Electrodeposition of Metallic Nanowire Thin Films Using Mesoporous Silica Templates**

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Nanostructured materials are one of the most active areas of materials science research. This interest is due to their unique properties (e.g., magnetic, optical, electronic, mechanical) and potential applications.[1] Metallic nanostructured materials, such as metal nanowires and nanoarrays, have potential applications in nanoscale devices, sensors, nonlinear optics, magnetic storage media, and anisotropic conductors.[1,2] Synthetic methods such as electron-beam lithography, step-edge decoration, and templated growth have been developed to prepare metallic nanostructured materials.[3] The templated growth method, which involves confined growth of metallic materials to a template (e.g., a pore) followed by removal of the template, provides a flexible and affordable synthetic route to a large variety of metal nanowires. Examples of such templates include hard templates[4] (e.g., porous alumina films, track-etched polycarbonate films, and mesoporous silica) and soft templates[1a,5] (e.g., liquid-crystalline phases and amphiphilic block copolymers). The hard templating approach is conceptually simple to implement; however, the use of porous alumina or polycarbonate membranes as templates usually results in polycrystalline nanowires or nano-

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wires with large wire diameters (20–1000 nm), which may preclude quantum confinement effects.

Surfactant-templated mesoporous silica possesses unique mesoscale pore channels and a controllable pore surface chemistry, which make it an ideal template for the synthesis of metal nanowires.[6–8] Electrodeposition is an efficient and ready technique for depositing metal coatings. In this Communication, we report the fabrication of metal thin films composed of ordered arrays of metal nanowires that are grown electrochemically within silica mesoporous channels. Although syntheses of metal nanowires by chemical reduction of metallic complexes and by chemical vapor infiltration of mesoporous silica pore channels have been reported previously,[8] as-synthesized metal nanowires usually lack macroscopic continuity. In this new method, nanowires are continually grown from the bottom conductive substrate upward until the mesoporous channels are filled. This provides a ready and efficient route to macroscopic, hierarchical metal nanowire thin films.

The metal nanowire thin films before and after removal of silica were characterized using X-ray diffraction (XRD). Figure 1 shows the XRD patterns of a mesoporous silica thin film (A) and a silica/metal thin film before (B) and after (C) re-
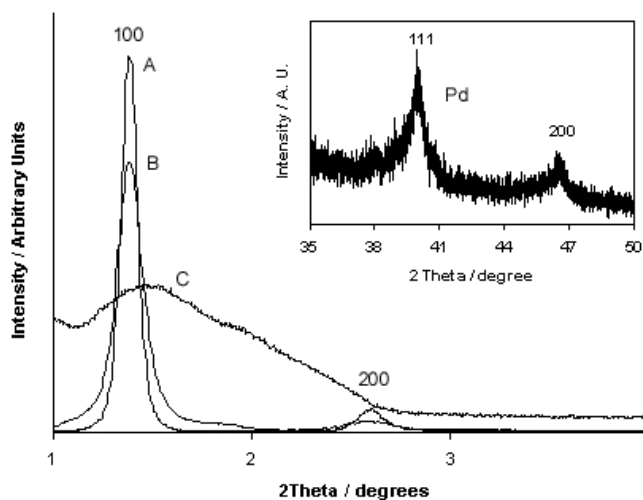

Fig. 1. XRD patterns of mesoporous silica (A), palladium deposited in mesoporous silica (B), and a palladium nanowire thin film (C). Inset: XRD patterns of palladium deposited in the mesoporous silica.

moval of the silica template. Trace A exhibits a typical one-dimensional hexagonal pattern with an intense (100) diffraction peak with a *d*-spacing of 67.4 Å and with a (200) peak of 35.6 Å. The mesostructured silica after metal deposition (trace B) shows a diffraction pattern similar to that for trace A, except for the expected decrease in the XRD peak intensity at low angles.[8b] The inset shows the XRD pattern of the silica/palladium thin film at higher 2θ angles. The presence of the characteristic diffraction peaks of palladium indicates the formation of palladium possessing a *Fm3m* crystalline structure within the mesoporous channels. The small crystalline grain sizes, resulting from confined growth of palladium within the mesoporous channels, may cause the broadened re-

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palladium diffraction peaks. Silica template removal results in a much broader (100) diffraction peak with a smaller *d*-spacing of 59.3 Å (trace C), indicating the presence of ordered palladium nanowire arrays. Partial collapse or aggregation of the nanowires may contribute to the broader (100) diffraction peak, the disappearance of the (200) peak, and the decrease in the *d*-spacing.

