Journal of Solid State Chemistry 214 (2014) 79–85

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Growth of oriented vanadium pentaoxide nanostructures on transparent conducting substrates and their applications in photocatalysis

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ARTICLE INFO

Available online 17 October 2013

Keywords:
Hydrothermal synthesis
VO_2 film
V_2O_5 film
Photocatalysis

ABSTRACT

A novel, hydrothermal and hard-template-free method was developed for the first time to grow oriented, single-crystalline monoclinic VO_2 (B) flower-like nanorod films on transparent conductive fluorine-doped tin oxide (FTO) substrates. The length and morphology of the nanorods can be tuned by changing the growth parameters, such as growth time and initial precursor concentration. The flower-like V_2O_5 films were obtained after post-calcination treatment of VO_2 (B) films. The photocatalytic activity of V_2O_5 films was investigated by the degradation of methylene blue (MB) under UV and visible light. The prepared V_2O_5 film exhibited good photocatalytic performance (74.6% and 63% under UV and visible light for 210 min, respectively) and more practical application in industry.

1. Introduction

Constructing one-dimensional (1D) metal oxide nanostructures on various substrates has attracted considerable attention because of their geometric and morphologic characteristics and proximity to the substrates. These nanostructures show diverse applications in nano devices [1–3], sensors [4], energy-conversion [5–8], field emission [9], and so on. Vanadium oxides (VO_x), an important class of transitional metal oxides, exhibit diverse physicochemical properties and usages based on their variable oxidation states and *V–O* coordination environments. For example, VO_2 (B) is cathode in lithium ion batteries [10,11]; VO_2 (R/M) is promising thermochromic candidate for smart energy-saving windows due to its temperature-responsive phase change at ~68 °C [12]. Among the vanadium oxides, V_2O_5 possesses good chemical and thermal stability, unique electrochemical and photoelectric properties, and has attracted considerable interest for the application as the electrodes of Li-ion batteries [13–15] and gas sensors [16–20]. Especially, V_2O_5 is well known as industrial catalysts for the oxidation of organics [21,22]. Interestingly, when these vanadium oxides appear as 1D nanostructure, novel local or collective properties may emerge. Prominent example can be found that 1D V_2O_5 on substrates shows better electrochemical/photocatalytic performance and easy-operating characters in practice usage due to excellent electron transport pathway and adhesion to the substrates [23–26]. Still, many novel fundamental physicochemical properties and technological applications based on 1D nanostructure of vanadium oxides remain to be discovered. However, the difficulty in the preparation of 1D nanostructure, especially with a specific orientation on substrates is a big obstacle to achieve the aforementioned goals.

Generally, the preparation methods for 1D nanostructure can be categorized into two classes, namely gas-phase-based and liquid-phase-based processing. Comparatively speaking, the liquid-phase-based process is quite attractive for the following considerations: it is low-cost, easy-operating and high-yield; the processing temperature is far lower than that in the gas-based methods; good control on the compositions and microstructures of the final products by modulating the growth parameters. Therefore, solution-based is a versatile and effective protocol to fabricate 1D metal oxides nanostructure and exploit their potential applications. Vanadium oxide films are usually obtained by expensive gas-phase based methodologies featuring with complex routines, sophisticated equipment, and rigorous conditions. There are only a few reports involved in solution-based preparation techniques [23–25].

Herein, we report a novel, hard-templates-free and versatile hydrothermal treatment-based routine to prepare 1D vanadium oxide nanostructures on FTO glass. Oriented monoclinic VO_2 (B) nanorod arrays or flower-like nanostructures films on FTO were grown by modulating the hydrothermal reaction parameters. The transparent

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http://dx.doi.org/10.1016/j.jssc.2013.10.020

conducting FTO substrates can induce the heterogeneous nucleation of vanadium oxides on the substrates and enhance the adhesion and uniformity of the films. The as-formed 1D VO_2 (B) nanostructures could be used as a general precursor to further transform into other vanadium oxides [27,28] with retained morphologies and sizes. As a typical example, 1D VO_2 (B) was converted into V_2O_5 by post-oxidation in air. The as-obtained 1D nanostructured V_2O_5 films on FTO showed good photocatalytic performance due to its hierarchical structure. The hierarchical structure consisted of 1D nanorod can enlarge the specific area for fast mass transfer, retard the recombination of photogenerated carriers, and particularly enhance the light absorption capability via allowing more light reflection and multiple-scattering inside the interior, which has proved to be favorable for the improvement of the photocatalytic activity of TiO_2 and other photocatalyst systems [29–31]. Also, V_2O_5 deposited on FTO substrates was easily separated and recollected from reactor, which is quite desirable in practical applications.

2. Experimental section

2.1. Synthesis

Fluorine-doped tin dioxide (FTO) conducting glass was purchased from Wuhan Georgi instruments Co., Ltd.; other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used as received without any further purification.

