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Synthesis and high gas sensitivity of tin oxide nanotubes

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Abstract

Semiconductor tin oxide (SnO_2) nanotubes have been synthesised in bulk quantities using a sol–gel template (AAO membrane) synthetic technique. The morphology and crystal structure of SnO_2 nanotubes were characterised by a field emission scanning electron microscope (FESEM) and a transmission electron microscope (TEM). The as-prepared SnO_2 nanotubes are polycrystalline with an outer diameter of 200 nm, an inner diameter of about 150 nm and a length extending to tens of micrometers. SnO_2 nanotube sensors exhibited high sensitivity towards ethanol gas.

Keywords: Tin oxides; Nanotubes; Sol–gel; Gas-sensors; Nanocrystallites

1. Introduction

One-dimensional (1D) nanostructures including nanotubes, nanowires, and nanoribbons have attracted both intensive and extensive research, which can be mainly attributed to their unique chemical and physical properties, and their intriguing technological applications [1,2]. In particular, 1D semiconductor nanostructures provide building-blocks for fabricating functional nanoscale electronic, optoelectronic, photonic, chemical and biomedical devices based on the bottom-up paradigm [3–7].

Among all the potential applications, nanoscale chemical and biological sensors are generally considered as one of the important areas for nanotechnology to enter into practical applications [8]. The high surface-to-volume ratio of 1D nanostructures induces extremely high sensitivity to adsorbed chemical or biological species on the surface of nanosensors. Lieber et al. have developed silicon nanowire sensors and implemented them as the real-time sensors for detecting pH and biological species [9]. The principle of the Si nanowire sensors is based on the conductance (surface charge) change caused by protonation and deprotonation associated with the adsorbed molecular species. Single and multiple In_2O_3 nanowire sensors have shown high sensitivity to NO_2 and NH_3 gas [10,11]. SnO_2 is a wide-bandgap (3.6 eV) semiconductor. The electronic conductivity of SnO_2 is significantly influenced by the effects on its surface states of molecular adsorption. It has been widely explored as an effective gas sensor, traditionally in the forms of thin or thick films with low sensitivity and long response time [12]. Recently, SnO_2 nanobelts have been tested for their sensitivity to environmental pollutants such as CO and NO_2 [13]. Photochemical SnO_2 nanoribbon sensors have been fabricated for detecting low concentration of NO_2 at room temperature under UV light [14]. Polycrystalline SnO_2 nanowire sensors were also developed for sensing ethanol, CO and H_2 gas [15]. SnO_2 nanohole array sensors exhibited reversible response to H_2 [16].

Herein, we describe the synthesis of polycrystalline SnO_2 nanotubes using the sol–gel template method, and the fabrication of SnO_2 nanotube sensors. Due to their one dimensional and tubular structure, SnO_2 nanotube sensors exhibited high sensitivity and quick response time for detecting ethanol and ammonia gas.

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2. Experimental

Anodic aluminium oxide (AAO) membranes (Whatman, 200 nm pore, 60 μm in thickness, and 47 mm in diameter) were used as the template for preparing SnO_2 nanotubes. The chemicals used were tin(II) chloride dehydrate ($SnCl_2{\cdot}2H_2O$, Aldrich, A.C.S. reagent), sodium hydroxide (Aldrich, 98%) and hydrochloric acid (36%, Merck). SnO_2 nanotubes were synthesised via a sol–gel and sintering process following these steps: (i) 3.38 g $SnCl_2$, 4.7 ml ethanol and 0.3 ml HCl were mixed together and aged for 24 h, during which time the colour of the solution changed from white to pale yellow and finally forming a transparent and highly viscous gel. Then, 0.3 ml deionised water was added to the as-prepared gel to form a solution; (ii) the AAO templates were impregnated by vacuum suction. The solution was forced to pass through the pores of the template and adhere on the pore walls; (iii) the impregnated template was dried at 100 °C and then sintered at 500 °C for 3 h to convert the tin hydroxide to tin oxide; (iv) after sintering, the AAO membrane was dissolved in 6 M NaOH solution. The undissolved SnO_2 nanotubes were collected and washed through a filtering process to remove Na^+ and Al^{3+}. The crystal structures and morphologies of the SnO_2 nanotubes were characterised using X-ray diffraction (XRD, Philips 1730), field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, JEOL 2011). The specific surface area was measured by the Brunauer–Emmett–Teller (BET) method at 77 K using a NOVA 1000 high-speed gas sorption analyzer (Quantachrome Corporation, USA). The gas sensing properties of the as-prepared SnO_2 nanotubes and SnO_2 nanopowders (61 nm in average particle size (APS), Nanostructured & Amorphous Materials Inc., USA) were measured using a WS-30A gas sensor measurement system. SnO_2 nanotubes and nanopowders were mixed with polyvinyl acetate (PVA) binder to form a slurry, and then pasted on to ceramic tubes (2 mm in diameter) between Au electrodes, which were connected with four platinum wires. The fabricated sensors were fitted into the gas-sensing measurement apparatus. Given amounts of ethanol and ammonia gas were injected into the testing chamber by a micro-syringe injector. The gas sensing response was defined as the ratio R_{air}/R_{gas}, where R_{air} and R_{gas} are the electrical resistance of the sensors in air and in gas, respectively. The gas sensing measurement was carried out at a working temperature of 200 °C.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of SnO_2 nanopowders and SnO_2 nanotubes. All diffraction lines can be indexed to the tetragonal rutile phase (JCPDS #41-1445). It should be noted that SnO_2 nanotubes have much broader diffraction peaks and lower diffraction intensities than that of SnO_2 nanopowders, indicating a much small crystal size for the nanotubes. The average crystal size of SnO_2 nanotubes was calculated to be about 15 nm using the Scherrer equation $d = \kappa\lambda/\beta\cos\theta$. The general morphology of SnO_2 nanotubes was observed by FE-SEM and is shown in Fig. 2. The as-prepared SnO_2 nanotubes have lengths of

