

Synthesis and room-temperature ferromagnetism in flower-like SnO₂ nanostructures

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Abstract. The flower-like nanostructures of SnO₂ were successfully synthesized by a simple hydrothermal method. The structure of the flower-like samples was investigated by X-ray diffraction (XRD). The samples revealed the single phase of SnO₂ tetragonal structure. The corresponding selected-area electron diffraction (SAED) analysis further confirmed the formation of the tetragonal structure of SnO₂ without secondary phases. The UV-visible spectroscopy showed the absorption peaks of SnO₂ flower-like samples in ultraviolet region centered at approximately 275 nm (4.37 eV). The estimated band gap of the samples was in the range of 3.47-3.52 eV. The magnetic properties were investigated by VSM. The flower-like sample prepared at 180°C for 48 h exhibits a diamagnetic behavior, whereas the sample prepared at 180°C for 24 h is ferromagnetic having the saturation magnetization of 0.574 memu/g at 15 kOe.

1. Introduction

Tin oxide (SnO₂) is one of most functional materials with a wide bandgap of about 3.6-4.0 eV [1, 2]. It is widely used for various devices such as transparent electrodes [3], gas sensors [4], photocatalysts [5], supercapacitors and dye-sensitized solar cells [6]. In addition, SnO₂ has been widely used for the development of multifunctional magneto-optoelectronic devices [7]. Recently, 3d transition metal doped SnO₂ nanostructures have been reported to exhibit ferromagnetism at room-temperature [8-10]. Surprisingly, the phenomenon of *d⁰* ferromagnetic semiconductors and insulators oxides have been reported by many researchers, such as thin films of HfO₂ [11] and nanostructures of TiO₂, CeO₂ and SnO₂ [12, 13], while the corresponding bulks are diamagnetic behaviour. Most recently, there are some studies reporting room-temperature ferromagnetism observed in pure SnO₂ nanostructures [13, 14]. At present, only few studies have been reported on magnetic properties of hierarchical flower-like SnO₂ nanostructures. Therefore, it is of great interest to investigate the ferromagnetic properties in hierarchical flower-like architectures of SnO₂ as it will be potentially useful for permanent nanomagnets and data storage.

In this article, we report a successful synthesis and magnetic properties of hierarchical SnO₂ flower-like architectures assembled by nanorods under hydrothermal conditions. The synthesized flower-like nanostructures were characterized by XRD, TEM and Optical absorption measured by UV-vis was carried out to estimate the bandgap energy (E_g). The magnetic properties of SnO₂ flower-like nanostructures were investigated using VSM at room-temperature. The origin of ferromagnetism in the flower-like nanostructures is also discussed.

2. Experimental procedure

In this study, high purity chloride of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (99.99%, Sigma-Aldrich) was used as starting material. In a typical procedure, 15 ml of deionized water and 5 ml of absolute ethanol were placed in a 100 ml beaker. Then 1g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was added to the beaker. The mixed solution was stirred with a magnetic stirrer at room-temperature for 3 h, followed by addition sodium hydroxide (NaOH) until its pH reaches 11. The homogeneous solution was transferred into a Teflon-lined stainless steel autoclave, sealed and maintained at 180°C for 24 and 48 h. After the autoclave was cooled naturally to room-temperature, the precipitate was collected and washed several times with deionized water and ethanol separately. The product was then dried in a vacuum at 70°C for 6 h. The final product obtained was white SnO_2 powders. The samples were characterized for crystal phase identification by powder X-ray diffraction (XRD) using a Philips X-ray diffractometer (PW3710, The Netherlands) with $\text{CuK}\alpha$ radiation ($\lambda = 0.15406$ nm). The morphology of SnO_2 flower-like samples were characterized by transmission electron microscopy (TEM) (Hitachi H8100 200 kV). The optical absorption spectra were measured in the range of 200-800 nm using a UV-vis spectrometer (T80/T80t, PG Instruments Limited, UK). The magnetic measurements were performed at room temperature using a vibrating sample magnetometer (Versa Lab VSM, Quantum Design).

3. Results and discussion

A detailed study was investigated to characterize the SnO_2 flower-like nanostructures prepared at varying treatment time conditions. The XRD patterns of the flower-like samples prepared by hydrothermal reaction at 180°C for 24 and 48 h are shown in Figure 1. It can be seen that the samples have the similar XRD patterns, which can be indexed to tetragonal structure of SnO_2 when compared to standard data (JCPDS 88-0287). There is no diffraction peak originating from impurity phase in the XRD pattern, indicating that SnO_2 was successfully synthesized via these procedures. The sharp peaks signify that the samples may have a high degree of crystallization [15]. No remarkable shift is detected in the diffraction peaks, indicating that the samples are of high purity.

