From Surfactant–Inorganic Mesostructures to Tungsten Nanowires**

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Surfactant–inorganic mesostructured composite materials[1–3] have attracted great interest over the past decade due to their potential applications as catalysts, separation membranes, chemical sensors, and in solid-electrolyte and optoelectronic devices.[3–8] However, to obtain these highly ordered mesoporous materials, removal of the surfactant species from the mesostructured composites is critical. Here we report on a simple and versatile vacuum-controlled pyrolysis procedure for the removal of the surfactant species from lamellar mesostructured composites of tungsten oxide with cetyltrimethylammonium surfactant cations (WO-L). In this process, pyrolysis and carbothermal reaction of WO-L take place in vacuo at 500–850 °C, and bulk quantities of uniform metallic tungsten nanowires with diameters of 20–80 nm and lengths ranging from 5 to 30 μm are obtained. We believe that raising the processing temperature induces curvature in the lamellar structure of the thermally unstable inorganic–surfactant precursor and finally leads to the formation of tubular structures. The inorganic–surfactant precursor may act as a template, which confines the carbothermal reaction and results in tungsten nanowires. This may represent a universal approach for the synthesis of nanowires of other transition metals, such as Co, Ni, and Cu, by vacuum pyrolysis/carbothermal (VPC) treatment of lamellar inorganic–surfactant precursors.

The discovery of carbon nanotubes[9] raised the question whether compounds with layered structures analogous to that of graphite can form nanotubes or one-dimensional nanowires. It was partially answered by the synthesis of WS_2, MoS_2,[10] and $NiCl_2$[11] nanotubes. We speculated that lamellar composites consisting, for example, of tungsten oxide or the oxide or sulfide of Ni, Co, or Cu and surfactants could serve as precursors for metallic nanowires or nanotubes by reduction.

Mesolamellar WO-L was prepared by the reaction of sodium tungstate (Na_2WO_4) and cetyltrimethylammonium bromide (CTAB) under mild hydrothermal conditions[12, 13] in 85–90 % yield. Elemental analysis and thermogravimetric/differential thermal analysis results showed a molar ratio of surfactant to tungsten of about 2:1. The lamellar nature of WO-L was confirmed by the low-angle X-ray powder-diffraction (XRD) pattern (Figure 1 a).

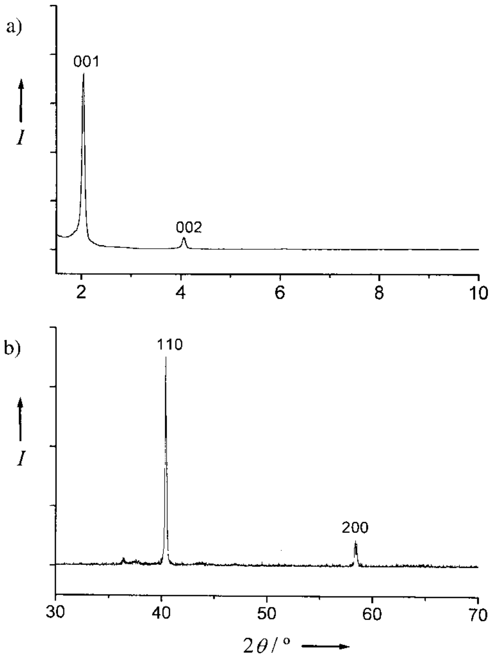

Figure 1. a) Low-angle XRD pattern of WO-L prepared under mild hydrothermal conditions. b) XRD pattern of the VPC product indicating the presence of bcc W.

The VPC treatment of WO-L was carried out in a conventional tube furnace (Figure 2). Control of the temperature gradient and gas pressure during the VPC reaction was a key factor, otherwise the precursors cracked into platelets or particles. The final black products were characterized on a Bruker D8-advance X-ray diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). In the XRD pattern of the final product (Figure 1 b), reflections could be readily indexed to the bcc phase of W with a lattice constant of $a = 3.165$ Å.