Electrodeposited metal nanowires were characterized by transmission electron microscopy (TEM), electron energy-loss spectroscopy (EELS), and scanning electron microscopy (SEM). Figure 2a shows a representative TEM image of palladium nanowires. The diameters of the nanowires observed by TEM range from 40 to 80 Å with an average diameter of 70 Å. This corresponds to the pore diameters of the silica template (47 to 89 Å) determined by nitrogen adsorption measurements.[9] These measurements indicate the feasibility of controlling the diameter of the nanowires via the pore size of the templates. Due to defects in surfactant liquid-crystalline structures, surfactant rods that are arranged in a hexagonal mesophase may cross and result in silica templates with interconnected pore channels and therefore in crossed nanowires (see the area marked by an arrow in Fig. 2a). This further demonstrates the efficiency of this templating approach and the possibility to characterize pore structures in detail by using metal electrodeposition.

Figure 2b shows a TEM micrograph of a single nanowire obtained by sonic dispersion. The inset shows the selected-area electron diffraction (SAED) pattern of the nanowire. It indicates the formation of local single-crystalline nanowires with a cubic structure. The average length of these metal nanowires after dispersion by sonication is greater than 1 μm with an aspect ratio larger than 125. After complete metal deposition, the length of the metal nanowires is identical to that of the pore channels. Compared with a templating method reported recently,[8] this technique may provide a simpler route to manufacture metal nanowires with high aspect ratios. Figure 2c shows a typical high-resolution transmission electron microscopy (HRTEM) image of a single Pd nanowire on a carbon grid. The HRTEM image shows (111) lattice fringes across the width of the entire nanowire, with an interplanar spacing of 0.22 nm, which is similar to that of bulk palladium. Both the SAED pattern and the HRTEM image indicate the absence of PdO on the surface, which is further confirmed by electron energy-loss spectroscopy (EELS).

Figure 3 shows the EELS spectra of a Pd nanowire, metallic Pd reference, and PdO reference. The Pd nanowire and Pd reference show similar EELS spectra. Comparing the spectrum of the Pd nanowire with that of PdO, the absence of oxygen K-edge peaks in the spectrum of the Pd nanowire indicates the absence of PdO on the Pd nanowire surface. The PdM$_{4,5}$ edge peaks
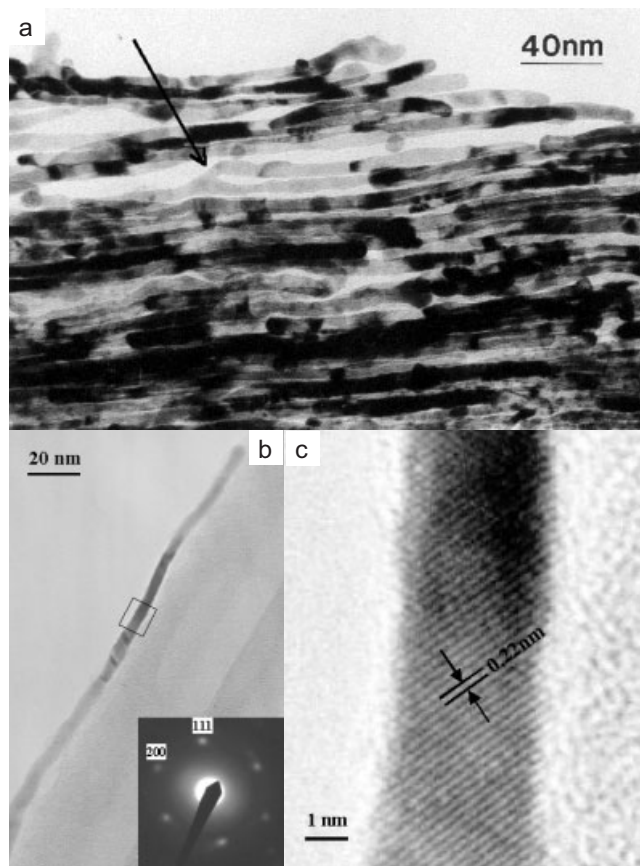

