Hydrothermal Synthesis of a Novel Sodium Vanadium Bronze with Single-crystalline Nanobelt-like Morphology

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A novel sodium vanadium bronze was successfully synthesized at 180 °C by a facile hydrothermal method. XRD, SEM, TEM, and XPS techniques were used to characterize the synthesized bronze. SEM and TEM analyses reveal that the bronze exhibits nanoblet-like morphology with an average width of ca. 55 nm and lengths from several to tens μm.

In the past decade, considerable efforts have produced significant advances in the fabrication of one-dimensional (1D) nanostructures. A variety of chemical methods, which are based on: i) use of the intrinsically anisotropic crystallographic structure of a solid to accomplish 1D growth; ii) introduction of a liquid–solid interface to reduce the symmetry of a seed; iii) use of various templates with 1D morphologies to direct the formation of 1D nanostructures; iv) use of supersaturation control to modify the growth habit of a seed; v) use of appropriate capping reagents to kinetically control the growth rates of various facets of a seed; and vi) self-assembly of 0D nanostructures, have been described for the production of wires, ribbons, corrugated wires, helical wires, tubules, etc. These 1D nanostructures have exhibited novel optical, electrical, magnetic, and mechanical properties that are very different from the bulk counterparts.[1]

Ternary vanadium oxide bronzes have exhibited versatile electronic, magnetic, and electrochemical properties as well as a wide range of applications for intercalating organic molecules, semiconductors, and active materials for batteries.[2] This leads to a large number of vanadium bronzes prepared by high-temperature solid state synthesis,[2f,3] sol–gel process,[4] hydrothermal synthesis,[5] and other soft chemical method.[6] Among these synthesis methods, soft chemical methods, like hydrothermal synthesis, often allow new and/or nanostructured materials to be produced that are often not able to be synthesized by using solid-state reaction at high temperature. Here, we report on hydrothermal synthesis of a novel sodium vanadium oxide bronze. This layered bronze exhibits single-crystalline nanobelt structure.

A typical synthesis for the bronze is as follows: 0.5 mmole of V_2O_5 powders and 0.5 mmole of $Na_2HPO_4 \cdot 12H_2O$ or $NaH_2PO_4 \cdot H_2O$ were loaded into a 20-mL capacity Teflon-lined stainless steel autoclave, and then 15 mL of deionized water was added into the Teflon-lined stainless steel autoclave. The autoclave containing the reactant solution was sealed and placed into a programmed furnace to be kept at 180 °C for 24 h, and then allowed to cool to room temperature. The resulting dark green precipitate was filtered and washed with deionized water and absolute ethanol to remove ions possibly remaining in the final product. The precipitate slurry was dried at 60 °C overnight in a vacuum oven.

The purity and crystallinity of the as-prepared product were determined using powder XRD (Bruker D8 Advance Power X-ray diffractometer). A typical XRD pattern of as-synthesized product is shown in Figure 1. As indexed in Figure 1, the diffraction peaks clearly exhibit pronounced 00*l* reflections, displaying typical 1D periodic lamellar ordering and a basal interlamellar distance of 10.58 Å. We checked the standard JCPDS cards for sodium vanadium bronzes or vanadium oxides, but could not find a matching card for the XRD pattern of the synthesized compound. However, two similar XRD patterns were found in the literature.[6,7] One is layered $V_2O_5 \cdot nH_2O$ with a basal interlamellar spacing of 11.5 Å.[7] As our product exhibits dark green in color, whereas reported $V_2O_5 \cdot nH_2O$ are red-brown. It appears that the synthesized product cannot be assigned as $V_2O_5 \cdot nH_2O$. The other is layered $Na_{0.33}V_2O_5 \cdot 1.3H_2O$,[6] which has a basal interlamellar spacing of 10.84 Å, and this compound has similar color to our product. Thus, the synthesized product may be isostructural vanadium bronze with layered $Na_{0.33}V_2O_5 \cdot 1.3H_2O$.

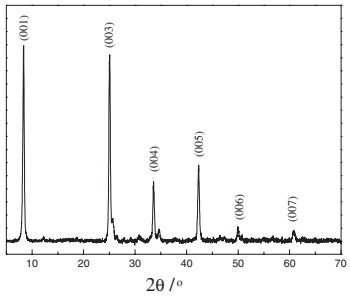

Figure 1. Typical XRD pattern of the synthesized bronze.

