Large-scale Synthesis of $SrCrO_4$ Nanowires and $PbCrO_4$ Nanorods by a Solution-phase Method at Room Temperature

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A facile, large-scale, solution-phase method has been developed to the synthesis of ABO_4-type chromate nanowires/rods at room temperature. Single-crystalline strontium chromate nanowires and lead chromate nanorods were fabricated by this method without heating or adding any surfactants or polymers. The structure and morphology of the nanowires/rods were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and selected-area electron diffraction (SAED). This simple method may also be extended to the synthesis of other ABO_4-type chromate one-dimensional nanostructures with a large-scale and low-cost production.

The synthesis and properties of one-dimensional (1D) nanostructures, such as wires, belts, tubes, and rods, have stimulated considerable interest owing to their unique properties and wide range of potential application in nanodevices.[1–3] During the past few decades, many attempts have been made to the synthesis of 1D nanostructures. Of the methods, solution-phase methods have emerged as powerful tools recently because of their significant advantages, including less-complicated techniques; cost-effective, low-temperature, and potential for large-scale production.[4] However, most of such controlling synthesis schemes reported need a microemulsion techniques or hydrothermal process, or polymer-assisted. The introducing of surfactants, templates, or other additives into the synthetic route undoubtedly leads to more synthetic procedures and might bring impurities into the final products. Thus, developing simple template-free solution-phase methods for the synthesis of the 1D nanostructures remains a challenge.

ABO_4-type ternary metal oxides, where A and B are two different metallic elements with oxidation states of +2 and +6, respectively,[5] are of importance owing to the unique properties and potential applications, including photoluminescence,[6,7] scintillation,[8,9] photosensitization,[10] stimulated Raman scatting behavior,[11] catalysis, etc.[12] Many solution-phase methods (mainly soft-template solution methods) have been developed to prepare 1D nanostructures of ABO_4-type materials. The soft methods to synthesize ABO_4-type nanostructures include the reverse micelle or microemulsion soft-template methods for the synthesis of $BaWO_4$,[13a] $BaCrO_4$,[13b] $BaSO_4$,[13c] and the polymer-assisted synthesis of $BaCrO_4$[13d] and $PbCrO_4$.[13e] Recently, hydrothermal synthetic route to $ZnWO_4$, $MnWO_4$, and $FeWO_4$ nanorods[14] and $CdWO_4$ nanorods[6] has been studied. $PbCrO_4$ nanorods synthesized by microwave-assisted ionic-liquid method have also been reported.[15] In this letter, we reported the large scale synthesis of single-crystalline strontium chromate nanowires by a facile method at room temperature without adding any surfactants or polymers. $SrCrO_4$ nanowires could be obtained from the reaction of aqueous $SrCl_2$ and Na_2CrO_4 solutions at room temperature. $PbCrO_4$ nanorods can also be fabricated by the same method, using $Pb(NO_3)_2$ instead of $SrCl_2$ precursor. In comparison with other conventional solution-phase methods, this new approach is simple and thus more suitable for industrial production. To the best of our knowledge, there has been no report on the solution-phase method to synthesize ABO_4-type 1D nanostructures at room temperature without adding any additives.

All chemicals were analytical grade and used as received without further purification. In a typical synthesis process, 5 mmol of $SrCl_2 \cdot 6H_2O$ and $Na_2CrO_4 \cdot 4H_2O$ were dissolved in 25 mL of distilled water in two beakers, respectively. Then, aqueous $SrCl_2$ solution was added dropwise into aqueous Na_2CrO_4 solution, with the assistance of strong magnetic stirring to form a homogeneous yellow solution at room temperature. The resulting suspension was placed at room temperature for 5 days without stirring. The final products containing nanowires were collected by centrifugation, washed several times with distilled water and absolute ethanol, and finally dried in vacuum at 60 °C for 60 min.

The products were characterized by X-ray diffraction pattern (XRD), recorded on a Rigaku D/max-rA diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). The morphology of the samples was examined by a scanning electron microscope (SEM, Hitachi S-4700). Transmission electron microscopic (TEM) and selected-area electron diffraction (SAED) studies were carried out with a Phillips Tecnai 20 microscopy. The as-synthesized powders were first dispersed in ethanol by ultrasonic treatment. A small drop of the dispersions was transferred to a holey carbon film supported on a copper grid for TEM observation.

Figure 1a shows the XRD pattern of the strontium chromate nanowires. All diffraction peaks can be perfectly indexed to the monoclinic phase of $SrCrO_4$ (JCPDC 15-0368), with lattice parameters of $a = 7.081$ Å, $b = 7.388$ Å, $c = 6.771$ Å, and $\beta = 103.4°$. A typical SEM image of the as-synthesized strontium chromate nanowires is shown in Figure 1b. The SEM image indicates that $SrCrO_4$ nanowires are highly uniform, and the length of the nanowires can reach up to tens of microns. The diameters of $SrCrO_4$ nanowires range from 50 to 230 nm, and the nano-

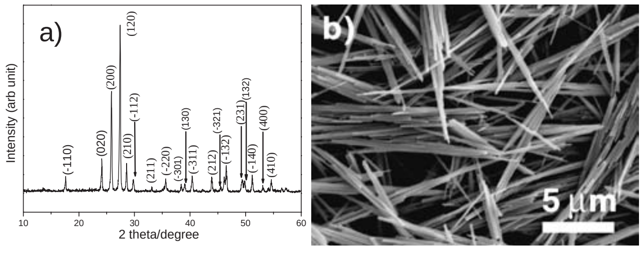

Figure 1. (a) XRD pattern and (b) a typical SEM image of $SrCrO_4$ nanowires.