Fig. 2. TEM images of the palladium nanowires. a) Electrodeposited Pd nanowires. b) A single Pd nanowire. The inset shows the selected-area electron diffraction of the single Pd nanowire. c) Selected-area (see b) high-resolution transmission electron microscopy (HRTEM) image of the Pd nanowire.

are labeled as A, B, and C in Figure 3. The shift of these peaks to higher energy in the PdO spectrum is due to the oxidation of Pd.

Previous research has suggested that mesoporous silica thin films containing one-dimensional hexagonal pore channels may form a swirling mesostructure due to the low bending
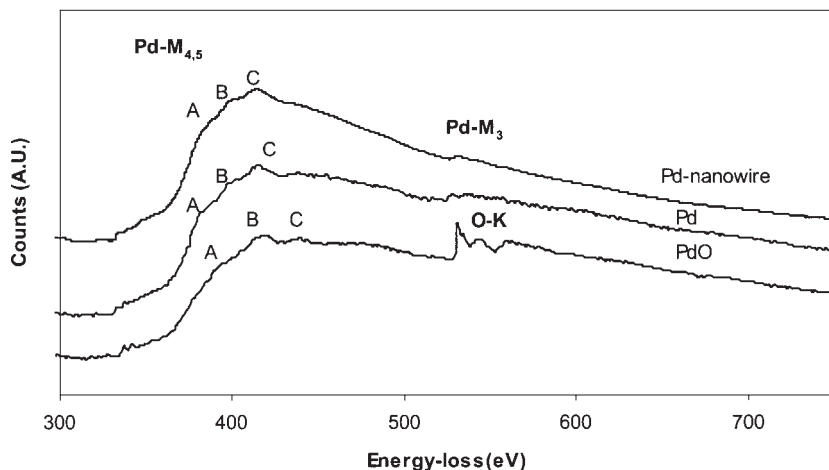

Fig. 3. Electron energy-loss spectra (EELS) of a Pd nanowire, Pd reference, and PdO reference.

energy of the surfactant tubules and the inability of the liquid–vapor interface to impose long-range order on the tubule assembly process.[6,10] Figure 4a shows a representative TEM plan-view image of the swirling mesostructured silica/surfactant thin film prepared with the surfactant P123. The swirling
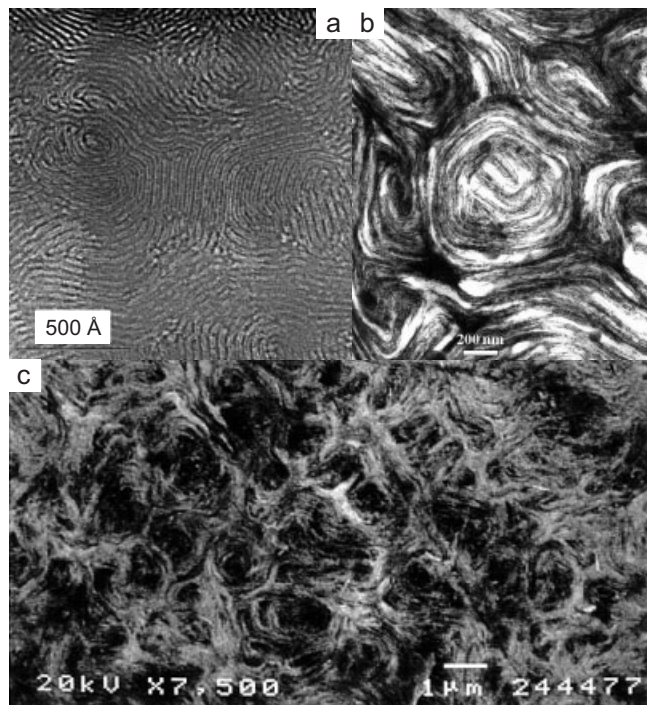

