Journal of Physical Sciences, Vol. 17, 2013, 185-190
ISSN: 0972-8791, www.vidyasagar.ac.in/journal
Published on 26 December 2013

Hydrothermal Synthesis of EDTA–capped Brain-like SnO_2 Nanoparticles

S. Gnanam and V. Rajendran

Department of Physics, Presidency College
Chennai – 600 005, Tamilnadu, India
E-mail: gnanam.sambatham@gmail.com

ABSTRACT

Brain-like morphology of EDTA assisted SnO_2 nanoparticles have been synthesized by facile hydrothermal process. The XRD analysis shows that well crystallized tetragonal rutile SnO_2 can be obtained and the crystal size was 7.5 nm for the sample calcined at 400ºC for 2h. Brain-like morphology of the prepared SnO_2 nanoparticles was observed in the SEM studies. We believe these brain-like SnO_2 nanostructures will offer new opportunities for the development of nanoscale electronics, optics and gas sensing applications. The significant optical properties of this material may be very interesting for further application on catalyst and chemical sensors.

Keywords: SnO_2; Nanoparticles; EDTA; Brain-like morphology; Optical properties

1. Introduction

Recently, synthesis of nanomaterials with controlled morphology, size, chemical composition and crystal structure, and in large quantity, is a key step toward nanotechnological applications [1]. Tin oxide (SnO_2) is an n-type semiconductor with excellent optical and electrical properties, partly due to its wide band gap (E_g = 3.6 eV). Nanosized SnO_2 has been extensively investigated in various areas, such as transparent conductive electrodes and transistors, Li-ion batteries, dye-sensitized solar cells, and chemical gas sensors [2]. Tin oxide nanoparticles were prepared by different wet chemical routes, such as precipitation, sol-gel, hydrothermal, spray pyrolysis, solvothermal, and microwave methods [3, 4]. Among the chemical methods, hydrothermal process is often used due to its simplicity, allowing the control of grain size, morphology and degree of crystallinity by easy changes in the synthesis procedure. Manna et al. [5] synthesized CdSe nanocrystals with rod, arrow, tear-drop and tetrapod morphologies, just by manipulating parameters related to crystal growth. Since the shape, size, and dimensionality of semiconductors are vital parameters for their properties, developing a facile method to prepare important nanomaterials with well-defined structures is of great interest and importance. To control the shape of nanocrystals in solution phase, many kinds of organic compounds such as surfactants and polymers have been used to direct or confine anisotropic growth. These capping reagents can bind with the various crystallographic surfaces to alter their growth rates. Furthermore, using solution-based route to prepare SnO_2 nanostructures such as nano-brain-like with branched structures have not been reported up to date. In this article, we report a facile hydrothermal route to control the size and shape of EDTA capped brain-like morphology

of SnO_2 nanoparticles. The introduction of a small quantity of capping agent in the reaction system was found to play a great role in the size- and shape-control. The influence of EDTA on morphology and optical properties of synthesized SnO_2 nanoparticles were discussed.

2. Experimental procedure

All chemical reagents were commercial with AR purity, and used directly without further purification. Initially, 0.78 g of ethylenediaminetetraacetic acid (EDTA) was dissolved in 35 ml of distilled water under magnetic stirring. Then, 0.15M of ammonium oxalate was added into 35 ml of water–ethanol mixtures (1:1, v/v) containing 0.1M of $SnCl_4.5H_2O$ and dissolved in above solution under stirring. After that, 5ml of ethylene glycol (polymerizing agent) was added into the above solution and stirred for 30 min to form a sol solution. After that, the sol solution was transferred into a Teflon-lined autoclave for hydrothermal reaction at 120 °C for 15 h. After that, the brownish-black hydrothermal product was filtered and washed several times with water-ethanol mixtures. Finally, the sandal colored SnO_2 nanoparticles were formed at 400°C for 2h.

The prepared SnO_2 samples were characterized by powder X-Ray diffractometer (XRD) using XPERT PRO with CuK_α radiation λ=0.154nm at scanning speed of 2^o/min from 20^o to 80^o. The Fourier transform infrared (FTIR) spectrum of the sample was collected using a Bruker IFS 66V FTIR spectrometer. Optical absorption spectrum of the sample was taken with Varian Cary 5E Spectrophotometer. The room temperature photoluminescence (PL) spectrum of SnO_2 was recorded with fluorescence spectrometer (FLS920) using Xe lamp as the excitation source at excitation wavelength λ_{ex}=250nm. The Scanning Electron Microscopy (SEM) image was taken using JEOL, JSM-67001. The Transmission electron microscopy (TEM) image was taken using an H- 800 TEM (Hitachi, Japan) with an accelerating voltage of 100 kV.

