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An Inorganic Route for Controlled Synthesis of $W_{18}O_{49}$ Nanorods and Nanofibers in Solution

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In this work, we describe a simple inorganic route for synthesis of monodispersed $W_{18}O_{49}$ nanorods with dimensional control in the quantum confinement regime. The single-crystalline $W_{18}O_{49}$ nanorods can be prepared into stable colloidal solutions, or assembled into fibrous and/or paper forms by tuning process parameters. The important role of Na_2SO_4 salt in the synthesis has been demonstrated. This inorganic route should be feasible for large-scale production of low-dimensional nanostructured $W_{18}O_{49}$.

In recent years, transition metal oxides have received increasing attention in the synthesis of nanostructured materials.[1−9] Among them, a significant fraction of the work has been devoted to fabrication of one-dimensional (1D) tungsten oxides (WO_{3-x}, $x \geq 0$) due to their many known applications such as in electrochromic windows, optical devices, secondary batteries, gas sensors, and photocatalysts.[2,3] In particular, monoclinic $W_{18}O_{49}$ (or $WO_{2.72}$) is of great interest owing to its unusual defect structure and promising properties in the nanometer regime.[4−10] Nonetheless, most of the synthetic work for this 1D nanostructure reported is limited to high-temperature methods with either vapor or vapor−solid processes.[4−9]

For the large-scale production, wet chemical methods need to be further developed. Most recently, colloidal $W_{18}O_{49}$ nanorods with excellent quality had been synthesized with $W(CO)_6$ at 250−270 °C in the presence of $Me_3NO{\cdot}2H_2O$ and excess oleylamine, followed by various treatments in organic solvents.[10] In addition to this organic route, it would also be desirable to search for inorganic alternatives using low-cost precursors and solvents. Herein, we describe a facile inorganic route for synthesis of uniform $W_{18}O_{49}$ nanorods or nanofibers in aqueous solution. This novel method is based on treating freshly prepared $H_2WO_4{\cdot}xH_2O$ in the presence of Na_2SO_4 salt under hydrothermal conditions at 160−200 °C for 2−24 h.

In a typical synthesis, 10 mL of hydrochloric acid (3 M) was added dropwise to 10 mL of sodium tungstate solution (0.125 M) under stirring. A light yellow precipitate of amorphous tungstic acid appeared gradually. The mixture was vigorously stirred for 15 min followed by centrifugation (3000 rpm, 5 min), after which deionized water (20 mL) and a certain amount of sodium sulfate (0−20 g) were immediately added to the solid precipitate. The mixture was then vigorously stirred for 1−2 h (a slurry form was observed after 1 h when 20 g of Na_2SO_4 was used); the mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 160−200 °C for a period of 2−24 h. After reaction, the autoclave was then cooled to room temperature under tap water. The final product was harvested by centrifugation and washed with deionized water (several times) and pure alcohol (one time) to remove Na_2SO_4 and any other possible remnant. The obtained products were characterized with scanning electron microscopy (SEM, JSM-5600LV), trans-

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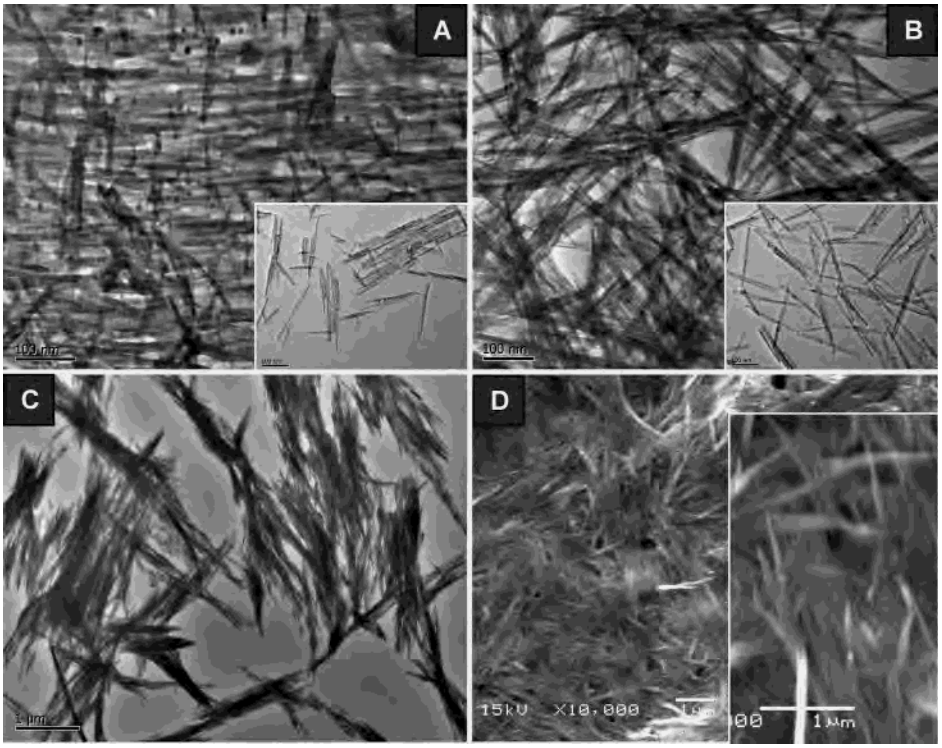

