

Fabrication and characterization of wire-like SnO₂

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Received 4 March 2006, in final form 24 April 2006

Published 2 June 2006

Online at stacks.iop.org/JPhysD/39/2494

Abstract

Wire-like SnO₂ is fabricated by the wet chemical method. X-ray diffraction measurements show that the obtained samples have rutile-type structure. Electron transmission microscopy experiments illustrate that the wire-like SnO₂ ranged from 10 to 50 nm in width and several microns (μm) in length. The high-resolution TEM indicates that SnO₂ wires are single crystals. The possible growth mechanism is proposed, and it is found that polyethylene glycol plays an important role in obtaining the wire-like and nano-rods morphology of SnO₂. The band gap is determined to be 3.56 eV. Two photoluminescence peaks located at 389 and 470 nm are observed. Our fabrication method promises a simple way of synthesizing wire-like SnO₂ at a low temperature of 350°C.

1. Introduction

Rutile-type SnO₂ is an important semiconductor with a wide band gap. It is widely used as gas sensor [1] and transparent conducting electrode [2]. Recently, more and more attention has been paid to the fabrication and characterization of one-dimensional (1D) SnO₂, such as nano-wires, nano-rods, nano-belts and nano-tubes [3–7]. The 1D SnO₂ is promising for nano-structured elements. Usually, 1D SnO₂ is fabricated using the vapour–liquid–solid (V–L–S) process, by thermal evaporation of pure Sn, SnO, SnO₂ powders or their mixture [3–8]. Zhang *et al* [9] presented a different way of synthesis of SnO₂ nano-belts by thermal evaporation of SnCl₂ at a temperature of 900°C. As indicated by Zhang *et al* [9], the presently reported routes require very high temperature or high post temperature treatment (above 800°C). However, using polyethylene glycol (PEG) as a morphology-director, vanadium oxide nano-belts were obtained by hydrothermal treatment of NH₄VO₃ at 180°C [10]. In this paper, we illustrate a simple way using PEG as morphology-director to obtain wire-like SnO₂ at a low temperature of 350°C.

2. Experiments

In a typical synthesis route, 0.05 mol tin chloride (hydrous SnCl₄·5H₂O(A.R.)) is dissolved in 96 ml distilled water firstly (pH is adjusted by citric acid to 1.5–2). The solution is stirred and heated up from room temperature to 50°C. When the solution is transparent, with or without 10 ml 100 g l⁻¹ PEG of average molecular weight, 6000 g mol⁻¹ (PEG6000) solution is added secondly. Then 20 ml aqueous ammonia solution (25–28% weight) is added to the above solution dropwise. The dropping rate must be well controlled for the chemical homogeneity. The dropping rate is about 0.7 ml min⁻¹. The reaction temperature is about 50°C. The solution is vigorous stirred during the reaction. The final pH is 7–8. The resulting gel is kept at 50°C for 2 h. After this, it is preserved at room temperature for 11 h, collected, washed with distilled water, and then dried at 100°C for several hours. Finally, heating treatments are conducted at 350°C in air for 1 h. One sample without PEG added and two samples with PEG added in the synthesis routes are investigated in this study.

The crystalline structure of the material is analysed by x-ray diffraction (XRD) using a Rigaku D/max-2400 diffractometer with curved crystal monochromator and Cu–K α radiation (=0.154 056 nm) operated at 40 KV and 60 mA.

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The samples' stoichiometry is measured by a KRATOS X SAM 800 x-ray photoelectron spectroscopy (XPS). The feature micrographs are obtained using a JEM 2010F transmission electron microscope (TEM). After the sample is well dispersed in distilled water suspension using a supersonic disperser, the absorption spectra of the samples are measured on a Shimadzu UV-2500 UV-Visible spectrophotometer. The photoluminescence (PL) spectra are measured with a Shimadzu RF-5301PC spectrofluorophotometer.

3. Results and discussions

Figure 1 shows the XRD pattern of SnO₂ obtained with PEG6000 added in the fabrication routes. The diffraction index is indicated in the figure. As seen in figure 1, XRD measurement reveals that the structure of the samples is rutile-type cassiterite (tetragonal) phase of SnO₂. No other impurity phase is detected in XRD measurements.

