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A simple preparation procedure for the synthesis of sodium hexaniobate nanorods

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Abstract

A simple hydrothermal method was used to synthesize crystalline sodium hexaniobate nanorods of high purity in gram quantity by treating Nb_2O_5 powder in 10 M NaOH at 150 °C without utilizing template molecules. The molecular composition of such material was identified as $Na_6H_2Nb_6O_{19}\cdot 2H_2O$. SEM revealed that the majority of these hexaniobate rods had a diameter distribution of 200–450 nm and a length distribution of 40–60 μm, though finer rods with a diameter of 50–100 nm could also be found in the product mixture.

Keywords: Sodium hexaniobate; Nanorods; Hydrothermal; Nb_2O_5

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1. Introduction

The recent rapid development in the science and technology of nanomaterial has generated tremendous excitement and expectation in the field. As the subject is of great academic and practical importance, there have been intensive research efforts in the synthesis, assembly, fabrication and applications of these nanomaterials. For example, numerous studies had concentrated on the bulk synthesis of oxidic nanotubes and nanorods. These included the synthesis of TiO_2 nanotubes by supramolecular assemblies and by Al_2O_3 membrane templating [1,2], CuO nanowires [3] and MgO nanorods by direct heating [4], Sb_2O_3 nanorods by microemulsion [5], SnO_2 nanorods by redox reaction [6], Eu_2O_3 nanorods by ultrasound irradiation [7], SiO_2 [8] and VO_x [9] nanotubes by surfactant templating, and ZrO_2 [10] nanotubes and GeO_2 [11] nanorods by carbon nanotube templating. However, these syntheses frequently required tedious synthesis procedure, harsh reaction condition or expensive reagents, and the purity and yield of the resulting nanomaterial were usually quite low. Recently, we had reported a simple hydrothermal method to prepare grams quantities of pure TiO_2 nanotubes. In this method, fine TiO_2 powder would dissolve and re-assembled themselves in a hot concentrated alkali solution producing long TiO_2 nanotubes [12]. Such method did not require the utilization of template molecules, and thus the removal of template molecules after the preparation was not necessary. More important, as long as the reaction time was sufficient, all the TiO_2 powder would ultimately transform into a nanotubular shape product and no separation of TiO_2 particles from the product mixture was required. We had applied the same preparation procedure to Nb_2O_5 powder and a sodium hexaniobate material in the shape of a solid rod could be obtained. It was reported that niobic acid powder, $H_8Nb_6O_{19}$, obtained by hydrolysis from aqueous $K_8Nb_6O_{19}$ solution with sulfuric acid displayed a high photocatalytic activity for H_2 gas evolution from an aqueous methanol solution without supporting any other materials, such as Pt (quantum yield; ca. 10% at 330 nm) [13]. As one of the research focuses in our laboratory is to produce H_2 gas photocatalytically [14], we plan to hydrolyze this sodium hexaniobate nanomaterial in order to prepare a new type nio-

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bic acid nanophotocatalyst and examine its ability to generate H_2 gas.

2. Experimental

In a typical preparation run, 10 g of Nb_2O_5 powder (Aldrich Chemical Co.) and 100 ml of 10 M NaOH solution were mixed in a perfluoroalkoxy container and stirred for 48–72 h at 150 °C. After cooling down, the resulting reaction mixture was filtered and washed thoroughly with 2.0 L of deionized water several times. After the final washing, the filtered cake was dried at 110 °C for 24 h. The pH of the deionized water used in the washing was around 6.5.

SEM images of the nanorods were obtained with a Hitachi S-2460N scanning electron microscope with an accelerating voltage of 30 kV. A Philips CM-200 TEM/EDX was used to record TEM images and to analyze the elemental composition of the nanorods. The oxidation state of the niobium was revealed by a VG Scientific ESCALAB-250 X-ray Photoelectron Spectrometer. The concentrations of sodium and niobium in the prepared niobate nanorods were determined by ICP-AES on the HF-digested samples. BET surface areas and pore volumes were estimated with an ASAP 2010 surface area and porosimetry analyzer. XRD experiments were performed on a Scintag DMS 2000 diffractormeter equipped with Cu Kα radiation. X-ray source ($\lambda = 1.54184$ A). TGA/DTA thermogravimetric analysis was performed with Perkin-Elmer Pyrisl TGA and Perkin-Elmer DTA7, respectively. FT-IR spectrum was recorded with Bio-Rad FTS-185 spectrometer using a KBr pellet.

