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Gas sensing properties of p-type semiconducting vanadium oxide nanotubes

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ABSTRACT

Vanadium oxide nanotubes (VONTs) were synthesized using the V_2O_5 powder as precursor with dodecylamine as structure-directing template via one-step hydrothermal way. The prepared VONTs sensors exhibit excellent sensing sensitivity and superior recovery property in detecting ethanol vapor. The response to the ethanol vapor and NO_2 gases confirms that the samples are of p-type behavior at 80 °C, which is associated with the presence of the protonated amine molecules in the VONTs. The sample changes to n-type behavior at 260 °C arising from the decomposition of the protonated amine molecules. The p-type VONTs have potential for development of a novel gas sensor.

1. Introduction

The increase concern over safety in industrial activities and in homes has generated great interest in reliable gas detection. Compared to bulk and nanoparticle sensor materials, one-dimensional (1D) nano-materials have been reported to make new semiconductor gas sensors for the higher surface-to-volume ratio and the size which is likely to generate a complete depletion of carriers in the materials [1–8]. 1D vanadium oxides have been reported for their interesting properties such as gas sensing, electrochemical, and optical properties [9–14]. The nanomaterials of vanadium oxide are considered as prominent sensor materials for the quantitative detection of ethanol vapor [15–17], nitric oxide, oxygen, nitrogen oxide [18], triethylamine (TEA) and dimethylmethylphosphonate (DMMP) [19], and so on. The tubular morphology of the vanadium oxide is particularly attractive since it provides access to the three different contact regions: inner and outer surface as well as the tube ends [20], and these make the VONTs likely to be good sensor materials.

Naturally, most metal oxides are n-type semi-conducting materials, and the gas sensing properties of the vanadium oxides have been shown to be consistently n-type semiconductor for the presence of the oxygen vacancy [16,17,19]. In this paper, we report the preparation of the VONTs and develop a novel p-type semiconducting gas sensing VONTs. We relate the formation of the p-type semiconductor to the protonated amine in our VONTs. And the p-type gas sensing behavior supplies a new clue for the variety and flexibility of the gas sensor based on the VONTs.

2. Experimental details

All the reagents were of analytical grade and were used without further purification. The sample was prepared by an initial sol–gel reaction followed by hydrothermal treatment based on the Ref. [21] reported with modification. Vanadium pentoxide (0.900 g) was dissolved in distilled water (45 ml), and the mixture was stirred magnetically for 3 h in air and aged for 12 h to obtain yellow suspension. Another solution was prepared by dissolving dodecylamine (0.916 g) in ethanol (55 ml) which was mixed with the yellow suspension followed by stirring for 36 h, and then the mixture was aged for 12 h to form a suspension with a pH value of about 7.00. And then the resulting solution was transferred into 80 ml Teflon-lined stainless-steel autoclave which was maintained at 180 °C for 3 d. After cooling to room temperature naturally, the final black precipitates were filtered off and successively washed with distilled water and ethanol to remove excess amine and any decomposed products. Finally, the resulting material was dried at 80 °C for 12 h in air and the sample was obtained.

Sensor devices were fabricated by dispersing the VONTs into ethanol and depositing one drop of the resulting suspension onto a ceramic tube on which a pair of Au electrodes was previously printed. Then, the sensor devices were dried at 150 °C for 3 h in air. Lastly, a Ni–Cr heating wire was inserted into the ceramic tube.

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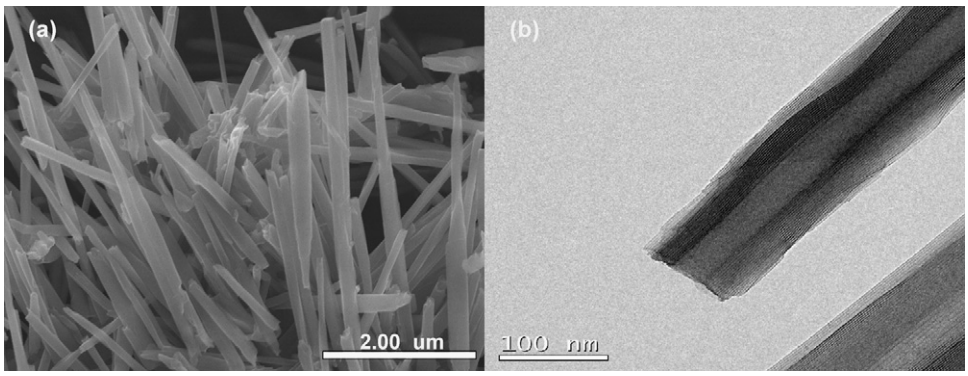

Fig. 1. Morphology of VONTs: (a) FE-SEM image and (b) TEM image.

