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Vanadium oxides nanostructures: Hydrothermal synthesis and electrochemical properties

I. Mjejri [a], N. Etteyeb [a], F. Sediri [a,b,*]

[a] Laboratory of Condensed Matter Chemistry, IPEIT, University of Tunis, 2 Jawaher Lel Nehru 1008, B. P. 229 Montfleury,Tunisia
[b] Chemistry Department, Sciences Faculty of Tunis, Tunis El Manar University, 2092 El Manar, Tunisia

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ABSTRACT

A facile and template-free one-pot strategy is applied to synthesize nanostructured vanadium oxide particles via a hydrothermal methodology. X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transforms infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) have been used to characterize the structure and morphology of the samples. The products are gradually changed from sheet-shaped VO_2(B) to rod-like $V_3O_7{\cdot}H_2O$ with decreasing cyclohexanediol as both protective and reducing agent. The specific surface area of the VO_2(B) nanosheets and $V_3O_7{\cdot}H_2O$ nanorods was found to be 22 and 16 $m^2\,g^{-1}$, respectively. Thin films of VO_2(B) and $V_3O_7{\cdot}H_2O$ deposited on ITO substrates were electrochemically characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The voltammograms show reversible redox behavior with doping/dedoping process corresponding to reversible cation intercalation/de-intercalation into the crystal lattice of the nanorods/nanosheets. This process is easier for the small Li^+ cation than larger ones Na^+.

1. Introduction

The synthesis of nanostructure materials with well-controlled phase, size and morphology has been of great interest because of their novel physical and chemical properties [1–5]. These properties make nanostructured metal oxides useful for a wide range of applications including lithium ion battery and catalysis [6–10]. The synthesis and characterization of one-dimensional (1D) nanostructures, such as nanowires, nanorods and nanobelts, have attracted considerable attention for advanced functional systems owing to their attractive properties [11–16]. Vanadium oxides and their derived nanostructural compounds show particularly rich chemistry because of the tunable vanadium oxidation state and flexible coordination environment [12,17,18]. Among these, VO_2 and $V_3O_7{\cdot}H_2O$ have attracted much attention due to its potential application in lithium ion battery [1,19,20]. VO_2 and $V_3O_7{\cdot}H_2O$ is a typical intercalation compound with a layered crystal structure and a large variety of atomic and molecular species that can be reversibly intercalated and de-intercalated between the layers have been intensively investigated as a cathode material for rechargeable lithium ion batteries because of its low cost, abundance, easy synthesis, and high energy density [19,20–22]. Various methods have been used to fabricate nanostructured vanadium oxide including microemulsion-mediated systems [23], arc discharge [24], laser-assisted catalysis growth [25], solution [26], vapor transport [27], solvothermal and hydrothermal [11–14] methods have been successfully explored to fabricate different kind of nanostructured vanadium oxides. Indeed, hydrothermal methods involving the reduction of V_2O_5 to $V_3O_7{\cdot}H_2O$ and VO_2 provide a new approach to synthesis of nanomaterials under mild conditions, which offers various morphologies and easy control [28–30]. Generally, vanadium oxide is prepared by reducing vanadium pentoxide with many reducteur agent [17] Ganganagappa and Siddaramanna [31] and Yifu Zhang et al. [32] have reported the preparation of $V_3O_7{\cdot}H_2O$ and VO_2(B) powders by a reduction process in solution reaction routes, but their results showed a limited success because only nano-sized powders in zero dimension were obtained. It is difficult for traditional methods to prepare such nanostructures in one, two or three dimensions. The performance of three dimensional nanostructure based vanadium oxide has been the subject of a tremendous amount of research [33]. Moreover, Dongliang Chao et al. [34] prepared V_2O_5 three-dimensional (3D) with various morphologie by solvothermal synthesis and electrodeposition. Vanadium pentoxide with layered orthorhombic structure has

* Corresponding author at: Chemistry Department, Tunis El Manar University, El Manar, Tunis 2092, Tunisia. Tel.: +216 71336641; fax: +216 71337323.
E-mail address: faouzi.sediri@ipeit.rnu.tn (F. Sediri).

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been thought to be one of the most promising cathode materials for lithium-ion batteries due to its low cost, high discharge rate, and long cycle life.

In this paper, by controlling 1,4-cyclohexanediol quantities, $V_3O_7{\cdot}H_2O$ and VO_2(B) have been synthesized via a simple hydrothermal route. The electroactivity of the $V_3O_7{\cdot}H_2O$ nanorods and VO_2(B) nanosheets has been investigated. Cyclic voltammetric and electrochemical impedance spectroscopy characterization of thin films of the nanostructured $V_3O_7{\cdot}H_2O$ and VO_2(B) have revealed reversible redox behavior with charge–discharge cycling corresponding to the reversible lithium intercalation/deintercalation into the crystal lattice. The as-synthesized nanosheets and nanorods exhibit good electrochemical behavior and promising to be used in lithium-ion battery.

2. Experimental

2.1. Hydrothermal synthesis

All of the chemical reagents were purchased from Acros Organic and used without further purification. Vanadium (V) oxide was used as vanadium source. The organics reagents, 1.4-cyclohexanediol, has been used as templates for the first time. VO_2(B) nanosheets and $V_3O_7{\cdot}H_2O$ nanorods were hydrothermally synthesized, from a mixture of V_2O_5, 1.4-cyclohexanediol and distilled water (5 mL) in a molar ratio 1:1:350 and 0.125:1:350 respectively. Reactants were introduced in this order and stirred a few minutes before introducing the resulting suspension in a Teflon-lined steel autoclave and the temperature set at 180 °C for 4 days. The pH of the solution remains close to pH ≈ 7 during the whole synthesis.

