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Large-Scale Synthesis of Tungsten Oxide Nanowires with High Aspect Ratio

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Through the controlled removal of surfactant from the presynthesized mesolamellar precursor (WO-L) at elevated temperature, tungsten oxide nanowires with diameters ranging from 10 to 50 nm and lengths up to several micrometers were obtained on a large scale. The structure, morphology, and composition of the nanowires were characterized by the XRD, TEM, HRTEM, EDX, and Raman spectra.

Introduction

Among the numerous transition metal semiconducting oxides, tungsten oxides are of intense interests and have been investigated extensively for their distinctive properties.[1-4] With outstanding electrochromic, optochromic, and gaschromic properties, tungsten oxides have been used to construct flat panel displays, photoelectrochromic "smart" windows, optical modulation devices, writing−reading−erasing optical devices, gas sensors, humidity and temperature sensors, and so forth.[1-4] Recently, some nonstoichiometric tungsten oxides have attracted considerable attention in physics, chemistry, and materials areas for their interesting electronic properties, especially the superconductivity and charge carrying abilities.[5]

Over the past few years, much effort has been devoted to the synthesis of semiconductor nanowires, nanorods, and nanobelts, because of the importance of understanding the dimensionality confined transport phenomena and fabricating nanodevices and nanosensors.[6] Many synthetic methodologies, including laser-assisted catalytic growth, thermal evaporation, and wet chemical reactions, have been investigated,[7-11] and various kinds of one-dimensional (1D) nanostructures, such as Si, GaN, ZnO, SnO_2, CdSe, and MnO_2, have been fabricated so far.[7-11] However, studies on nanoscaled tungsten oxides were comparatively rare because of lack of preparation methods for such materials. Very recently, Liu et al. met the challenge and developed a simple method to prepare tungsten oxide nanowires directly from tungsten metal.[12] In this manuscript, we reported a large-scale synthesis strategy of tungsten oxide semiconductor nanowires through the controlled removal of surfactant from the mesolamellar precursor (WO-L) at high temperature. With diameters ranging from 10 to 50 nm and lengths up to several

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micrometers, as-synthesized nanowires have a high aspect ratio of more than 50. This strategy may offer an opportunity for the further investigation of some fundamental properties of 1D tungsten oxides and may also serve as a general method for the synthesis of 1D nanostructures.

Experimental Section

I. Materials. All chemicals used in this work, such as sodium tungstate (Na_2WO_4), cetyltrimethylammonium bromide (CTAB), and hydrochloric acid (HCl), were analytical grade reagents.

II. Synthesis of Tungsten Oxide Nanowires. Mesolamellar tungsten oxide (referred to as WO-L) with intercalated cetyltrimethylammonium (CTA^+) cations was prepared through the co-condensation reaction of sodium tungstate (Na_2WO_4) and cetyltrimethylammonium bromide (CTAB) under mild hydrothermal conditions.[13,14] The surfactants were removed with high temperature treatment in a conventional tube furnace. The as-prepared WO-L precursor was loaded in a quartz boat and put in the hot zone of the quartz tube. After calcination at 720 °C for 2 h with a pressure range from 10^{-1} to 10^{-2} atm, the system was cooled to room temperature, and tungsten oxide nanowires were finally obtained. During the whole process, Ar (99.9%) was used as the protecting medium, and the flow rate was kept at about 60 mL/min. By controlling argon flow rate and temperature rising speed, the final products could be tungsten or tungsten oxides. Generally, high argon flow rate and low temperature rising speed are favorable for the formation of tungsten oxide nanowires.

III. Characterization. Powder X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). The 2θ range used in the measurement of tungsten oxides was from 10° to 70° in steps of 0.02° with a count time of 1 s. The low-angle XRD pattern of the lamellar precursor was recorded in 2θ ranges from 1.5° to 10°. The size and morphology of tungsten oxide nanowires were determined by using a Hitachi model H-800 transmission electron microscope, with a tungsten filament at an accelerating voltage of 200 kV. Structure and composition of the nanowires were measured by high-resolution transmission electron microscopy (HRTEM, JEOL-2010F) and electron-induced X-ray fluorescence (EDX). Raman spectra were obtained by using an RM 2000 microscope confocal Raman spectrometer (Renishaw PLC., England) employing a 632.8 nm laser beam and a CCD detector with 4 cm^{-1} resolution.

