O U R N A L O F

Ceramic Processing Research

Single-crystalline tungsten oxide nanoplates

Deliang Chen^{a,*}, Hailong Wang^a, Rui Zhang^a, Lian Gao^b, Yoshiyuki Sugahara^c and Atsuo Yasumori^d

^aSchool of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China

^bThe State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China

^cDepartment of Applied Chemistry, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan

^dDepartment of Materials Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba 278-8510, Japan

Tungsten oxide nanocrystals are important semiconductor materials with a suitable energy band gap (*ca.* 2.5 eV) for visible-light utilization. Though there are a great amount of reports on the synthesis of WO₃ nanocrystals, no effective routes to two-dimensional (2D) WO₃ nanocrystals have been reported. We here developed a novel and efficient route to synthesize free-standing single-crystalline WO₃ nanoplates on a large scale and in a repeatable way. The proposed route involved a rational transformation of tungstate-based inorganic-organic hybrid nanobelts to single-crystalline WO₃ · H₂O nanoplates, and then to single-crystalline monoclinic WO₃ nanoplates with an inhibited crystal growth direction of [004]. The sizes of the as-obtained WO₃ nanoplates are (200-500) nm × (10-30) nm. The WO₃ nanoplates as-synthesized have high specific surface areas (up to 180 m² g⁻¹) and showed remarkably enhanced visible-light photocatalytic properties in water splitting for O₂ generation.

Key words: Tungsten oxide nanoplates, Tungstate nanoplates, Two-dimensional nanostructures, Inorganic-organic hybrids, Layered compounds.

Introduction

Low-dimensional nanocrystals have unique shape- and size-dependent properties and have attracted an increasing interest from chemists and materials scientists [1-3]. In the past decades, a great number of routes were developed to synthesize various nanocrystals with low-dimensional morphologies, including zero-dimensional (0D) quantum dots [4], one-dimensional (1D) nanowires and nanorods [5, 6] and two-dimensional (2D) nanosheets and nanodisks [7, 8].

Tungsten oxide nanocrystals have unique electro-chromic, field-emission, photoluminescent, and photocatalytical properties, offering important applications in smart windows, catalysis and as sensors [9, 10]. Tungsten oxide thin films, mesostructures, nanoparticles, nanorods, nanoneedles, nanowires and nanotubes were reported by various research groups [11-13]. Recently, WO₃ nanodisk films and hexagonal WO₃ nanosheets were also reported [14, 15]. No effective routes, however, towards free-standing monoclinic 2D WO₃ nanocrystals are available till now. The proceeding introduces an efficient route to large-scale synthesis of free-standing single-crystalline WO₃ nanoplates [16, 17].

Tel : +86-371-63818662

Experimental

The protonated phase of $H_2W_2O_7 \cdot xH_2O$ (0.8 $\leq x \leq 4.5$) was derived by treating $Bi_2W_2O_9$ powders in a hydrogen chloride aqueous solution via a selective leaching process [18]. The tungstate-based inorganic-organic hybrid nanobelts were synthesized according to the process reported previously [19], in which the $H_2W_2O_7 \cdot xH_2O$ as-obtained was allowed to react with n-octylamine in a nonpolar media of heptane. The molar ratio of *n*-alkylamine to $H_2W_2O_7 \cdot xH_2O$ was maintained at *ca*. 20-40 and the volume ratio of heptane to n-alkylamine was maintained at ca. 2-5 [20]. The tungstate-based inorganic-organic hybrid nanobelts were used as the precursor to fabricate H₂WO₄ and WO₃ nanoplates through a rational conversion process [16]. The tungstate-based inorganic-organic hybrid belts assynthesized were dispersed in a HNO₃ aqueous solution (20-30 mass%) and kept for a reaction time of more than 2 days under a magnetic stirring condition at room temperature. The yellow solids collected were washed with H₂O and ethanol before drying at 120 °C. The 120 °C-dried product was H₂WO₄ nanoplates. The 120 °C-dried product was then calcined in air at 250-450 °C for 2 h (heating rate: 2 K minute⁻¹), and the pale yellow product obtained was WO₃ nanoplates [17].