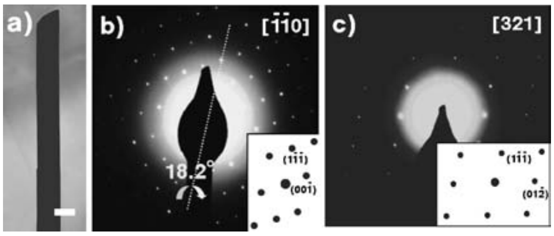

Figure 2. (a) TEM image and (b and c) corresponding selected-area electron diffraction (SAED) patterns of an individual $SrCrO_4$ nanowire tilted to zone axes $[\bar{1}\bar{1}0]$ and [321], respectively. Scale bar in Figure 2a: 100 nm. Dashed line indicates the tilting axes rotated to obtain the needed orientation, and circular arrows give the tilting angles.

wires tend to form bundles (Figures S1 and S2, Supporting Information). The results also demonstrate that strontium chromate nanowires in high yield, almost 100%, can be easily obtained by this simple method.

A typical TEM image of an individual strontium chromate nanowire is shown in Figure 2a. The diameter of the studied nanowire is about 100 nm. Selected-area electron diffraction (SAED) patterns taken from different positions from individual nanowires are essentially the same, indicating that the nanowire is single-crystalline in nature. Figures 2b and 2c show two electron diffraction patterns taken from the same nanowire (shown in Figure 2a) and their relative orientational relationships. The zone axes are $[\bar{1}\bar{1}0]$ (Figure 2b) and [321] (Figure 2c), respectively. The [321] zone axis electron diffraction pattern was obtained by rotating the nanowires of 18.2° about its $[1\bar{1}\bar{1}]$ direction (marked by dash line in Figure 2b), which is in agreement with the calculated value of 17.7°, and thus, the growth direction of the selected nanowire was determined as its $[1\bar{1}\bar{1}]$ crystallographic direction.

It is expected that this simple method can be extended to fabricate other ABO_4-type 1D nanostructures. Similarly, lead chromate nanorods are prepared with an identical method, using $Pb(NO_3)_2$ instead of $SrCl_2$ precursor. XRD pattern (Figure S3, Supporting Information) indicates that the synthesized nanowires are phase-pure $PbCrO_4$. A typical SEM image of the as-synthesized $PbCrO_4$ nanorods is shown in Figure 3a. The product consists of a wealth of nanorods with more uniform diameter distribution of 80–100 nm and length in the range of 1 to 5 µm. The morphology and structure of the $PbCrO_4$ nanorods were further examined with TEM and SAED. The diameter of an individual $PbCrO_4$ nanorod shown in Figure 3b is about 90 nm. The corresponding SAED pattern (inset in Figure 3b), could be attributed to the $[2\bar{1}4]$ zone axis diffraction of monoclinic $PbCrO_4$ with lattice parameters of $a = 7.12$ Å, $b = 7.44$ Å, $c = 6.8$ Å, and $\beta = 102.4°$, and it confirms that the nanorods are essential single-crystalline.

The solution reaction time has a key influence on the formation of nanowires/rods in this study. When 1 mL of aqueous $SrCl_2$ solution was added into Na_2CrO_4 solution, the products consist of lots of nanoparticles with average diameter of 40 nm and only a few nanorods. The nanoparticles tend to vanish and plentiful nanorods form as the reaction proceeds. On the basis of our results, we think that the formation of $SrCrO_4$ nanowires can be divided into two stages. Firstly, $SrCrO_4$ nucleates immediately and forms small nanoparticles when $SrCl_2$ was added into aqueous Na_2CrO_4 solution. Secondly, these nanoparticles grew and/or oriented attached to nanowires in the direction of their energetically favored crystallographic axes, by oriented attachment mechanism, which is proposed by Penn and Banfield.[16] The detailed formation mechanism of the nanowires/rods needs to be further studied.

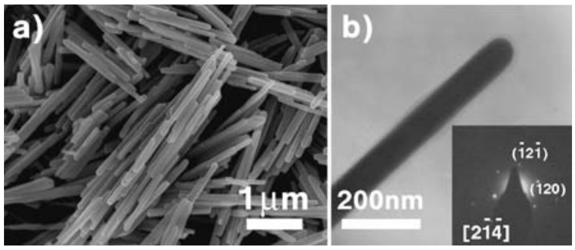

Figure 3. (a) SEM image of $PbCrO_4$ nanorods. (b) TEM image of an individual $PbCrO_4$ nanorod. Inset: corresponding selected-area electron diffraction (SAED) pattern.

In conclusion, we have reported a facile, solution-phase method to the large-scale synthesis of strontium chromate nanowires with a diameter of 50 to 230 nm and length up to tens of microns at room temperature without heating or adding any surfactants. Lead chromate nanorods were also prepared by this simple method. The facile method may be a versatile approach that can be extended to synthesize other ABO_4-type 1D nanostructures with a large-scale and low-cost production.

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