3. Results and discussion

Fig.1 shows the XRD pattern of EDTA-capped SnO_2 sample. It demonstrates that the SnO_2 tetragonal rutile structure with lattice constants a=b=0.4743 nm and c=0.3186 nm, which match well with the standard XRD data file of SnO_2 (JCPDS file no.041-1445). No extra peaks were observed in the XRD pattern due to either tin metal or surfactants that implies the formation of pure and single-phase of tin oxide. The width of the reflections is considerably broadened, which indicates a small crystalline domain size. The average size of the sample prepared at 400ºC using Debye-Scherrer's formula was about 7.5 nm.

Fig. 2 shows the FTIR spectrum of as-synthesized SnO_2 samples. It shows strong vibrations at ~3423 and 1614cm^{-1}, which can be related to ν (O-H) and δ (O-H), respectively. The vibrations at 2919-2800 cm^{-1} (i.e., ν (C-H)) and at 1387-900 cm^{-1} (i.e., δ (C-H)) can be ascribed to minor amounts of residual additives. However, the lower wave number region exhibits a very strong vibration at ~547cm^{-1}, which can be assigned to ν (Sn–O–Sn) of the tin oxide framework.

Fig.3 shows the UV absorption spectrum of EDTA-capped SnO_2 samples calcined at 400 ºC. The band gap energy (E_g) is calculated to be 4.2 eV, which is larger than that of the reported value for bulk SnO_2 (3.6 eV) [6]. It indicates a blue shift in the prepared samples from that of bulk but a prominent shift was occurred in the case of the sample synthesized using EDTA. Considering the blue shift of the absorption position

from the bulk SnO_2, the absorption onsets of the present samples could be assigned to the direct transition of electron in SnO_2 nanocrystals. Adding a chelating agent consisting of a higher band gap energy semiconductor (or smaller) can eliminate dangling bonds and drastically increase quantum yield. The increasing trends of the band gap energy upon the decreasing particle size are well presented for the quantum confinement effect [7].

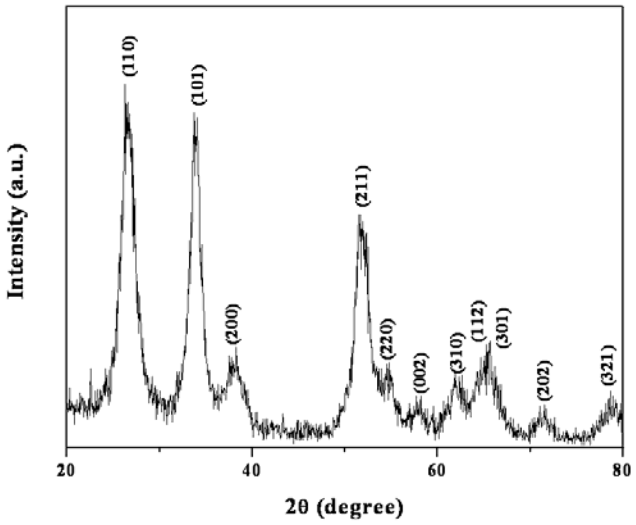

Figure 1: XRD pattern of EDTA–capped SnO_2 nanoparticles calcined at 400°C for 2h

