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A study on the precursor of vanadium pentoxide by the hydrothermal method

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Abstract

Different morphologies including bulk, layer by layer structure and nanosheets-like spheres of vanadium pentoxide (V_2O_5) precursor have been synthesized via a simple and direct hydrothermal method. Field emission scanning electron microscopy, X-ray powder diffraction and UV–vis diffuse reflectance were used to characterize the fabricated materials. The results showed that the reaction time had a great influence on the morphology evolution processes of the as-synthesized precursors. The photocatalysis measurements showed that the nanosheet-like spheres exhibited the highest activity for degrading rhodamine B under UV light. The possible morphology transformation mechanism and the schematic representation of the precursor are also discussed.

Keywords: Morphology transformation; Precursor; Hydrothermal; Formation mechanism; Photocatalysis

1. Introduction

Nanomaterials, which are often superior to their corresponding bulk materials [1–4], have attracted much attention due to their crucial roles in future technological applications. It is well known that the properties of materials such as physical, optical and electronic ones are greatly dependent on their shapes when their sizes were reduced to micrometer or nanometer scale [5]. So, many efforts have been devoted to the synthesis of materials with different shapes and sizes. To achieve the desired shapes and sizes, some surfactants, including different organic or inorganic oxidants and reductants, were effectively used. For instance, different inorganic salts, such as KNO_3, $Ca(NO_3)_2$, $La(NO_3)_3$, etc. were used to synthesize molybdenum trioxide nanobelts and prism-like particles. All these inorganic salts were added to control the morphologies of the final products [6]. Thiol, cetyltrimethyl ammonium bromide (CTAB), polyvinylpyrrolidone, $C_{12}H_{25}SO_3Na$ and H_2S, strontium nitrate and sodium tungstatsodium poly (4-styrenesulfonate) were used to obtain MoO_3 SWCNTs (single-walled carbon nanotubes) [7], V_2O_5 nanorod and nanoparticles [8], ZnO nanocrystals, ZnS nanomaterials [9–11] and hollow nanospheres and microspheres structure of tungsten trioxide [12], respectively.

Among the transition metal oxides, vanadium pentoxide (V_2O_5) has attracted great attention due to its good property for application on lithium-ion batteries [13] and photocatalysis [14,15]. In order to obtain vanadium pentoxide nanomaterial, different surfactants such as $KBrO_3$ [16], hydrogen peroxide (H_2O_2) [17], polyethyleneglycol (PEG) [18] and polyvinylpyrrolidone (PVP) [19] were used. Except for these surfactants mentioned above, oxalic acid is also a feasible and facile surfactant to prepare V_2O_5 in hydrothermal condition with the final process of calcination. While even using the same surfactant of oxalic acid as the reductant, different morphologies of vanadium pentoxide precursor were obtained during the preparation of V_2O_5 nanostructure, such as vanadium oxide microspheres [20–22], similar roselike nanostructures and nanorods [23]. However, the morphology mechanism and the morphology transformation process of vanadium pentoxide precursor have been rarely reported. In this work, we used the

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facile and controllable hydrothermal method to prepare the precursor of vanadium pentoxide, and observed the morphology transformation processes of the vanadium pentoxide precursor by increasing the reaction time without the change of the other parameters. In addition, the morphology transformation mechanism was discussed.

2. Experimental

2.1. Synthesis

Comparative experiments in the different reaction times with the other experimental parameters unchanged were carried out to approach different precursor morphologies of V_2O_5 via the hydrothermal method in a Teflon-lined autoclave. Four experimental programs were designed, which are named S1, S2, S3 and S4. Their detailed processes are as follows:

0.002 mol of ammonium metavanadate ($NH_4 \cdot VO_3$) was dissolved in 50 ml ethanol solution containing 0.02 mol of oxalic acid. After vigrous stirring for 2 h until the solution turned to brick-red suspension, it was transferred to a 25 ml stainless steel Teflon lined autoclave maintained at 180 °C for different reaction times. Later on, the obtained blue precipitates were collected and washed with deionized water and anhydrous ethanol for several times and then dried at 60 °C in air for 10 h. The precipitates which were maintained for 4 h, 8 h, 12 h and 24 h are named S1, S2, S3 and S4, respectively.

