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Preparation of Ultralong $SrCrO_4$ Nanowires by a Surfactant-Free Solvothermal Reaction

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One-dimensional nanostructures with very large aspect ratios, such as nanotubes, nanowires, nanorods, and nanobelts, have attracted significant interest due to their potential applications in electronic and optoelectronic nanodevices.[1-5] Generally, a variety of surfactants as soft-templates have been used for preparing one-dimensional materials. The surfactant-assisted synthetic method provides the outstanding crystal morphology and low agglomeration of one-dimensional nanomaterials. However, the use of these surfactants may block surface reaction sites of nanomaterials and lead to significant decrease of their catalytic and physical properties of nanomaterials. Therefore, a simple method without the use of surfactants must be developed for the large-scale preparation of one-dimensional materials.

Strontium chromate ($SrCrO_4$) is an important material used as photocatalysts, photoluminescence materials, and yellow pigments.[6,7] $SrCrO_4$ was normally synthesized by conventional solid state reaction with $SrCO_3$ and Cr_2O_3 at 1200 °C.[8] $SrCrO_4$ was also synthesized using a microwave-assisted reaction with $SrCl_2$ and $Na_2Cr_2O_7$.[9] Recently, one-dimensional $SrCrO_4$, such as nanowires, nanorods, and nanobelts, have been synthesized *via* different synthesis routes.[10-12] $SrCrO_4$ nanorods with maximum length of 1.6 μm were prepared by a hydrothermal reaction in the presence of PVP (poly(vinylpyrrolidone)).[13] The average aspect ratio of $SrCrO_4$ nanorods ranges from 8.7 to 22.7. Most of one-dimensional $SrCrO_4$ obtained comprised of lengths of a few micrometers. To the best of our knowledge, the longest length of $SrCrO_4$ nanowires with length of about 10 μm and the aspect ratio of 100 was obtained from the reaction of aqueous $SrCl_2$ and $Na_2Cr_2O_7$ solution at room temperature.[14] In this paper, we reported a simple solvothermal method without the use of any surfactant for the preparation of ultralong $SrCrO_4$ nanowires with lengths up to 50 μm and the aspect ratio of 1000.

Figure 1 shows the XRD patterns of the two $SrCrO_4$ products using the simple precipitation and solvothermal reaction. For the case of the simple precipitation reaction, the $SrCrO_4$ product was obtained from a reaction of $Sr(NO_3)_2$ and Na_2CrO_4 aqueous solutions at room temperature. For the case of the solvothermal reaction, the $SrCrO_4$ product was obtained by heating the mixed ethanol solution of powder $SrCrO_4$ precursor prepared from a simple precipitation at 160 °C for 24 h. All the peaks in Figure 1 corresponded to monoclinic $SrCrO_4$ and were in good agreement with the reported data for this system (JCPDS 15-0368, a = 0.7081 nm, b = 0.7388 nm, c = 0.6771 nm, β = 103.4°).

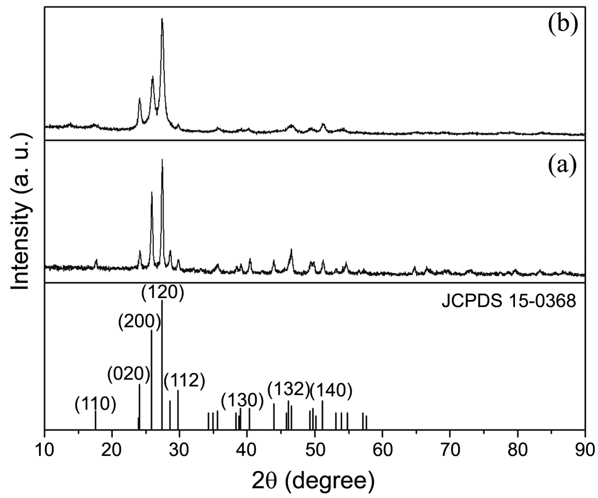

Figure 1. XRD patterns of the $SrCrO_4$ products prepared by (a) simple precipitation and (b) solvothermal reaction.

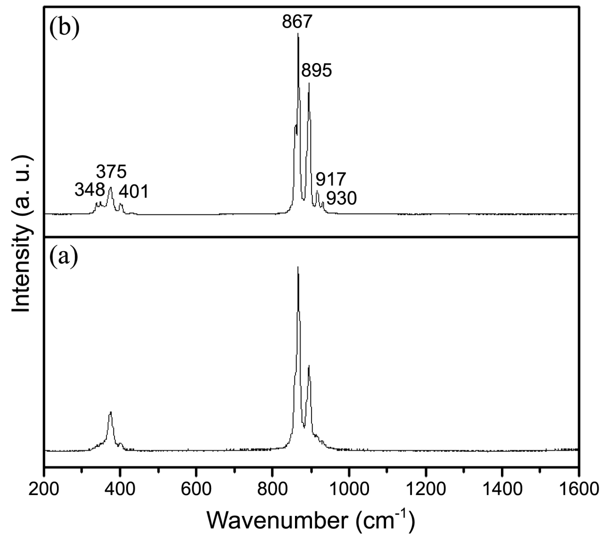

Figure 2. Raman spectra of the $SrCrO_4$ products prepared by (a) simple precipitation and (b) solvothermal reaction.

