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Hydrothermal synthesis of vanadium pentoxide nanostructures and their morphology control

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Abstract

Different morphologies of vanadium pentoxide (V_2O_5) from 1D to 3D, including nanospheres, nanowires, urchin-like and flower-like nanostructures, have been synthetized by a simple hydrothermal method. Some parameters, such as the reaction temperature, the volume of polyvinyl pyrrolidone (PVP) and possible formation mechanisms of different V_2O_5 nanostructures were discussed. The results demonstrate that PVP and the reaction temperature play a critical role on the morphology of vanadium pentoxide.

Keywords: Morphology-controlling; V_2O_5 nanostructures; Hydrothermal; Formation mechanism

1. Introduction

As a layered structure, vanadium pentoxide V_2O_5 with an energy gap of 2.3 eV [1] have attracted great attention due to its novel properties such as lithium batteries [2,3] and gas sensor [4]. Thereby, V_2O_5 has been selected as a model system for the description of nanostructured materials [5,6]. Recently, various different nanostructures were synthetized by adding different inorganic or organic agents including hexamethylenetetramine (HMT) [7], cetyltrimethyl ammonium bromide (CTAB) [8,9], polyvinyl pyrrolidone (PVP) [10], $Cu(acac)_2$ [11]. Vanadium compounds such as $K_2V_8O_{21}$ [12], $LiNiVO_4$ [13], V(C,N) [14] were successfully synthetized by adding different agents. All the results suggest that surfactants play an important role on the morphologies and properties of the products. Usually, PVP polymer is regarded as the simplest crystal growth modifier, because it can selectively anchor on certain surfaces and thus kinetically control the growth rates of various planes [15]. In addition, PVP can also serve as a new class of reductants to kinetic control over both nucleation and growth [16]. Therefore, PVP is used as capping reagent owing to a strong interaction between the surfaces of nanocrystals and PVP based on the strong coordination ability of the O and N atoms in the pyrrolidone ring. It is believed that the selective adsorption of PVP on various crystallographic planes can effectively control and change the morphologies of the nanocrystals [17].

However, the effects of the PVP on the vanadium oxides morphology are investigated rarely, especially the volume of the PVP to the formation of vanadium pentoxides morphology and the reaction temperature. In this work, we used the so-called control variable method to prepare various morphologies of V_2O_5 nanocrystals. The main purpose of current work is to understand the effect of PVP on the formation of V_2O_5 nanostructures.

2. Experimental

2.1. Synthesis

Vanadium pentoxide (V_2O_5) was synthetized by a simple hydrothermal method in a Teflon-lined autoclave. So-called control variable method was used to prepare various morphologies of V_2O_5 nanocrystals. Experiment condition of different volumes of PVP at the same temperature and that of the same volume of PVP at different temperatures were adopted. In this work,

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Table 1
Materials and synthetic conditions of different experimental programs.

Number	NH_4VO_4 (mol)	pH value	PVP (g)	Temperature (°C)
S1	0.003	2	0.15	180
S2	0.003	2	0.05	180
S3	0.003	2	0.15	140
S4	0.003	2	0.05	140

we designed four experimental programs named as a, b, c and d, respectively. Their detailed experimental parameters are shown in Table 1 and their detailed processes are as follows.

0.003 mol of ammonium metavanadate ($NH_4 \cdot VO_3$) was dissolved in distilled water containing 2 ml of 30% H_2O_2. Nitric acid was added dropwise to adjust the pH value of the solution to 2. After that, 0.15 g of analytical grade polyvingl pyrrolidone (PVP, K30) was added to the solution under vigorous magnetic stirrer to form a clear pure orange solution. Then, about 20 ml of the mixture was transferred to a 25 ml autoclave with a Teflon liner and maintained at 180 °C and 140 °C for 24 h, respectively. Afterwards, the resulting dark blue precipitates were washed with deionized water and anhydrous ethanol for several times and then dried at 60 °C in air for 10 h. The precipitate maintained at 180 °C was labeled as S1 and the other one maintained at 140 °C was labeled as S2.