3. Results and discussion

After being contacted with 10 M NaOH at 150 °C for the stated amount of time, almost all the Nb_2O_5 powder was transformed into a rod-shape product. Fig. 1a and b were the lower and higher magnification SEM images of the resulting tubular-shape products, respectively. As could be seen from the image in Fig. 1a, a large number of fiber-like material could be easily found everywhere on the silicon substrate surface. Such fiber-like material seemed to be of high purity as no starting Nb_2O_5 powder material could be found among them in these SEM images. In addition, XRD data also indicated that no starting Nb_2O_5 material was present in the product mixture (compare Fig. 3a and b). Upon closer examination of this fiber-like material, we found that many of them were actually made up of a bundle of rod-shape substance (Fig. 1b). A high magnification SEM image in Fig. 1c verified that these rod-shape substances were indeed nonporous solid rods instead of hollow tubes. Fig. 1c showed that the cross-section of these rods was quite smooth, but their cylindrical external surface was not. Most of these rods had a diameter distribution of 200–450 nm and a length distribution of 40–60 μm. It should be pointed out that some rods with diameter smaller than 100 nm could also be found in the product mixture (Fig. 1d). By assuming an average length

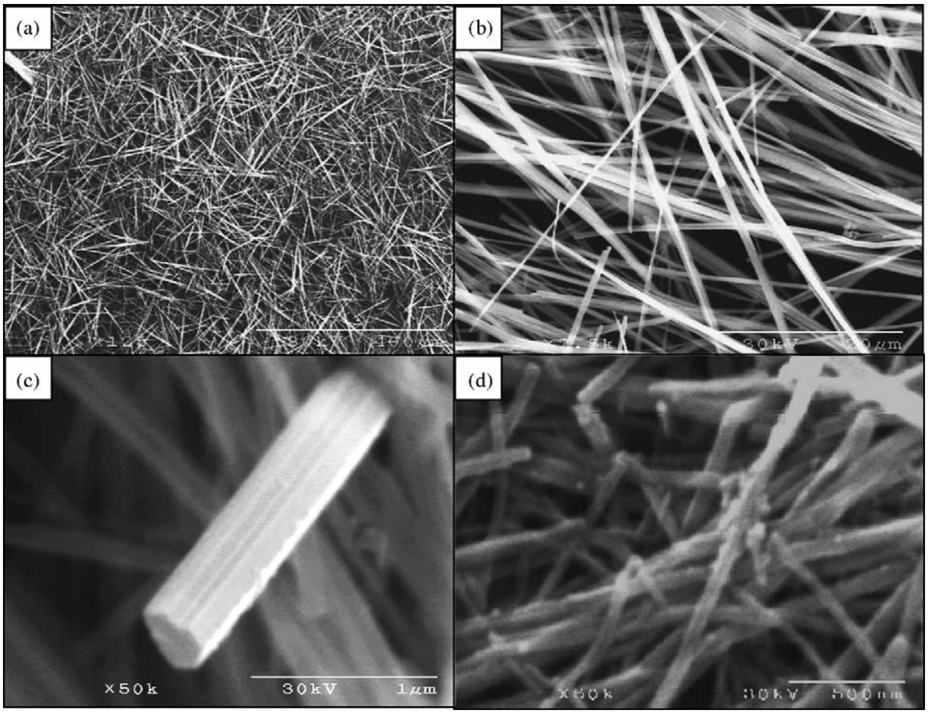

Fig. 1. (a) SEM image of sodium hexaniobate nanorods at a lower magnification; (b) SEM image of the material in (a) at a higher magnification; (c) SEM image of a single sodium hexaniobate nanorod; (d) SEM image of sodium hexaniobate nanorods of smaller outer diameter.