Like those reported in [3, 4], the two obtained samples with PEG6000 added in the fabrication routes are rich in

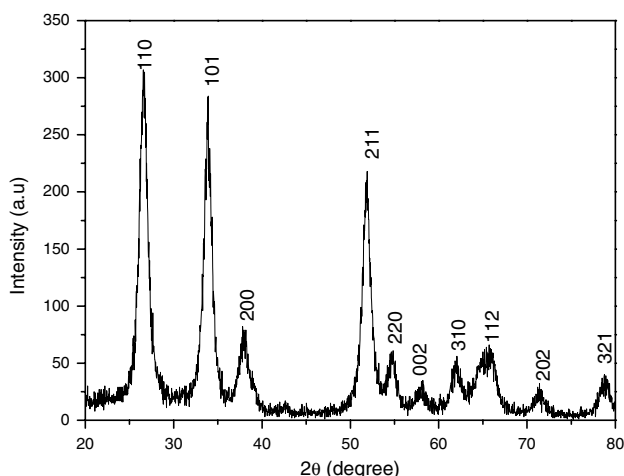


Figure 1. The XRD pattern of SnO₂ with PEG6000 added in the fabrication routes.

morphologies: there are spherical granules, nano-rods and wire-like structures. There are at least 10% fractions of the TEM graphs exhibiting the wire-like structures. The morphologies of the SnO₂ sample with PEG6000 added in the fabrication routes are shown in figures 2(a) and (b). The morphology in figure 2(b) is the most prevalent pattern of the TEM graphs. There are about 90% of the TEM patterns representing this morphology in figure 2(b). As seen in figure 2(a), the wire-like SnO₂ has a width ranging from 10 to 50 nm and length of several microns. Some of the wires are uniform in length, while others have many branches. Furthermore, the wire-like SnO₂ connects with each other and forms a dendritic structure. As indicated by figure 2(b), besides some spherical nano-particles, there are a large number of nano-rods granules. The nano-rods have a length of about 50–400 nm, and a width of about 10–50 nm. The length of nano-rods may be depends on the chain length of the PEG6000. The morphology of the sample without PEG6000 added in the synthesis routes is shown in figure 3. There is no wire-like structure or nano-rods in figure 3, and the grain size is about 50 nm. The difference in characteristics shown between figures 2 and 3 implies that PEG6000 plays a crucial role in determining the morphology of SnO₂. In the report on the synthesis of vanadium oxide nano-belts [10], the PEG polymer acts as heterogeneous nucleation sites for V₂O₅·nH₂O due to the fact that lower activation energy is required for heterogeneous nucleation at the polymer/water interface. And, the more or less extended polymer chain of PEG serves as the template directing the assembly and 1D growth of vanadium oxide to form belt-like nano-structures. In the formation of ZnO nano-rods [11], it seems that PEG has special interaction with some facets of ZnO. PEG seems to have strong interaction with the side planes of the hexagonal prismatic ZnO (which are {100} facets) and relatively weak interaction with the end planes (bounded by {001} facets). This difference will cause the change of the relative growth rate of different facets, which causes ZnO to grow fast along the [001] direction. Ma *et al* [12] indicated that the more or less extended order of PEG polymer chain could provide a new sort of organization to metal atoms along the polymer

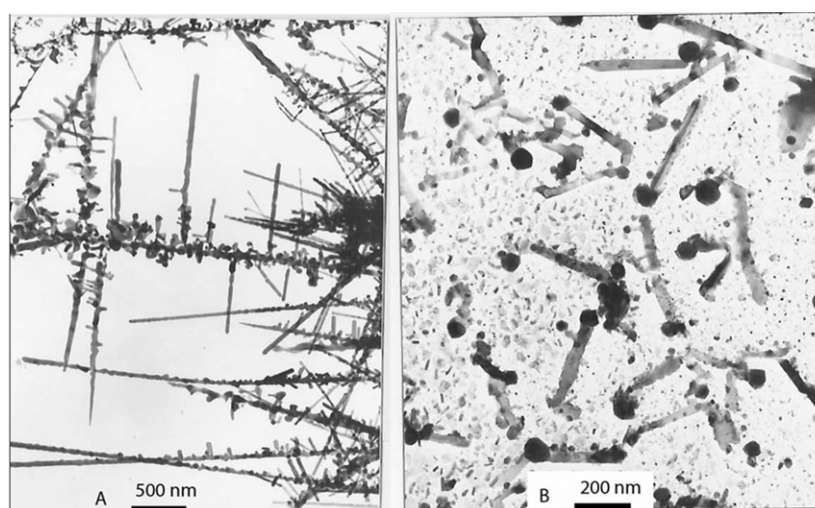


Figure 2. The TEM morphology of SnO₂ with PEG6000 added in the fabrication routes: (a) nano-wire like structures and (b) nano-rods and spherical particles.

