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Hydrothermal Synthesis of Tungsten Oxide Nanowires: Effect of Precursor's Condition

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Abstract

Hexagonal WO_3 nanowires have been hydrothermally fabricated in the presence of K_2SO_4 using tungstic acid hydrate as a precursor. It is evident that the K_2SO_4 played a crucial role in the formation of the uniform hexagonal WO_3 nanowires with an average diameter of 7 nm and length up to several hundreds nanometers. Based on comparative experiments under different precursor condition, it was found that residual cation and anion of the starting materials and also pH of the precursor's condition had strong effects on crystal structure and morphology of the resulting products. In spite of the excess amount of K_2SO_4 used, platelets of WO_3 and triclinic crystallites were formed as a mixture indicating that the residual ions present in the precursor's condition controlled the reaction route during hydrothermal process of the tungstic acid hydrate.

Keywords: Tungsten oxide, Nanowire, Hexagonal tungsten oxide, Hydrothermal process

1. Introduction

Among a number of metal oxides, tungsten oxide (WO_3) is of intense interest due to its well- known applications in electrochromic devices [1], gas sensors [2] and catalysts [3]. For these applications, the morphological characteristics of the materials such as grain size or shape are very important and strongly depend on preparation method. Of special interest is a preparation of nanostructured WO_3 since nano-scaled particles exhibit novel properties thanks to the large number of surface atoms and/or three-dimensional confinement of electrons.

The studies in recent years have shown the possibility of functional devices from one-dimensional materials. The design and performance of these functional devices are based on the electrical properties of one-dimensional materials. Therefore, more recent research on WO_3 nanostructures (nanowires, nanobelts and nanorods) has been investigated. Meanwhile, with the development of one-dimensional nanostructures, dimensionality and size of the materials have also been regarded as crucial factors that may bring some novel properties. Subsequently, the synthesis of WO_3 with well-controlled dimensionality, size, as well as crystal structure has become the subject of great attention.

Many efforts have been focused on the exploration of new synthetic routes for the synthesis of WO_3 nanowires/nanorods, including chemical vapor deposition [4], electrochemically etching method [5], template directed synthesis [6], solution-based colloid approach [7] and hydrothermal reaction [8]. However, in most cases the hydrothermal process provides significant advantages in the preparation of monodispersed nanoparticles with a control over size and morphology [9], low processing temperature, and easy synthesis.

In this present work, WO_3 nanowires were prepared by treating (hydrous) tungsten oxide precursor in the present of potassium sulfate (K_2SO_4) salt under hydrothermal condition. The effects of pH of the reaction system, ammonium (NH_4^+) and chlorine (Cl^-) ions present and potassium sulfate (K_2SO_4) on crystal structure and morphology of the product were also investigated.

2. Materials and Methods

2.1 Materials

Ammonium tungstate para pentahydrate ($(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$, Wako) and hydrochloric acid (HCl, Merck) were employed for the preparation of tungstic acid hydrate precursor. The K_2SO_4 (Univar) was employed in the hydrothermal reaction.

2.2 Sample Preparation

WO_3 nanowires were synthesized via hydrothermal process by using precipitated tungstic acid hydrate gel as the precursor. The tungstic acid hydrate was prepared according to the scheme in Fig. 1. In method 1, the tungstic acid hydrate precipitate was separated by centrifugation to NH_4^+ and Cl^- in the starting precursor for hydrothermal synthesis.

The mixed slurries were transferred into a Teflon-lined stainless steel autoclave, and a hydrothermal treatment was carried out at 180 °C for 12 h. The final products were washed with de-ionized water and ethanol repeatedly to remove sulfate ions (SO_4^{2-}) and other remnants and finally dried at 100 °C.

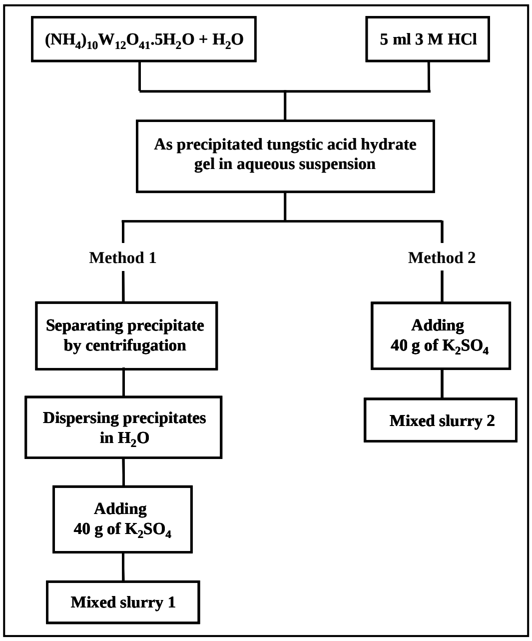


Fig. 1 Steps in preparation of tungstic acid hydrate, the precursor used to fabricate WO_3 nanowires.

