A New Approach to Prepare VO_2 (B) Nanoribbons

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The VO_2 nanoribbons have been successfully prepared via hydrothermal reaction of V_2O_5 and poly(vinyl alcohol) (PVA) solution. The products consist of a large number of ribbon-like nanostructures, and nanoribbons are 100–200 nm in width, 0.8–1.9 μm in length and about 20–30 nm in average thickness. The influence on the morphology of the as-obtained products was briefly discussed on the basis of the experimental results.

Recently, one-dimensional (1-D) nanomaterials, such as nanobelts, nanowires, and nanotubes attracted more and more attention because of their specific properties and their wide potentials in nanodevices.[1–4] Moreover, hydrothermal synthesis is an effective method to fabricate 1-D nanostructures not only because of its critical temperature and pressure, but also the low cost, large scale, and wide suitability for various materials.

Vanadium oxides usually is composed of a variety of binary oxides with the general formula VO_{2+x} ($-0.5 \leq x \leq 0.5$), such as V_2O_5, V_6O_{13}, V_4O_9, V_3O_7, VO_2, and V_2O_3. They have attracted special interest due to their applications in oxidation catalysis of hydrocarbons,[5] cathode materials for reversible lithium batteries,[6] intelligent thermochromic windows,[7] and so on.

In the past decade, several methods have been reported to fabricate 1-D nanostructures of VO_2. Liu et al.,[8] reported the fabrication of VO_2 (B) nanoribbons through ammonium metavanadate as a reagent. Using VO_2 powder as a starting material, nanowires[9] were prepared at high temperature in an argon atmosphere. VO_2 (R) nanorods were obtained via the hydrothermal reaction of KOH, V_2O_5, and hydrazine.[10] Recently, nanorods of B phase VO_2 were made from metal alkoxide with laurylamine hydrochloride (LAHC) as organic surfactant.[11] Among them, metastable VO_2 (B) was especially interesting because of its layer structure and potential applications in lithium battery materials[12] and the capability of transformation to thermochromic VO_2 at high temperature.[13]

Herein, we report a surfactant-assisted hydrothermal method to prepare large scale VO_2 nanoribbons using commercial V_2O_5 as reagents by a soft chemical process. The influence of reaction media, reductant PVA on the morphology was briefly discussed on the basis of the experimental results.

All the reagents used in the experiments were of analytical grade and were used without further purification. In a typical procedure, commercial V_2O_5 powder (0.90 g), 30 mL of deionic water and 10 mL of 5 wt % PVA solution were vigorously agitated for 0.5 h, and then transferred into a 50-mL stainless steel autoclave. The autoclave was sealed and maintained at 180 °C for 96 h. After cooling to room temperature on standing, the deep-blue products were filtered off, washed with distilled water and absolute ethanol several times, and dried in vacuum at 80 °C for 8 h.

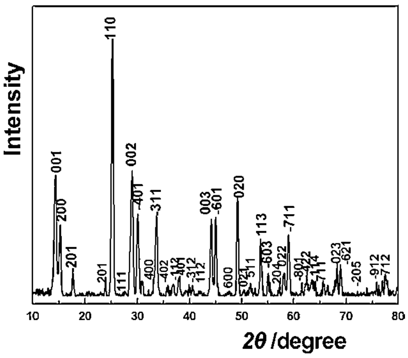

Figure 1. XRD pattern of VO_2 (B) nanoribbons.

The overall crystallinity and purity of as-obtained products were characterized by X-ray diffraction (XRD) carrying out on a Shimadzu XRD-6000 diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.54060$ Å). The morphology and size distribution of the samples were examined by TEM carrying out on a JEM-100CXII and JEM-2010 transmission electron microscope with an accelerating voltage of 100 kV. SEM image was collected by employing a Quanta 200 scanning electron microscope operated at 30 kV.

Figure 1 shows the X-ray powder diffraction profile of the product obtained after hydrothermal treatment. The peaks from the sample can be indexed as monoclinic VO_2 (space group $C2/m$) with lattice parameters $a = 12.05$, $b = 3.69$, $c = 6.43$ Å, $\beta = 107.18°$. It corresponds to the VO_2 (B) (JCPDS Card No. 81-2392, $a = 12.09$, $b = 3.702$, $c = 6.433$ Å, $\beta = 106.97°$) already described in the literature.[14] It can be observed from the XRD pattern that 001, 002, and 003 peaks are extraordinarily strong compared with other peaks, which differ greatly from the XRD data of the standard power sample (JCPDS Card No. 81-2392), indicating that as-prepared VO_2 (B) may have special morphologies. No impurity phases are detected from the XRD pattern such as V_2O_5, V_2O_3, VO_2 (A), and VO_2 (M), indicating that VO_2 (B) nanoribbons with high purity were obtained under current synthetic conditions.

The size and morphology of the products were examined by TEM and SEM. The TEM images (Figure 2a) revealed that the VO_2 nanoribbons were 0.8–1.9 μm long, typically 100–200 nm wide and 20–30 nm thick. Flexible nanoribbons with uniform diameter were also observed in typical SEM image (Figure 2c), which was in agreement with the TEM results. The SAED pattern from an individual nanoribbon (inset in Figure 2b) revealed it as single crystal and the growth direction of nanoribbons as [001].