2.2. Measurements

The structure and morphology of the precipitates were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). A Rigaku D/Max-1200X diffractometry with the Cu Kα radiation operated at 30 kV and 100 mA was employed for the structure analysis. A Hitachi S-4300 SEM was operated for the surface morphologies observation. Diffuse reflectance UV–vis absorption spectra were obtained using a XPA photocatalytic reactor.

2.3. Photocatalytic activity

The photocatalytic performance of different morphologies of the precursors were evaluated via degradation of rhodamine B (RhB) under the irradiation of UV light. A 300 W Hg lamp was used as the UV source. The lamp was placed beside the RhB solution with a distance of 10 cm. In a typical protocol, 0.01 g catalyst was added to 100 ml of 1.0×10^{-5} M RhB dye solution. After that, the mixture was magnetically stirred in the dark for 30 min to establish an adsorption/desorption equilibrium and a 4 ml suspension was centrifuged to get clear RhB solution as a primary sample and then the mixture was exposed to UV light at room temperature. A 4 ml suspension was centrifuged to remove the catalysts every 20 min. The clear RhB solution was analyzed by UV–vis spectra with a Shimadzu UV-spectrophotometer 2100.

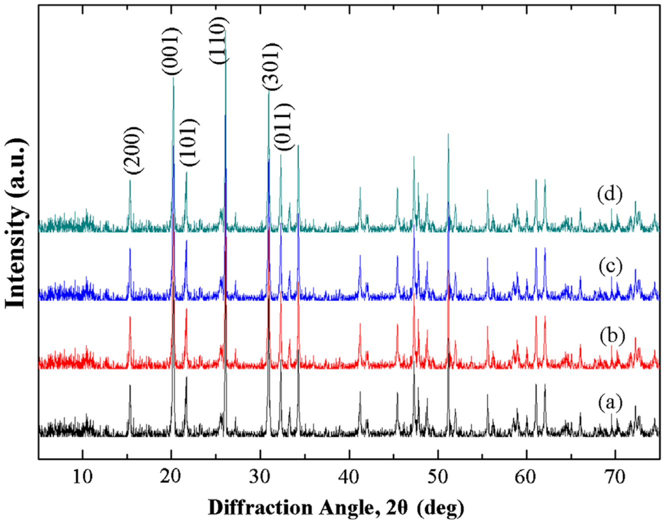

Fig. 1. XRD results of the four precipitates after calcined under 450 °C for 1 h at (a) S1 program (suspension liquid react at 180 °C for 4 h), (b) S2 program (suspension liquid react at 180 °C for 8 h), (c) S3 program (suspension liquid react at 180 °C for 12 h), (d) S4 program (suspension liquid react at 180 °C for 24 h).

3. Structural characterization and mechanism analysis

3.1. XRD analysis

Fig. 1 shows the XRD results of the calcined precipitates. The main diffraction peaks of 15.32°, 20.26°, 21.71°, 26.12°, 31.01° and 32.36° correspond to the characteristic diffraction of the (200), (001), (101), (110), (301) and (011) planes of the vanadium pentoxide, respectively. The diffraction peaks match well with those of the standard V_2O_5 pattern (PDF No. 65-0131). These XRD results demonstrating that the precipitates of four experimental programs were pure V_2O_5 powder.

3.2. SEM analysis

The morphology and structure of the samples were further investigated by FESEM. By increasing the reaction time with the other conditions unchanged, we successfully observed the morphology transformation process of vanadium pentoxide precursor, which are shown in Fig. 2. The results obtained from different reaction times are given on the left side in Fig. 2 and the corresponding magnified images of these results are given on the right side in Fig. 2, respectively. When the reaction time is 4 h, the morphology of the precursor powder is a bulk with edges and corners as shown in Fig. 2(a). The size of this bulk powder is more than dozens of micrometers. High resolution SEM observation reveals that the edges of the bulk are stacked by layers, which is marked by the yellow arrow (the right image in Fig. 2a). Fig. 2(b) is the morphology of the product which is obtained at 180 °C for 8 h. It is clearly seen that the primary bulk marked by the yellow arrow in the right image splits apart into many layers and some top layers start to bend. The thicknesses of the layers are about 30 nm and the split behavior starts at the end of the bulk. Then the