Single-crystalline $PbCrO_4$ Nanowires and Their Hydrothermal Transformation to Amorphous $PbCr_3O_{10}$ Nanotubes

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Single-crystalline $PbCrO_4$ nanowires have been successfully synthesized by a simple solution method at room-temperature. Amorphous $PbCr_3O_{10}$ nanotubes could be hydrothermally prepared from $PbCrO_4$ nanowires in the presence of PVP. This simple method needs no any seed, catalyst, or template, and may also be extended to the fabrication of other 1-D chromates.

Lead chromate ($PbCrO_4$) exists in two crystal structures: the stable monoclinic structure and the unstable orthorhombic structure.[1] $PbCrO_4$ is widely used in decorative and protective systems, and mass coloration of fibers, plastics, papers, elastomers, and rubbers.[2,3] In addition, $PbCrO_4$ is used as a host material for photosensitizer, humidity-sensing resistor and so forth.[4,5] The properties of lead chromates are determined predominantly by crystal structure, composition, particle size, and morphology.[1,3] Therefore, the synthesis of lead chromates with well-controlled size and shape is of great significance for their applications. Since the discovery of carbon nanotubes in 1991, one-dimensional (1-D) nanostructures have aroused intensified interest because of the unique size- and shape-dependent properties.[6] It is expected that 1-D nanostructures of lead chromates will find new applications or improve the performance of existing applications.

There have been few reports on the preparation of $PbCrO_4$. Spherical $PbCrO_4$ nanoparticles were prepared by water-in-oil microemulsion method.[4] $PbCrO_4$ nanorods were synthesized by hydrothermally treating an aqueous solution of $Pb(CH_3COO)_2$, $K_2Cr_2O_7$, NaOH, and poly(vinylpyrrolidone) at 140 °C for 20 h.[7] In this communication, we demonstrate a room-temperature route to the synthesis of single-crystalline $PbCrO_4$ nanowires and hydrothermal transformation of $PbCrO_4$ nanowires to amorphous $PbCr_3O_{10}$ nanotubes. To the best of our knowledge, there has been no report on the room-temperature synthesis of single-crystalline $PbCrO_4$ nanowires or on the synthesis of $PbCr_3O_{10}$ nanotubes.

All chemicals used were of analytical grade and used as received without further purification. In a typical experiment, 33 mg of $Pb(NO_3)_2$ and 34 mg of poly(vinylpyrrolidone) (PVP, $M_W \approx 55000$) were dissolved in 10-mL deionized water under constant magnetic stirring at room temperature. Then, a solution containing 20 mg of K_2CrO_4 dissolved in 10-mL deionized water was added dropwise and the addition process took ≈5 min. The resulting solution was stirred for 10 min. Yellow precipitate was obtained (sample 1). The precipitate was separated by centrifugation, washed with deionized water and absolute ethanol three times, respectively, and dried in a vacuum at 60 °C. For the preparation of $PbCr_3O_{10}$ nanotubes, the above as-prepared precipitate together with its mother solution was transferred into a 40-mL Teflon-lined stainless steel autoclave. The autoclave was heated and maintained at 220 °C for 20 h, and then was allowed to cool to room temperature (sample 3). Sample 3 can be subsequently separated into two parts by centrifugation, which was grey (sample 3a) and red (sample 3b).

X-ray powder diffraction (XRD) was performed with a Rigaku D/max 2550V X-ray diffractometer using graphite-monochromatized high-intensity Cu Kα radiation ($\lambda = 1.54178$ Å). The XRD pattern of sample 1 is shown in Figure 1. All the reflections can be indexed to a single phase of monoclinic $PbCrO_4$ [space group: $P2_1/n$ (no. 14)] with lattice constants $a = 7.10$ Å, $b = 7.42$ Å, $c = 6.77$ Å, and $\beta = 102.35°$, consistent with the reported data (JCPDS 74-2304). The yield of the $PbCrO_4$ powder is about 95%.

