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Influence of pH on the Properties of SnO_2 Nanoparticles Synthesized by Sol-Gel Process†

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SnO_2 nanoparticles with different pH values ranging from 6-10 were synthesized using sol-gel process. The influence of pH on the structural and optical properties of SnO_2 nanoparticles were studied using X-ray diffraction, scanning electron microscopy, energy dispersive X-ray, Fourier transform infrared spectroscopy, UV-VIS and photoluminescence spectroscopy studies. X-Ray diffraction study revealed the formation of nano-metre scale SnO_2 particles with tetragonal rutile structure in the range of 3-5 nm. The particle size was found to be small for the pH value 8.3. FTIR study indicates the structural confirmation of SnO_2 nanoparticles. UV and photoluminescence studies also support our result. SEM study shows plate like morphology. Energy dispersive X-ray analysis confirms the elemental composition of SnO_2 nanoparticles. It was concluded that tin oxide nanoparticle prepared at pH value around 8 can be used for various potential applications.

Key Words: Tin oxide nanoparticles, Sol-Gel method, pH Values.

INTRODUCTION

Various classes of nanoparticles (metals, semiconductors and insulators) have provided us to play around and reproduce nanostructured materials with the desired properties. Semiconductor particles have attracted more interests because of their size-dependent optical and electrical properties.

Tin oxide is an important material due to its properties such as high degree of transparency in the visible spectrum, strong physical and chemical interaction with adsorbed species, low operating temperature and strong thermal stability in air. It is an *n*-type semiconductor with a band gap of 3.6-3.8 eV. Tin oxide has been used as gas sensing material for gas mixture such as CO, H_2 and NO. Tin oxide is widely used in optoelectronic devices, fabricating solar cells, electrochemical applications, electrode materials for lithium batteries and catalysts for redox reactions. During the past decade, SnO_2 nanostructures have been one of the most important oxide nanostructures due to their properties and potential application.

Many methods have been developed for the synthesis of SnO_2 nanoparticles[1-5]. Sol-gel processing is a relatively simple way of preparing chemically homogeneous, high-purity and phase-pure powders at lower temperature.

In the present paper, the influence of pH on the structural and optical properties of SnO_2 nanoparticles synthesized by sol-gel process were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) Fourier transform infrared spectroscopy (FTIR), UV-VIS and photoluminescence spectroscopy studies.

EXPERIMENTAL

The experiment was followed by a simple sol-gel method. Hydrous tin(IV) chloride [$SnCl_4 \cdot 5H_2O$ (AR)] was dissolved in deionized water. Certain amount of Ammonia solution was added into the mixture under constant stirring. The reaction took place as follows.

$$SnCl_4 + 4NH_4OH \rightarrow SnO_2 \cdot nH_2O + 4NH_4Cl + (2-n)H_2O \quad ^6$$

The resulting solution was aged at room temperature for 24 h. The pH value was set between 6-10. The obtained opal gel was washed with deionized water and ethanol several times to remove impurities. Then it was dried at 80 ºC for several hours . The resulting product was grind well using mortar and pestle. Finally it was calcined at 300 ºC for 2 h.

RESULTS AND DISCUSSION

XRD: The XRD pattern (Fig. 1) is in excellent agreement with a reference pattern (powder diffraction file No. 21-1250). The crystallite size of the as-prepared powder was calculated from XRD line broadening using Debye Scherrer formula (Table-1).

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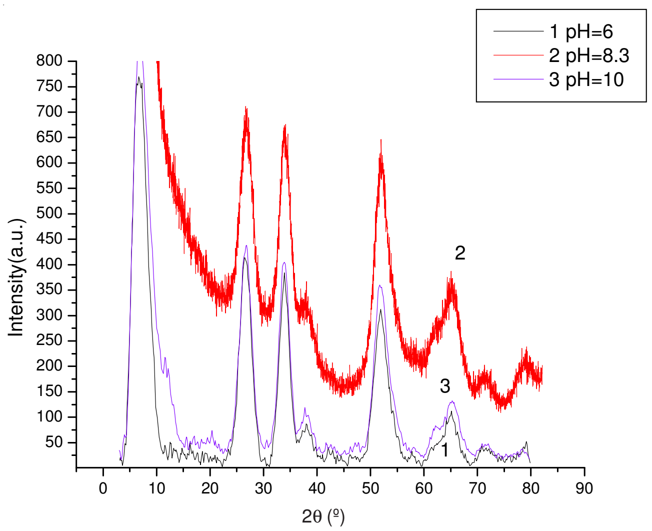