Results and Discussion

The low-angle XRD pattern of the precursor (WO-L) is shown in Figure 1a, and the lamellar nature of WO-L was confirmed. The XRD pattern showed one weak peak and one very intense diffraction peak, which have been safely attributed to a typical lamellar structure. Figure 1b shows the XRD pattern of as-synthesized tungsten oxide nanowires. It has been undisputedly indexed to monoclinic $W_{18}O_{49}$ (JCPDS card no. 36-101), despite the broadened peaks.

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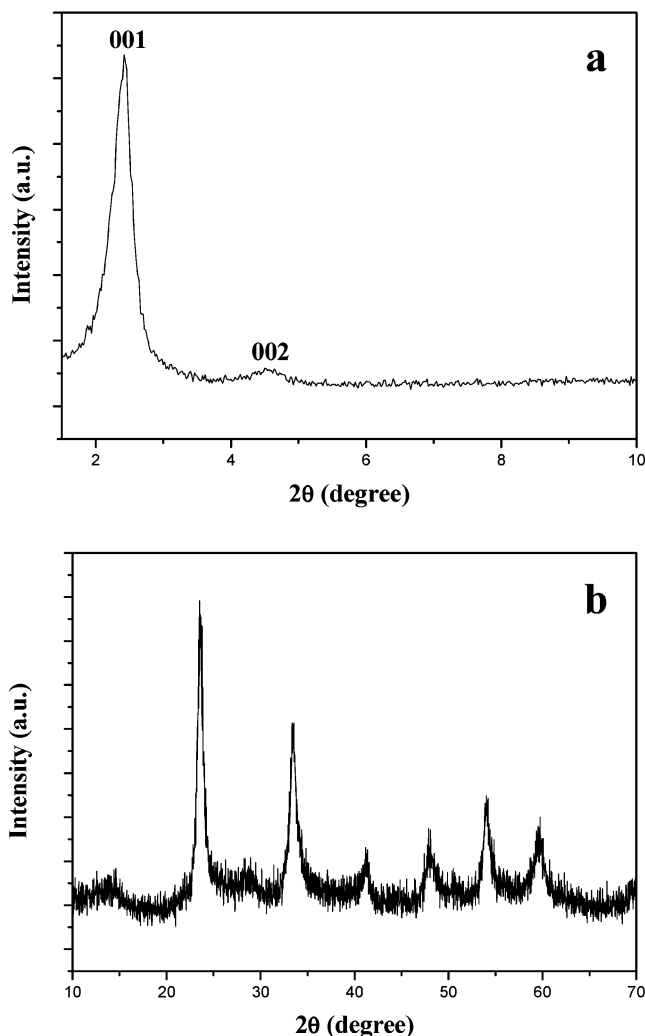
Figure 1. (a) Low-angle XRD pattern of the mesolamellar precursor (WO-L), which was prepared under mild hydrothermal conditions. (b) Typical XRD pattern of the final tungsten oxides.

The morphologies of the final products were demonstrated in Figure 2a−c. On the basis of the TEM check, the proportion of the nanowire morphology was estimated to be about 95%. As shown in the TEM images, the average diameter of these uniform nanowires was about 17 nm (Figure 2c) and the length of the nanowires was up to several microns (Figure 2a). Therefore, the nanowires reached a high aspect ratio of more than 50. An HRTEM image was taken on a single nanowire with diameter of about 30 nm (Figure 2d), which provided further insight into the structure of the tungsten oxide nanowires. The spacing of the lattice fringes was found to be about 0.378 and 0.373 nm, respectively, shown in the inset of Figure 2d. These two planes could be indexed best as {010} and {103} of a monoclinic $W_{18}O_{49}$ crystal, respectively, according to JCPDS card no. 36-101, in agreement with reported results.[1,15] The nanowires grew along the [010] direction, which was reasonable because the close-packed planes of monoclinic $W_{18}O_{49}$ crystal were {010}. The selected area electron diffraction (SAED) pattern

