



Effect of precursor morphology on the hydrothermal synthesis of nanostructured potassium tungsten oxide

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ABSTRACT

$K_2W_4O_{13}$ with nanorod and nanowire structures were selectively-prepared by the alteration of starting precursors under hydrothermal treatment at 180 °C for 6 h in the presence of K_2SO_4 . The uniform $K_2W_4O_{13}$ nanowires with a diameter of ~10 nm and a length in a range of hundreds nanometers were obtained when the amorphous-like $WO_3 \cdot 0.33H_2O$ precipitate was employed as the precursor, while non-uniform $K_2W_4O_{13}$ nanorods with diameter in a range of ~10 nm and diverse length ranging from tens to few hundreds nm were obtained when the well-crystalline, platelet $WO_3 \cdot H_2O$ precursor was employed. The experimental finding is discussed based on solubility of the two precursors, which led to different crystallization behavior during the hydrothermal treatment.

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1. Introduction

The discovery of carbon nanotubes (CNTs) in 1991 [1] has opened up the research interest for low-dimensional nanostructure not only the CNTs but other materials as well. A number of nanostructural inorganic materials have been synthesized because of their superior mechanical properties, unique electronic behaviors and high potential in making nanodevices for an advanced technology. For these reasons, the synthetic methods of one-dimensional nanostructures such as nanorods, nanowires, nanotubes and nanobelts, have expanded rapidly.

Potassium tungsten bronzes (K_xWO_3 , $0 < x < 1$) are one type of non-stoichiometric tungsten bronzes that are formed when potassium atoms partially occupy tunnels in the WO_3 host framework formed by corner sharing of WO_6 octahedra [2,3]. Similar to other tungsten bronzes, the K_xWO_3 exhibit wide range of electronic properties and thus have been studied for many applications such as electrodes in electrochemical device, rechargeable lithium battery and solar filter [4–6].

Typically, the one-dimensional K_xWO_3 are synthesized by high-temperature reaction such as a vapor deposition, vapor-transport reaction, vapor–solid or vapor–liquid–solid growth and electrolysis which require the operating temperature in a range of 450–950 °C depending on the methods employed [7–11]. The cost for material preparation by these methods can be expensive as the operation is conducted at high temperature and under vacuum for some processes. In comparison, chemical methods provide more advantages

in large-scaled synthesis, simple operation and low-cost apparatus. Among those chemical methods, a hydrothermal has been the most widely employed because its high pressure and temperature promotes a crystal growth in a certain direction leading to low-dimensional morphology of the product. Like other chemical processes, phase, size and shape of the product are dependent on the synthesis condition such as reactant concentration, pH and temperature.

Despite a lot of studies reported on the preparation of tungsten oxide nanorods/nanowires under hydrothermal condition, to our knowledge the effect of precursor having similar chemical composition but different particle morphology on crystallization behavior has never been studied. Thus, the objective of this present work is to investigate the effect of precursor for hydrothermal treatment on the crystallization and morphology of the product.

2. Experimental

2.1. Preparation of $WO_3 \cdot 0.33H_2O$ and $WO_3 \cdot H_2O$ precursors

A $WO_3 \cdot 0.33H_2O$ precursor was prepared by precipitation reaction taking place at room temperature of a tungstate salt and hydrochloric acid as follows: 1 g of ammonium tungstate paraperhydrate ($(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$, WAKO) was dissolved in 30 mL of deionized water. Then, 5 mL of 3 M hydrochloric acid (HCl, AR grade, 37%, Merck) was added dropwise to the tungstate solution under stirring. The resulting mixture was kept stirring for 30 min at room temperature. The precipitate was washed thoroughly with deionized water and then was separated from the supernatant by centrifugation.

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A $\text{WO}_3 \cdot \text{H}_2\text{O}$ precursor was prepared by precipitation reaction of the tungstate salt and nitric acid following the previous study [12]. To explain briefly, an acidic aqueous solution of 10 mM $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$ prepared by dissolving $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$ in 2 M nitric acid (HNO_3 , AR grade, 65%, Scharlau) was slowly heated to 80 °C under vigorous stirring. The acidic tungstate solution was aged at 80 °C for 1 h. The resulting precipitate was thoroughly washed with deionized water and then was separated from the supernatant by centrifugation.

2.2. Preparation of nanostructured $\text{K}_2\text{W}_4\text{O}_{13}$

For a typical synthesis, 1 g of the hydrous tungsten oxide precursor was dispersed in 100 mL of deionized water. Then, 60 g of potassium sulfate (K_2SO_4 , 99.0%, Ajax Finechem) was added. After stirring for 30 min, the mixture was transferred into a 450-mL stainless steel vessel. The hydrothermal treatment was conducted in a pressure reactor (Parr Instrument) at 180 °C for 6 h. After cooling down to room temperature, the final product was washed with deionized water repeatedly, separated by means of vacuum filtration using a 0.1- μm cellulose membrane and finally dried at 105 °C overnight.

2.3. Characterizations

Crystal structure was identified by using an X-ray diffractometer (XRD, JDX 3530). Crystal morphology and microstructure were investigated by using a transmission electron microscope (TEM, JEM 2010). Photoluminescence (PL) study was carried out at room temperature by using a fluorescence spectrometer (LS 55, Perkin-Elmer, Waltham, USA) using a Xenon lamp as the excitation source at an excitation wavelength of 275 nm.