The techniques of scanning electron microscopy (SEM) (JEOL JSM-5600), field-emission scanning electron microscopy (FE-SEM) (Hitachi S-4500S), transmission electron microscopy (TEM) (JEOL JEM-2100F) and atomic force microscopy (AFM) (Nanosurf Easyscan) were used

^{*}Corresponding author:

Fax: +86-371-63818662

E-mail: dlchennano@hotmail.com; dlchen@zzu.edu.cn

Single-crystalline tungsten oxide nanoplates

to characterize the microstructures of the tungstate-based inorganic-organic hybrid precursors and their derived products. The phases and compositions of the products were examined by X-ray diffraction (XRD) (Rigaku RINT-2500), thermogravimetry (TG) (Perkin-Elmer TGA-7), Fourier transform infrared spectroscopy (FT-IR) (Jasco FT-IR 460 Plus), and CHN analysis (Perkin-Elmer PE2400II). The specific surface areas of the products were measured by N_2 adsorption-desorption (Quantachrome Autosorb1).

Results and Discussion

A SEM image of the tungstate-based inorganic-organic hybrids derived by a reaction between $H_2W_2O_7$ · xH_2O and *n*-octylamine in heptane is shown in Fig. 1. As Fig. 1 shows, the typical morphologies are 1D belt-like structures with lengths larger than 10 µm. Most of these 1D belts



Fig. 1. SEM image of tungstate-based inorganic-organic hybrid nanobelts.



Fig. 2. AFM image of a tungstate-based inorganic-organic hybrid nanobelt.



Fig. 3. XRD patterns of (a) tungstate-based hybrid belts, (b) H_2WO_4 and (c) WO_3 nanoplates.

are half-scrolled along their lengths. Fig. 2a shows an AFM image of an individual tungstate-based inorganicorganic hybrid belt. The thickness of the belt is 20-35 nm and its width is 400-800 nm, as shown as Figs. 2b and c.

Fig. 3a shows a typical XRD pattern of the tungstatebased inorganic-organic hybrid nanobelts. There are a series of reflections located in the low 20 angle region. These sharp peaks can be indexed as (00*l*) reflections from a highly ordered lamellar structure [19]. The interlayer distance of the hybrid belts is estimated to be ca. 2.56(2) nm according to the (00*l*) reflections in Fig. 3a. According to our previous results [19, 20], the hybrid nanobelts consist of alternant inorganic layers (O-W-O)



Fig. 4. FE-SEM image of H_2WO_4 nanoplates derived from tungstate-based inorganic-organic hybrid belts.



Fig. 5. AFM image of the H₂WO₄ nanoplates as-obtained.

and organic layers (*n*-octylammonium ions). The mass loss of the inorganic-organic hybrid between room temperature and 873 K was 52.9%. CHN analysis indicated the amounts of C, H and N in the hybrid were 42.48, 8.57 and 6.16%, respectively. The composition of the tungstate-based inorganic-organic hybrid was close to $(C_8N_{17}NH_3)_2WO_4$ [16, 19].

After the organic species of the tungstate-based inorganicorganic hybrid nanobelts were removed by HNO₃ oxidization, an inorganic product of tungstate was obtained. Fig. 3b shows the XRD pattern of the inorganic product as-obtained. It can be readily indexed to the phase of orthorhombic H₂WO₄ (JCPDS No. 43-0679). Fig. 4 shows a typical FE-SEM image of the as-obtained H₂WO₄ powders. It is clear that the H₂WO₄ as-obtained possesses a plate-like morphology. The areas of the plates are ranged in (200-500) nm × (200-500) nm. Fig. 5 shows an AFM image of the H₂WO₄ nanoplates as-obtained, the thicknesses of which are 10-30, as shown in Fig. 5b.

The crystal water of H_2WO_4 nanoplates can be removed by calcination at a low temperature of 250-450 °C [17]. Fig. 3c shows the XRD pattern of the product derived by calcining the H_2WO_4 nanoplates at 450 °C for 2 h. It can be indexed to monoclinic WO₃ according to the literature data (JCPDS No. 43-1035). The FE-SEM image of the WO₃ as-obtained is shown in Fig. 6. As shown as Fig. 6, the calcined product of WO₃ phase presents a 2D plate-like morphology with



Fig. 6. FE-SEM image of WO_3 nanoplates derived from the H_2WO_4 nanoplates as-obtained.

sizes of (200-500) nm × (200-500) nm × (10-30) nm, which are similar to those of their precursors of H_2WO_4 nanoplates. It suggests that the 2D platelike morphology is retained during the conversion from H_2WO_4 to WO_3 nanocrystals.