Fig. 4. a) Plan-view TEM image of a silica/surfactant thin-film template. b) TEM image of the palladium nanowire array thin film. c) Typical SEM top-view image of a palladium nanowire thin film.

bundles are oriented parallel to the substrate. Figure 4b shows a TEM micrograph of a free-standing thin film that is composed of parallel nanowires after removal of silica. These nanowires swirl and partially aggregate, which results in nanowire bundles that are similar to those in the mesoporous silica template shown in Figure 4a. Figure 4c shows a representative top-view SEM image of the nanowire thin film after removal of the silica template. The aggregated nanowire bundles spread across the thin film, which is consistent with the TEM observation. Therefore, we propose that these swirling bundles are composed of aggregated Pd nanowires that macroscopically manifest the swirling structure of the mesoscale pore channels. Additionally, aggregation of the nanowires in the swirling bundles broadens the (100) diffraction peak of the nanowire thin film (see curve C in Fig. 1).

The TEM, SEM, EELS, and XRD results indicate that it is possible to synthesize macroscopically hierarchical metal nanowires. We found that annealing is necessary to achieve a mechanically strong nanowire thin film upon removal of the silica template. It is believed that the annealing process promotes structural rearrangement of the nanowires and enhances their structural strength. Free-standing metallic nanowire thin films were successfully prepared by treating the annealed silica/palladium thin films with a HF solution.

In conclusion, we have demonstrated a general approach to prepare metal nanowire thin films by electrodeposition into porous silica thin-film templates. Macroscopically hierarchical thin films consisting of ordered arrays of metal nanowires can be readily obtained by using this technique. These metal nanowire thin films have many potential applications, such as electrodes, optical hosts, catalysts, magnetic materials, photovoltaic devices, and sensors. Further research is underway to synthesize different metal nanowire and nanomesh thin films with various templates and to study their magnetic and optical properties.

Experimental

The mesoporous silica films serving as templates were prepared by spin coating silicate/surfactant sols on conductive glass substrates (e.g., conductive TEC Glass slides from Pilkington). The triblock copolymer surfactant P123 (PEO_{20}-$PPO_{70}PEO_{20}$, where PEO is poly(ethylene oxide) and PPO is poly(propylene oxide), from BASF) was used to template the pore structure of the silica templates. Typically, the sols were prepared by mixing tetraethoxysilane (TEOS), H_2O, P123, HCl, and ethanol in a molar ratio of 1:5:0.0096:0.0089:22 at room temperature for 30 min. Surfactant removal by calcining the spin-coated thin films at 400 °C for 2 h in air resulted in conductive glass-supported mesoporous silica thin films.

The electrodeposition was conducted in 0.5 wt.-% $PdCl_2$–HCl solutions using a galvanostatic electroplating circuit that consisted of a mesoporous silica coated conductive glass slide as the working electrode, a standard Ag/AgCl electrode as the reference electrode, and a platinum wire as the counter electrode. Constant current densities of 1–20 mA cm^{-2} were used to achieve deposition rates of 1–10 nm s^{-1}.

The thickness of the nanowire thin film was determined by calculating the electric current versus time. By controlling the nanowire deposition such that the deposited nanowire was thinner than the mesoporous silica thin film, metal deposition on the external surface of the silica thin film was avoided. The silica/Pd nanowire thin film deposited on TEC Glass was annealed at 400 °C in a nitrogen atmosphere for 30 min. After removal of the silica template, an unsupported nanowire thin film was left on the acid-resistant conductive coating. The silica template was removed by submersing the film in a 2 % HF solution followed by rinsing with water. The template removal was confirmed by energy-dispersive X-ray spectroscopy (EDX).

XRD measurements were carried out on a Philips Xpert X-ray diffractometer using Cu Kα radiation ($\lambda = 0.1542$ nm). TEM measurements were performed with a JEOL 2010 TEM microscope operated at 200 kV. SEM micrographs were obtained on a JEOL JSM 5410 SEM at 20 kV. EELS spectra were obtained by using a JEOL 2010F FASTEM with a Gatan GIF system at the University of New Mexico.

