A Simple Approach for the Fabrication of $Na_{1+x}V_3O_8$ Nanoribbon Thin Film

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(Received March 7, 2005; CL-050303)

$Na_{1+x}V_3O_8$ nanoribbon thin films have been obtained through a thermal treatment of the V_2O_5 xerogel thin films prepared on sodium silicate glass substrates which also serve as a kind of sodium source at 450 °C for a certain time. The synthesized $Na_{1+x}V_3O_8$ nanoribbon thin films were characterized by XRD, SEM, and TEM. The nanoribbons uniformly distribute on the glass substrates and have an average of several to tens of micrometers in length, hundreds of nanometers in width and tens of nanometers in thickness.

One-dimensional (1D) nanostructured materials including nanorods, nanotubes, nanowires, and nanoribbons have been considered as promising candidate materials in nanoscale electronics and photonics owing to their novel chemical and physical properties.[1] Vanadium oxide bronzes have attracted many attentions because of their diverse structure and unusual electronic, photonic, and magnetic properties.[2] On account of their layered structures, they have been seen some potential application as cathode materials in rechargeable lithium batteries.[3] Most recently, a few 1D nanostructured vanadium oxide bronzes including $Na_2V_6O_{16}{\cdot}3H_2O$ nanobelts[4a] and nanowires,[4b] $CaV_6O_{16}{\cdot}3H_2O$ nanoribbons,[4c] NaV_6O_{15} nanowires[4b] and β-$AgVO_3$ nanowires[4d] have been synthesized through hydrothermal reactions. Here, we report a novel approach to synthesize $Na_{1+x}V_3O_8$ and form nanoribbon structure by an analogous solid-state interface chemical reaction between vanadium oxide and sodium silicate glass. Along with the synthesis, these 1D ribbons were fabricated into thin films. This route is rapid, low-cost and large-scale growth of nanoribbons. The structure of $Na_{1+x}V_3O_8$ consists of V_3O_8 layers which are built up with VO_6 octahedral and V_2O_8 units of edge-sharing VO_5–VO_5 trigonal bipyramids and the layers are strongly held together by Na^+ ions residing in the octahedral sites.[5]

First, vanadium oxide gel was synthesized following a quenching-like route.[6] In a typical route, 3 g of divanadium pentaoxide powder (99%, Zhonglian Chem&Ind. Reagent Factory, Beijing) was put into a ceramic crucible and maintained at $\approx 1000\,°C$ for 15 minutes, and then the molten liquid was quickly poured into 240 mL of deionized water while being stirred. The concentration of the sol solution is 0.05 M, determined through thermogravimetric analysis. If the concentration is higher than 0.1 M, gelation occurs,[7] and this is not benificial to synthesize nanoribbon structure. Second, a sodium silicate glass substrate has been precleaned and was dipped into the V_2O_5 sol several times to form a xerogel film. The thickness of the film was controlled around 1–2 µm. Finally, the film was heated to 450 °C at a rate of 3–4 °C/min in a furnace and maintained at 450 °C for 30 min or longer. After cooling down to the room temperature slowly, a translucent brown thin film was obtained.

X-ray powder diffraction (XRD) patterns were recorded on a Philips X' pert diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). X-ray photoelectron spectroscopy (XPS) measurements were conducted on an AXIS ULTRA system (Shimadzu-Kratos Co.) using a monochromatized Al Kα radiation as excitation source ($h\nu = 1486.6$ eV). Scanning electron microscopy (SEM) image was taken on a JSM-5600LV scanning electron microscope. The transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) pattern were obtained on a JEOL JEM-2010 transmission electron microscope at 200 kV.

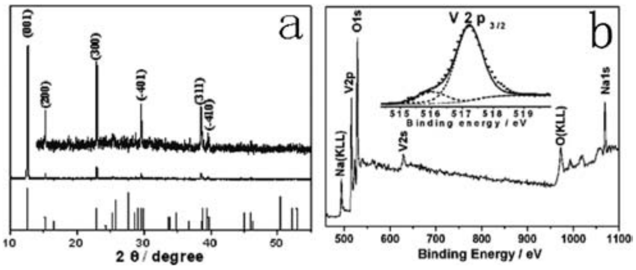

Figure 1. (a) XRD patterns of the $Na_{1+x}V_3O_8$ nanoribbon thin film. (b) XPS spectra of the $Na_{1+x}V_3O_8$ nanoribbon thin film. The inset shows the $V2p_{3/2}$ XPS core level spectra of the film.

Figure 1a shows the XRD pattern of the film obtained by thermal treated at 450 °C for 2 h. All the peaks in Figure 1a can be readily indexed to a pure monoclinic crystalline phase [space group: $P2_1/m(11)$] of $Na_5V_{12}O_{32}$ (JCPDS No. 24-1156, which can be considered as $Na_{1.25}V_3O_8$ compared with the cell parameters and the space *hkl* of $Na_{1+x}V_3O_8$ refined by Kawakita et al.[5a]) with calculated lattice constants $a = 12.14(4)$ Å, $b = 3.66(1)$ Å, $c = 7.31(6)$ Å, $\beta = 107.48(9)°$. The XRD result shows that the nanoribbons are $Na_{1+x}V_3O_8$ with a high degree of crystallinity and the film is highly oriented for there are only some special peaks existing. The XPS spectra (Figure 1b) show that the nanoribbons consist of Na, V (in a ratio of ca. 1:2.3) and O. Furthermore, a $V2p_{3/2}$ binding energy of 517.2 eV is characteristic of V^{5+} and a relevant amount (ca. 10%) of V^{4+} at a characteristic $V2p_{3/2}$ binding energy of 515.95 eV can also be seen.[8] Calculated from the ratio of Na, V, and the content of V^{4+}, x, is determined about 0.3.