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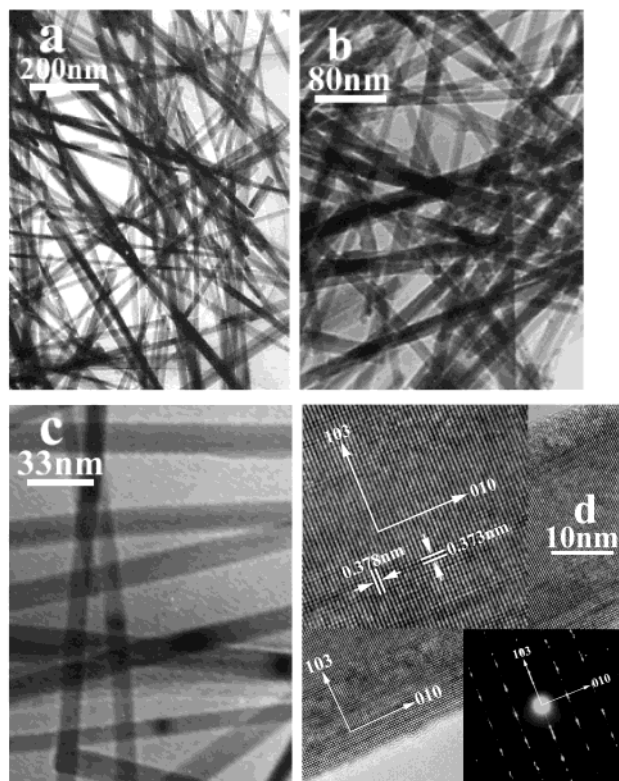
Figure 2. TEM images of as-synthesized tungsten oxide nanowires: (a, b) low magnification images, (c) high magnification image, and (d) HRTEM image of an individual tungsten oxide nanowire. Insets show the SAED pattern and the enlarged HRTEM pattern.

Figure 3. (a) EDX analysis of a representative tungsten oxide nanowire with the diameter of about 30 nm. (b) Raman spectrum of the as-synthesized products.

shown in the inset of Figure 2d indicated the existence of shear defects, which was coincident with the HRTEM results.

The electron-induced X-ray fluorescence (EDX) analysis was employed to determine the composition of the tungsten oxide nanowires. As shown in Figure 3a, only oxygen and tungsten elements existed in the nanowires with the molar ratio of about 2.73 (O/W) (the signals of copper and carbon came from the TEM grid).

The Raman spectrum of the as-synthesized products is shown in Figure 3b. According to the reported literature,[2,15] the strong and well-defined bands at 806, 708, 417, 348, 269 cm^{-1} could be assigned to monoclinic tungsten oxide. The bands at 268 cm^{-1} correspond to O$-$W$-$O bending modes of the bridging oxygen, and the bands at 708 and 806 cm^{-1} are ascribed to the corresponding stretching modes.