Figure 1. $W_{18}O_{49}$ nanorods and fibers synthesized with 20 g of Na_2SO_4 salt at 180 °C for different reaction times: (A) 2 h (TEM images), (B) 8 h (TEM images), (C) sample from part B with additional 16 h in deionized water (i.e., 8 + 16 h, TEM image), and (D) 16 h (SEM images).

mission electron microscopy and electron diffraction (TEM/ED, JEM-2010F, 200 kV), high-resolution transmission electron microscopy, energy-dispersive X-ray spectroscopy (HRTEM/EDX, Philips-CM200 FEG, 200 kV), and powder X-ray diffraction (XRD, Shimadzu XRD-6000, Cu Kα radiation).[11] The room temperature photoluminescence spectra of $W_{18}O_{49}$ nanorods were obtained with a fluorescence spectrometer (LS-55 Perkin-Elmer) with xenon (300 nm; 150 W pulsed xenon lamp) as an excitation source.

Figure 1 shows various $W_{18}O_{49}$ products synthesized as a function of reaction time in this work. After only 2 h, single-crystalline $W_{18}O_{49}$ nanorods in 100% morphological yield had readily formed with the diameter and length in the ranges 3−10 and 100−250 nm. Due to their small sizes, the individual tiny rods easily form parallel aggregates, such as raftlike arrangement (inset, Figure 1A) or "monolayer" settlement largely through interactions of their highly unsaturated sidewalls.[12] The continuous growth is evidenced in samples with longer reaction times. In Figure 1B, the nanorods have increased their diameter and length to 3−15 and 150−300 nm, respectively. The diameters reported here are only nominal owing to the rod aggregation, which will be addressed by the HRTEM technique (Figure 2C) shortly. It should be mentioned that this type of aggregation is mainly physical, and monodispersed nanorods can be obtained simply with more solvents in ultrasonic treatments; colloidal solutions of $W_{18}O_{49}$ nanorods in acetone solvent are stable for days. For example, the diameters of monodispersed $W_{18}O_{49}$ nanorods are on average 6.9 ± 1.6 nm (2 h, Figure 1A) and 7.3 ± 2.1 nm (8 h, Figure 1B), respectively. More permanent connectivity among these nanorods can be generated by hydrothermal treatment. In Figure 1C, for example, fiberlike $W_{18}O_{49}$ was prepared from the same sample used in Figure 1B, but with an additional heat treatment in deionized water at 180 °C for 16 h. This fibrous morphology is well preserved even with extensive ultrasonic treatments with surfactants (e.g., cetyl-trimethylammonium-bromide had

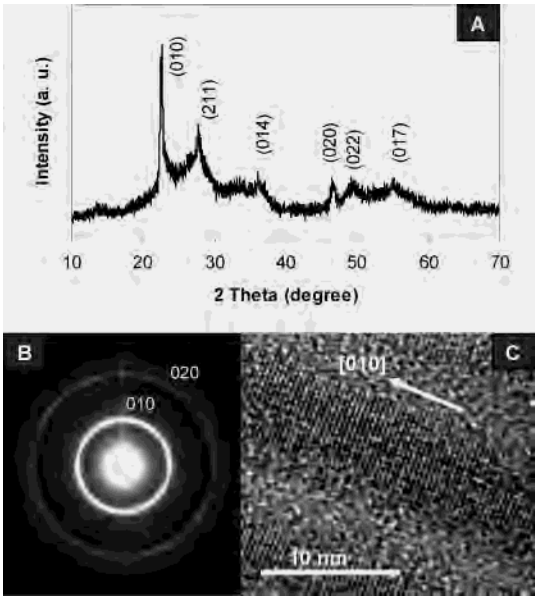

Figure 2. (A) XRD pattern for $W_{18}O_{49}$ nanorods, (B) ED pattern for randomly distributed $W_{18}O_{49}$ nanorods, and (C) HRTEM image for $W_{18}O_{49}$ nanorods (from Figure 1B).

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been tested in this work); our TEM investigation indicates that the $W_{18}O_{49}$ nanorods had attached to one another forming fiber bundles through their side crystal planes during the treatment. Longer reactions (e.g., 16−24 h, 20 g of Na_2SO_4) result in the formation of fibrous $W_{18}O_{49}$ with the length up to a few micrometers. Figure 1D displays two SEM images of the "$W_{18}O_{49}$ paper" prepared from a prolonged synthesis; details on the fiber length and "paper" texture can be obtained from the inset. Our TEM results reveal that the paperlike morphology is also composed of aggregated shorter nanorod bundles (separable in solvents). Although the length of nanorods can be varied by reaction time, the diameter of individual nanorods shows much weaker time dependence.