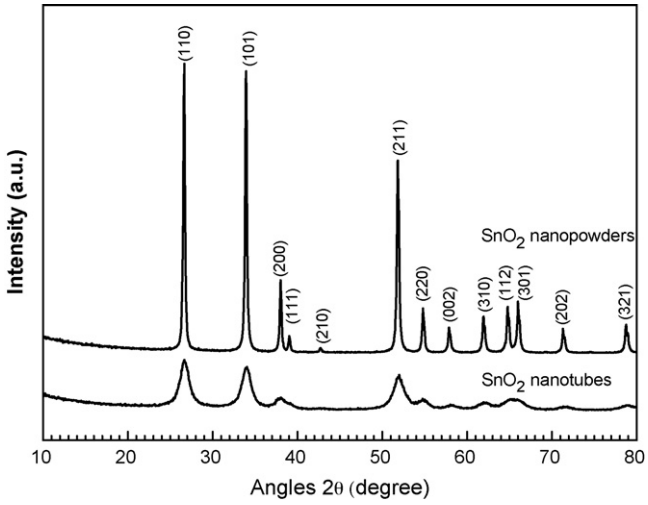

Fig. 1. X-ray diffraction patterns of SnO_2 nanotubes and nanopowders.

a few micrometers. The SnO_2 nanotubes were partially broken, which could have been induced during the sintering process or the subsequent filtering process. The inset in Fig. 2 is a top view of the SnO_2 nanotube bundle, from which we can clearly see the hollow and tubular structure with an outer diameter of 200 nm. We measured the BET surface areas of commercial nanosize SnO_2 powders and as-prepared SnO_2 nanotubes. SnO_2 nanosize powders have a BET surface area of 15.2 m^2/g, while SnO_2 nanotubes have a surface area of 45.6 m^2/g. The crystal structure of the SnO_2 nanotubes was further analysed by TEM and high resolution TEM (HRTEM). A general TEM image of a SnO_2 nanotube is shown in Fig. 3(a). The SnO_2 nanotubes are polycrystalline, with the small nanosize crystals bonded together through the sintering process. Selected area electron diffraction (SAED) was performed on the individual SnO_2 nanotubes (the inset in Fig. 3(a)). The indexed ring patterns confirmed the tetragonal crystal structure of the SnO_2 nanocrystals that form the nanotube. Fig. 3(b) shows a high resolution TEM image of a SnO_2 nanotube, in which the individual crystal sizes are in

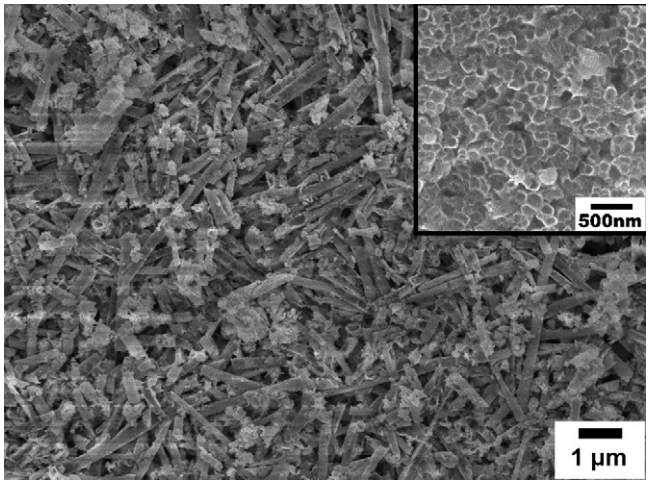

Fig. 2. FESEM image of SnO_2 nanotubes. The inset is a top view of SnO_2 nanotube bundle.