On the basis of the TEM check, there were no nanoparticles found at the ends of tungsten oxide nanowires. The vapor$-$liquid$-$solid (VLS) growth mechanism[16] cannot be applied for our tungsten oxide nanowires growth, because a metal particle is necessary at the growth front of the nanowire to act as the catalytic active site. On the basis of the growth mechanism of other rodlike materials and our experiment results,[13−14,17] we found that the artificial mesolamellar nanostructure played an important role in the formation of the tungsten oxide nanowires. In control experiments using mechanically mixed tungstate and surfactants instead of the
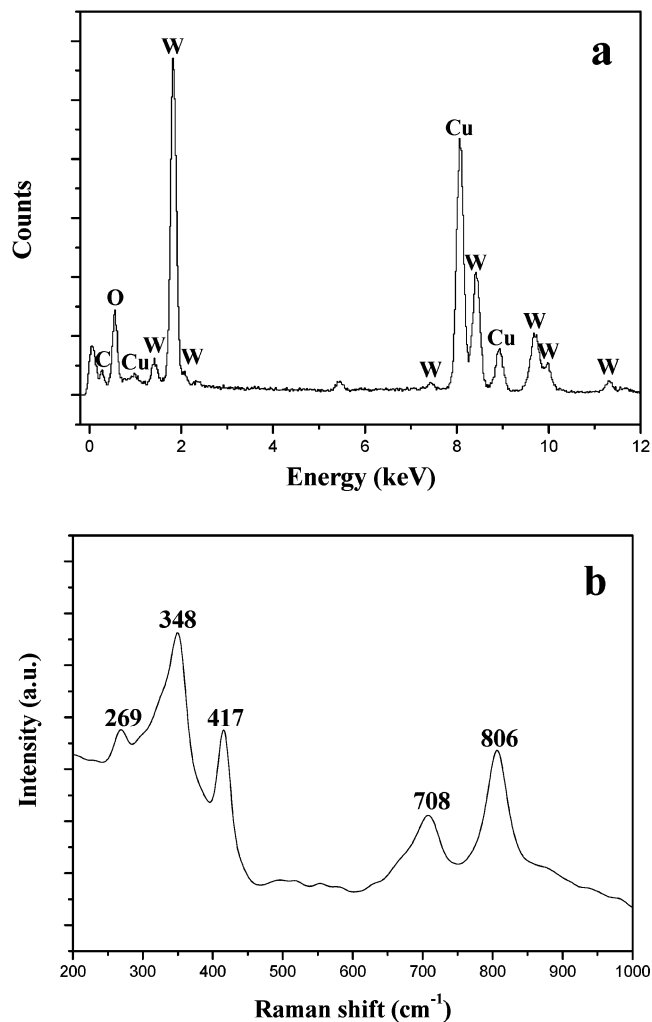
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lamellar precursor, almost no tungsten oxide nanowires were found in the final products. The mechanism was somewhat similar to the mechanism proposed by us in the formation of WS$_2$ nanotubes and W nanowires.[14] On the basis of the similar principle that a piece of foliage or a piece of wet paper curls during its drying process, a layered compound might shrink, fold, or roll from the edges of the layers and form scrolls under appropriate conditions. If the interaction between neighboring layers could be reduced at the edges of the layer, while keeping the interactions of in-layer atoms or molecules, tubular structures might form through the rolling of these lamellar structures. Thus, formed cylinders might serve as microreactors, which direct and confine the growth of the nanowires or nanotubes. In some cases, the tubular structure maintained and transformed to 1D nanotubes when the surfactants were removed, as we have found in the synthesis of WS$_2$ nanotubes.[14] However, in other cases, the layered structure or the scrolls would collapse or condense into one-dimensional solid wires or rods during the removal of the surfactant. Under such circumstances, with elevated temperature the surfactant was removed and tungsten oxide nanowires were obtained under appropriate conditions. Recently, similar processes for the formation of

aluminum-based nanorods have been reported by Yada et al.,[17] which further strengthened the possibility of the rolling process of a lamellar structure.

Conclusions. In summary, tungsten oxide nanowires with relatively uniform diameters ranging from 10 to 50 nm and lengths up to several micrometers were synthesized on a large scale. With the distinctive and promising properties of tungsten oxide, the as-synthesized nanowires may serve as functional materials in the fabrication of nanosized sensors and flat panel display systems. Additionally, tungsten oxide nanowires could be facilely converted to W nanowires, WS_2 nanotubes, or highly conductive bronzes, which may find more significant applications, such as STM tips.[18] It is foreseeable that the novel growth strategy will probably become a general method for the synthesis of 1D nanostructures.

Supporting Information Available: More TEM images confirming that the tungsten oxide nanowires obtained were on a large scale. This material is available free of charge via the Internet at http://pubs.acs.org.

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