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Hydrothermal synthesis of vanadium oxide nanorods and their electrochromic performance

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ABSTRACT

Nanorod-like V_2O_5 was fabricated using a simple one-step hydrothermal method using NH_4VO_3 and oxalic acid as precursors. The morphology and structure of the as-prepared V_2O_5 nanocrystals were characterized by different techniques. Furthermore, based on the analyses of cyclic voltammetric curves and electrochromism test, the thin V_2O_5 nanorod film have been found to exhibit promising electrochromic performance, which can be attributed to their nanorod architecture. The as-prepared V_2O_5 nanocrystals are promising electrochromic candidate for potential application in smart window.

1. Introduction

Vanadium oxide (V_2O_5) is an important transition metal oxide in different areas, such as lithium ion battery, supercapacitor, gas sensors, photocatalyst, electrochromic devices and so on [1–6]. Due to its layered structure, which facilitates ion intercalation, the electrochromic behavior of V^{5+} and V^{4+} oxides is well known [7]. V_2O_5 can reversibly change from one colored state to another upon supplying a suitable charge, which made it a promising candidate for smart window [8].

There has been always a strong correlation between the structure and its electrochemical properties. It is well known that the nanosized materials have better electrochemical performance than the large size particles, which will provide more effective electrical transport continuity and facilitates Li^+ ion intercalation [9]. Specially, thin film is one of the most favorite structures for smart window applications [10]. Obviously, fabricating high quality electrochromic thin films in low cost is very important for applications. Therefore, many attempts have been adopted to enhance the electrochromic performance of V_2O_5 such as controlled morphology, composite materials and different synthesis methods [11–13]. Hydrothermal technique is a low-cost, environmental friendly approach to prepare materials in different nanoarchitectures such as nanorods, nanowires and nanoparticles and so forth [14,15].

Here in this paper, the electrochromic V_2O_5 film with organized nanostructures are prepared by hydrothermal treatment so as to get the best electrochemical properties.

2. Experimental

V_2O_5 nanorod array was grown on a fluorine-doped tin oxide (FTO) glass substrate using a hydrothermal method. The substrates were cleaned with acetone, ethanol, finally rinsed with deionized water and dried in air. Hydrothermal synthesis was carried out for V_2O_5:0.5850 g NH_4VO_3 dissolved in 50 mL deionized water and then 1.1206 g oxalic acid was added to the system to form an orange solution. The resulting solution was stirred at for 15 min before the addition of 50 mL deionized water. Then 10 drop of HCl was added. The resultant solution was transferred to a Teflon-lined stainless steel autoclave and the FTO substrate was placed at an angle against the wall of the Teflon lined with the conductive side facing down. The hydrothermal was conducted at 180 °C for 3.5 h and then cooled overnight. After rinsed extensively with deionized water and dried in ambient air, a V_2O_5 nanorod array film was uniformly coated on the FTO glass substrate. The samples were

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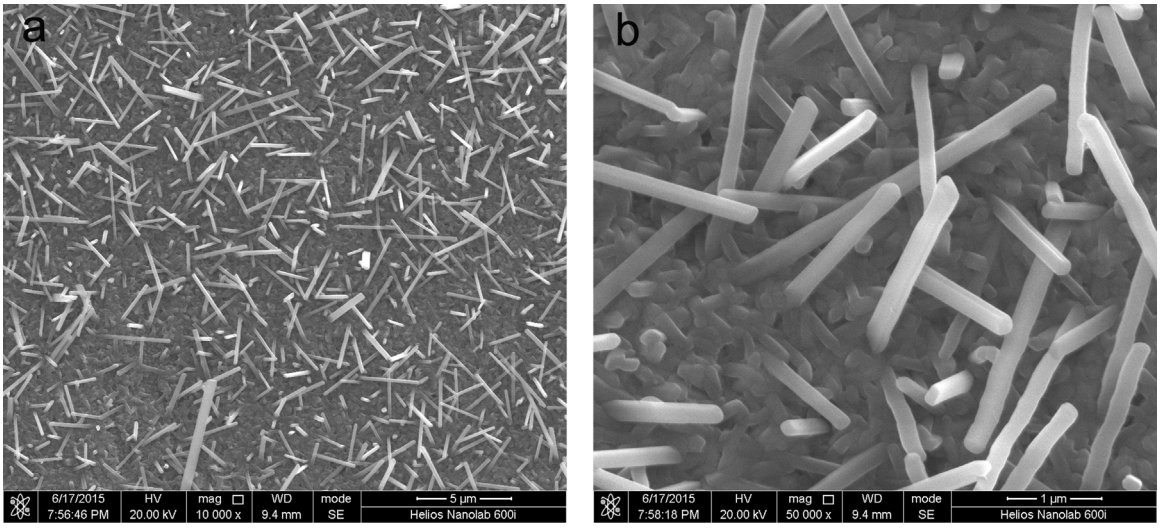

Fig. 1. SEM images of the as-synthesized V_2O_5 at (a) low and (b) high magnification.

annealed at 300 °C for 1 h then 500 °C for 2 h to create a V_2O_5 layer.

