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Hydrothermal synthesis and characterization of mesoporous rod-like hybrid organic-inorganic nanocrystalline based vanadium oxide

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Abstract

We describe a simple route to mesoporous rod-like nanocrystalline of hybrid organic–inorganic based vanadium oxide through the hydrothermal method using V_2O_5 as vanadium source and 2-phenylethylamine as reducing and structure-directing agent. Techniques X-ray diffraction (XRD), scanning electron microscope (SEM), thermal analysis (TG-DTA), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, UV–visible spectroscopy and nitrogen adsorption/desorption isotherms (BET) have been used to characterize the structure, morphology and the texture of the samples. The nanorods are up to several hundred nanometers in length, the width and the thickness are 280–300 and 60 nm, respectively. The molar ratio plays a key role on the structure and the morphology of the materials.

Keywords: A. Hydrothermal synthesis; B. X-ray methods; D. Transition metal oxides

1. Introduction

Vanadium oxides have been extensively studied for their interesting physicochemical properties such as electrochemical performance [1–3]; a high capacity for lithium insertion makes it attractive to be used as cathodes in high-capacity batteries [4–8]; as well as in the field of catalysis [9,10]. The wide range of oxidation state and coordination polyhedra in the system vanadium/oxygen and the use of soft chemical process, in particular the mild hydrothermal method (120–250 °C) allows the synthesis of large amounts of vanadium oxide with open structure intercalated simple cation metal or organic molecules. Recently, several studies have been reported on the hydrothermal synthesis of hybrids organic-vanadium oxides materials using linear diamines molecules [11–16] ammonium cations [17–22] or alkyloviologen [23]. The organic molecules are sandwiched between the inorganic frameworks, where this latter has a lamellar structure formed by vanadium oxide layers with negative charge. The negative charges are then balanced by cations present in the interlayer space. More, pH plays a critical role in the formation of structure layers and the coordination of vanadium centers. Indeed, the vanadium may exhibit both V^{4+} and V^{5+} oxidation states and the layers are currently built from $[VO_5]$ square pyramids and $[VO_4]$ tetrahedral, at a pH close to 7 [24].

Furthermore, the physicochemical properties of solid state materials mainly depend on their size, structure and morphology [25]. Subsequently, nanostructured materials have attracted considerable attention due to their remarkable physicochemical properties, which differs considerably to dense materials, thereafter their use in great potential applications [26–28]. Among them, one-dimensional (1D) nanostructure vanadium oxides, such as nanotubes, nanowires, nanobelts and nanorods, have been extensively studied the past few years [25,29–33].

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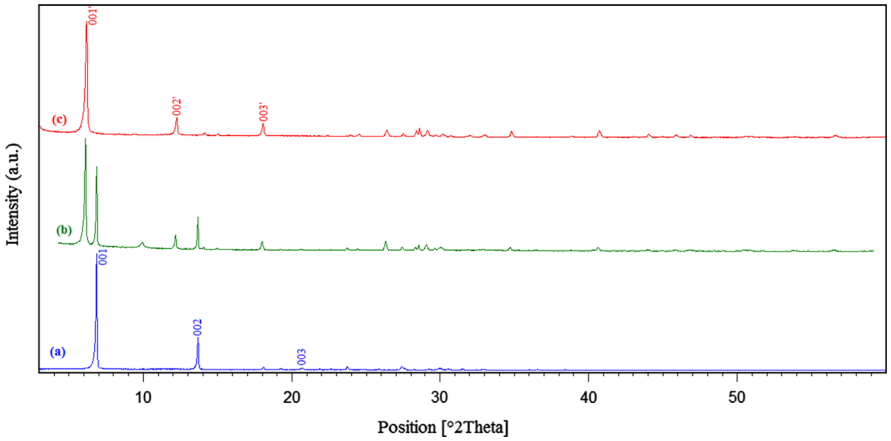

Fig. 1. Powder X-ray diffraction patterns of the resulting products synthesized at different molar ratio V_2O_5:2-phenylethylamine (a) 1:1, (b) 0.5:1 and (c) 2:1.

This paper deals with the synthesis of rod-like hybrid organic–inorganic nanocrystalline based vanadium oxide by hydrothermal reaction of V_2O_5 as a vanadium source and 2-phenylethylamine which acts as structure-directing, size and morphology-controlling agent. The impact of the molar ratio on the particles size and the morphology has been investigated. Although many methods have been developed to elaborate hybrid organic-inorganic nanocrystalline based vanadium oxide, to the best of our knowledge, this is the first report of hybrid organic–inorganic nanomaterial based vanadium oxide synthesis using V_2O_5 and 2-phenylethylamine as a structure-directing template.

2. Experimental section

2.1. Characterization techniques

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 59.98°), the scanning rate is 0.017 s^{-1} and the step time is 12 s. Scanning electron microscopy (SEM) studies were recorded on a Cambridge Instruments Stereoscan 120 at an accelerating voltage of 10 kV. 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. Raman spectroscopy was performed using a Jobin Yvon T 64000 spectrometer (blue laser excitation with 488 nm wavelength and <55 mW power at the sample). Thermogravimetric analyses were carried out under an oxygen flux of 5 cm^3 min^{-1} at a heating rate of 10 °C min^{-1} between room temperature and 600 °C, using a Netsch STA 409 thermogravimetric analyzer. X-ray photoelectron spectroscopy (XPS) experiments were performed using a Shimadzu ESCALAB, at room temperature. The optical parameters of sample were calculated from the optical absorbance data recorded in the wavelength range from 200 to 800 nm using a UV–visible spectrophotometer Shimadzu-3101PC.

2.2. Hydrothermal synthesis

All of the chemical reagents were analytical grade. They were purchased from Acros Organics and used without further purification.

The detailed process for the synthesis was as follows. In a typical synthesis, the preparation was made from a mixture of V_2O_5, 2-phenylethylamine and distilled water (5 mL) at different molar ratio of V_2O_5 to 2-phenylethylamine. Reactants were introduced in this order and stirred a few hours before introducing the resulting mixture in a Teflon-lined steel autoclave and the temperature set at 180 °C for 2 days under autogenous pressure. The pH of the reaction mixture remains close to pH≈10. The resulting black powder was washed with water and acetone to remove the residues of 2-phenylethylamine and then dried at 80 °C for 6 h. The black color of the powder suggests that some V^{5+} ions have been reduced to V^{4+} by the decomposition of the organic compound [34]. Comparative experiments were carried out to investigate the influence of the molar ratio of V_2O_5 to 2-phenylethylamine on the crystallinity, morphology and texture of the materials.

3. Results and discussion

3.1. X-ray diffraction

The crystallinity of the resulting samples synthesized at 180 °C for different molar ratio of V_2O_5 to 2-phenylethylamine (a) 0.5:1, (b) 1:1 and (c) 2:1, were studied by X-ray powder diffraction (XRD), as shown in Fig. 1. It is obvious that the crystalline phases for vanadium oxide nanocrystals are discriminatory at different molar ratios. Indeed, when the molar ratio R=0.5:1 (Fig. 1a), the patterns predominantly consist of a series of peaks with high intensity corresponding to the stacking of the layers along a direction perpendicular to the substrate which have d-spacings of the type d_{001}/l, where l is