2.2. Structure and morphology characterizations

X-ray powder diffraction data (XRD) were obtained on a X'Pert Pro Panalytical diffractometer with CuKα radiation (λ = 1.5418 Å) and graphite monochromator. The XRD measurements were carried out by applying a step scanning method (2θ range from 3° to 70°), the scanning rate is 0.017° s^{-1} and the step time is 1 s. Scanning electron microscopy (SEM) study was recorded on a Cambridge Instruments Stereoscan 120. Fourier-transform infrared spectra (FTIR) were recorded from 4000 to 400 cm^{-1} on a Nicolet 380 spectrometer in pellets of samples dispersed in KBr. X-ray photoelectron spectroscopy (XPS) experiments were performed using a Shimadzu ESCALAB at room temperature.

2.3. Electrochemical measurement

The electrochemical measurements were carried out using one compartment cell and a BioLogic SP150 potentiostat/galvanostat apparatus. Ag/AgCl electrode and a stainless grid were used as reference and counter-electrode electrode, respectively. The working electrode is a film of $V_3O_7{\cdot}H_2O$ and VO_2(B) deposited on a plate of indium tin oxide (ITO). The electrode was obtained: 0.5 mg of nanostructured was dispersed in 1 mL of water by ultrasonic treatment to obtain a suspension. 100 μL of this suspension were deposited on a 1 cm^2 area ITO-coated glass plate then the water evaporated. The layer obtained was about 1 μm thick and was dried after being covered with 10 μL of a Nafion solution (obtained by dissolving in ethanol a commercial Nafion solution 9/1 v/v). The final working electrode is an ITO-coated glass plate covered by a thin layer of vanadium oxide nanomaterial protected by Nafion membrane order to prevent the degradation of the material into the solution. The operating voltage of nanosheets and nanorods was controlled between (−1, 1 V) and (−0.2, 1.2 V) respectively, at different scan rates at room temperature. $LiClO_4$ and $NaClO_4$ were used as electrolytic salts at 1 M in PC. The supporting electrolytes were degassed with argon.

3. Results and discussion

3.1. Structure and morphology

Powder X-ray diffraction patterns of the resulting samples synthesized with cyclohexanediol at 180 °C for different molar ratios (R) of cyclohexanediol to V_2O_5 (a) 1:1, (b) 0.5:1, (c) 0.25:1 and 0.125:1, were determined by X-ray powder diffraction (XRD), as shown in Fig. 1. It is obvious that the crystalline phases for vanadium oxide nanorods are discriminatory at different molar ratio. Indeed, when the synthesis was carried out with R = 1:1 (Fig. 1a), the diffraction pattern shows the presence of VO_2(B) (JCPDS card no.31-1438). The diffractogram (Fig. 1a) reveals the presence of narrow peaks, suggesting that this material has high crystallinity. When the molar ratio decreased to R = 0.5:1 (Fig. 1b), the diffraction pattern always shows the presence of VO_2(B) (JCPDS

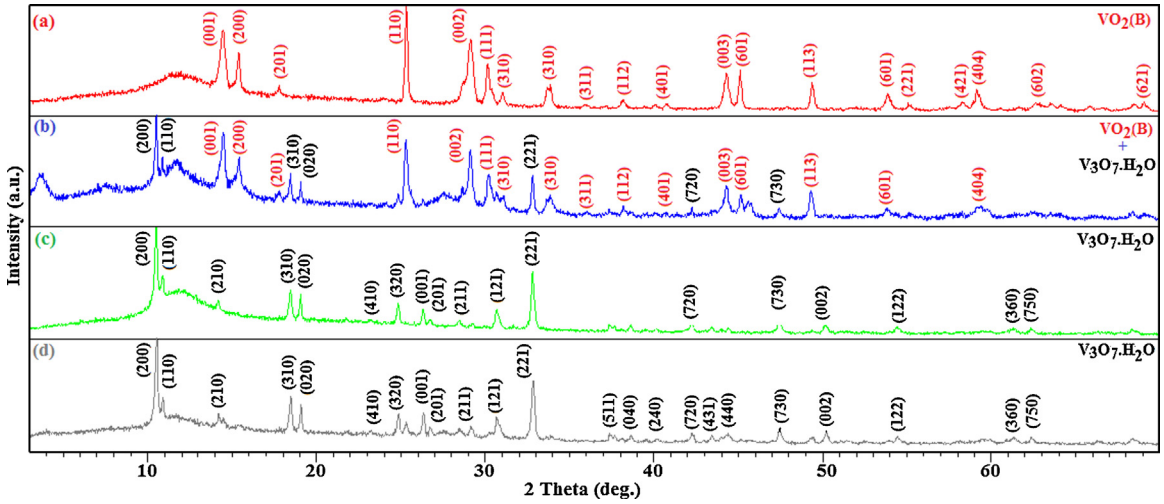

Fig. 1. XRD patterns of the samples synthesized at different molar ratio cyclohexanediol: V_2O_5 (a) 1:1, (b) 0.5:1, 0.25:1 (c) and 0.125:1 (d).