2.3 Characterization

X-ray diffraction (XRD) analysis was performed using a JEOL JDX 3530 diffractometer with Cu*Kα* radiation. The sizes and shapes of the nanowires were observed by a transmission electron microscope (JEOL, JEM-2010) operated at 200 kV.

3. Results and Discussion

XRD pattern of the hydrothermal product derived from method 1 is shown in Fig. 2. All the diffraction peaks are indexed to pure hexagonal WO_3 (JCPDS# 33-1387). The intensity of (001) peak increased distinctly in the obtained XRD pattern, implying the preferential growth along the [001] direction. This supposition can be confirmed by high-resolution TEM (HRTEM) image.

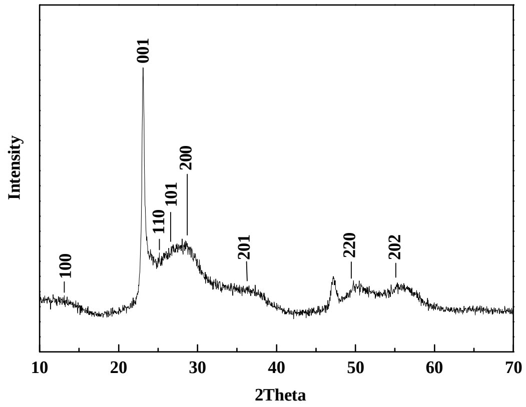
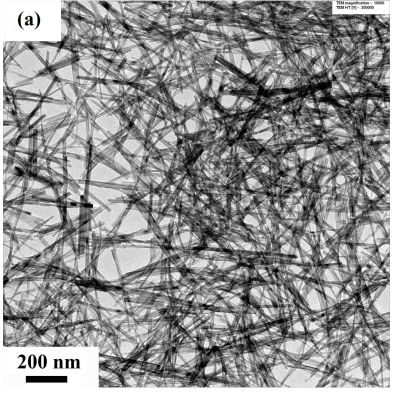


Fig. 2 XRD pattern of hexagonal WO_3 resulted from hydrothermal treatment of mixed slurry 1.

The morphology of the product was observed using low-magnification TEM. The overall morphology of the sample is shown in Fig. 3(a), which shows that the product consists of a large amount of uniform nanowires with an average diameter of 7 nm and length from 100 nm to several hundred nanometers. It was also found that these nanowires had a uniform diameter along their entire length and a narrow diameter distribution.

To have further insight into the structure of hexagonal WO_3 nanostructures, an individual nanowire was analyzed by HRTEM measurement. As shown in Fig. 3(b), the spacings of the lattice fringes were found to be 0.393 nm, which correspond to the (001) plane of hexagonal WO_3 crystal. This result confirms the growth of the nanowires along the [001] direction.



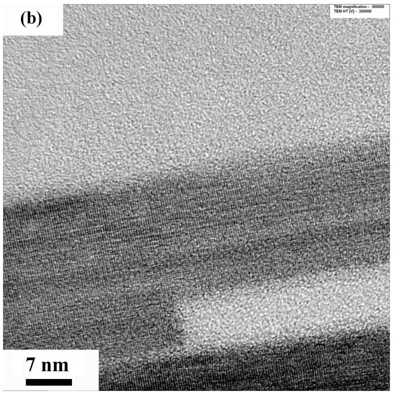


Fig. 3 (a) TEM image of hexagonal WO_3 nanowires; (b) HRTEM image of an individual nanowire with [001] growth direction.

In a comparative experiment, preparation of WO_3 nanowires by using method 2 was carried out to investigate the influential factors on the growth of WO_3 nanowires. It was found that the pH value, as well as NH_4^+ and Cl^- present in the system, had dramatic effects on the crystal structure and morphology of the final product. When the experiment was performed in the reaction system of which pH value was 1.8 (in mixed slurry 1), the uniform hexagonal WO_3 nanowires were obtained. With a decrease of pH value to lower than 0.5 (in mixed slurry 2), the products identified by XRD analysis (Fig. 4) as hexagonal WO_3 (JCPDS# 33-1387), triclinic WO_3 (JCPDS# 20-1323), K_2WO_4 (JCPDS# 24-0905) and $K_2W_6O_{19}$ (JCPDS# 31-1115) were obtained. Their morphologies are shown in Fig. 5. Based on the result of the previous experiment, the nanowire was hexagonal WO_3, while platelet nanoparticles were triclinic WO_3, K_2WO_4 and $K_2W_6O_{19}$. This result is in good agreement with the result reported by Gu *et. al*. [8].