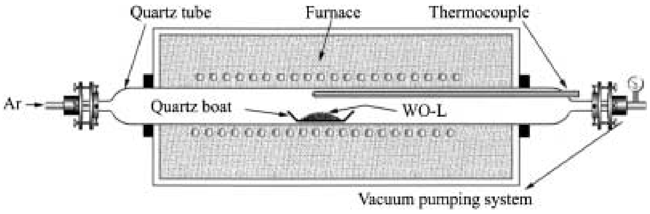

Figure 2. Schematic representation of the tube furnace used for VPC treatment of WO-L.

Transmission electron microscopy (TEM) images were taken with a Hitachi H-800 transmission electron microscope operated at 200 kV. The TEM image of a typical product (Figure 3 a) showed primarily wirelike structures with diameters of 20–80 nm and lengths ranging from several micrometers to 30 μm. In addition to the nanowires, platelets and particles were obtained. Analysis by electron-induced X-ray

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[**] The authors thank Prof. G. D. Stucky for helpful discussions. This work was supported by the National Science Foundation of China and the State key project of Fundamental Research for Nano-materials and Nano-structures.

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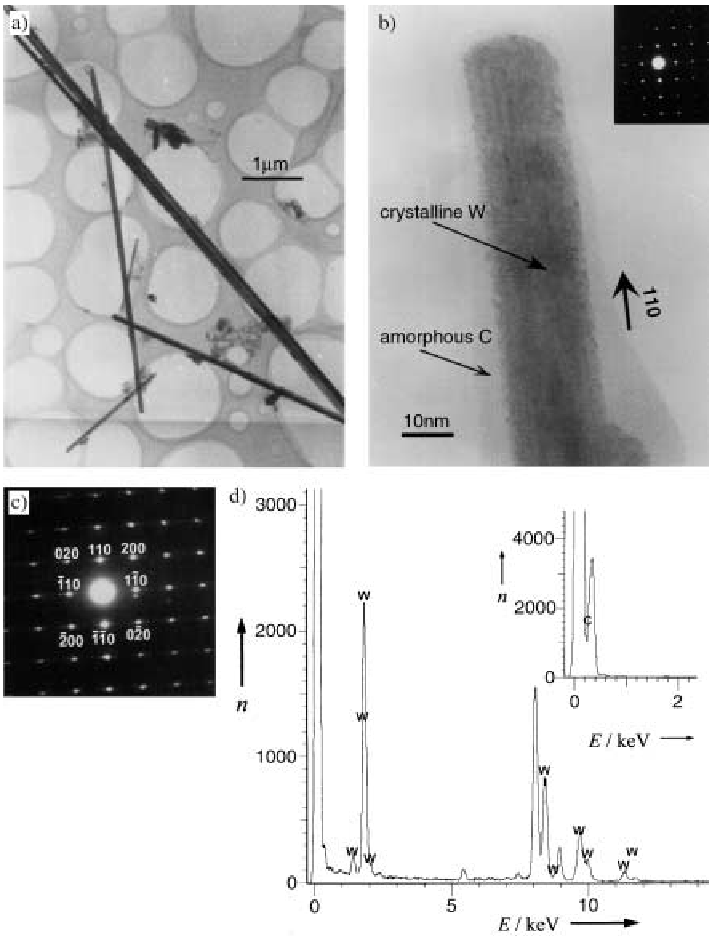

Figure 3. a) TEM image showing the morphology of the W nanowires obtained by the VPC method. b) HRTEM image of an individual W nanowire. The SAED pattern (inset) reveals the [110] growth direction of the bcc W nanowire. c) Diffraction indexes of the SAED pattern in (b). d) Compositions of the core and sheath (inset) parts of the W nanowire shown in (b), obtained by EDX analysis.

fluorescence (EDX) showed that the platelets were composed of tungsten, and the particles were usually composed of tungsten or amorphous carbon. The average yield of the nanowires, estimated from TEM images of samples from different syntheses, was about 20%. The coexistence of platelike and granular W products in the samples, as well as the relatively large mean diameters (about 50 nm, based on TEM images) of the W nanowires, might explain why inhomogeneous peak broadening was not observed in the XRD patterns. The reproducibility of the synthesis was satisfactory. Under optimal experimental conditions, the yield of tungsten nanowires was never less than 10%. The mean dimensions and size distributions of nanowires obtained in different synthetic batches under the same reaction conditions (hydrothermal precursor synthesis and VPC) were about the same.