Fig. 1. XRD pattern of SnO_2 nanoparticles prepared at 300 ºC for various pH values

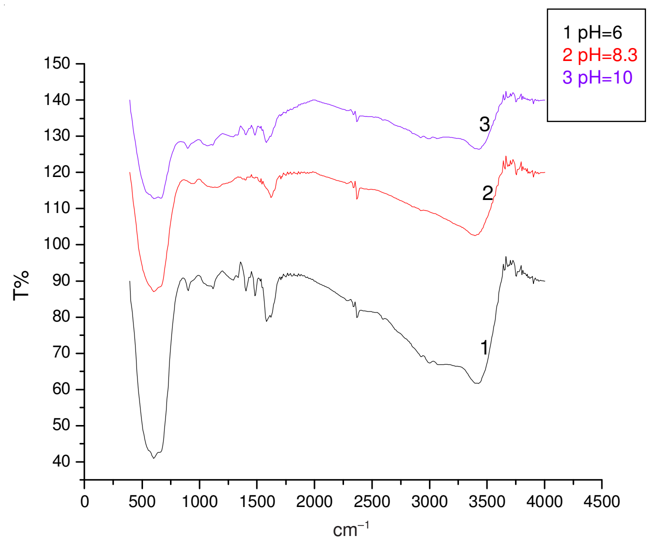


Fig. 2. FTIR spectra of SnO_2 nanoparticles prepared at 300 ºC for various pH values

TABLE-1
PARTICLE SIZE OF SnO_2 NANOPARTICLES PREPARED AT 300 ºC FOR VARIOUS pH VALUES

pH	Crystallite size along the phases (nm)			Average crystallite size (nm)
	110	101	211	
6.0	4.3034	5.634	4.168	4.7018
8.3	3.0361	3.624	3.569	3.398
10.0	3.9627	4.7615	6.7245	5.1496

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (2)$$

The particle size obtained is found to be smaller than those reported earlier[7].

FTIR: (Fig. 2) At low pH values (< 6) stretching vibrations of Sn-OH group occur at 521 cm^{-1}. At higher pH values Sn-OH disappear and the band at 630 cm^{-1} which correspond to Sn-O-Sn becomes stronger[7,12,13] indicating the following reaction has taken place.

$$SnOH + SnOH \rightarrow Sn\text{-}O\text{-}Sn + H_2O \quad (3)$$

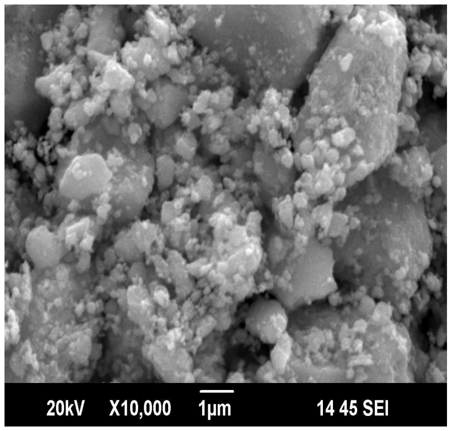
Table-2 shows that for the pH value 8.3 the band assignments mostly coincide with the characteristic frequency than the other pH values.

SEM: SEM morphology of SnO_2 nanoparticles prepared at 300 ºC (Fig. 3) at different pH.

