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Rapid communication

Synthesis and characterization of vanadium oxides nanorods

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Abstract

Vanadium oxides nanorods with high crystallinity and high surface area were synthesized by hydrothermal method using laurylamine hydrochloride, metal alkoxide and acetylacetone. The samples characterized by XRD, nitrogen adsorption isotherm, SEM, TEM, and SAED. Uniformly sized B phase VO_2 nanorods had widths about 40–80 nm and lengths reaching up to 1 μm. V_2O_5 rodlike structured with the widths about 100–500 nm and the lengths of 1–10 μm were obtained by calcination at 400 °C for 4 h. This synthesis method provides a new simple route to fabricate one-dimensional nanostructured metal oxides under mild conditions.

Keywords: Vanadium oxides; Nanorods; Nanowires; Characterization; Mild conditions

1. Introduction

The synthesis and characterization of one-dimensional (1-D) nanostructured (nanotubes, nanowires, and nanorods) have received considerable attention due to their unique properties and novel application [1–5]. Much effort has concentrated on the important metal oxides such as TiO_2, SnO_2, WO_3, ZnO, and ZrO_2. Among them vanadium oxides are especially interesting since they are widely used for various applications like electrochemical device and catalysis [6–8]. Their functional properties are influenced by many factors such as crystallinity, surface area, and preparation methods [6–13]. A large number of vanadium oxides nanotubes were successfully synthesized via a sol–gel reaction followed by hydrothermal treatment [10–13]. Important progress was achieved in producing nanofibers and nanotubes of vanadium oxides using carbon nanotubes as template [14,15]. Owing to high cost of carbon nanotubes, the use of titanate nanotubes as template via hydrothermal synthesis (200 °C) was investigated; however, the products were composite of vanadium oxide and titanate nanorods [16]. V_2O_5 nanorods from $VOSO_4$ aqueous solution using template-based electrodeposition were also successfully synthesized [17]. In our previous works, mesoporous metal oxides nanopowders with controlled pore size (3–6 nm) were synthesized by a modified sol–gel method in aqueous phase using a surfactant assisted process under mild conditions, offering a high photocatalytic activity [18–20]. This process has also been applied to a semiconductive material in dye-sensitized solar cells and hydrogen evolution [21–26].

In this study, the surfactant-assisted process has been expanded to prepare nanostructured vadadium oxides by hydrothermal method. The characteristic of the prepared nanopowders will be reported.

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2. Experimental

2.1. Synthesis

Nanostructured vanadium oxides were synthesized using laurylamine hydrochloride (LAHC)/metal alkoxide modified with acetylacetone (ACA). Vanadium triethoxide oxide (VTO, Hokko Chemical Industry Co., Ltd.) was mixed with the same mole of ACA (Nacalai Tesque, Inc.) to slowdown the hydrolysis and condensation reactions [18,21,25]. Subsequently, 0.1 M LAHC (Tokyo Chemical Industry Co.) aqueous solution (as the surfactant, pH 4–4.5) was added in the solution (molar ratio of VTO to LAHC was 4), and it was stirred at room temperature for 1 h. After kept stirring at 40 °C for 24 h, it was put into a Teflon-lined stainless steel autoclave and heated at 150 °C for 1 week. The obtained black green product was washed with 2-propanol and distilled water, followed by freezed drying.

2.2. Characterization

The crystalline structure of samples was evaluated by X-ray diffraction (XRD, RIGAKU RINT 2100). The microstructure of the prepared materials was analyzed by scanning electron microscopy (SEM, JEOL JSM-6500FE), transmission electron microscopy (TEM, JEOL JEM-200CX), and selected-area electron diffraction (SAED). The Brunauer–Emmett–Teller (BET) specific surface area was determined by the nitrogen adsorption (BEL Japan, BELSORP-18 Plus). Thermal analytical measurements were carried out on a thermongravimetric analyzer (Perkin Elmer, Pyris 1 TGA). Infrared spectra were obtained with Fourier Transfer Infrared Spectroscopy (FTIR, Perkin Elmer. Spectrum One) using KBr technique.