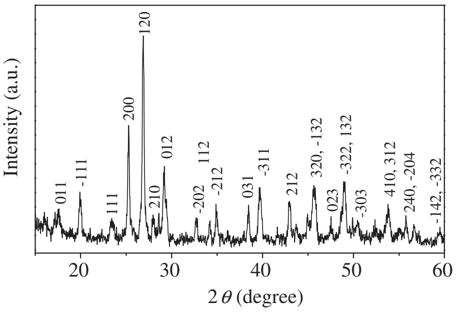

Figure 1. XRD pattern of $PbCrO_4$ nanowires prepared at room temperature (sample 1).

The morphologies of the as-prepared products were investigated by transmission electron microscopy (TEM, JEOL JEM-2010). Figure 2a shows TEM micrograph for sample 1. One can see $PbCrO_4$ nanowires with diameters of ≈20 to ≈120 nm and lengths up to ≈2 µm. The aspect ratios of $PbCrO_4$ nanowires were up to ≈65. Each nanowire is straight and has a uniform diameter along its entire length. Selected area electron diffraction (SAED) patterns taken from different positions from an individual nanowire or different $PbCrO_4$ nanowires were essentially the same, indicating that $PbCrO_4$ nanowires were single-crystalline. Figure 2b shows a typical single nanowire and its corresponding SAED pattern (inset of Figure 2b). The SAED pattern can be indexed as the $[1\bar{1}0]$ zone axis of monoclinic $PbCrO_4$, which is consistent with the XRD result (Figure 1). Figure 2c shows the high-resolution TEM (HRTEM) micrograph of an individual nanowire. It shows that the nanowire is structurally single-crystalline with a periodic fringe spacing of 5.09 Å along the longitudinal direction of the nanowire, which corresponds to the (110) planes of monoclinic $PbCrO_4$. This indicates that $PbCrO_4$ nanowires had a preferential growth direction along the *c* axis of the crystal lattice.

We have investigated the influence of hydrothermal treat-

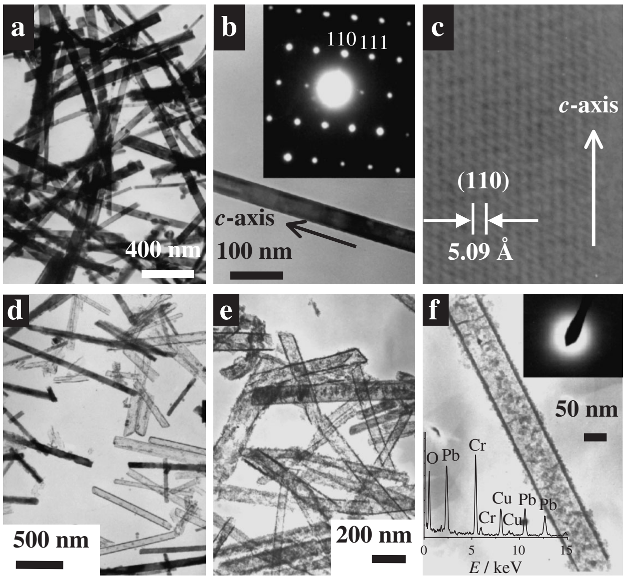

Figure 2. (a) TEM micrographs of some typical samples. (a) $PbCrO_4$ nanowires (sample 1); (b) a single nanowire with a diameter of 40 nm (sample 1). Inset: SAED pattern of the same nanowire; (c) HRTEM micrograph of an individual nanowire; (d)–(f) samples prepared by hydrothermally treating the same solution as that of sample 1 at various temperatures for 20 h. (d) at 180 °C (sample 2); (e) and (f) at 220 °C (sample 3a, grey product); (f): an individual nanotube, its corresponding SAED pattern (the inset,upright) and EDS spectrum (the inset, left bottom).

ment on the morphology and composition of the products. XRD studies show that the product obtained at 140 °C (sample 4) consisted of a single phase of monoclinic $PbCrO_4$. When the temperature was increased to 180 °C (sample 2), the sample consisted of a mixture of monoclinic $PbCrO_4$, monoclinic Pb_2CrO_5 and amorphous $PbCr_3O_{10}$. When the temperature was further increased to 220 °C (sample 3), the sample consisted of monoclinic Pb_2CrO_5 and amorphous $PbCr_3O_{10}$. Pb_2CrO_5 was red in color and could be easily removed from samples by centrifugation owing to its large sizes (micrometer-sized rods).