High-resolution transmission electron microscopy (HRTEM) images of W nanowires were taken on a JEOL-2010 transmission electron microscope. The HRTEM image of an individual nanowire (Figure 3b) provided further insight into the structure of these products. The selected-area electron diffraction (SAED) pattern recorded perpendicular to the growth axis of the single nanowire (Figure 3c) could be attributed to the [001] zone axis diffraction of bcc W, and this suggested that the nanowire grew along the [110] direction. This conclusion was also confirmed by the [110] lattice fringes perpendicular to the nanowire axis, with a spacing of 2.24 Å. We also employed SAED to characterize the nanowires obtained in different syntheses, as well as different parts of the same nanowire. All electron diffraction patterns indicated exclusively the same [110] orientation of the nanowire, and this implies that these W nanowires are single crystallites rather than multidomain polycrystallites (random orientations would usually be expected in different parts of a multidomain nanowire).

An additional important detail was found in the HRTEM image: a clear amorphous coating sheath on the nanowire core. The EDX analysis of these individual nanowires showed that they contained only W and a trace of C (Figure 3d). The amorphous outer sheath was composed only of C (inset of Figure 3d). We attribute the amorphous C coatings on the W nanowires to residues of the vacuum-pyrolysis carbothermal treatment of the inorganic–surfactant precursor.

How are atoms or other building blocks assembled into such structures with nanoscale diameters but long lengths, and how can we understand the mechanism by which the nanowires are formed in this novel VPC approach? On the basis of the needle morphology, we propose a new growth model for these W nanowires (Figure 4). The nanowire formation can be divided into four steps. 1) The CTA^+ cations condense into aggregates in which the tungstate anions are intercalated in the interspaces between the head groups of CTA^+ to form $CTA-WO_4$ ion pairs. 2) The continuing condensation process generates more highly ordered lamellar assemblies. These mesolamellar structures were confirmed by low-angle X-ray diffraction (see Figure 1a). 3) When heated in vacuo with gradually increasing temperature, these lamellar sheets begin to roll onto themselves and finally form separate scrolls

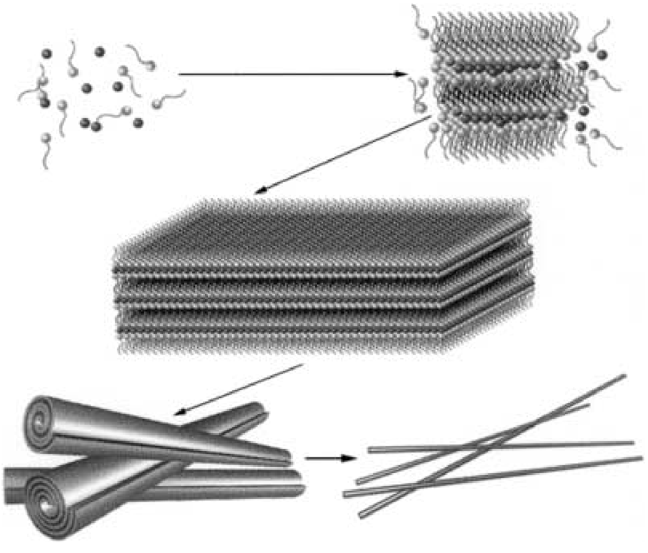

Figure 4. Schematic depiction of different periods in a typical VPC process. The dark balls represent inorganic components such as WO_4^{2-}, and the light balls correspond to the head groups of the CTA^+ cations.