3. Results and discussion

Fig. 1 shows XRD patterns of the prepared samples. As-synthesized sample was composed of monoclinic B phase VO_2 (JCPDS card No: 31-1438). The peaks were rather sharp, which indicated relatively high crystallinity. Metastable B phase VO_2 was found to have good performance in lithium batteries [27–29]. Nanocrystal B phase VO_2 had been obtained by an ambient temperature reduction of aqueous vanadate ions with potassium borohydride and sodium dithionite followed by heating in vacuum at 230 °C [29]. However, B phase VO_2 nanorods were obtained by this method.

The SEM image (Fig. 2(a)) reveals that the prepared VO_2 without ACA display rodlike morphology with 100–400 nm in width and 500 nm–2 μm in length. The BET surface area was about 28 m^2/g. More uniform

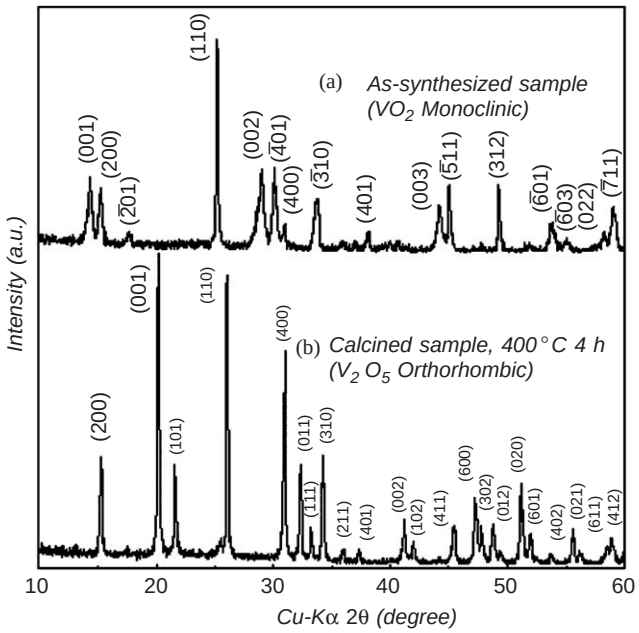

Fig. 1. XRD patterns for (a) the as-synthesized sample, (b) the calcined sample at 400 °C for 4 h.

shape and finer size of nanorods were obtained with ACA addition (Fig. 2(b)).

The widths of rods decreased between 40 and 80 nm, the thickness of 15–50 nm, and the lengths of nanorods range from 500 nm to 1 μm (Fig. 3(a)). Because the condensation reaction speed was much faster under without ACA condition, it is predicted that the crystal growth occurred before the surfactant molecules were adsorbed on the nanostructured vanadium oxide [25]. VO_2 nanorods are frequently grown together in the form of bundles, however individual nanorod can also be observed, which can be confirmed by the HRTEM and SAED investigation. Lattice fringes of 001, 200, and 110 were confirm, (Fig. 3(b–d)) ($d = 0.61$, 0.58, and 0.35 nm) allowing for the identification of the monoclinic phase. HRTEM images of nanorods with clear lattice fringes, again confirming its high crystallinity.

In order to confirm the essential of LAHC for the nanorods formation, lower molar ratio of VTO to LAHC and other amine surfactant have been used. In the condition of [VTO]/[LAHC] = 1, nano-micro plate-like structured vanadium oxide was obtained (Fig. 4(a)). Without LAHC condition (no surfactant), vanadium oxide nanorods were not obtained (Fig. 4(b)). It can be deduced that lower molar ratio of precursor to surfactant may destroy the dynamic equilibrium of microemulsions, resulting in the loss of microemulsion function [30]. Needle-like nanostructured could be observed with the used of myristylamine as the surfactant condition (Fig. 5(a, b)), however, B phase VO_2 has not been obtained.