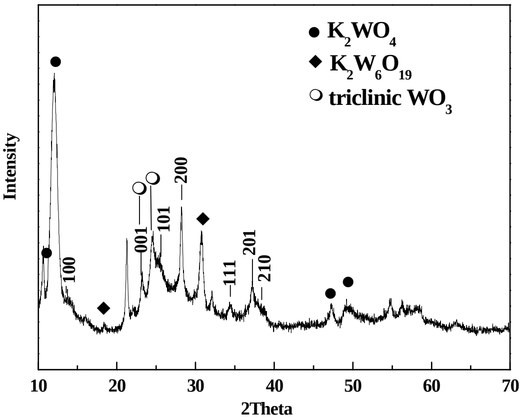


Fig.4 XRD pattern of the products resulted from hydrothermal treatment of mixed slurry 2. The indexed peaks are hexagonal WO_3.

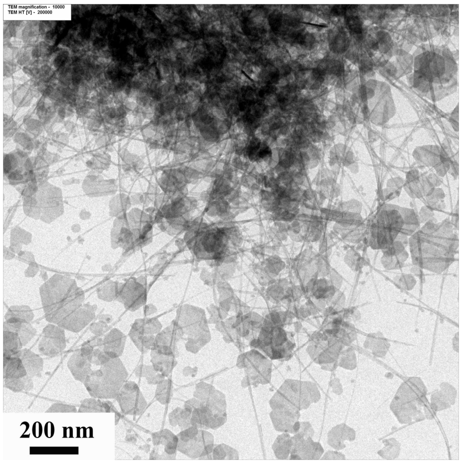


Fig. 5 TEM image of the products resulted from hydrothermal treatment of mixed slurry 2.

The experiment in method 1 was also conducted in the absence of the K_2SO_4. TEM image of the product is shown in Fig. 6. Although the same pH value of 1.8 was employed, the product was irregular in shape which was significantly different from the product prepared under the same condition but in the presence of the K_2SO_4 (nanowire, Fig. 3). Therefore, it is evident that the K^+ and/or SO_4^{2-} played a vital role in controlling the one-dimentional growth of the final product. The detail of the effect of these ions on the formation of nanowire structure is not well understood. However, it is believed that the SO_4^{2-} may adsorb onto the crystal faces parallel to the c-axis ([001] direction) of the WO_3 nanocrystal, therefore, inhibiting the growth of these faces and leading to preferential growth along the c axis [10].

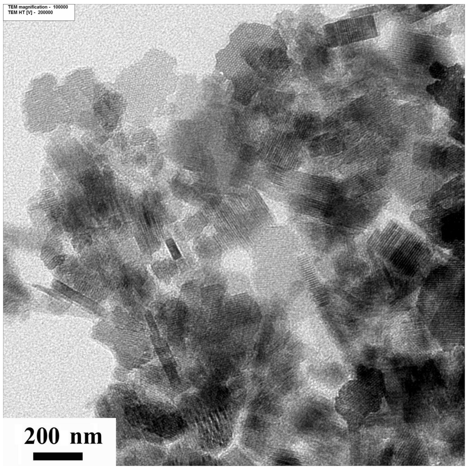


Fig. 6 TEM image of WO_3 nanoparticles resulted from hydrothermal treatment of mixed slurry 1 without K_2SO_4.

Based on the experimental results, it is clear that both pH and the SO_4^{2-} have strong influence on the crystal structure and morphology of the products. In case of the products resulting from preparation method 2, the effect of pH seemed to be more pronounced than the effect of SO_4^{2-}.

4. Conclusions

The WO_3 nanowires were synthesized using the tungstic acid hydrate as a precursor for hydrothermal reaction. It was found that the conditions in which tungstic acid hydrate precursor was present strongly affected crystal structure and morphology of the final hydrothermal products. The K_2SO_4 was proved to be a crucial factor that promoted the formation of a nanowire structure, while the pH of precursor as well as the presence of residual cation and anion of the starting materials also determined the morphology and crystal structure of the final product.

5. Acknowledgement

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6. References

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