Figure 2 illustrates that ribbon-like materials, with several to tens of micrometers in length, around hundreds of nanometers in width and tens of nanometers in thickness, are uniformly distributed, and the ribbons are isolated from each other with amorphous tropism. The rectangle-like cross section of the materials is clearly visible in the SEM image.

These nanoribbons can be peeled off from the glass substrate by ultrasonic and dispersed into some organic solvent. Figure 3a shows a TEM image of a nanoribbon's cleavage end. The SAED pattern (inset in Figure 3a) is well consistent with monoclinic

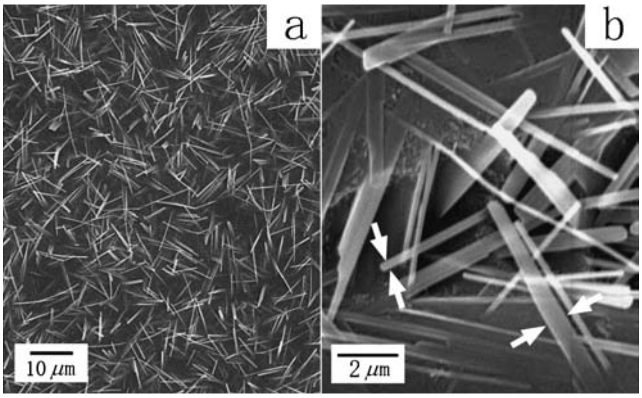

Figure 2. Typical SEM images of the $Na_{1+x}V_3O_8$ nanoribbon thin film. (a) Low magnification; (b) High magnification.

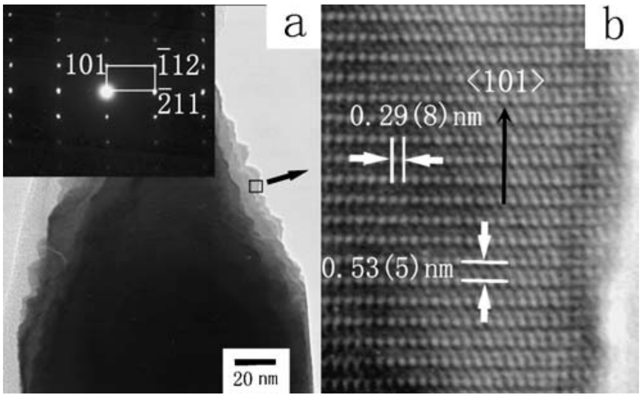

Figure 3. (a) A TEM image of a nanoribbon's cleavage end. The inset shows the corresponding SAED pattern. (b) An HRTEM image from the boxed region in (a) indicates the space of 0.53(5) nm between the (101) crystal planes with the growth direction ⟨101⟩ shown by the arrow.

phase $Na_5V_{12}O_{32}$ (JCPDS No. 24-1156, another chemical formula: $Na_{1.25}V_3O_8$) and indicates that the nanoribbons grow along the [101] direction. Figure 3b is a representative enlarged HRTEM image of the boxed region in Figure 3a, which shows the clearly resolved interplanar distances $d_{101} = 0.53(5)$ nm and $d_{\bar{2}11} = 0.29(8)$ nm.

Further experiments have been carried out for understanding the growth mechanism. When a very thin xerogel film (dipped once) was used and heated at 450 °C, only a thin *a* axis-oriented $NaVO_3$ film could be obtained (not shown in the paper). This implies that the films must be thick enough to obtain the nanoribbons and one layer of $NaVO_3$ may form at the interface of vanadium oxide film and the sodium silicate glass substrate in the case of thick films. The formation of $NaVO_3$ may be similar to Mekki's reports[9] that Na^+ could be removed from the silicate network through the formation of metavanadate units of $NaVO_3$ when adding V_2O_5 into the sodium silicate glasses. $NaVO_3$ can further react with vanadium oxide to form NaV_3O_8. And Na^+ ions can diffuse across the interfacial layer of $NaVO_3$ and the upper vanadium oxide layer. On the other hand, studying the films heated at different temperature shows that the film already turns into $Na_{1+x}V_3O_8$ film treated at 350 °C for about 2 hours but no ribbon-like structure exists. Heated at 400 °C for 2 hours the film contains a few ribbon-like materials. Heated at 450 °C for 30 min large amounts of ribbon-like materials appear on the film. It may be through a vapor-solid (VS) growth mechanism that $Na_{1+x}V_3O_8$ could grow into a ribbon-like structure with high length-to-width ratio. However, heated at 450 °C for more than 24 hours only a very thin *a* axis-oriented $NaVO_3$ film is obtained. This indicates that the $Na_{1+x}V_3O_8$ nanoribbons are somewhat unstable and subliming at 450 °C. So a competitive process of subliming and depositing of $Na_{1+x}V_3O_8$ may occur on the surface of the film at high enough temperature and the nanoribbons begin to form just below at 450 °C. Further studies will be summarized in our next paper.

In summary, $Na_{1+x}V_3O_8$ nanoribbon thin films have been obtained through a thermal treatment of the vanadium oxide films prepared on sodium silicate glass substrates at 450 °C. Sodium silicate glass serves as a kind of sodium source. Through XRD, XPS, and TEM characterization the compound was identified as $Na_{1+x}V_3O_8$ of high crytallinity. The growth direction of the nanoribbon was determined and the growth mechanism was discussed.

This work is supported by the National Key Basic Research "973" Plan of China (No. 2002CCC02700) and the Natural Science Foundation of China (No. 90306010 and 20371015).

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