Fig. 7a shows a typical TEM image of the H_2WO_4 nanocrystals as-obtained. They are quadrangular nanoplates, the edge lengths of which are 200-500 nm. The selected area electron diffraction (SAED) pattern of an individual nanoplate, as shown in the inset of Fig. 7a, is a set of ordered diffraction lattices, which can be indexed to orthorhombic H₂WO₄ with a single-crystalline structure along the [020] zone axis. The inhibited growth direction of the H_2WO_4 nanoplate can be determined to be [020], because the H₂WO₄ nanoplate with a large area lies along the Cu grid. A typical HR-TEM image of the H₂WO₄ nanoplate as-obtained is shown in Fig. 7b. Its clear crystal lattice indicates that the H₂WO₄ nanoplate is singlecrystalline, agreeing with the result of the SAED pattern. Fig. 7c shows a TEM image of the WO₃ nanocrystals asobtained derived from the H₂WO₄ nanoplates. As the Fig. 7c shows, the product possesses a plate-like morphology, which is very similar to that of the precursor of the H₂WO₄ nanoplates. The ordered diffraction lattice of a SAED pattern in the inset of Fig. 7c indicates that the WO₃ nanoplate also has a single-crystalline structure with a zone axis of [020]. Fig. 7d gives a HR-TEM image of the WO3 nanoplate. The clear 2D crystal lattice suggests that the WO₃ nanoplate is a perfect single crystal. The interplanar distances of 0.364 nm and 0.376 nm ought to be attributed to (200) and (020) crystal planes, respectively. Considering the results of the SAED pattern and HR-TEM image, the inhibited growth direction of the WO₃ nanoplates obtained can be determined to be [004].

Orthorhombic H_2WO_4 consists of layers of $[WO_6]$ octahedra, and the normal direction of the layers of $[WO_6]$ octahedra is the crystal direction of [020] [16]. H_2WO_4 commonly forms plate-like nanocrystals with an inhibited growth direction of [020] because of its layered structure



Fig. 7. (a,c) TEM and (b,d) HRTEM images of (a,b) H_2WO_4 and (c,d) WO_3 nanoplates (the insets are the SAED patterns of the corresponding individual nanoplates).

along (020) crystal planes. Monoclinic WO₃, on the other hand, is of a distorted ReO₃ structure with corner-sharing distorted and tilted [WO₆] octahedral, and it is usually difficult to form shape-anisotropic crystals [16]. In this study, the successful achievement of plate-like WO₃ nanocrystals with an inhibited growth direction of [004] is predominantly attributed to the preservation of the 2D plate-like shapes in the conversion of H₂WO₄ nanoplates into monoclinic WO₃ nanocrystals [16, 17].

The WO₃ nanoplates as-obtained are loose aggregates and easily redispersed in liquid solutions. The BET measurements indicated the WO₃ nanoplates as-synthesized have a super high specific surface area (up to 180 m² g⁻¹), higher than that of the corresponding mesostructural WO₃ ever reported [16, 17]. The WO₃ nanoplates have an energy band gap of ca. 2.66 eV, and showed a remarkably enhanced photocatalytical property in water splitting for oxygen generation driven by visible light [16, 17].

Conclusions

Single-crystalline monoclinic 2D WO₃ nanoplates were successfully synthesized for the first time via an inprocess product of H_2WO_4 nanoplates, which were derived from tungstate-based inorganic-organic hybrid nanobelts. The 2D WO₃ nanoplates as-obtained took on an inhibited growth direction of [004]. The single-crystalline WO₃ nanoplates with high specific surface areas are expected to have enhanced performance in visible-light photocatalysis and as chemical sensors.

Acknowledgements

This work was supported by the Introduced Talent Project of Zhengzhou University and the 21st Century COE Program. D. Chen acknowledges Dr. Yan Shan (Qingdao University of Science and Technology), Dr. Songwang Yang (Shanghai Institute of Ceramics), Dr. Seiichi Tahara (Waseda University), Mr. Kazutoshi Sekiguchi (Tokyo University of Science), Mr. Ryota Goto (Waseda University), and Prof. Dr. Erika Kalman (Hungarian Academy of Science) for their kind help in some of the experiments.

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