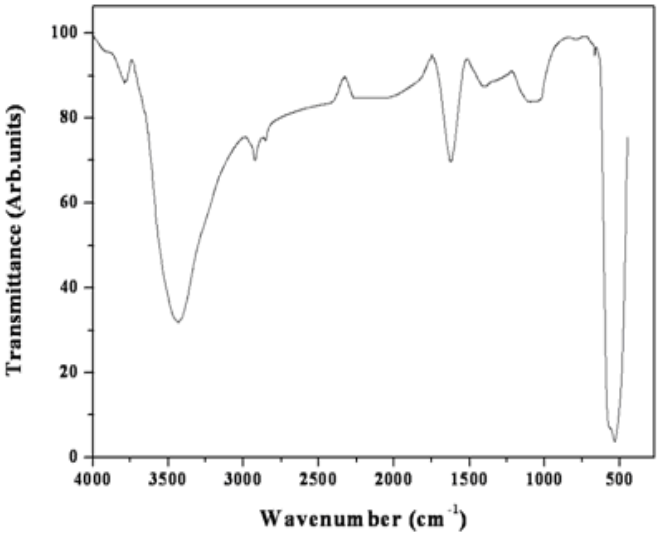

Figure 2: FTIR spectrum of as-synthesized EDTA–capped SnO_2 nanoparticles

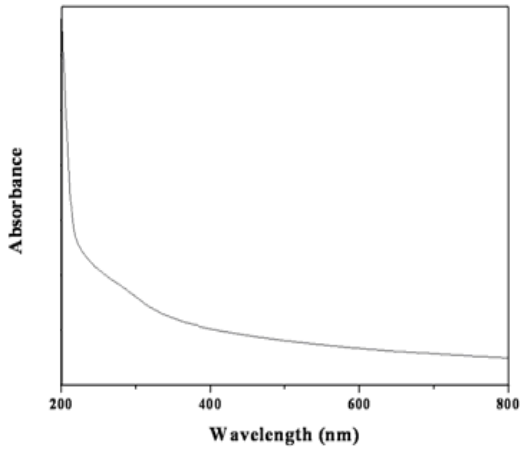

Figure 3: UV-vis absorption spectrum of EDTA-capped SnO_2 nanoparticles

Fig. 4 shows the room temperature PL spectrum of EDTA-capped SnO_2 nanoparticles with an excited wavelength at 250nm. The emission band is composed of a strong UV band located at 377 nm and a strong blue-green band around 450nm. The UV emission band must be explained by a near-band-edge transition of wide band gap SnO_2 nanoparticles, namely the free excitons recombination through an exciton-exciton collision process. The blue-green emissions are attributed to surface defects in the SnO_2 nanoparticles [8]. The visible emission of SnO_2 nanoparticles is related to the defect levels within the band gap of SnO_2, associated with an oxygen vacancies or tin interstitials that formed during the synthesis process.

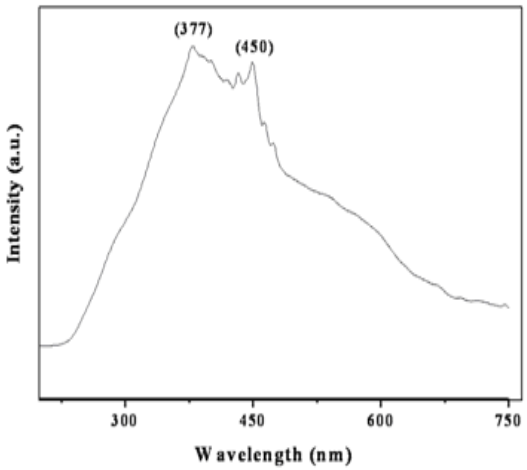

Figure 4: PL emission spectrum of EDTA–capped SnO_2 nanoparticles

Fig. 5a) shows the SEM image of EDTA assisted SnO_2 nanoparticles. Brain-like morphology of aggregated spherical particles was observed in EDTA mediated SnO_2 samples. It demonstrates that the content of EDTA that acts as the complexing agent has influence on the morphology of SnO_2 nanoparticles. Fig.5b shows the TEM image of EDTA assisted SnO_2 nanoparticles. The aggregated spherical-like morphology was observed with particle size in the range of ~7–8 nm, which is good agreement with the XRD analysis.