The synthesized sample was investigated by a FEI Quanta 200FEG SEM. FT-IR spectrum was collected on a Perkin-Elmer spectrometer. Raman spectra were collected on a Renishaw inVia Raman microscope with an Ar+ laser (532 nm) excitation source. The cyclic voltammetry test was carried out in a three-electrode environment with the V_2O_5 on FTO/glass as the working electrode, neat FTO glass as the counter electrode. 1 M lithium perchlorate in propylene carbonate was used as the electrolyte. The electrochromic behavior of V_2O_5 films was examined using an Autolab PGSTAT30 potentiostat with the UV–vis spectrometer (SHIMADZU UV2550).

3. Results and discussion

After calcination of the hydrothermal sample, a nanorod-like V_2O_5 structure can be seen lying on the FTO glass as shown in the SEM image of Fig. 1. It is clearly shown that the product is made up of nanorods with widths about 80–100 nm and lengths of 1–10 μm The SEM image demostrate that V_2O_5 tends to form 1-D nanostructure under the hydrothermal conditions as reported in previous literature [16].

The FT-IR spectrum of V_2O_5 is presented in Fig. 2a. The peak at 1000 cm^{-1} and 818 cm^{-1} correspond to V=O terminal oxygen and V–O–V asymmetric stretching modes [17,18]. The peak at 474 cm^{-1} is related to the stretching mode of the oxygen atom shared between three vanadium atoms. Raman spectroscopy is a useful technique to give the in-situ vibrational spectra of V_2O_5. A number of well-defined bands assigned to V_2O_5 crystal phase were found in the region of 200–1400 cm^{-1}, as shown in Fig. 2b. The Raman spectrum of V_2O_5 film shows features that are consistent with the positions and assignments of the bands for nano-crystalline nature of the previously reported V_2O_5 [19,20]. The peaks at 285 cm^{-1}, 403 cm^{-1} are assigned to the bending vibration of the V=O bonds. The peak at 529 cm^{-1} and 489 cm^{-1} are assigned to the terminal oxygen (V_3–O) stretching mode and the V–O–V stretching mode. The peak present at 997 cm^{-1} corresponds to the stretching mode of the V–O bonds.

Cyclic voltammetry measurements were carried out at various sweep rates between −1.0 and 1.0 V to determine the oxidation–reduction peak potentials of the V_2O_5, as presented in Fig. 3a. The measurements were carried out at various sweeping rates from 10 to 50 mV/s. During the test, the film exhibits well reversible color change from yellow–green to pale blue reversibly. This process is in accordance with insertion (extraction) of the Li^+ into (out from) the V_2O_5 films:

$$V_2O_5 + xLi^+ + xe^- = Li_xV_2O_5$$

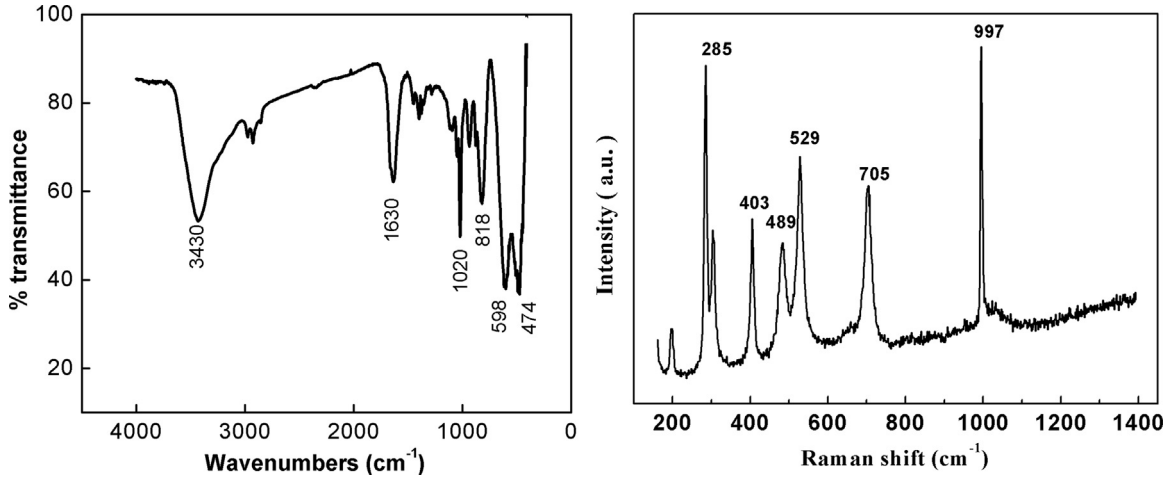

Fig. 2. (a) FTIR spectra and (b) Raman spectra of the as-synthesized V_2O_5 film.