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consisting of CTA$^+$ cations and tungstate anions. 4) With increasing furnace temperature, tungstate is reduced by pyrolytic carbon derived from CAT$^+$ to give W metal with a shape defined by the scrolls, which could serve as microreactors for the VPC process and thus are responsible for the ultimate wirelike shape of W. The VPC process should involve a tubular intermediate that results from confinement of the scrolls. However, with the removal of surfactant molecules and crystallization of tungsten metal, these tubular nanostructures would finally transform into the nanowire products.

To substantiate our hypothesis, we performed control experiments. The tungstate and surfactants were mixed mechanically, but no lamellar composite structures were present in these mixtures according to low-angle XRD data. The same VPC operations were performed on these mixtures. However, only W particles were observed. In addition, we performed a more stringent test of our model by preparing Ni, Co, Cu, and Cd nanowires (see Supporting Information). The fundamental experimental results were in good agreement with our suggested VPC model (see Supporting Information). The above studies illustrate that the controlled VPC treatment of inorganic–surfactant lamellar precursors might be a general approach for the synthesis of crystalline nanowires or nanotubes.

Experimental Section

Analytical-grade Na_2WO_4 (3 mmol) and CTAB (9 mmol) were dissolved in distilled water to form a homogeneous solution. The pH of the solution was adjusted to the range of 8–10 by addition of aqueous NH_3 or HCl. The mixture was stirred vigorously for 1 h and then sealed in a Teflon-lined stainless steel autoclave and kept at 140 °C for 6 d. The solid WO-L product was collected by filtration, washed with distilled water and absolute ethanol, and then dried in vacuo at 80 °C for 12 h. The calculated yield was about 85–90 % on the basis of W.

The VPC treatment was carried out in a conventional tube furnace (see Figure 2). The as-prepared WO-L (400 mg) was placed in a quartz boat. The quartz boat was placed in the hot zone inside the quartz tube and the content calcined and pyrolyzed for 10 h at 100 to 850 °C in a high-purity argon atmosphere (99.999 %) with a pressure range of 10^{-2}–10^{-3} atm. The furnace temperature was first increased to 400 °C over 4 h and then held at that temperature for 2 h to ensure completion of the rolling process of the lamellar precursor. Then the temperature was raised to 850 °C over 2 h and kept at that temperature for 2 h. Finally, the temperature was allowed to descend to room temperature. In the whole process, the reaction temperature was controlled exactly at ± 1 K by a built-in temperature-control unit in the tube furnace.

Received: July 17, 2001
Revised: November 5, 2001 [Z17528]

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Dynamic Kinetic Resolution and Desymmetrization of Enantiotopic Groups by Cyclodehydration of Racemic or Prochiral δ-Oxoesters with (*R*)-Phenylglycinol: Enantioselective Synthesis of Piperidines[**]

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The development of efficient methods to produce an optically pure enantiomer is of fundamental importance, particularly for the synthesis of bioactive natural or synthetic products. Today, enzyme-mediated desymmetrizations of either prochiral or *meso* substrates, generally diesters, and enzyme-catalyzed kinetic resolutions of racemates constitute classical approaches for the synthesis of enantiopure compounds, and have become powerful synthetic tools.[1] In contrast, in spite of the impressive advances in the field of chemical, nonenzymatic, enantioselective desymmetrizations over the last few years, the chemical differentiation of two enantiotopic functional groups has been little developed.[2] On the other hand, the major drawback of kinetic resolution, like conventional resolution processes, is that the maximum yield of one enantiomer is always limited to 50 %. However, this situation dramatically changes when racemic substrates have a chirally labile stereogenic center that is capable of undergoing racemization in situ during the reaction (dynamic kinetic resolution (DKR)).[3]

In the context of our studies on the synthesis of enantiopure piperidine derivatives from chiral nonracemic bicyclic lactams formed by cyclodehydration of δ-oxoesters and (*R*)- or (*S*)-

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[**] This work was supported by the DGICYT, Spain (BQU2000-0651), and the CUR, Generalitat de Catalunya (2001SGR-0084). We also thank the Ministry of Education, Culture, and Sport for fellowships to M.C. and M.P., as well as the CICYT, Spain, for a postdoctoral fellowship to V.P.

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