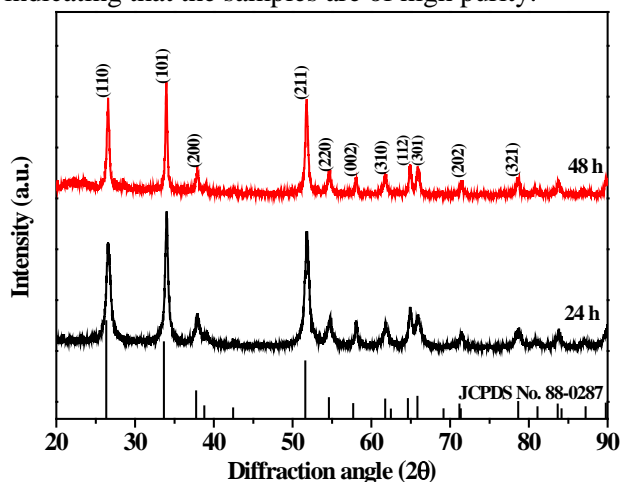


Figure 1. The XRD patterns of SnO_2 flower-like nanostructures prepared at 180°C for 24 and 48 h

The morphology and structure of SnO_2 flower-like samples were investigated by TEM as shown in Figure 2. Figure 2(a) show TEM bright field images of hierarchical flower-like architectures. The flower is assembled by nanorods and hierarchical structures are uniformly distributed across the whole sample. This result is similar to the work reported by Zeng et al. [15], in which flower-like SnO_2 assembled by nanorods were synthesized by hydrothermal treatment. The unique flower is found to consist of many well-ordered nanorods with a length of $\sim 29\text{-}38$ nm and a width of $\sim 12\text{-}17$ nm (Figure 2(a)). When the reaction time is 48 h (Figure 2(b)), the sample presents the multi-shaped and flower morphologies. The flower morphology is assembled by thicker nanorods with irregular diameters. These results indicate that the treatment time play an important role in the size and morphology of SnO_2 samples. The corresponding SAED patterns of the flower-like samples (inset in Figure 2(a) and (b)) reveal spotty ring patterns typical of polycrystalline materials of the tetragonal structure of SnO_2 , which is in agreement with the XRD results and no secondary phases exist. The measured interplanar spacing (d_{hkl}) from SAED

patterns is good agreement with the values in the standard data (JCPDS:88-0287). This result confirms the formation of SnO₂ flower-like nanostructures indicating polycrystalline character.

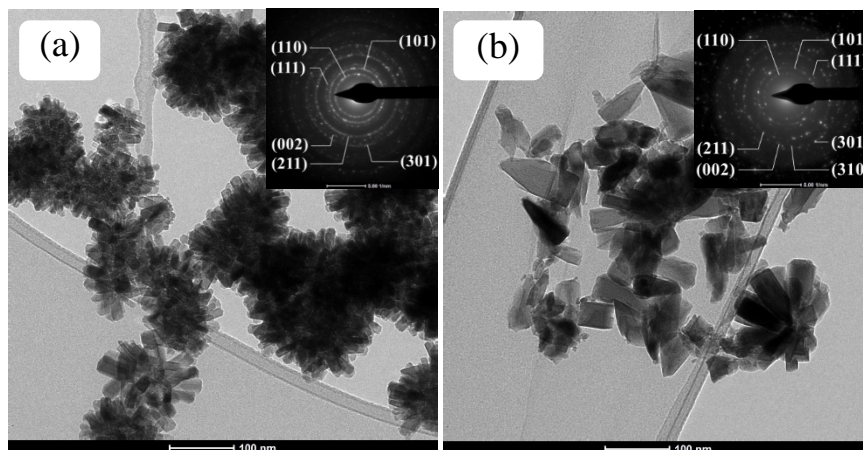


Figure 2. TEM images with corresponding selected area electron diffraction (SAED) patterns of SnO₂ flower-like nanostructures prepared at 180°C for (a) 24 h and (b) 48 h