The addition of PVA may be the decisive factor in the fabrication of VO_2 (B) nanoribbons. PVA could serve as both

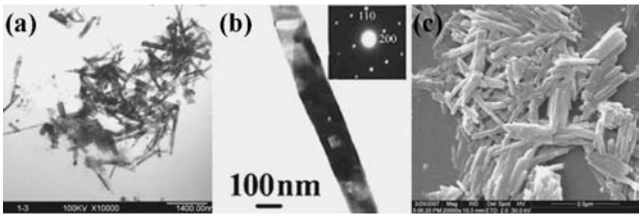

Figure 2. VO_2 (B) nanoribbons: (a) TEM images; (b) TEM image of a typical nanoribbon (inset:the corresponding SAED); (c) SEM images.

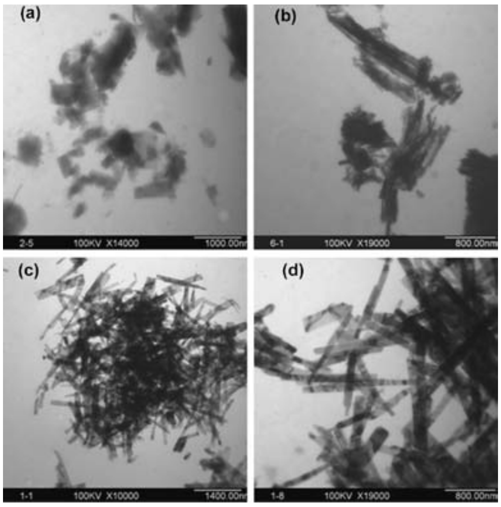

Figure 3. TEM images of samples obtained at different reaction times: (a) 6 h; (b) 48 h; (c) 72 h; (d) 168 h.

reducing reagent and capping reagent in the present synthesis. Firstly, V_2O_5 was reduced by PVA at 180 °C into VO_2. Secondly, the VO_2 obtained could further grow into nanoribbons with the assistance of PVA. PVA contains lots of hydrophilic (–OH) and the chain has high flexibility. The flexible chain and its hydroxy groups enable it to couple with VO_2 by hydrogen bonding, to minimize the surface energy and to form thermodynamically favorable polymer complex, which induces the preferential orientated growth of VO_2 (B) nanoribbons along the [001] direction under hydrothermal conditions.[15] Comparative experiment was made without the participation of PVA while keeping other parameters unchanged, and no VO_2 were obtained, indicating that the addition of PVA is indispensable in our synthetic route.

Figure 3 shows TEM images of the products obtained under different reaction times. There is a large difference among the VO_2 (B) prepared at various conditions. After the mixture of V_2O_5, water and PVA was hydrothermally treated for 6 h, a large number of irregular nanosheets (Figure 3a) in the product were found. When the reaction time was increased to 48 h, numerous nanoribbons were observed in addition to the sheets (see Figure 3b). Figure 3c revealed the presence of a large number of nanoribbons, which indicated that the purity of the nanoribbons in the products increased with prolonging the reaction time. From Figure 3d these uniform nanoribbons, with a long length ranging from several hundred nanometers to several micrometeters, were observed.

Based on the above-mentioned analysis and experimental results, it was speculated that the addition of PVA and the hydrothermal reaction time might decide the formation of 1-D nanostructures, while other factors during the preparation just influenced slightly the morphology.

The as-obtained VO_2 (B) was calcined at 450 °C under high purity N_2 (99.999%) atmospheric to obtain VO_2 (M) powder (the XRD pattern can be seen in Supporitng Information: Figure 2).[16] The as-prepared VO_2 (M) exhibited a strong crystallization peak around 68.7 °C (the DSC image in Figure 3 of Supporting Information),[16] which was agreed well with the result reported by Morin.[17]

In summary, a hydrothermal method assisted by PVA solution has been developed to synthesize metastable VO_2 (B) in nanoribbon form. The resulting nanoribbons had uniform width in the range of 100–200 nm, length in the range of 0.8–1.9 µm and thickness about 20–30 nm, which provided an ideal mode to study the fundamental properties of VO_2 nanoribbons. According to comparative experimental results, the morphology could be controlled by altering reaction conditions. This simple synthetic route will offer great opportunities for the large-scale fabrication of 1-D nanostructure materials. The metastable VO_2 (M) was obtained by post-annealing the VO_2 (B) at 450 °C under high purity N_2 (99.999%) atmosphere. Moreover, VO_2 (B) nanoribbons are interesting due to its layer structure and potential applications in lithium battery and VO_2 (M) can be used as intelligent materials on account of its metastable nature. The relative work is being proceeded by our research team.

This work was partially supported by PLA (No. 51420030505JW1214), Key Laboratory of Catalysis and Materials Science of Hubei Province (No. CHCL06003) and Natural Science Foundation of Hubei (No. 2005ABA034).

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Published on the web (Advance View) October 20, 2007; doi:10.1246/cl.2007.1366