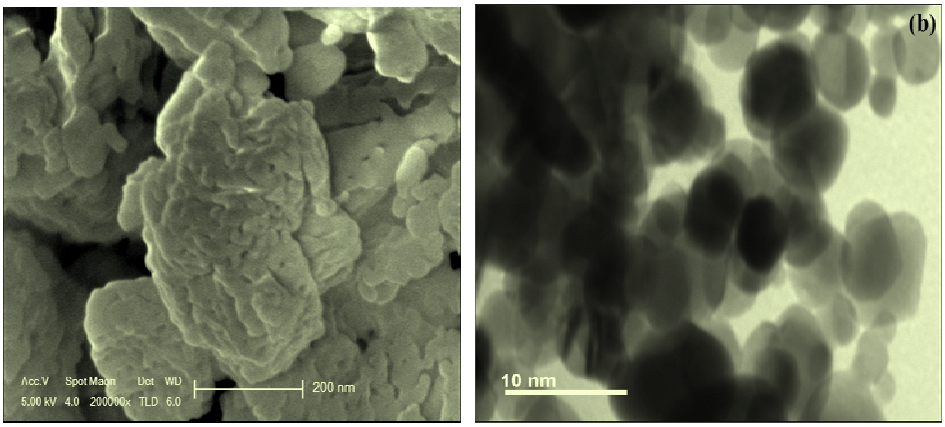

Figure 5: (a) SEM and (b) TEM images of EDTA–capped SnO_2 nanoparticles

The possible formation mechanism is described as follows: when the content of EDTA is low and the solution containing the tin ion is slowly put into the ethylene glycol solution which contains EDTA, the chelating agent rapidly gathers around the tin ion, gradually forming the loose complex compound by stirring. The tin ion can penetrate the loose complex compound to interior, and then it causes the continuous growth of tin oxide nanoparticles toward some directions. Because the two chelate rings occur, the spatial volume of growing units is expanded. It has been known that the adsorption of growth units on crystal surfaces strongly affects the growth speed and orientation of crystals [9]. When the precursors are calcined, the molecules of complex compound tend to be perpendicular to the absorbed surface, the growth units would tend to face-land onto the growing interface. Since this kind of landing and dehydration will result in three Sn-O-Sn bonds, which make the face-landing of growing units on axial energetically preferable to both vertex and edge landing along radial direction [10]. The chelating agent EDTA acts as an anionic compound. The electrostatic attraction is insufficient to form clusters when the two solutions (i.e. tin tetrachloride and ammonium oxalate) are mixed. The EDTA molecule can bind to tin metal ions by forming six bonds to it - two from nitrogen atoms. Therefore, we used a polymerizing agent (ethylene glycol)-aided counter ion complexation method, which may promote the interaction between tin metal ions and EDTA. Addition of ethylene glycol leads to the closeness of the tin metal chains to EDTA molecules because of the desolvation of Sn^{4+} ions resulting in formation of nanoparticles in amino groups and four from oxygen atoms in carboxyl groups.

4. Conclusion

In summary, we have successfully synthesized the tetragonal rutile structure of EDTA-capped SnO_2 nanoparticles via hydrothermal method. It is cleared that EDTA plays the key role in the formation of the SnO_2 nanoparticles. The value of band gap energy obtained from UV absorption spectrum is 4.2 eV, which was also attributed to the formation of nanocrystalline SnO_2 particles. Brain-like morphology of the prepared SnO_2 nanoparticles was observed in the SEM studies. We believe these brain-like SnO_2 nanostructures will offer new opportunities for the development of nanoscale electronics, optics and gas sensing applications. The significant optical properties of this material may be very interesting for further application on catalyst and chemical sensors.

REFERENCES

1. S.H. Ng, D.I. dos Santos, S.Y. Chew, D. Wexler, J. Wang, S.X. Dou and H.K. Liu, Polyol-mediated synthesis of ultrafine tin oxide nanoparticles for reversible Li-ion storage, Electrochemistry Commun., 9 (2007) 915–919.
2. S. Mathur, S. Barth, H. Shen, J.C. Pyun and U.Werner, Size-dependent photoconductance in SnO_2 nanowires, Small, 1 (2005) 713–717.
3. K.Gupta, P.C. Jana and A.K.Meikap, Synthesis and properties of polyaniline samarium nanocomposite, J. Phys. Sci., 16 (2012) 209–216.
4. K. Anandan and V. Rajendran, Rose-like SnO_2 nanostructures synthesized via facile solvothermal technique and their optical properties, J. Phys. Sci., 14 (2010) 227–234
5. L. Manna, E.C. Scher and A.P. Alivisatos, Synthesis of soluble and processable rod-, arrow-, teardrop-, and tetrapod-shaped CdSe nanocrystals, J. Amer. Chem. Society, 122 (2000) 12700–12706.
6. J. Kaur, S.C. Roy and M.C. Bhatnagar, Highly sensitive SnO_2 thin film NO_2 gas sensor operating at low temperature, Sensors Actuators B, 123 (2007) 1090–1095.
7. S. Ferrere, A. Zaban and B.A. Gregg, Dye Sensitization of Nanocrystalline Tin Oxide by Perylene Derivatives, J. Phys. Chem. B., 101 (1997) 4490–4493.
8. J. Portier, G. Campet, C. Kwon, J. Etourneau and M. Subramanian, Relationships between optical band gap and thermodynamic properties of binary oxides, Inter. J. Inorg. Mater., 3 (2001) 1091–1094.
9. S. Das, S. Kar and S. Chaudhuri, Optical Properties of SnO_2 Nanoparticles and Nanorods Synthesized by Solvothermal Process, J. Appl. Phys., 99 (2006) 1–7.
10. J. Hu, Y. Bando, Q. Liu and D. Goldberg, Laser-ablation growth and optical properties of wide and long single-crystal SnO_2 ribbons, Adv. Func. Mater., 13 (2003) 493–496.