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Morphology-controlled synthesis of tungsten oxide hydrates crystallites via a facile, additive-free hydrothermal process

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Abstract

Tungsten oxide hydrates crystallites with a diversity of morphologies were successfully synthesized by employing peroxo-polytungstic acid as the precursor via a facile and additive-free hydrothermal process. The crystal structure, morphology and orientation relationship were investigated by using X-ray diffractometer, scanning electron microscopy and transmission electron microscopy. Results show that with the increase of the hydrothermal reaction time, the product morphology shows an obvious evolution from hexagonal plates to round angular blocks and to hexagonal gears, through irregular nanosheets and to cuboid rods finally. Furthermore, the driving force of this morphology evolution was found to be correspondent with the interesting change of the orientation growth and the phase transition of tungsten oxide hydrates under the hydrothermal process.

Keywords: A. Grain growth; D. Transition metal oxides; Morphology evolution; Hydrothermal process

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1. Introduction

The past decade has witnessed a rapid development of the activities in the synthesis of new nanoparticles, driven both by the intense interest of exploring new science and by the hope for the potential applications and economic impacts [1,2]. At present, one of the largest activities in this field has been focused on the size and morphology design and controlling of the metal oxide particles in order to achieve fascinating properties in technological applications. Thus, an increasing number of works have been reported to successfully synthesize these materials with desired morphologies using solution-based method, such as ZnO [3], CuO [4], TiO_2 [5], Fe_2O_3 [6], CeO_2 [7], and WO_3 [8]. Nevertheless, as difficulties in practicability and economical proficiency remain, it is still of great significance to develop the synthesis of nanostructured materials with shape-dependent properties, which will result in a wide range of electrical, optical, catalytic, or thermal properties and inspire new domains of theoretical research and better their technological applications.

As one kind of well-known functional metal oxides, tungsten oxide and its hydrates ($WO_3{\cdot}nH_2O$, $n = 0$–2) have been extensively researched and employed in various fields including supercapacitors [9], photo catalysts [10,11], gas sensors [10,11], chromic devices [10,11], and water treatment [10,11]. These applications highlight the profound significance of the morphology control to exhibit the strong connections between the product morphology and properties [12]. However, contaminations are usually created during production and economic efficiency loss is unavoidable in practical applications, for organic [13] or inorganic [14] templates are often necessary to achieve the specific morphologies. Thus, the synthesis of $WO_3{\cdot}nH_2O$ particles by template-free methods have made great achievements [14–16] but still have limitations in controlling specific morphologies, which involves extremely poisonous starting materials [17,18], or expensive tungsten sources like $W(CO)_6$ [19] and $W(Cl)_6$ [14,15,20–23]. As a tungsten-base water-soluble precursor, peroxo-polytungstic acid can be obtained by simply mixing tungsten powders with hydrogen peroxide solution. This acid has been reported to

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synthesize sheets-like $WO_3 \cdot nH_2O$ particles before [14], but few works of controlling different morphology using this acid have been reported yet. Therefore, the synthesis of $WO_3 \cdot nH_2O$ particles using peroxo-tungstic acid by solution-based method, especially without any additives, are expected to widely enhance the practical applications of tungsten oxide hydrates materials. In the present work, a facile, additive-free synthesis of $WO_3 \cdot nH_2O$ particles with controlled morphology evolution and phase transition under hydrothermal conditions is reported. Peroxo-polytungstic acid was used in this method as the precursor to achieve three-dimensional morphology evolution for the first time. A possible growth mechanism of the morphology evolution was suggested to reveal the growth habits of $WO_3 \cdot nH_2O$ particles when peroxo-polytungstic acid is used as the precursor in hydrothermal reactions.

2. Experimental

2.1. Preparation of peroxo-polytungstic acid solution

The $WO_3 \cdot 0.33H_2O$ particles were synthesized by a hydrothermal reaction using peroxo-polytungstic acid as precursor solutions. In a typical synthesis process, finely powdered tungsten (4 g, wako, 12 μm) was slowly added to hydrogen peroxide (20 mL, 30 wt%, wako) in a cold water bath (10 °C) to stabilize the reaction temperature below 40 °C. This produced a clear and colorless peroxo-polytungstic acid solution.