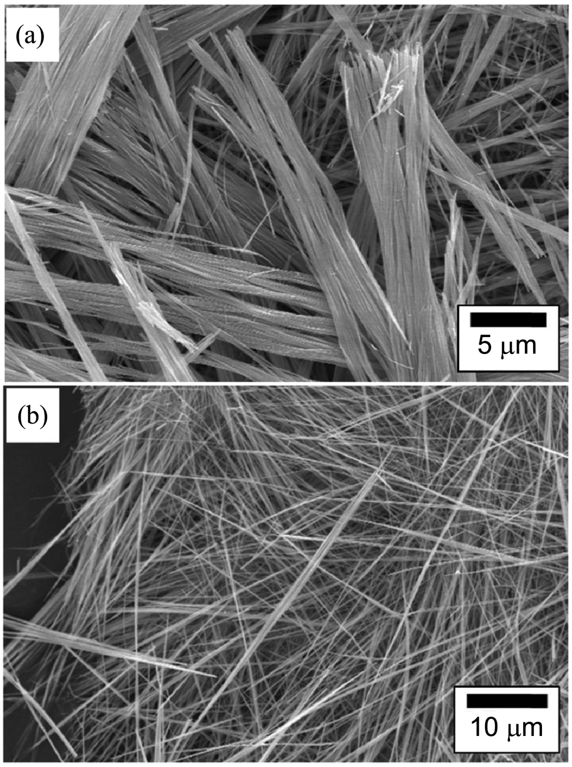

Figure 3. SEM images of the $SrCrO_4$ products prepared by (a) simple precipitation and (b) solvothermal reaction.

Figure 2 shows the Raman spectra of the two $SrCrO_4$ products using the simple precipitation and solvothermal reaction. All of the Raman peaks in Figure 2 were in good matched with the reported data for $SrCrO_4$.[15,16] The Raman peaks at 930 cm^{-1} (917 cm^{-1} and 895 cm^{-1}) and 867 cm^{-1} corresponded to antisymmetric stretching vibration modes (ν_3) and symmetric stretching vibration mode (ν_1) of the CrO_4 group in the $SrCrO_4$, respectively.[17] The Raman peaks at 401 cm^{-1} and 375 cm^{-1} (348 cm^{-1}) corresponded to antisymmetric bending vibration modes (ν_4) and symmetric bending vibration mode (ν_2) of the CrO_4 group, respectively.[17] No other peaks were observed in the XRD patterns and Raman spectra, indicating that $SrCrO_4$ has been successfully synthesized.

Figure 3 shows the SEM images of the $SrCrO_4$ products prepared by two different methods. When the simple precipitation reaction was used, the products were composed of bundles of microdrods with a mean diameter of 50 nm and a length of 25 μm (the aspect ratio is 500), as shown in Figure 3(a). This indicates that the $SrCrO_4$ crystals are easily grown to form microrods due to its unique crystalline properties even at room temperature. The bundle-like morphology was plausibly obtained by face to face oriented attachment of each microrod. When the thermal heating was used in ethanol solvent for solvothermal method at 160 °C with the $SrCrO_4$ precursors, the ultralong $SrCrO_4$ nanowires with a mean diameter of 50 nm and a length of 50 μm were obtained, as shown in Figure 3(b). Therefore, the aspect ratio of the $SrCrO_4$ product was significantly increased by the solvothermal reaction. The thermal heating treatment in ethanol *via* the solvothermal reaction may be an efficient way to prepare the ultralong $SrCrO_4$ precursors nanowires without any self-assembled orientated attachment.

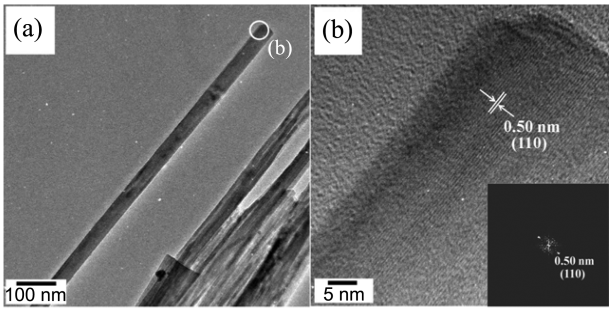

Figure 4. (a) HRTEM image and (b) high-magnification HRTEM image of an individual $SrCrO_4$ nanowire prepared by the solvothermal reaction. The inset of (b) shows the FFT pattern of an individual $SrCrO_4$ nanowire.

