Vanadium pentoxide nanofibers by electrospinning

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Abstract

New vanadate fibers with nano- to submicron diameter were prepared by electrospinning using vanadium sol and poly(vinylacetate) (PVAC) solutions followed by thermal treatment. The PVAC has been applied as structure directing template for the synthesis of vanadium oxide fibers. The fibers were characterized by SEM, AFM, XRD and IR spectra.
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1. Introduction

Nanostructured materials which are considered as intermediates between classical molecular scale and microsized entities, constitute a rapidly growing field of scientific interest and industrial applications. Chemical structures and systems within the size range from about 1 to 100 nm in one, two, or three dimensions are typical for such materials. They are attracting considerable attention, because they present new challenges for the chemist, they frequently exhibit novel properties, and some nanoscale systems offer interesting device applications as a consequence of their size,

properties and topology. Nanoparticles may be of quite different shapes such as spheroids, mushrooms [1], platelets, rods, or tubes; the form adopted plays a large role in determining the basic properties, for example, isotropic or anisotropic behavior and region dependent surface reactivity.

The tubular form has attracted a great deal of interest because they might turn out to become very useful in future nanodevice technology [2]. Another very interesting family are the nanoporous MCM-aluminosilicates [3,4] with continuous framework structures that have tunnel dimensions between 3 and 10 nm, extending the range of zeolite-like materials. The synthesis of these mesostructured molecular sieves relies on surfactant micelles or liquid crystal arrays of micelles as structure directing agents for the assembly and subsequent polymerization of inorganic aluminosilicate precursors at the surfactant solution interface. The application of complementary electrostatic interactions between surfactant molecules

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and charged or polarized metal oxy precursors as the inorganic component has opening a way to new metastable modifications of metal oxides [5]. Quite recently it has been shown that hydrogen bonding [6] or real coordinative interactions [7–9] between the ligand liquid crystal template and the metal center offer new perspectives for the controlled synthesis of surfactant based periodic inorganic structures.

The vanadium–oxygen system is an interesting and complex subject for study, involving as many as 13 distinct phases, each identifiable by its lattice structure and spacings. A further complication is the substantial variability in stoichiometry occuring in some structures, most notably the Magneli phases based on rutile, with compositions of V_nO_{2n-1}, where n is an integer [10]. Semiconductor to metal transitions have been reported in at least eight vanadium oxygen compounds at temperatures ranging from −147 to 68 °C. These changes are associated with a first order crystallographic transition affecting the electrical, magnetic and optical properties of the materials, permitting them to be used as switches. VO_2 and V_2O_3 exhibit the largest changes in properties and are therefore the most useful compositions, with VO_2 receiving the most attention. This is perhaps because the transition temperature of VO_2 is conveniently close to room temperature, at 68 °C, making it useful for a variety of applications [11–16]. Studies involving the transition of V_2O_3 require measurements in the range of −121 °C, and a few properties have been reported through its transition [17–22].

In this work, we present a relatively simple method [23–25] to prepare V_2O_5 nanofibers, which have good electrical transport properties [26,27] besides these are useful materials for the preparation of V_2O_3 and VO_2.

2. Experimental

Sol–gel method was used to prepare the electrospinning solution, in which the starting material was commercial vanadium oxideisopropoxide, $(VO(OC_3H_7)_3)$, a clear liquid soluble in a variety of organic solvents. Brifely, 5 g of vanadium oxide isopropoxide was added to 5 g of dry ethanol to produce a clear pale yellow fluid. 0.24 g of distilled water was added into this with rapid agitation. The contents stirred continuously for 12 h. The exchange of isopropyl and ethyl groups was evident, as the pale yellow solution became green. Then this vanadium sol solution was mixed with PVAC (1:3 by wt ratio) under stirring for 5 h to give the final electrospinning solution.

The electrospinning solution was delivered at a constant flow rate to a plastic capillary connected to a high-voltage power supply. Upon applying a high voltage (15 kV), a fluid jet was ejected from the capillary. As the jet accelerated towards a grounded collector, the solvent evaporated and a charged fiber was deposited on the collector in the form of a non-woven fabric. The fibers are collected and then calcined at different temperatures. Scanning electron microscopy (SEM) images of the products are collected with a JOEL GSM-5900 scanning electron microscope. Atomic force microscope (AFM) pictures are taken using XE-100 (PSIA Co.) instrument. X-ray diffraction (XRD) pattern of the fibers are obtained with Shimadzu Lab-X 600 X-ray diffractometer with Cu-Kα irradiation. The infrared (IR) spectra are recorded in Bio-Rad Win FT-IR spectrophotometer at room temperature.

