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Hydrothermal synthesis of mesoporous $VO_2 \cdot ½(H_2O)$ nanosheets and study of their electrical properties

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ABSTRACT

Layered sheet-like nanocrystalline $VO_2 \cdot ½(H_2O)$ has been synthesized by hydrothermal process using V_2O_5 as vanadium source and 2-phenylethylamine as a reducing agent and a structure-directing template. Techniques X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and nitrogen adsorption/desorption isotherms have been used to characterize the structure, morphology and composition of the materials. Electrical conductivity measurements showed that the as synthesized $VO_2 \cdot ½(H_2O)$ nanosheets has a conductivity value which goes from $75 \times 10^{-6}\,\Omega^{-1}\,cm^{-1}$ at 298 K, to 68 $10^{-5}\,\Omega^{-1}\,cm^{-1}$ at 386 K with activation energy of 0.24 eV.

1. Introduction

Layered transition metal oxides have attracted considerable attention due to their applications in ion exchange, catalysis, semiconductor, pillaring and active cathode materials [1]. Of these inorganic oxides, vanadium oxide is a good host material, capable of intercalating a variety of neutral and charged species such as alkali metal ions, organic amines, surfactants, alcohols, etc. [2–4]. The resulting intercalation compounds usually retain a lamellar structure, with the guest species occupying the interlayer region [5–7]. Livage et al. have reported synthesis of several reduced vanadium oxide xerogels using organic and inorganic cations as intercalate [8–10]. Mild hydrothermal conditions (120–250 °C) appear to be ideal for the formation of organic/inorganic hybrid materials based on vanadium oxides [11–14].

The binary vanadium oxides, VO_x ($1 \leq x \leq 2.5$), exhibit a wide variety structure type [15]. Many of them are of technological importance, being used in oxidation catalysis, high-energy density battery electrodes, etc. [16,17]. These oxides also show interesting electronic properties, from metallic behaviour in some VO_2 to semiconducting behaviour in V_2O_5. The rutile-type VO_2 displays a metal-insulator transition with increasing temperature [18,19]. The most oxygen-rich phase, V_2O_5, has been characterized with a layered structure, which can be reduced by intercalation reactions to derive novel materials [3]. B-VO_2 also exists as an intermediate in the course of the thermal reduction of V_2O_5 by H_2 or SO_2 gas [20]. It has a layered structure and shows good performance as an anode host for rechargeable lithium cell with aqueous electrolytes [21]. Vanadium oxide hydrate, $VO_2 \cdot ½H_2O$ has been prepared as a single phase from the hydrothermal reaction of the hydrolyzate of VCl_4 and NaOH at 200 °C [22]. Several intermediate metastable phases, such as $V_2O_5 \cdot H_2O$ and $V_3O_7 \cdot H_2O$, have been identified [23,24]. The metastable $VO_2 \cdot H_2O$ has been synthesized by hydrothermal treatment of NH_4VO_3 and N_2H_4 at 170 °C for 15 days [25].

This paper deals with the synthesis of $VO_2 \cdot ½H_2O$ by hydrothermal reaction of V_2O_5 and 2-phenylethylamine which, acts as a reducing agent and could also allows control the size and morphology. The products obtained hydrothermally consist of phase-pure sheets-like nanocrystallites. A study of the electrical properties is reported. Although many methods have been developed to elaborate nanostructured vanadium dioxide, to the best of our knowledge, it is the first report of $VO_2 \cdot ½H_2O$ nanosheets preparation using 2-phenylethylamine as reducing agent and no report on the electrical properties of $VO_2 \cdot ½H_2O$ has been conducted so far.

2. Experimental

2.1. Hydrothermal synthesis

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

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The material was prepared from V_2O_5 (0.15 g), 2-phenylethylamine (g) (0.1 g) and distilled water (5 mL) in a molar ratio of 1:1:366. 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 6 days. 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 4 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 [26]. The material obtained after hydrothermal treatment was characterized by different techniques. To investigate the formation process of $VO_2{\cdot}½H_2O$ sheet-like nanocrystalline, time dependent experiments were carried out at180 °C for different reaction times.