backbone, which affords the diverse assembling ways for the 1D growth of the final products. The chain of every PEG may be extends and interacts with each other in an end-to-end way when the amount of PEG is sufficient and thus can form 1D further longer chain. Liu *et al* [13] showed that in the presence of alkalescence, Zn^{2+} can link with O atom in the chain of C–O–C, which induced the change of the nucleation energy and led to the yield of ZnO seed crystal along the direction of the chain of PEG by the reaction between $Zn(NH_3)_4^{2+}$ and OH^- . $Zn(NH_3)_4^{2+}$ is the reaction results of $Zn(NO_3)_2 \cdot 6H_2O$ and $NH_4 \cdot H_2O$ ($Zn^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4^{2+}$). As far as our case is concerned, the role played by ammonia may be similar to that played by $NH_4 \cdot H_2O$ in [13]. Like that presented by Liu *et al* [13], we suppose that Sn^{4+} can link with O atom in the chain of C–O–C, which induced the change of the nucleation energy and led to the yield of SnO_2 seed crystal along the direction of the chain of PEG. After heat treatment, the wire-like structure and nano-rods of SnO_2 are formed. On the other hand, PEG may have special interaction with some facets of SnO_2 , which is similar to that proposed by [11]. Thus, the

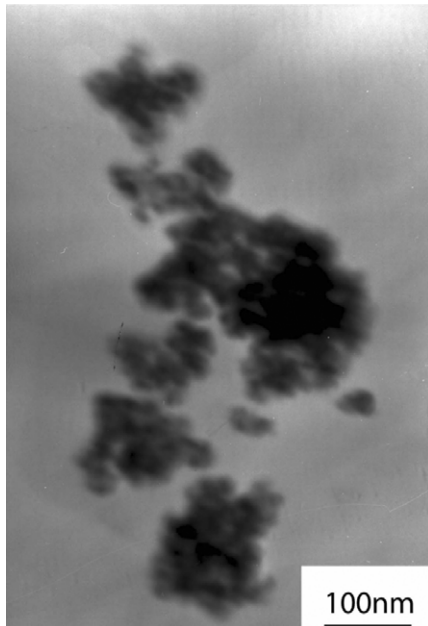


Figure 3. The TEM morphology of SnO_2 without PEG6000 added in the fabrication routes.

soft-template function of PEG is the very reason for obtaining wire-like and nano-rods SnO_2 . The chain structures of PEG are the morphology-directors in the growth process of nano-rods and wire-like SnO_2 . The high-resolution TEM (HRTEM) morphology of an individual wire is shown in figure 4, which reveals that the wire is single crystal.

To determine the absorption band edge, we fit the absorption data to equation (1) for the SnO_2 sample with PEG6000 added in the fabrication routes:

$$(\alpha\hbar\omega)^2 \propto (\hbar\omega - E_g), \quad (1)$$

in which $\hbar\omega$ is the photon energy, α is absorption coefficient and E_g is the absorption band gap energy. E_g is given by extrapolating the linear regions to zero absorption. As determined in figure 5, the band gap energy is 3.56 eV, which is the same as that of the bulk SnO_2 material.

PL spectrum is convenient to investigate the structure and defect or impurity levels [14]. Figure 6 shows the room temperature PL spectrum for the SnO_2 sample with PEG6000 added in the fabrication routes. The excitation wavelength used for the PL measurements is 350 nm (3.54 eV). The PL spectrum shows a strong UV emission peak at 389 nm (3.188 eV) and a broad blue emission near 470 nm (2.638 eV). Since the excitation and emissions are both lower than the band gap of SnO_2 ($E_g = 3.56$ eV), the emissions cannot be assigned to the direct recombination of a conduction electron in the Sn 4p band and a hole in the O 2p valence band. This is similar to that reported by Gu *et al* [15]. Kim [16] reported a weak peak at 3.13 eV emitted from undoped SnO_2 at low temperature and room temperature, and they thought that the origin of the peak was related to defects or nano-crystal grains or to defect levels associated with oxygen vacancies or tin interstitials resulting from the nano-size of the SnO_2 film. Thereafter, Jin [14] concluded that the PL peak at 3.1 eV was related to the structural defects and the peak at 2.4 eV was due to oxygen vacancies. Furthermore, Wang [17] reported that the oxygen vacancies do not play an important role in the origin of the UV emission at 3.16 eV of Sb doped SnO_2 . As far as our samples are concerned, the SnO_2 sample may have a large number of defects: vacancies of oxygen, vacancy clusters and local lattice disorder at the interface and interior