3. Results and discussion

Fiber microstructure was determined by scanning electron microscopy and atomic force microscopies. Figs. 1 and 2 summarise results of material prepared using 50 wt% V_2O_5 in as-synthesised and calcined form. The SEM images of as-synthesised fibers shows that the fibers have smooth, uniform surfaces and uniform diameter in the whole length. The fibers obtained after calcination at 400 °C exhibit spiral like structure. The diameters are reduced by about 40% due to the decomposition of the PVAC component. After calcination at 500 °C any shrinkage is minimal but the fibers can be seen to have rougher surfaces. It is thought that this is due to the complete decomposition of PVAC components. In this stage the fibers appear to consist of linked particles or
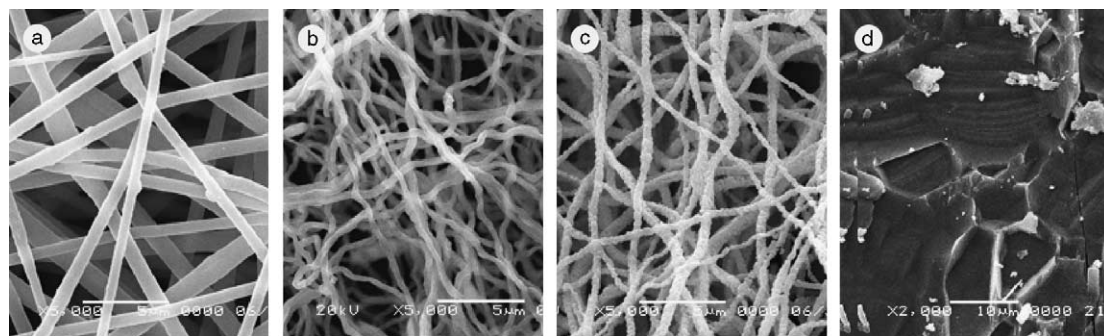
Fig. 1. SEM images of the V_2O_5 fibers: (a) as-synthesised material, 50 wt% of V_2O_5/PVAC composite; (b) 50 wt% of V_2O_5/PVAC composite fibers calcined at 400 °C; (c) 50 wt% of V_2O_5/PVAC composite fibers calcined at 500 °C; (d) 50 wt% of V_2O_5 /PVAC composite fibers calcined at 700 °C.
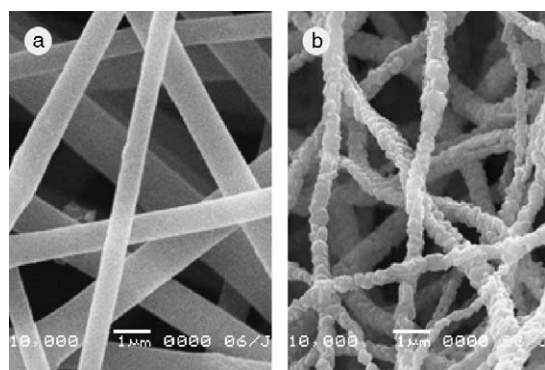

Fig. 2. SEM images of 50 wt% V_2O_5/PVAC fibers at higher magnification: (a) as-synthesised material, PVAC-inorganic composite; (b) calcined at 500 °C.

crystallites. When the fibers subjected to calcination at 700 °C, the fiber structure is disappeared due to the melting of V_2O_5 fibers at about 670 °C [28].

The surface topography of the fibers was also studied by atomic force microscopy (AFM). The surface morphological image obtained for as-synthesised form is shown in Fig. 3. The AFM data demonstrated that the fibers are homogeneous, smooth and uniform with regard to surface topography. The strip at the right hand side part of Fig. 3 indicates the Z-axis height from which it is possible to estimate the fiber roughness. The height profiles shown corresponded to the marked directions from top to bottom and the reference positions are marked 0.

The fiber crystallinity was determined by X-ray diffraction. Fig. 4a–c shows the XRD spectra of V_2O_5 fibers in the as-synthesised form, after calcination at 400 and 500 °C respectively. XRD patterns of the as-synthesised fibers indicated that the structure is amorphous in nature. Following calcination at 400 °C well defined features appear due to the crystallisation of vanadium pentoxide. XRD spectra of the fibers after calcination at 500 °C shows that the features become sharper and well defined although position does not alter significantly. This would suggest a higher degrees of crystallinity and larger particle sizes. The data here is fitted to reveal the presence of V_2O_5 phase (JCPDS 9-387) [28].