Furthermore, XPS analyses (VEGSCALAB MKII X-ray photoelectron spectrometer with nonmonochromatized Mg Kα radiation as the excitation source) provided additional insight into the composition and vanadium atom valence state of the synthesized bronze. The XPS survey spectrum (Figure 2a) reveals that this dark green precipitate consists of sodium, vanadium, and oxygen. No phosphorus element can be detected. The atomic ratio of sodium to vanadium to oxygen is 1:6:16, close to the stoichiometry of $Na_{0.33}V_2O_5 \cdot 1.3H_2O$ bronze. The small difference ($\Delta d = 0.26$ Å) between the basal interlamellar spacings can be attributed to the difference in the amount of interlayered water. Thus, the present bronze can be depicted as $Na_{0.33}V_2O_5 \cdot nH_2O$ ($n < 1.3$). The high resolution XPS region spectrum (Figure 2b) further confirms that the bronze consists of mixed valance state vanadium atoms, and V^{5+} should be a major part in this bronze. The peaks centered at 517.30, 524.33, and 530.05 eV correspond to V2p$_{3/2}$, V2p$_{1/2}$, and O1s, respectively. These binding energies represent the V^{5+} and O^{2-} valence

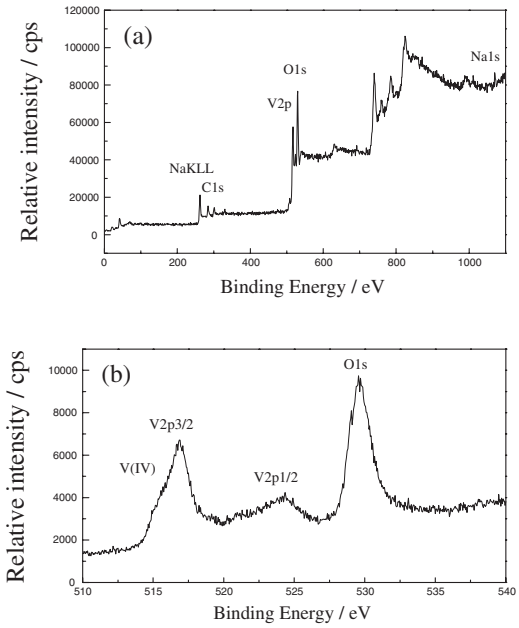

Figure 2. XPS survey spectrum (a) and V2p to O1s region spectrum (b) of the as-prepared bronze.

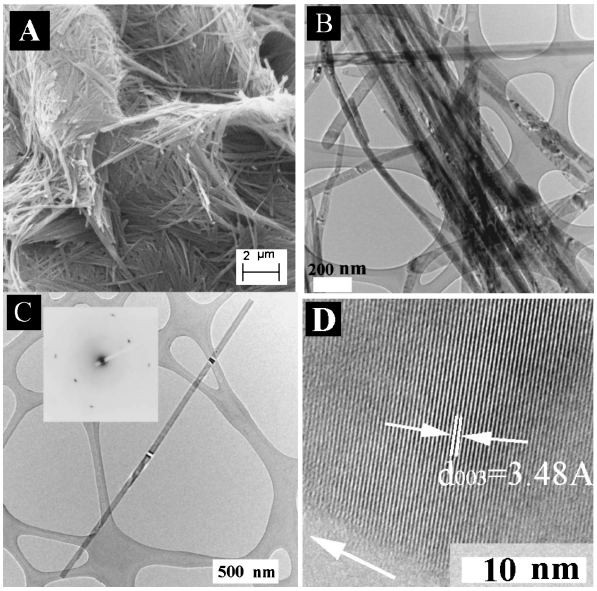

Figure 3. Typical SEM (A) and TEM (B, C) and HRTEM (D) images of the synthesized bronze, the inset is SAED pattern of the single bronze.

states, whereas a week intensity peak centered at 515.34 eV indicates the existence of a small amount of V^{4+} in the bronze.[2f,8]

The size, morphology and structure of the product were also examined by SEM (LEO 1450VP) and TEM (JEOL JEM-2010F field emission transmission electron microscope). Figure 3a is a representative SEM image. It clearly shows that the sample is in form of nanobelt-like morphology, which is different from the plate-like $Na_{0.33}V_2O_5 \cdot 1.3H_2O$ prepared by the refluxing method.[6] TEM observation found that the nanobelts are uniform with an average width of ca. 55 nm and lengths from several to tens μm, as shown in Figure 3b. Selected area electron diffraction (SAED) analyses taken from different parts of a single nanobelt give similar ED patterns, revealing the single crystalline nature of the nanobelts. The typical SAED pattern is presented in inset of Figure 3c. HRTEM observations for individual nanobelt provide additional information on the structure of these materials. The HRTEM image (Figure 3d) taken from a single nanobelt (Figure 3c) shows the clearly resolved lattice fringes, corresponding to the (003) planes of the $Na_{0.33}V_2O_5 \cdot nH_2O$. These substantiate that the nanobelts are single-crystalline.

Although the exact mechanism for the formation of these uniform nanobelts is still unclear, we believe that the intrinsical layered structure of the bronze may facilitate 1D nanobelt formation. It is well known that many 1D nanostructures (nanotubes or nanorods) have been synthesized from the layered structures.[9]

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