In Figure 2A, a representative XRD pattern for our as-synthesized tungsten oxide nanorods is displayed. All the main peaks can be indexed undisputedly to monoclinic $W_{18}O_{49}$ (JCPDS card 05-0392).[4−10] Consistent with general features of nanomaterials,[1] the overall diffraction intensity is weak, and peak broadening is pronounced. Diffraction peaks of (0*k*0) are stronger compared with the rest, indicating that the ⟨010⟩ is the major growth direction. EDX analysis gives an O/W atomic ratio of 2.6 ± 0.2, which is in good agreement with the theoretical value of $W_{18}O_{49}$. Furthermore, the ED pattern in Figure 2B shows two strong (0*k*0) rings, confirming that the ⟨010⟩ is indeed the preferential growth direction.[10] Figure 2C presents an HRTEM image of nanorods with the diameters 3−7 nm. The lattice spacing along ⟨010⟩ is determined to be $d_{010} = 0.38 \pm 0.01$ nm, in excellent agreement with the reported lattice constant of monoclinic $W_{18}O_{49}$.[4−10]

It is apparent that the sodium sulfate plays a crucial role in controlling the 1D growth and substoichiometric phase.[13] Without adding this salt, only the hexagonal phase of WO_3 (verified by XRD; JCPDS card 33-1387)[14] is formed; the products are showed as elongated hexagonal platelets and irregular nanoparticles. In Figure 3, the effect of salt is further demonstrated. With 2.5 g of Na_2SO_4, the hexagonal WO_3 still coexists with monoclinic $W_{18}O_{49}$ nanorods. With 3.5 g of the salt, phase-pure $W_{18}O_{49}$ can be achieved, but 100% rod morphology can only be obtained with 5 g of Na_2SO_4 added. Above 5 g, however, further modification on rod morphology is not pronounced. Other stable inorganic salts such as NaCl and $NaNO_3$ had also been tested in this work, but no obvious effects were observed. We have also carried out syntheses at 160 and 200 °C. Reactions at 160 °C (16−24 h) produce more monodispersed short $W_{18}O_{49}$ nanorods (about 100 nm in length) but are generally mixed with nanoparticles. On the other hand, reactions at 200 °C (16 h) give large fiberlike rod bundles with the length up to a few micrometers owing the more permanent interconnectivity generated at high temperature.

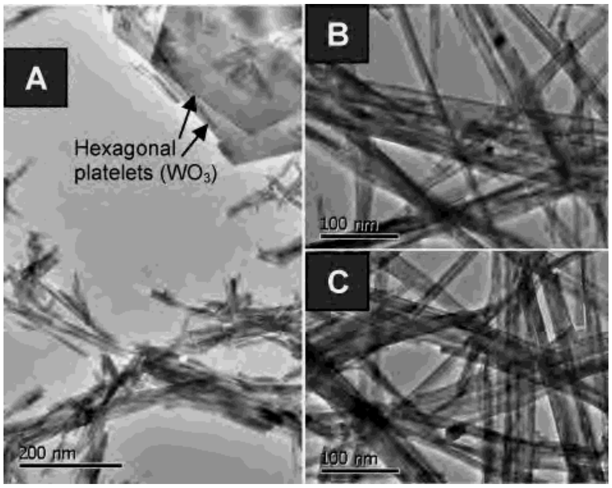

Figure 3. $W_{18}O_{49}$ nanorods synthesized at 180 °C for 16 h with different amounts of Na_2SO_4 salt: (A) 2.5 g, (B) 5 g, and (C) 10 g.

The room-temperature photoluminescence (PL) emission spectra of the $W_{18}O_{49}$ nanorods generally exhibit two emission maxima over the studied wavelength range, which is quite similar to a previously reported pattern for $W_{18}O_{49}$ nanorods synthesized via an organic route,[10] although the energy levels of the two emission peaks are less separate owing to different measurement conditions. For example, the higher energy peaks of the sample series of Figure 1 appear at 3.43 eV (360.6 nm; 4 h), 3.39 eV (364.9 nm; 8 h) and 3.38 eV (366.8 nm; 16 h) respectively, while the lower energy peaks are essentially constant at around 2.95 eV (ca. 420 nm). The slight blue-shift observed in the samples synthesized with a shorter reaction time indicates that the nanorods prepared in this work are entering the quantum confinement regime, as their size effect has been noticed.

Though little is known about the general growth mechanism of 1D $W_{18}O_{49}$, the crucial role of sodium sulfate has been clearly demonstrated in the current case. For instance, sulfate ions might adsorb on side surfaces of the nanocrystals or modify the ionic strength of reactant species in solution,[15] preventing the rods from radial enlargement. Furthermore, these anions could also be involved in possible redox reactions in forming $W_{18}O_{49}$ under hydrothermal conditions. Further investigation on these mechanistic aspects is needed.

In summary, we have developed a simple inorganic route to prepare monodispersed $W_{18}O_{49}$ nanorods with dimensional control in the quantum confinement regime. The single-crystalline $W_{18}O_{49}$ nanorods can be prepared into stable colloidal solutions, or be assembled into fibrous and/or paper forms by tuning process parameters. The important role of Na_2SO_4 salt in the synthesis has been demonstrated. This aqueous route should be feasible for large-scale production of low-dimensional nanostructured $W_{18}O_{49}$.

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