FT-IR spectra of as-synthesised PVAC/V_2O_5 composite fibers and calcined at different temperatures are shown in Fig. 5. These spectra recorded in the wave number range 450–2300 cm^{-1}. In Fig. 5a (as-synthesised form) strong bands are observed between 1000 and 2000 cm^{-1} which can be assigned to bend and stretching frequencies of PVAC. There is no band corresponding to bending frequencies of water-suggesting the as-synthesised products are dry. After calcination at 400 and 500 °C, all these strong features are removed (Fig. 5b and c). No sign of adsorbed water or hydroxy, carbonate or hydrocarbon impurity can be observed. Instead, well defined features are observed due to vanadium oxide. The evidence for the structural quality of V_2O_5 is the peak position of the vanadyl (V=O) mode located at 1018 cm^{-1}
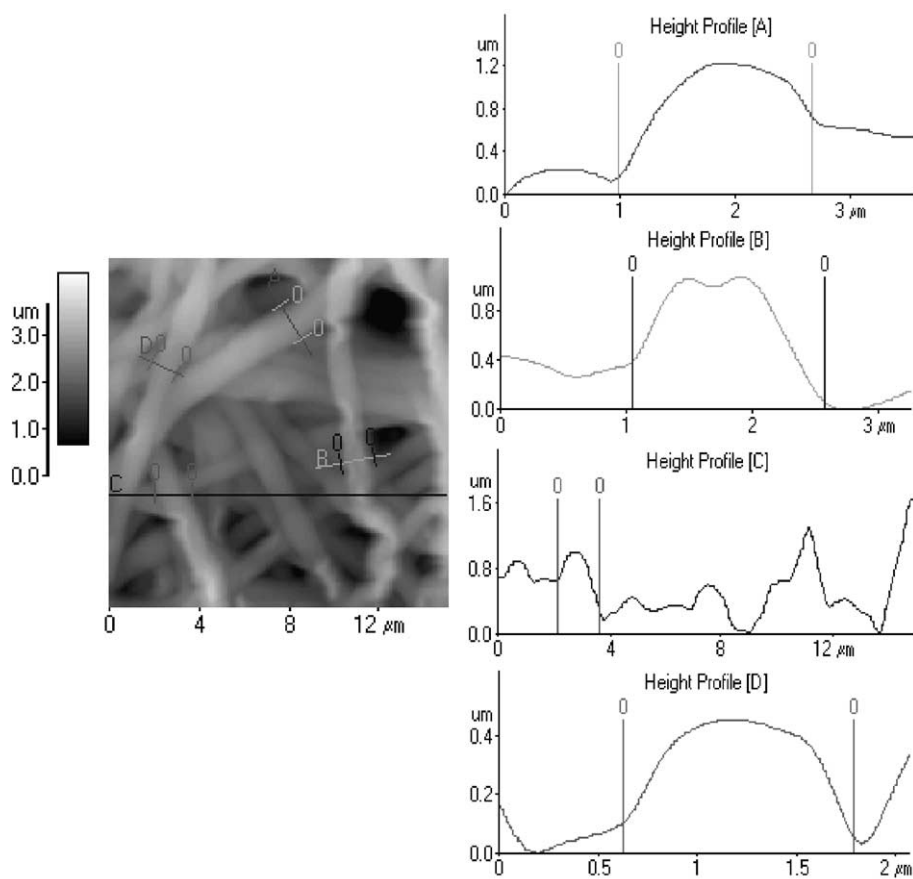
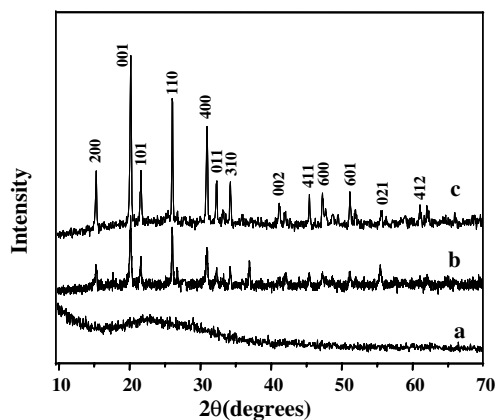Fig. 3. AFM image of 50 wt% V_2O_5/PVAC composite fibers.

Fig. 4. X-ray diffraction patterns of the 50 wt% V_2O_5 fibers: (a) as-synthesised material, PVAC-inorganic composite; (b) after calcination at 400 °C; (c) after calcination at 500 °C.
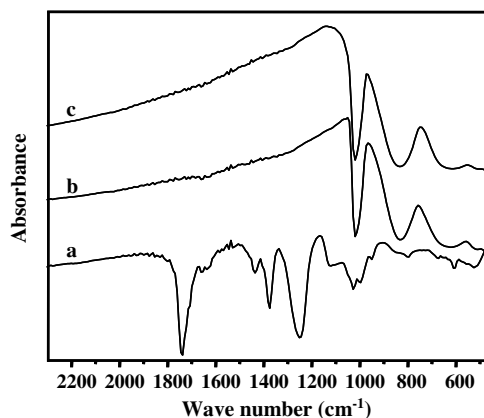
Fig. 5. FT-IR spectra of 50 wt% V_2O_5 fibers: (a) as-synthesised material, PVAC-inorganic composite; (b) following calcination at 400 °C; (c) following calcination at 500 °C.

[29,30]. This band corresponds to the stretching of the shortest bond between vanadium and oxygen. Unlike other oxygen atoms, this terminal oxygen is strongly bonded to only one vanadium atom. The other band at 834 cm^{-1} due to V–O–V stretching vibration.

4. Conclusions

By using the electrospinning technique, through sol–gel process, PVAC/V$_2$O$_5$ composite fibers have been prepared. After calcination of the composite fibers, pure crystalline V$_2$O$_5$ nanofibers were obtained. The morphology of the fibers are determined by the calcination temperature. By controlling the parameters of the calcinations, one could also expect to be able to make V$_2$O$_3$ and VO$_2$ nanofibers.

Acknowledgement

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