Nanostructures of tin oxide by a simple chemical route: synthesis and characterization

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Abstract. Tin oxide (SnO₂) nanostructures have been synthesized by a simple chemical route. The morphology and crystallization of the samples can be controlled by changing the mixed solution of tin chloride. The precursors were calcined at 600 °C for 2 h in air to obtain the SnO₂ nanorods and nanoparticles. The phase composition of the samples was investigated by XRD and electron diffraction analysis. The results confirmed the formation of a SnO₂ phase with tetragonal structure. The optical properties of the nanostructures were investigated by UV-vis spectroscopy. The estimated band gaps of nanorods and nanoparticles were 3.39 and 4.23 eV, respectively. The results revealed that the morphologies and band gaps of the samples varied with the mixed solution of tin chloride.

1. Introduction
Nanostructures of metal oxides have received significant attention because of their size-dependent properties and great potential for a variety of applications such as transparent electrodes, liquid crystal displays, solar cell and supercapacitors [1, 2]. The morphology of metal oxides, either rod, spherical or fiber shaped, will have an effect on properties [3]. Therefore, the experimental conditions are very important [4]. Nanostructures of tin oxide (SnO₂) have wide range of applications as an n-type semiconductor with band gap of about 3.6-4.0 eV [5]. Nanostructured SnO₂ have been synthesized by several methods including hydrothermal, sol-gel and precipitation [6]. Among these methods, a simple effective route to synthesize nanoscale of SnO₂ by the use of nontoxic and environmentally benign precursor is still the key issue [2].

In this article, we report a successful synthesis SnO₂ nanorods and nanoparticles by a simple chemical route using tin chloride dihydrate and PVA as the starting materials. The synthesized nanostructures were characterized by TG-DTA, XRD, TEM, HRTEM and optical absorption measured by UV-vis was carried out to estimate the bandgap energy (Eg). The effect of the condition for preparation in the morphology and optical properties is also discussed.

2. Experimental procedure
Tin oxide nanoparticles and nanorods were synthesized by a simple chemical route. SnCl₂.2H₂O and polyvinyl alcohol were used as starting chemicals. In typical procedure for SnO₂ nanoparticles, 4.513 g SnCl₂.2H₂O solution prepared in 200 ml deionized water (DI water) was stirred at 80 °C for several hours in air until dry. The resultant material of primary calcination was ground and sieved to give yellow
powder. For SnO$_2$ nanorods, PVA-polymer solution was prepared by dissolved 4 g PVA in a mix solution of 100 ml DI water. Subsequently, this solution was mixed with the solution of tin chloride dihydrate. Throughout the whole process described above, no pH adjustment was made. Then, the mixed solution was continuously stirred at 80 °C until the dried precursor was obtained. Finally, the dried precursor was calcined in air at 600 °C for 2 h to obtain SnO$_2$ powders. The as-synthesized SnO$_2$ powders were characterized by thermogravimetric-differential thermal analysis (TG-DTA) (TA Inc., SDT 2960). The calcined samples were characterized for crystal phase identification by powder X-ray diffraction (XRD) using a Philips X-ray diffractometer (PW3710, The Netherlands) with CuK$_\alpha$ radiation ($\lambda$=0.15406 nm). The particle size and morphology of SnO$_2$ powders were characterized by transmission electron microscopy (Hitachi H8100 200kV). The optical absorption spectra were measured in the range of 200-800 nm using a UV-vis spectrometer (T80/T80t, PG Instruments Limited, UK).

3. Results and discussion

Figure 1(a) and (b) show the simultaneous TG-DTA curves of the nanoparticles and nanorods precursors. The TG curve exhibits two weight loss steps: the first step (~5.75%) is between ~50 and 141 °C and second weight loss step (~29.03%) is between ~141 and 382 °C. The weight loss between ~50 and 141 °C is related to the loss of water. The major weight loss (~141-382 °C) is related to the combustion of chloride as shown in figure 1(a). On the DTA curve of figure 1 (a), the exothermic peak is observed to have maximum at ~ 380 °C confirmed the major weight loss of chloride [3]. For the precursor of nanorods, the TG curve shows two weight loss steps: the first step (~31.58%) is between ~50 and 363 °C and second weight loss step (~34.79%) is between ~363 and 557 °C. The weight loss between ~50 and 363 °C is related to the loss of water and chloride. The weight loss (~363-557 °C) is related to the combustion of organic residues from PVA as shown in figure 1(b). On the DTA curve of figure 1(b) the main exothermic effect was observed at 360 and 493 °C, indicating that the thermal events can be associated with the burnout of organic species involved in the precursor powders (organic mass remained from PVA), of the residual carbon or due to direct crystallization SnO$_2$ from the amorphous component [6]. No further weight loss and no thermal effect were observed above ~ 557 °C, indicating that no decomposition occurs above this temperature. In this work, the precursor was calcined in air at 600 °C for 2 h in order to develop crystallization.