2.2. 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 70°), the scanning rate is 0.017° s^{-1} and the step time is 1 s. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) studies were recorded on a Cambridge Instruments Stereoscan 120. Transmission electron microscopy (TEM) was carried out with a JEOL 100 CX II Microscope at an accelerating voltage of 200 kV. One droplet of the powder dispersed in CH_3CH_2OH was deposited onto a carbon-coated copper grid and left to dry in air. 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. The Brunauer–Emmett–Teller (BET) specific surface area, average pore diameter and pore size distributions were determined by nitrogen physisorption at 77 K using a Micrometrics ASAP-2000 instrument. The electrical conductivity study was carried out on a pellet of the samples with a diameter of 13 mm and a thickness of 2.27 mm compacted under a pressure of 9 ton and annealed at 100 °C for 12 h. The conductivity was determined by an alternative current method using a Hewlett Packard 4192 A impedance analyzer at oscillation amplitude of 0.1 V in the frequency range 100 Hz–13 MHz.

3. Results and discussion

3.1. X-ray diffraction

Powder X-ray diffraction patterns of the resulting samples synthesized at 180 °C for different reaction times: 2 days (a), 4 days (b) and 6 days (c), are shown in Fig. 1. It is obvious that the crystalline phases for vanadium oxide nanosheets are discriminatory at different reaction times. Indeed, after a two-day synthesis process (Fig. 1a), the product presents a layered structure, probably with water and 2-phenylethylamine in the interlayer region resulting in the larger d_{001} spacing of 14.454 Å. When the reaction process is extended up to four days (Fig. 1b), diffraction peaks can be seen and indexed to monoclinic crystalline $V_{14}O_6$ (JCPDS # 83-2141) and another phase identified as tetragonal $VO_2{\cdot}½H_2O$ (JCPDS # 89-6930). On the other hand, Fig. 1c shows the tetragonal phase of $VO_2{\cdot}½H_2O$ with lattice constants $a = b = 3.721$ Å and $c = 15.421$ Å (JCPDS # 89-6930), which is obtained when a sex-day synthesis process is carried out, suggesting that the V^{5+} ions in the layered compound have been further reduced to V^{4+} ions by 2-phenylethylamine during the reaction. These results indicate that the formation of nanocrystalline $VO_2{\cdot}½H_2O$ goes through a layered intermediate.

The XRD patterns shown in Fig. 1c indicate that the d-spacing values of all diffraction peaks are identical to those of $VO_2{\cdot}½H_2O$ according to JCPDS card 89-6930. No peak of any other phase or impurity was detected from the XRD pattern. This shows that the $VO_2{\cdot}½H_2O$ with high purity can be obtained via the hydrothermal treatment at 180 °C. The diffractogram (Fig. 1c) reveals the presence of narrow peaks, suggesting that this material has high crystallinity. Besides, the presence of the typical diffraction peaks ($d_{0\,0\,l}$) in the XRD patterns of the compound indicates a layered framework. The XRD pattern displays a 0 0 l set of reflections with high intensity corresponding to the stacking of the layers along a direction perpendicular to the substrate: a characteristic of well-ordered layered structure with a layered distance equal to 15.452 Å.

3.2. Scanning and transmission electronic microscopy

The morphology of synthesized materials was studied using the scanning electron microscopy (SEM). Fig. 2 shows SEM images of

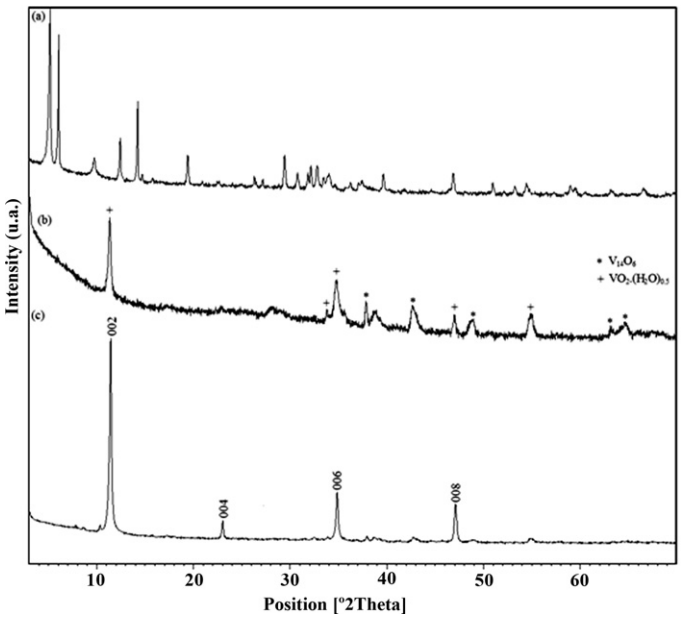

Fig. 1. Powder X-ray diffraction patterns of the resulting products synthesized at 180 °C for different reaction times: 2 days (a), 4 days (b) and 6 days (c).