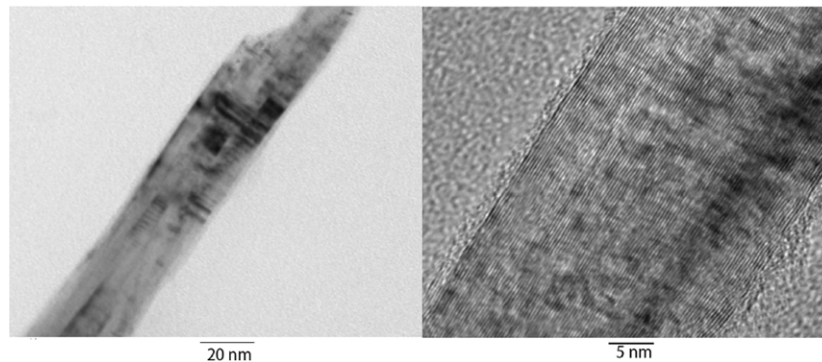


Figure 4. The HRTEM morphology of one individual SnO_2 wire.

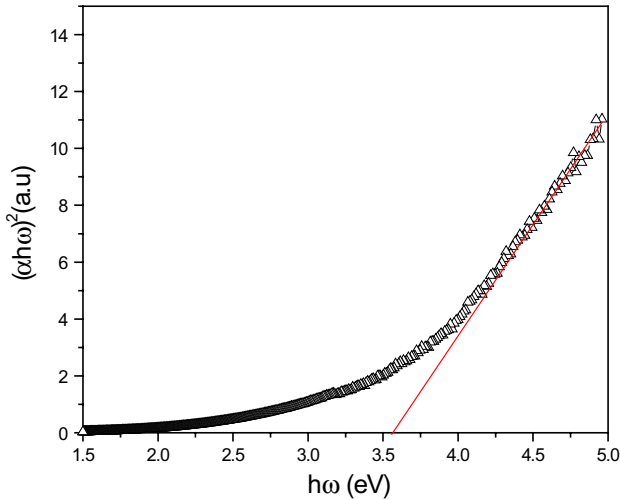


Figure 5. The $(\alpha\hbar\omega)^2$ as a function of $\hbar\omega - E_g$ for SnO₂ with PEG6000 added in the fabrication routes. The solid line is a linear fitting to the experimental data.

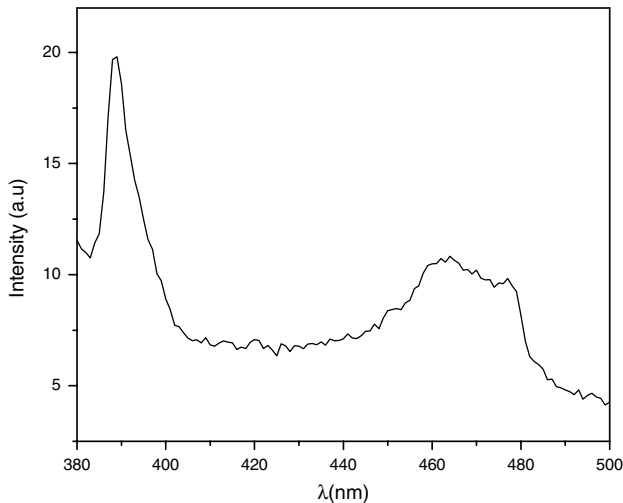


Figure 6. The PL spectra of SnO₂ with PEG6000 added in the fabrication routes.

surface. So it is difficult to identify the origin of UV and blue emission.

4. Conclusion

In this paper we present a simple way of fabricating wire-like SnO₂ at a low temperature of 350 °C. It is found that PEG plays a crucial role in this synthesis route. The chain structure of PEG is the morphology-director in the growth process. The band gap is determined to be 3.56 eV. There are two PL peaks at 389 and 470 nm. Our synthesis method is different from the V–L–S process and promising.

Acknowledgments

This study was supported financially by the NSAF Joint Foundation of China (10376006) and by the Program for New Century Excellent Talents in University and the PhD Funding Support Program of the Education Ministry of China (20050614013).

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