uniform Ag nanowires have been synthesized within nanoscale channels of mesoporous silica SBA-15 by a simple chemical approach, which involves AgNO₃ impregnation, followed by thermal decomposition.

Owing to their high surface areas and uniform pore sizes, mesoporous silica materials have been widely used as host materials for loading catalysts, polymers, metals and semiconductor nanoparticles that have potential catalytic, environmental and optoelectrical applications. While there was certain success with the formation of continuous polymer nanofibers within mesoporous silica, inorganic metal or semiconductor nanowire formation within mesoporous MCM-41 materials has been largely elusive and in many cases incomplete filling or nanoparticles were observed. Here we report a simple chemical methodology for the formation of uniform Ag nanowires within mesoporous silica SBA-15. This process involves AgNO₃ solution impregnation followed by thermal decomposition. Transmission electron microscopy studies on these samples show unambiguously that these continuous Ag nanowires are made of long polycrystalline domains. They have uniform diameters of 5–6 nm, and large aspect ratios between 100 and 1000. Thus, the current process represents a viable approach for synthesizing uniform metallic nanowires and may be applicable for making other inorganic nanowires with complex compositions.

Mesoporous silica SBA-15 was synthesized in accordance with the published procedure using tri-block copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) EO₂₀PO₇₀EO₂₀ as template in acidic conditions. Briefly, a solution of EO₂₀PO₇₀EO₂₀ + 2 M HCl + TEOS + H₂O = 2:60:4.25:15 (mass ratio) was prepared, stirred for several hours at 40 °C, and then heated at 100 °C overnight. The solid products were filtered off and calcined at 500 °C for 5 h. Low-angle X-ray diffraction [Fig. 1, inset (a)] and transmission electron microscopy [TEM, Fig. 2(a)] studies on these samples indicate they are mesoporous silica consisting of well-ordered hexagonal packed channels with diameters of 5–6 nm.

To prepare nanowires within these nanoscale channels, 20 mg of SBA-15 powder was soaked in 10 ml of 0.2 M AgNO₃ EtOH-H₂O (1:1 v/v) solution and the suspension was stirred overnight at room temperature. The product was filtered off, rinsed with deionized water, and subjected to thermal treatment.

Fig. 1 High-angle X-ray diffraction pattern (Siemens, D5000) of the silver nanowire/SBA-15 composite. The low-angle X-ray diffraction patterns for SBA-15 before (a) and after (b) Ag nanowire loading are shown in the inset.

Fig. 2 (a) TEM (Topcon 002B, 200 KeV) image of the as-made SBA-15 mesoporous silica recorded along the [110] zone axis. (b) Low magnification TEM image of SBA-15 mesoporous silica after the Ag nanowire loading; Ag nanowires appear as dark lines in the image. (c) High-magnification TEM image of the Ag nanowires within the SBA-15. A selected area electron diffraction pattern recorded on several Ag nanowires is shown in the inset of (c).
at 300 °C in air for 2 h to decompose the impregnated AgNO₃ and form Ag nanowires.

The AgNO₃ impregnated sample was colorless while a brown/grey color appeared once the sample was treated at 300 °C. X-Ray diffraction indicates the mesoscopic ordering of SBA-15 was maintained after the AgNO₃ loading and the thermal treatment with the observation of low angle peaks that can be indexed as (100), (110) and (200) reflections of the hexagonal mesostructure of SBA-15 [Fig. 1, inset (b)]. Meanwhile, high angle diffraction peaks were observed after the thermal treatment. These diffraction peaks can be readily indexed according to the crystalline Ag structure with cubic lattice constant of a = 4.07 Å.

The thermally treated sample was also characterized by TEM [Fig. 2(b), (c)]. While there is a small amount of spherical Ag particles (5–30 nm in diameter) on the external surface of the SBA-15, extensive Ag nanowire formation can be seen in the large area view of the sample [Fig. 2(b)]. A high-magnification image of the sample [Fig. 2(c)] clearly indicates that these nanowires are continuous and essentially follow the curvature of nanoscale channels. They have uniform diameters of 5–6 nm, which are consistent with the sizes of the nanoscale channel templates. These nanowires also possess large aspect ratios from 100 to 1000, which have not been seen previously in many studies using MCM-41.8 carbon nanotubes18 or porous alumina19 as host matrices. By performing an over-focus and under-focus imaging series in the microscope, it is confirmed that these nanowires are actually embedded within the channels instead of being located on the external surface. Furthermore, the highly crystalline nature of the Ag nanowires was confirmed by selected area electron diffraction measurement made on these nanowire arrays [Fig. 2(c) inset]. The diffraction spots/rings can be again indexed as (111), (200), (220) and (311) reflections according to the cubic structure of Ag. The appearance of diffraction rings/spots indicates that the Ag nanowires are comprised of polycrystalline domains with large aspect ratios.

It was found that in order to achieve complete filling of the mesopores within SBA-15, a proper selection of the initial impregnation solution is critical. For example, we attempted using AgNO₃ solution in pure water or EtOH – H₂O (3:7 or 8:2 v/v), in all cases, only spherical Ag particles were obtained after the thermal treatment with a low percentage of channel filling. This incomplete filling is directly related to the very different surface tensions of H₂O and ethanol (71.99 and 21.97 mN m⁻¹, respectively, at room temperature). 

N₂ sorption measurements were also carried out on the samples before and after the Ag loading. It was found that the pore volumes decrease from 0.93 cm³ g⁻¹ for as-made SBA-15 to 0.61 cm³ g⁻¹ for Ag-loaded samples. This further confirms that Ag nanowires are indeed located inside the host channels and the loading efficiency is comparable with previous experiments using MCM-41.4,9,11 The capability of nanowire array formation within SBA-15 clearly indicates that the mesopores used to template Ag nanowires are highly ordered with few local defects [Fig. 2(a)] and they are also robust enough to sustain the thermal treatment. Thus we believe SBA-15 should be an ideal host material for making nanowire arrays of metals and many other systems. Initial results indicate that it is possible to form Co, Ni, NiO, Fe₂O₃ and polymer nanowire arrays within the SBA-15 matrix using a similar procedure.

We have also characterized the optical properties of these Ag nanowire arrays. Two plasmon absorption bands (410 and 580 nm) were observed in our preliminary studies. Further studies of the physical properties of these nanowires are currently in progress.

This research was funded by Camille and Henry Dreyfus Foundation, 3M Corporation and University of California, Berkeley. We thank Dr C. Nelson for the help during transmission electron microscopy studies, Professor G. D. Stucky at University of California, Santa Barbara for helpful discussions, Professor J. R. Long for use of the UV–VIS spectrometer and Professor Don T. Tilley for use of the surface area measurement unit. We also thank the National Center for Electron Microscopy for the use of their facilities.

Notes and references