2.2. Synthesis of tungsten oxide hydrates particles

The as-prepared solution was then diluted in deionized water to obtain a tungsten concentration of 0.127 mol/L. After that, the diluted solution was transferred into a Teflon-lined stainless steel autoclave (25 mL, filling ratio 60%), and the autoclave was then sealed and maintained at 180 °C for 1 h. After cooled to room temperature, the as-prepared precipitates were isolated by centrifugation and repeatedly washed with absolute ethanol (5 mL) for four times. Finally, the as-obtained precipitates were dried at 40 °C in a drying cabinet for 1 h. To explore the morphology evolution, the reaction times varied from 1 h to 96 h while other conditions were kept unchanged.

2.3. Characterization

The phase composition of the samples was characterized via X-ray powder diffraction (XRD) on a Ultima IV X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) at a scanning rate of $8^\circ \ \text{min}^{-1}$ (Rigaku, Japan) in the 2θ range from 10° to 70°. A JSM-6500F field-emission scanning electron microscope was used for the observation of field emission scanning electron microscopic (FESEM) images. Transmission electron microscopic (TEM) images, high-resolution transmission electron microscopic (HRTEM) images and selected area electron diffractions (SAED) were taken on a JEM-3010 high-resolution transmission electron microscope operated at 300 kV.

3. Results and discussion

3.1. The phase transition

The XRD patterns of the products prepared at different hydrothermal reaction time are shown in Fig. 1. The sample prepared at first 4 h give rise to similar XRD pattern that can be indexed to orthorhombic $WO_3 \cdot 0.33H_2O$ phase (JCPDS Card No. 87-1203). When the reaction time reaches to 24 h, three XRD peaks of monoclinic WO_3 (JCPDS Card No. 71-2141) are observed, revealing the existence of a phase transition from orthorhombic $WO_3 \cdot 0.33H_2O$ to monoclinic WO_3. This transition are further demonstrated with hydrothermal reaction time increased to 96 h, at which the strong peak intensity XRD peaks of monoclinic WO_3 with weak peak intensity of orthorhombic $WO_3 \cdot 0.33H_2O$ are found.

3.2. The morphology evolution

By using the peroxo-polytungstic acid as the precursor, we aim to take advantage of the chelating peroxo ligands to achieve three-dimensional microstructure with potential different functional properties. In the course of our research, it is shown that this precursor can lead to obvious different morphologies compared with other previous reports [14]. With the reaction time increased, the SEM images of the crystallites are shown in Fig. 2, which exhibit obvious morphology evolution, from flat hexagonal $WO_3 \cdot 0.33H_2O$ plates (Fig. 2a) to round angular blocks (Fig. 2b) and to hexagonal gears (Fig. 2c), through irregular nanosheets (Fig. 2d), and to, ultimately, cuboid WO_3 rods (Fig. 2e). At short reaction time (1 h), the sample appears to be orthorhombic $WO_3 \cdot 0.33H_2O$ with flat hexagonal plate-like morphology with branch-like structure inside (Fig. 2a). It is found that every hexagonal plate-like structure has sheets-like structures in six symmetric oriented growth directions parallel to the plane of the plates. When the reaction time is controlled at 2 h (Fig. 2b), the hexagonal plates become thicker and are more like spheres with hexagonal edges and corners. This indicates that the crystal growth direction may switch to a

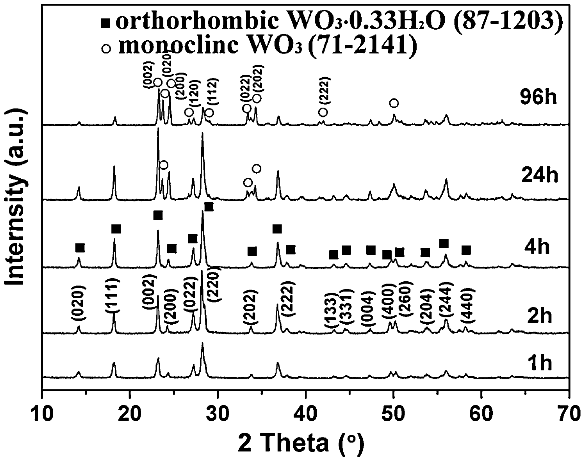

Fig. 1. XRD patterns of the products prepared by using peroxo-polytungstic acid with different hydrothermal reaction times.