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The Combination of Colloid-Controlled Heterogeneous Nucleation and Polymer-Controlled Crystallization: Facile Synthesis of Separated, Uniform High-Aspect-Ratio Single-Crystalline BaCrO4 Nanofibers**

By *Shu-Hong Yu,* *Helmut Cölfen*, and *Markus Antonietti*

A recent trend in chemistry is to learn about the opportunities of controlling the architecture, morphology, and patterning of inorganic materials at all dimensions from the nanoscale to macroscopic scale by mimicking the processes of biomineralization.[1] Due to their promise as advanced materials and in advanced technologies, in particular the fabrication of one-dimensional nanoscale building blocks, such as nanotubes, nanowires, and nanorods with uniform sizes and aspect ratios, has been intensively explored.[2–8] For example, the preparation of high-aspect-ratio nanofibers from cheap and commonly available inorganic materials is of interest as such fibers are very promising polymer filler materials for the alteration of a material's mechanical and rheological properties at elevated temperatures. The hybrid material is generally strengthened while retaining its optical transparency.[9] Furthermore, it is highly interesting to study the influence of particle shape on electrical or optical inorganic nanoparticle properties. Thus various studies on the synthesis of nanorods of such materials have been reported.[2–5,10,11] Other synthetic routes include the use of hard templates,[3] laser-assisted catalytic growth (LCG),[2] controlled solution growth at elevated temperature,[6,11] and oriented nanoparticle fusion.[10,11]

As an environmentally benign strategy, bioinspired morphosynthesis has been recognized as a very promising route to templating inorganic materials with controlled morphologies. Here, self-assembled organic superstructures, organic additives, and/or templates with complex functionalization patterns are used under near natural conditions.[1] However, a facile universal way for the preparation of separated nanofibers by biomimetic mineralization routes has rarely been found: the nanofibers described up to now are always made as rather thick bundles, thus removing the most important advantages of nanofibers for the improvement of materials.

We have demonstrated that a special class of crystal-surface-active polymers, the so-called double-hydrophilic block copolymers (DHBCs),[12] allows the facile and systematic morphosynthesis of inorganic materials by employing different patterns of functional polyelectrolyte groups. In previous studies, we reported the preparation of nanofibers of calcium phosphate,[13a] barium sulfate,[13b–d] and barium chromate[13e] using DHBCs as additives for the crystal morphosynthesis. Nevertheless, also with these improved crystal modifiers, it was not possible to generate single fibers.

Here, we report on a new and potentially facile strategy for morphology control of inorganic materials using a combination of crystal growth control by DHBCs and controlled nucleation. This results for the first time in the fabrication of uniform, separated BaCrO4 single-crystalline nanofibers with extremely high aspect ratios of > 5000, breaking the previous constraint of bundle formation.

The concept was to add a minor amount of a cationic colloidal structure, thus enriching the Ba-loaded DHBCs in a confined area of space and reaching higher supersaturation and nucleation close to those spots. Indeed, if small amounts of PSS/PAH (PSS/PAH: poly(styrene sulfonate, sodium salt)/ polyallylamine hydrochloride) polyelectrolyte capsules (20 μL, concentration 0.5 vol.-%, approximate total particle number 2×10^9, i.e., 1.32×10^6 capsules per μg of BaCrO4) 5 μm in size (surface area per capsule 7.85×10^{-11} m^2, total surface area of the capsules 0.157 m^2) with a positive surface charge[14] are added to a solution containing phosphonated poly(ethylene oxide)-*block*-poly(methacrylic acid) (PEO-*b*-PMAA-PO$_3$H$_2$) and BaCrO4 precursor salts,[13e] separated and highly extended single-crystalline nanofibers with diameters in the range of 8–20 nm and lengths of up to several hundred micrometers were obtained. Their aspect ratio is larger than 5000. The ξ-potential measurements underline that the capsule was positively charged (+28.3 mV) and the pure polymer solution (pH 5) was negatively charged (–42.5 mV), also after the addition of Ba^{2+} (–30.0 mV), underlining incomplete counterion condensation onto the polyelectrolyte block. Adding the capsules to a Ba-loaded polymer solution did not alter the ξ-potential much (–30.9 mV). This is indicative of polymer adsorption onto the capsule with simultaneous release of Ba^{2+}, which could be precipitated as BaCrO4 (–34.8 mV).

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