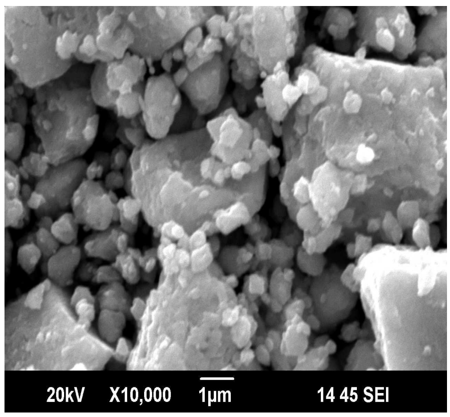
Nano plate like morphology was well observed in the SEM analysis for pH = 8.3[8,14].

EDA: EDA results showed that the obtained SnO_2 nanocrystallites is without other impurities (Table-3).

UV-absorbance spectra (Fig. 4): When the size of SnO_2 nanocrystallites is smaller or comparable to the exciton Bohr



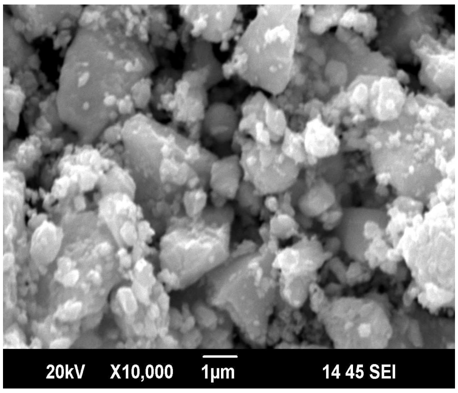
(a)



(b)

TABLE-2
FTIR SPECTRA OF SnO_2 NANOPARTICLES PREPARED AT 300 ºC FOR VARIOUS pH VALUES

Characteristic frequency	Observed frequency (cm^{-1})			Band assignments[8-11,15]
	pH = 6	pH = 8.3	pH = 10	
667-600	601.79	601.79	601.79	Stretching modes of Sn-O-Sn
1232-900	1357.88	995.26, 1157.28	–	Hydroxyl-tin vibrations
1635-1619	1581.63	1620.20	1581.63	Bending vibrations of water molecules
1737, 1401, 3135	–	1450.46	1450.46	Water and ammonia
3394-3409	3425.57	3394.71	3425.57	Stretching vibration of O-H bond



(c)

Fig. 3. (a) For pH = 6, (b) for pH = 8.3, (c) for pH = 10

TABLE-3
ELEMENTAL COMPOSITION OF SnO_2 NANOPARTICLES PREPARED AT 300 °C FOR VARIOUS pH VALUES

Element	Elemental composition for various pH values (At.%)		
	6	8.3	10
O K	20.30	23.24	14.79
Cl K	02.52	09.75	02.72
Sn L	77.18	67.01	82.49

radius, the quantum confinement would occur and blue shift in energy is observed[5]. Band gap calculation shows that for the pH value 8.3, the quantum size effect is well observed and the band gap energy obtained is 4.255 eV which is greater than the bulk tin oxide (3.6-3.8 eV) and also greater than that obtained at pH = 6 and pH = 10[11]. The band gap energy is particle size dependent and increases with decreasing particle size. This confirms the XRD result (Table-4).

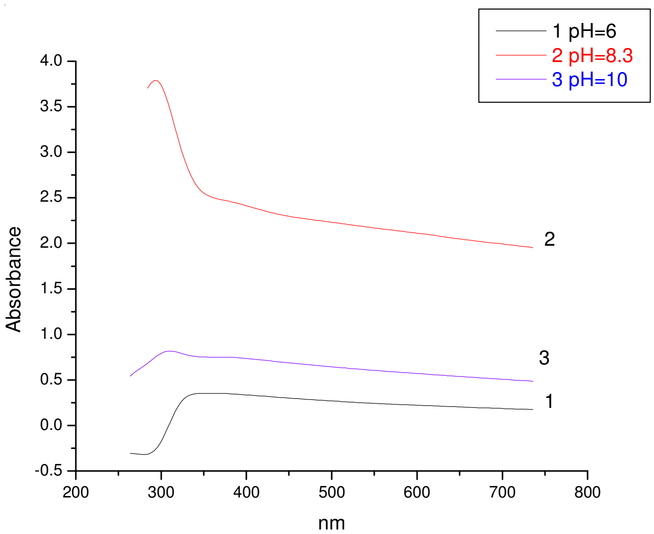


Fig. 4. UV absorbance spectra of SnO_2 nanoparticles prepared at 300 °C for various pH values