The collected sample was characterized by field emission-scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscope (TEM, JEM-2010). X-ray diffraction (XRD) patterns were acquired using a Rigaku D/MAX-2400 diffractometer (Cu Kα, λ = 1.54187 Å). X-ray Photoelectron Spectroscopy (XPS) was done with a PHI-5702 XPS-SAM (PHI Co. Ltd., USA). Fourier transform-infrared (FT-IR) spectra were conducted within the 4000–400 cm^{-1}. Wavenumber range using a Nicolet 360 FT-IR spectrometer with the KBr pellet technique. Gas sensing tests were performed by a WS-30A Gas Sensing Measurement System.

3. Results and discussion

3.1. Characterization

The morphology of the sample was studied by FE-SEM and TEM which is shown in Fig. 1. It shows that the sample exhibits the tubular-like morphology. As shown in Fig. 1(a), the VONTs, which are mostly grown-together in the form of bundles, are composed of uniformly tubular-like morphology with a length from 2 to 4 μm. As can be seen from the TEM (Fig. 1(b)), the VONTs present multiple layered walls. The XRD pattern of the product is shown in Fig. 2. It is possible to see three reflections at low angle (lattice structure indexed here as (0 0 1), (0 0 2) and (0 0 3)). These reflections indicate the layered structure of the walls within the VONTs, and the interlayer distance is 2.780 nm for VONTs, which is approximately the same as the d value (2.80 nm) reported by Nesper [22]. At higher angles, the diffractograms are typical of the two dimensional structure of the VO_x layers which form the walls of VONTs [23].

In general, the nanotubes are formed by the scrolling of several vanadium oxide walls with the amine molecules located in-between such layers. During hydrothermal treatment a partial reduction of vanadium from V^{5+} to V^{4+} occurs, owing to the difference in ionic radius between the V species the layers begin to scroll. The prepared sample was analyzed by x-ray photoelectron spectroscopy (XPS), as shown in Fig. 3(a), and the fitted-curves about $V2p_{3/2}$ and $V2p_{1/2}$ are illustrated in Fig. 3(b). No peaks of elements other than C, O, N and V are observed on the survey spectrum and the core level binding energies of $V2p_{3/2}$ and $V2p_{1/2}$ spectra are located at 516.2 and 524.0 eV, respectively. The $V2p_{3/2}$ peak of the sample is divided into two peaks at the binding energies of 517.4 and 516.1 eV, assigned to V^{5+} and V^{4+}, and the V $2p_{1/2}$ peak of the sample is divided into two peaks at the binding energies of 524.2 and 522.3 eV, assigned to V^{5+} and V^{4+}, respectively [24–27].

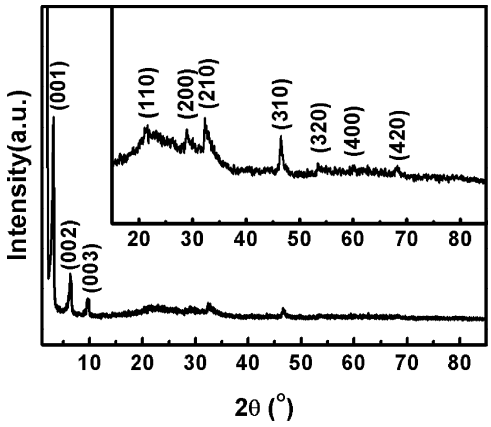

Fig. 2. XRD pattern of the VONTs. The inset shows an enlargement of the weak reflections appearing at high diffraction angles.

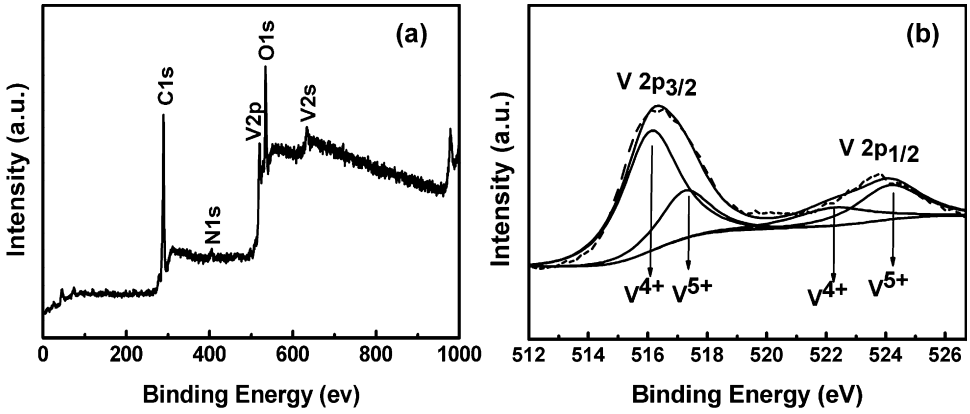

Fig. 3. XPS of the VONTs: (a) survey spectrum and (b) core-level spectrum of V 2p.