![Figure 1. TG-DTA curves of thermal decomposition of tin chloride dihydrate (SnCl$_2$.2H$_2$O) (a) in DI water and (b) PVA system.](image)

The XRD patterns of the samples are shown in figure 2. It can be seen that the samples have similar XRD patterns, which can be indexed to tetragonal structure of SnO$_2$ with lattice constant $a = 0.4755$ Å and $c = 0.3189$ Å for the nanoparticles and $a = 0.4744$ Å and $c = 0.3190$ Å for nanorods (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 shape peaks signify that the samples may
have a high degree of crystallization [7]. The morphology and structure of SnO$_2$ samples were investigated by TEM as shown in figure 3(a) and (b). Figure 3(a) shows TEM bright field image, selected area electron diffraction pattern (SAED) and high resolution TEM (HRTEM) of SnO$_2$ nanoparticles. TEM bright field image of SnO$_2$ sample shows the agglomerated nanoparticles with particle size of 15-20 nm. The SAED pattern of the sample reveals spotty ring patterns of tetragonal structure of SnO$_2$. The high-resolution TEM image in figure 3(a) reveals the details of the SnO$_2$ nanoparticles with the measured spacing of the lattice fringe of ~0.2649 nm corresponding to the (101) plane of SnO$_2$. Figure 3(b) reveals TEM bright field image, SAED and HRTEM of SnO$_2$ nanorods sample. The rod size of the sample estimated from TEM bright field image are around 56-75 nm (width) and 146-204 nm (length). The SAED pattern shows spotty ring patterns of tetragonal structure of SnO$_2$. The HRTEM image reveals the measured spacing of the lattice fringe of ~0.2646 nm (figure 3(b)) corresponding to the (101) plane of SnO$_2$. This is in agreement with the standard data (JCPDS: 88-0287).

![Figure 2](image2.png)  
**Figure 2.** XRD patterns of the SnO$_2$ nanostructures synthesized in DI water and PVA system.

![Figure 3](image3.png)  
**Figure 3.** TEM and HRTEM images with corresponding selected area electron diffraction (SAED) patterns of SnO$_2$ nanostructures obtained (a) in DI water and (b) PVA system.

![Figure 4](image4.png)  
**Figure 4.** Optical absorbance spectra (a) and $(ahv)^2$ as a function of photon energy for SnO$_2$ samples (b) produced in DI water and PVA system.

The UV-vis absorption spectra of SnO$_2$ nanostructures are shown in figure 4(a) and (b). The optical absorption of the samples increases as the wavelength decreases. The position of the absorption edges were calculated by the peak positions of the first derivative of the spectra. In DI water and PVA solvents have peaks centered at about 261 nm (4.75 eV) and 294 nm (4.22 eV). The optical absorption increases as the wavelength decreases. The absorption spectra for the samples show absorption below 350 nm.
(3.54 eV) as shown in Figure 4(a). The optical band gap \(E_g\) of each sample was estimated using the following equation [4] and Tauc plot method [8]:

\[
\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}}
\]

where \(\alpha\) is the optical absorption coefficient, \(h\nu\) is the photon energy, \(E_g\) is the direct band gap and \(A\) is a constant [9]. The optical band gap of the samples can be obtained by extrapolating the linear portion of the plot \((\alpha h\nu)^2\) versus \(h\nu\). Figure 4(b) shows the extrapolation of the linear portion of the curves toward absorption equal to zero \((y = 0)\) give \(E_g\) for direct transitions [10]. The estimated optical band gap energy for SnO\(_2\) samples are 3.39 eV and 4.23 eV for nanorods and nanoparticles. The optical band gap of nanoscale oxide materials depend on the size of particle, which related to two factors: the quantum size effect and interface effect [11]. In this work, the difference in the optical band gap is not due to the quantum size effect because the size of SnO\(_2\) samples are larger than a few nanometer. The optical band gap of the samples is blueshifted from 3.39 to 4.23 eV for nanorods and nanoparticles. These results indicate that the morphology plays an important role in the optical band gap of SnO\(_2\) nanostructures. The band gap in this work is close to that reported in the literatures [11, 12, 13].

4. Conclusion

Nanostructured SnO\(_2\) was successfully synthesized by a simple chemical route. The XRD and SAED results of the samples suggested the formation of a tetragonal structure and that no secondary phase was detected. The direct band gap of SnO\(_2\) samples was determined to be in the range of 3.39 to 4.23 eV. The results indicate that the condition of preparation can be controlled morphology and optical properties of the samples. The method has the important advantage to be simple, fast, nontoxic and can be extended to synthesis of many other oxide materials.

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References

[1] Liu J, Huang J, Li X, Liu H and Zhang Y 2013 Mater. Sci. Semicond. Process. 16 742
[2] Wu S, Wang M, Li C, Zhu Y and Wang H 2014 Mater. Chem. Phys. 147 184
[3] Al-Gaashani R, Radiman S, Tabet N and Daud A R 2012 Mater. Sci. Eng. B 177 462
[4] Das S, Kar S and Chaudhuri S J. 2006 Appl. Phys. 99 114303
[5] Pal J and Chauhan P 2009 Mater. Charact. 60 1512
[6] Wongsaprom K, Bornphotsawatkun R and Swatsitang E 2014 Appl. Phys. A 114 373
[7] Zeng W, Zhang H, Li Y, Chen W and Wang Z 2014 Mater. Res. Bull. 57 91
[8] Tauc J, Grigorovici R and Vancu A 1966 Phys. Solid State 15 627
[9] Ziegler E, Heinrich A, Oppermann H and Stöver G 1981 Phys. Solid State 66 635
[10] Ahmed A S, Azam A, Shafeeq M M, Chaman M and Tabassum S 2012 J. Phys. Chem. Solids 73 943
[11] Barreca D, Bruno G, Gasparotto A, Losurdo M and Tondello E 2003 Mater. Sci. Eng. C 23 1013
[12] Agrahari V, Mathpal M C, Kumar M and Agarwal A 2015 J. Alloys Compd. 622 48
[13] Kimura H, Fukumura T, Kawasaki M, Inaba K and Hasegawa T 2002 Appl. Phys. Lett. 80 94