TABLE-4
UV AND PL SPECTRAL ANALYSIS OF SnO_2 NANOPARTICLES PREPARED AT 300 °C FOR VARIOUS pH VALUES

pH	UV-Absorbance (nm)	PL-Emission (nm)	Band gap energy (eV)	Quantum Yield
6	352	352.5	3.529	1.021161
8.3	292	295.0	4.255	0.946461
10	312	314.0	3.982	0.959725

Quantum yield is the efiiciency of the flurophore. The fluroscence quantum yield is defined as the ratio of the number of photons emitted to the number of photons absorbed. Since not all photons are absorbed productively, the typical quantum yield will be less than 1.

Conclusion

Nano-metre scale SnO_2 particle with tetragonal rutile structure was successfully prepared by a simple sol-gel method. The crystallite size of about 3-5 nm at 300 °C was obtained by varying the pH values. Thus the band gap of the material can be tuned in a controllable manner. We came across only a few papers dealing with the pH values. In the present work the particle size was found to be small at pH value 8.3. This result was supported by spectroscopic studies also. Hence the pH value 8.3 can be chosen as an optimal value which will enhance the optical properties of the tin oxide nanoparticle.

REFERENCES

1. D. Wang, S. Wen, J. Cehn, S. Zhang and F. Li, *Phys. Rev. B*, **19**, 14282 (1994).
2. R.D. Tarey and T.A. Raju, *Thin Solid Films*, **128** 181 (1995).
3. T. Minami, H. Nanto and S. Takata, *Jpn. J. Appl. Phys.*, **27**, L287 (1998).
4. V. Schlosser and G. Wind, In: Proceedings of the Eighth EC Photovoltaic Solar Energy Conference, Florence, Italy, p. 998 (1998).
5. K. Anandan and V. Rajendran, *J. Non-Oxide Glasses*, **2**, 81 (2010).
6. X.H. Vu, T.H.A. Ly, Q.T. Khuc, D.V. Dang and D.C. Nguyen, *Adv. Nat. Sci.: Nanosci. Nanotechnol.*, **1**, 025014 (2010).
7. J. Zhang and L. Gao, *J. Solid State Chem.*, **177**, 1425 (2004)
8. M.A. Farrukh, P. Tan and R. Adnan, *Turk. J. Chem.*, **34**, 537 (2010).
9. Bharat G. Pawar, D.V. Pinjari, S,S. Kolekar, A,B. Pandit and S.H. Han, *ISRN Chem. Eng.*, **2012**, Article ID 954869 (2012).
10. R. Adnan, N.A. Razana, I.A. Rahman and M.A. Farrukh, *J. Chin. Chem. Soc.*, **57**, 222 (2010).
11. F. Gu, S.F. Wang, M.K. Lu, Y.X. Qi, G.J. Zhou, D. Xu and D.R. Yuan, *Inorg. Chem. Commun.*, **6**, 882 (2003).
12. K.C. Song and Y. Kang, *Mater. Lett.*, **42**, 283 (2000).
13. A.C. Ibarguen, A. Mosqeura, R. Parra, M.S. Castro and J.E. Rodriguez-Paez, *Mater. Chem. Phys.*, **101**, 433 (2007).
14. X. Yang and L. Wang, *Mater. Lett.*, **61**, 3705 (2007).
15. F. Gu, S.F. Wang, C.F. Song, M.K. Lü, Y.X. Qi, G.J. Zhou, D. Xu and D.R. Yuan, *Chem. Phys. Lett.*, **372**, 451 (2003).