FTO glass substrates were cleaned by ultrasonication in acetone, ethanol and deionized water respectively for 10 min in progression, and finally dried in air. Before hydrothermal treatment, FTO substrates were firstly pretreated with ammonia water and then rinsed in distilled water. The preparation of 1D nanostructured VO_2 films on FTO was as follows: Vanadium pentaoxide (V_2O_5) and oxalic acid were used as raw materials and mixed under a stirring of 30 min at 80 °C to obtain yellowish slurry [32]. Then the slurry was transferred to 100 mL Teflon-liner in stainless-steel autoclave and the pretreated FTO substrates were placed at an angle against the wall of Teflon-liner with the conducting side facing down. The autoclave was maintained at 200 °C for 8–20 h, after that, air-cooled to room temperature. The reactions were performed according to the conditions presented in Table 1. The black VO_2 (B) film deposited on the FTO substrate was washed with water and ethanol for several times and then dried at 80 °C for 12 h. Finally, the coated FTO substrates were calcined at 500 °C for 30 min in air with a heating rate of 8 °C min^{-1} to obtain the orange–yellow V_2O_5 films.

2.2. Characterization

The crystal structure of the prepared film was investigated using a Japan Rigaku D/max 2550V X-ray diffractometer (Cu-*K*a, λ= 0.15406 nm). Morphological and size information were examined by field emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Tokyo, Japan). The microstructure was further analyzed by a transmission electron microscope (TEM, JEM2010, JEOL, Tokyo, Japan). Diffuse reflection spectra were obtained using a UV–vis spectrometer (HITACHI U-3010).

Table 1
The conditions of hydrothermal reaction times (8 h, 10 h, 12 h, 16 h, 18 h, 20 h) and the concentration of vanadium atomic (0.02 M and 0.03 M) under which the hydrothermal reactions were carried out, and the V_2O_5 films samples calcined from VO_2 films.

Conc. (*V*)	Time					
	8 h	10 h	12 h	16 h	18 h	20 h
0.03 M	VO_2-A	VO_2-B	VO_2-C	VO_2-D	VO_2-E	VO_2-F
0.03 M calcined in air				V_2O_5-D	V_2O_5-E	V_2O_5-F
0.02 M					VO_2-G	

2.3. Photocatalytic evaluation

The photocatalytic activities of as-prepared V_2O_5 flower-like nanostructured films were measured through the photodegradation of methylene blue (MB) under UV and visible light. V_2O_5/FTO film plate (2.5 cm × 2.5 cm, the mass of V_2O_5 is ~2.0 mg) was immersed in aqueous MB solution (20 mg/L, 50 mL) (placed at 60° angle against the wall of the beaker). Before photodegradation, the samples were kept in the dark for 2 h to achieve absorption–desorption equilibrium, which means there is no obvious change in the UV–vis spectrometer. Then the solution with V_2O_5 /FTO film was radiated with a 300 W Xe lamb equipped with a cut-off filter behind to selectively obtain UV (λ ~365 nm) or visible-light (λ > 420 nm). The reactor was placed 10 cm away from the light source. At fixed time intervals, a given amount of solution was sampled and the time-course concentration of MB was measured by the absorbance maximum recorded on an UV–vis spectrometer (Hitachi U-3010) according to the Lambert–Beer Law. TOC was measured using a TOC/TN analyzer (Jena 3000 Germany) to evaluate the mineralization extent of the MB.

3. Results and discussion

3.1. Morphology and structure of VO_2 and V_2O_5 films on FTO

Our strategy to prepare oriented 1D nanostructures of vanadium oxides is described in Fig. 1, which includes the following steps: (a) the pre-treatment of FTO substrate and the heteronucleation of vanadium dioxide on the substrate during the hydrothermal reaction (Fig. 1a); (b) controllable growth of vanadium dioxide (VO_2) on FTO by modulating the reactant concentrations and reaction times (Fig. 1b); (c) chemical transformation of VO_2 (B) into other vanadium oxide species, among which V_2O_5 is obtained by calcining VO_2 (B) films in air with well-preserved morphologic information.

The as-obtained nanostructured product on FTO (sample VO_2-E) is first examined to confirm the phase using XRD analysis. Fig. 2a shows the XRD patterns of the FTO substrate, which is attributed to tetragonal SnO_2 (JCPDS No. 41-1445). After hydrothermal reaction, new characteristic diffraction peaks of monoclinic phase VO_2 (B) (JCPDS No. 31-1438) appeared (Fig. 2b), indicating that the VO_2 (B) was deposited on the FTO substrate. The intense and sharp diffraction peaks suggest the high crystallization degree of VO_2.

Fig. 3 shows the typical scanning electron microscopy (SEM) images of the surface and cross-section of VO_2 (B) films on FTO substrates. It is found that the morphologies of 1D nanostructured VO_2 films are in fact dependent on reactant concentrations when the reaction time is kept the same. In a low concentration (0.02 M of vanadium atom), vertically oriented VO_2 nanorod arrays (sample VO_2-G) were formed densely on the FTO substrate (Fig. 3a). It could be observed from the cross-sectional view image of the film (Fig. 3b) that order nanorod with a length of ~3 μm and an average diameter of 150 nm grew vertically on the substrate. However, in a high concentration (0.03 M), one kind of high uniform discrete flower patterned architecture (sample VO_2-E) was fabricated, as shown in Fig. 3c. The flower-like morphology was composed of VO_2 nanorods, which leaned on the substrate and hierarchically accumulated closely (Fig. 3d).