For comparison, in other two experimental programs, the volume of polyvingl pyrrolidone (PVP, K30) was changed from 0.15 g to 0.05 g while other parameters were kept invariant. The resulting dark blue precipitate maintained at 180 °C was labeled as S3 and the other one maintained at 140 °C was labeled as S4. Finally, the precipitates in all reactions were calcined under 500 °C for 1 h.

2.2. Measurements

The structure and morphology of the precipitates were characterized by X-ray diffractometry (XRD) and field emission scanning electron microscopy (FE-SEM). 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 employed for the surface morphologies observation.

3. Structural characterization and morphologies 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°, respectively correspond to the characteristic diffraction of the (200), (001), (101), (110) and (301) planes of the vanadium pentoxide. The diffraction peaks match well with those of the standard V_2O_5 pattern (PDF no. 65-0131). This demonstrates that the precipitates of four experimental programs were pure V_2O_5 powder.

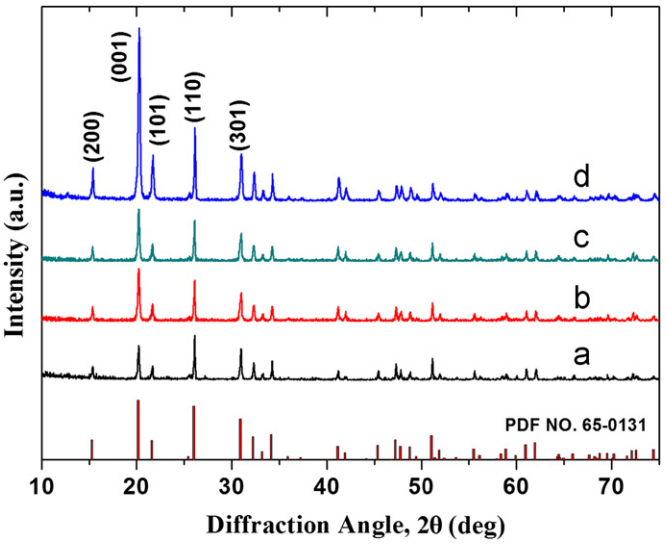

Fig. 1. XRD results of the four precipitates after calcined under 500 °C for 1 h at four programs: (a) S1 program (containing 0.15 g PVP at 180 °C), (b) S2 program (containing 0.15 g PVP at 140 °C), (c) S3 program (containing 0.05 g PVP at 180 °C), (d) S4 program (containing 0.05 g PVP at 140 °C).

3.2. SEM analysis

The morphologies of the samples of different programs were further investigated by FE-SEM. Four different morphologies of V_2O_5 nanostructures, including nanospheres, urchin-like, nanowires and nanoflowers, were obtained and showed in Fig. 2. One can see in Fig. 2(a) a large quantity of nanospheres were assembled of nanosheets. High resolution SEM observations reveal that these straight nanospheres are of width of ~2 μm and some of the nanosheets stick together (the inset image in Fig. 2(a)). Fig. 2(b) shows an urchin-like nanostructure of V_2O_5, which are composed of radially aligned nanorods. In a higher-magnification SEM image (the inset of Fig. 2(b)), it is clearly seen that the geometrical shapes of cross section of V_2O_5 are rectangular. The thickness and width of V_2O_5 nanorods are estimated to be 60~100 nm and 40~60 nm, respectively. The ends of the nanorods are regular. One can see in Fig. 2(c) a large quantity of nanowires. Their length and width are about several micrometers and ~100 nm, respectively. Along the nanowires, many particles adhere to the nanowires and some nanowires are broken. We suppose that the nanowires are broken by reason of heat treating at a high temperature. Fig. 2(d) shows flower-like V_2O_5 nanostructures which are assembled of petals. The diameter and thickness of the petals are about 1 μm and 60 nm, respectively.

4. Mechanism

In allusion to the four different morphologies of V_2O_5, including nanospheres, urchin-like, nanowires and nanoflowers, their formation mechanisms are discussed and the schematic representations are shown in Fig. 3.