3. Results and discussion

3.1. Preparation of $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ and $\text{WO}_3 \cdot \text{H}_2\text{O}$ precursors

For the precursor prepared by precipitating reaction of the $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$ and HCl, it was observed that a pale yellow precipitate was formed instantly after HCl was added into the tungstate solution. Obviously, fast precipitation took place in this system. On the other hand, much slower precipitation was observed for the precipitate prepared according to the latter method which involved dissolving $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$ in mild HNO_3 solution followed by aging at 80 °C to promote the hydrolysis and homogeneous precipitation. A pale yellow precipitate was observed after aging the solution for ~ 5 min. The difference of precipitation behavior can be attributed to a different method of mixing the tungstate and acid solutions in addition to different type of acid employed. By dropping 3 M HCl solution into the tungstate solution, it was most likely that local inhomogeneity took place although the solution was vigorously stirred. This type of mixing led to fast precipitation, particularly in the region where the acid was introduced because it became localized supersaturation. In contrast, by dissolving the tungstate salt in HNO_3 solution at room temperature before slowly brought to 80 °C, more homogeneous mixing and therefore more complete hydrolysis reaction was achieved uniformly throughout the entire solution volume.

Fig. 1 shows XRD patterns of the precipitates prepared by dropping HCl into the tungstate solution (Fig. 1(a)) and by dissolving the tungstate salt in mild HNO_3 solution followed by aging at 80 °C (Fig. 1(b)). The XRD pattern of the precipitate prepared by the former method has weak reflection peaks and strong background indicating poor crystallinity. Its reflection peaks correspond to those of an orthorhombic tungsten oxide hydrate,

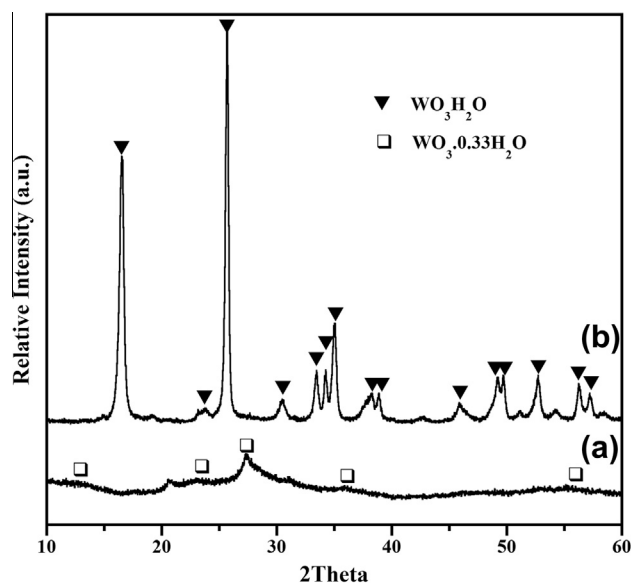


Fig. 1. XRD patterns of the precursors prepared by (a) dropping HCl into the tungstate solution, and (b) dissolving the tungstate salt in mild HNO_3 solution followed by aging at 80 °C.

$\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ (JCPDS#54-1012). In contrast, the XRD pattern of the precipitate prepared by the latter method consists of well-defined reflections with high relative intensities indicating high crystallinity. This precipitate was identified as orthorhombic tungstate, $\text{WO}_3 \cdot \text{H}_2\text{O}$ (JCPDS#43-0679). Note that the difference in a number of water molecule associated with the WO_3 structure may be resulting from a different acidification behavior of the paratungstate anion precursor in the acidic solution, and subsequent condensation to form the hydrolyzed species such as $\text{W}_6\text{O}_{20}(\text{OH})^{5-}$, $\text{W}_{12}\text{O}_{39}^{6-}$, $\text{W}_{12}\text{O}_{38}(\text{OH})_2^{6-}$ or $\text{W}_{12}\text{O}_{41}^{10-}$ [13]. Stability of these species is sensitive to the solution pH.

Fig. 2 shows TEM micrographs of the $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ and $\text{WO}_3 \cdot \text{H}_2\text{O}$ precursors. A distinct difference in morphology is clearly observed. The $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ precursor (Fig. 2(a)) is in the form of very fine, irregular-shaped particles, and an amorphous feature is observed at large extent. Its selected-area electron diffraction pattern (SAED, inset) consists of very diffused, broad pattern indicating amorphous structure. On the other hand, the $\text{WO}_3 \cdot \text{H}_2\text{O}$ (Fig. 2(b)) is seen as well-defined platelet particle with the size of ~ 70 – 100 nm wide and ~ 20 -nm thick. Its SAED pattern consists of discrete rings of crystalline structure. The result of TEM observation is consistent with the result of XRD analysis that the precipitate prepared by aging the acidic tungstate solution is much more well-crystalline than the one prepared by direct mixing of the HCl in the tungstate solution because of much slower hydrolysis reaction attained in the former condition.

3.2. Preparation of nanostructured $\text{K}_2\text{W}_4\text{O}_{13}$

Fig. 3 shows XRD patterns of the hydrothermal products obtained by hydrothermal treatment of the $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ and $\text{WO}_3 \cdot \text{H}_2\text{O}$ precursors. The two products show the same diffraction patterns regardless of the precursor employed, indicating the same crystal structure. The XRD patterns consist of sharp reflections at $2\theta = 23.1^\circ$ and 47.2° that could be best matched with the standard pattern of a hexagonal $\text{K}_2\text{W}_4\text{O}_{13}$ (JCPDS No. 20-0942). Relative intensity of the (001) peak is highest, instead of the (320) for the standard powder diffraction, indicating a preferred orientation along the (001) direction. In addition, very broad, amorphous-like feature in the range of ~ 25 – 40° is observed. The patterns

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