The typical high-resolution transmission electron microscopy (HRTEM) images of an individual $SrCrO_4$ nanowire prepared by the solvothermal reaction are shown in Figure 4. The width of the $SrCrO_4$ nanowires is about 50 nm. The observed lattice spacing of 0.50 nm corresponds to the (110) plane. The Fast Fourier transformation (FFT) pattern corresponds to the lattice fringe, as shown in the inset of Figures 4(b). This indicates that the single crystalline $SrCrO_4$ nanowire preferentially grows along with the (110) plane.

Figure 5 presents a proposed schematic diagram for the formation of ultralong $SrCrO_4$ nanowires through a simple precipitation and followed by the solvothermal reaction. At first, $SrCrO_4$ nuclei were formed from the reaction between

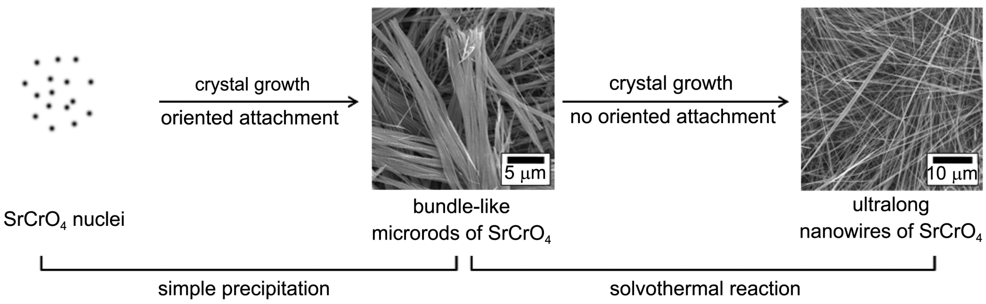

Figure 5. The schematic diagram for the formation of ultralong $SrCrO_4$ nanowires through a simple precipitation and followed by the solvothermal reaction.

Sr^{2+} and CrO_4^{2-} ions in the aqueous solution. After the initial nucleation process, microrods of $SrCrO_4$ were formed by the crystal growth. The bundle-like shape of $SrCrO_4$ was obtained by the self-assembled oriented attachment of each microrod of $SrCrO_4$ in the aqueous solution. Finally, ultralong $SrCrO_4$ nanowires were formed by thermal heating treatment in ethanol *via* the solvothermal reaction from the bundle-like microrods of $SrCrO_4$ precursor.

In conclusion, we develop a simple synthetic method for fabricating ultralong $SrCrO_4$ nanowires without the need of surfactants. The bundle-like microrods of $SrCrO_4$ were obtained by face to face oriented attachment of each microrod in the simple precipitation reaction. Ultralong $SrCrO_4$ nanowires with a mean diameter of 50 nm and a length of 50 μm were prepared using the solvothermal method with the $SrCrO_4$ precursor at 160 °C. The solvothermal reaction played an important role in the formation of ultralong $SrCrO_4$ nanowires without any agglomeration and oriented attachment. HRTEM images were used to confirm that the single crystalline $SrCrO_4$ nanowire preferentially grows along with the (110) plane.

Experimental Section

$Sr(NO_3)_2$ (99%, Aldrich), Na_2CrO_4 (98%, Aldrich), and ethanol (99%, Aldrich) were used as received. The $SrCrO_4$ precursor was prepared by a precipitation reaction from a mixture of 100 mL of 0.10 M $Sr(NO_3)_2$ aqueous solution and 100 mL of 0.10 M Na_2CrO_4 aqueous solution at room temperature for 2 h. The $SrCrO_4$ precipitate was obtained through filtration and several washed with water at room temperature, and then dried at 60 °C for 12 h. For the preparation of ultralong $SrCrO_4$ nanowires, 70 mL of ethanol was added to 1.0 g of the precipitated $SrCrO_4$ precursor, and the mixed solution was then transferred to a 100 mL Teflon-lined autoclave and heated at 160 °C for 24 h. The autoclave was naturally cooled down to room temperature. The ultralong $SrCrO_4$ nanowires were obtained through filtration, washed with ethanol, and then dried at 60 °C for 12 h. The yield for the preparation of $SrCrO_4$ precursor and ultralong $SrCrO_4$ nanowires are 69.1% and 50.1%, respectively.

The structure of the $SrCrO_4$ products was characterized by powder X-ray diffraction (XRD, PANalytical, X'pert-pro MPD). The Raman spectra were obtained using a Jobin-Yvon T64000 Raman spectrometer. The morphologies and crystalline structures of the $SrCrO_4$ products were observed by scanning electron microscopy (SEM, Hitachi S-4300) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM 3010), respectively.

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