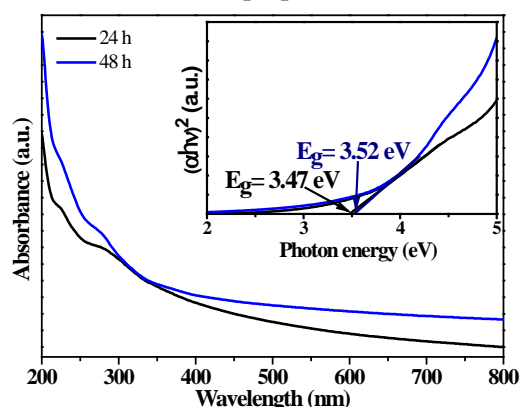


Figure 3. Optical absorbance spectra and plot of $(ahv)^2$ as a function of photon energy for SnO₂ samples (inset)

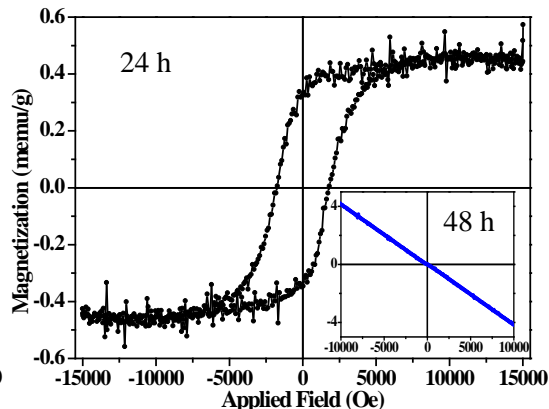


Figure 4. Magnetization of SnO₂ flower-like nanostructures

The UV-vis absorption spectra of SnO₂ flower-like nanostructures are shown in Figure 3. The optical absorption of the samples increases as the wavelength decreases. The absorption spectra for the samples show absorption below 350 nm (3.54 eV). The optical band gap of the samples can be obtained by extrapolating the linear portion of the plot $(ahv)^2$ versus $h\nu$. The inset of Figure 3 shows the extrapolation of the linear portion of the curves toward absorption equal to zero ($y = 0$) give E_g for direct transitions [16]. The estimated optical band gap energy for SnO₂ samples are 3.47 eV and 3.52 eV. The optical band gap of SnO₂ flower-like nanostructures is blueshifted from 3.47 to 3.52 eV as the treatment time is increased from 24 to 48 h. The different condition of preparation effects on defect formation in SnO₂ structure lead to an increase in the carrier concentration [17]. Figure 4 shows the field dependence of magnetization (M-H curve) of the SnO₂ flower-like samples prepared at 180°C for 24 and 48 h obtained from room-temperature VSM measurement (with the removal of any diamagnetic contribution). The flower-like sample of SnO₂ prepared at 180°C for 24 h exhibits room-temperature ferromagnetism with the saturation magnetization (M_s) of ~ 0.574 memu/g and the coercivity (H_c) of ~ 1775 Oe. However, the sample of SnO₂ prepared at 180°C for 48 h shows diamagnetic behaviour at room-temperature (the inset in Figure 4) which may be due to the valence state of tin which favors the $4d^{10}$ (Sn⁴⁺) electronic configuration in SnO₂. Therefore, there are no unpaired d electrons in the host system for ferromagnetic

ordering [18]. This result indicates that the different treatment times may attribute to oxygen vacancies and surface defects in the SnO₂ flower-like nanostructures. The phenomena have been observed in SnO₂ nanowires and nanoparticles [13, 14, 17]. In addition, the existence of room-temperature ferromagnetism in metal oxides is strongly dependent on the preparation route chosen. The origin of ferromagnetism in the nonmagnetic oxides nanoparticles results possible from the exchange interaction between unpaired electron spin and oxygen vacancies on the surface of the oxide nanoparticles [19]. This direct ferromagnetic coupling is called the F-center exchange (FCF). Therefore, the possible mechanism of intrinsic ferromagnetism in SnO₂ system can be explained on the model of the FCF interaction, as tin can have three variable valence states (Sn⁴⁺/Sn³⁺/Sn²⁺) and oxygen vacancies on the surface. It is possible that oxygen vacancies can create magnetic moments on neighboring Sn ions [17, 20]. The high value of H_c in the SnO₂ flower-like sample might be related to the magnetic moments of Sn ions at the cores of nanorod-flower. This make the sample response to the applied field will be slow [17].

4. Conclusion

Room-temperature ferromagnetism of flower-like SnO₂ nanostructures was synthesized by a simple hydrothermal method. The XRD and SAED results of flower-like samples prepared at 180°C for 24 and 48 h suggested the formation of a tetragonal structure and that no secondary phase was detected. The direct band gap of SnO₂ samples was determined to be in the range of 3.47 to 3.52 eV. The sample synthesized at 180°C 24 h show room-temperature ferromagnetism with M_s value of 0.574 memu/g.

Acknowledgments

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