$PbCrO_4$ nanowires hydothermally prepared at 140 °C (sample 4) have diameters of 80–140 nm and lengths of 1–2 µm. Compared with sample 1 prepared at room temperature, the diameters of $PbCrO_4$ nanowires increased. When the hydrothermal temperature was increased to 180 °C, a mixture of grey ($PbCrO_4$ and $PbCr_3O_{10}$) and red (Pb_2CrO_5) products was obtained (sample 2). Figure 2d shows the grey product (separated from sample 2) consisted of both nanowires ($PbCrO_4$) and nanotubes ($PbCr_3O_{10}$). Nanowires and nanotubes have similar sizes, with diameters of 50–110 nm and lengths of 0.5–4 µm. Figure 2e shows that the grey product (sample 3a hydrothermally prepared at 220 °C) consisted of exclusive $PbCr_3O_{10}$ nanotubes with diameters of 30–90 nm and lengths of 0.2–1 µm. The SAED pattern (inset of Figure 2f) shows that $PbCr_3O_{10}$ nanotubes were amorphous. Energy dispersive spectroscopy (EDS) (inset of Figure 2f) shows that the nanotube consisted of lead, chromium, and oxygen with a Pb/Cr/O molar ratio of 1:3:10, thus giving a formula of $PbCr_3O_{10}$ (copper came from copper grid of TEM sample holder). It is interesting to note that the $PbCr_3O_{10}$ nanotubes have open ends, which may be rather meaningful for their further functionalization and filling with nanoparticles. The XRD showed that sample 3b was composed of the monoclinic Pb_2CrO_5. The morphology of Pb_2CrO_5 was rods with diameters and lengths in the micrometer range.

The general reaction for the hydrothermal process at 220 °C for 20 h may be simplified as Eq 1:

$$\begin{aligned} &PbCrO_4 \text{ (nanowires, PVP-assisted)} \\ &\quad \rightarrow PbCr_3O_{10} \text{ (nanotubes, grey)} + Pb_2CrO_5 \text{ (microrods, red)} \end{aligned} \tag{1}$$

PVP has a key influence on the formation of $PbCrO_4$ nanowires and $PbCr_3O_{10}$ nanotubes. Without using PVP, $PbCrO_4$ nanowires with diameters of 30–160 nm and lengths of 0.6–2.8 µm were formed at room temperature. Compared with sample 1 prepared using PVP, the distribution range of diameters and lengths for $PbCrO_4$ nanowires increased without PVP. $PbCr_3O_{10}$ nanotubes could not be generated from the $PbCrO_4$ nanowire precursor by hydrothermal treatment at 180 °C or above in the absence of PVP. We suggest that the adsorption of PVP on the surface of $PbCrO_4$ nanowires played a crucial role in the formation of $PbCr_3O_{10}$ nanotubes, acting as both a directing reagent and surface-passivating reagent. The detailed formation mechanism of $PbCr_3O_{10}$ nanotubes needs to be further studied.

In summary, we have successfully developed a room-temperature synthetic route to single-crystalline $PbCrO_4$ nanowires and demonstrated that amorphous $PbCr_3O_{10}$ nanotubes could be hydrothermally prepared from $PbCrO_4$ nanowires in the presence of PVP. It was found that the hydrothermal temperature and surfactant (e.g., PVP) played key roles in determining the morphology and phase of lead chromates. This simple method does not need any seed, catalyst, or template, thus is promising for large-scale and low-cost production. The method demonstrated in this paper may also be extended to the fabrication of other 1-D chromates.

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