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A SIMPLE SOL GEL PROTOCOL TOWARDS SYNTHESIS OF SEMICONDUCTING OXIDE NANOMATERIAL

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Nanostructured Tin oxide (SnO₂), powders was synthesized by employing a novel Sol-gel protocol at RT. A wide variety of techniques such as energy – dispersive spectroscopy(EDX), N₂ sorption, X-ray diffraction (XRD), have been used to study the formation process and characterization of the nanoparticles obtained. Transmission electron microscopy (TEM) has been applied to find out about the shape and size distribution of the particles. The nanoparticles thus synthesized were monodispersed, with an average particle size of ~ 10 nm and spherical in shape. The EDX analysis revealed the presence of Sn, O signal in the synthesized nanoparticles confirming the purity of the synthesized samples. This protocol appears promising for application in large-scale synthesis of nanoparticles.

Keywords: SnO₂, NANOPARTICLES, SEMICONDUCTORS, XRD, TEM, BET.

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1. INTRODUCTION

The size and shape dependent properties of nanomaterials provide a challenge to synthetic chemists for obtaining highly functional advanced materials. It is well known that shape and size of inorganic nanocrystals control their widely varying electrical, optical and catalytic properties [1-3]. Consequently, one of the emerging challenges in materials synthesis is achieving control over the morphology of nanocrystals. Since the discovery of mesoporous silica molecular sieves in 1992 [4-5] several supramolecular assembly pathways have been reported and extended to the synthesis of a variety of mesoporous metal oxide compositions [6]. Mesoporous materials have attracted considerable attention because of their remarkably large surface area and narrow pore size distribution, which make them ideal candidate for catalysts, molecular sieves, chemical sensors and as electrodes in solid state ionic devices. A number of related synthetic strategies, thermal evaporation [7], laser ablation [8], solution phase growth [9] and supra molecular templating methods [10] have been developed and a variety of materials, in terms of both composition and structure, have been prepared [11-13]. Among various metal oxides tin oxide is a wide band gap ($E_g = 3.6$ eV) semiconductor and has potential technological

applicability in solid state gas sensors, [14] transparent conducting electrodes, [15] transistors solar cells and optical electronic devices [16]. The success in many of these applications relies critically on the preparation of crystalline SnO_2 with nanosize pore structure. Thus the objective of this study was to synthesize mesoporous SnO_2 stable at high temperature.

2. EXPERIMENTAL WORK

Nanosized tin oxide powder was synthesized using $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ as tin source and sodium dodecyl sulfate as surfactant. In a typical procedure 5 mmol of the surfactant was dissolved in deionized (DI) water ($\rho = 18 \text{ M}\Omega$) and then 1 M aqueous SnCl_4 solution was added to the above surfactant solution with stirring for 10 min, which resulted in a milky white suspension. After another 10 min. of stirring, the mixture was aged for 24 h at room temperature. The resulting product was centrifuged, washed with water and dried at 80°C . The resultant tin oxide powders were calcined in the temperature range $400\text{-}700^\circ\text{C}$ for 2h at an heating rate of 5°C min^{-1} crystal phase and crystallite size of SnO_2 were characterized by X-ray diffraction (XRD) (Siemens / 0-5000, $\Theta = 2\theta$) using $\text{CuK}\alpha$ radiation. Specific Surface area and pore size distribution were measured by a BET method using N_2 sorption isotherm determined at 77 K on a micromeritics pulse ASAP 2010 instrument The samples were degassed in a vacuum at 300°C for 3h prior to measurement. Composition was analyzed by EDX analysis. Morphology of the SnO_2 powders was observed by transmission electron microscope (TEM; - Tech nai - 12 operated at 120 KeV).

3. RESULTS AND DISCUSSION

3.1 Characteristics of nanostructured SnO_2 powder EDS spectra

The composition of SnO_2 powder calcined at 400°C was analyzed by EDS measurement as shown in Fig. 1.

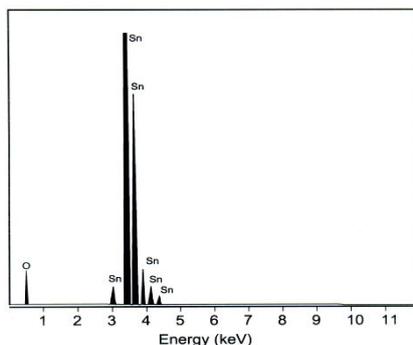


Fig. 1 – EDS analysis of SnO_2 calcined at 400°C

The energy dispersive X-ray spectroscopy (EDS) analysis of nanoparticles dispersion confirmed the presence of Tin and oxygen signal no peaks of other impurity were detected.

3.2 X-ray diffraction (XRD) spectra

The X-ray powder diffraction pattern of the as-synthesized nanoparticles and calcined at elevated temperatures are shown in Fig. 2

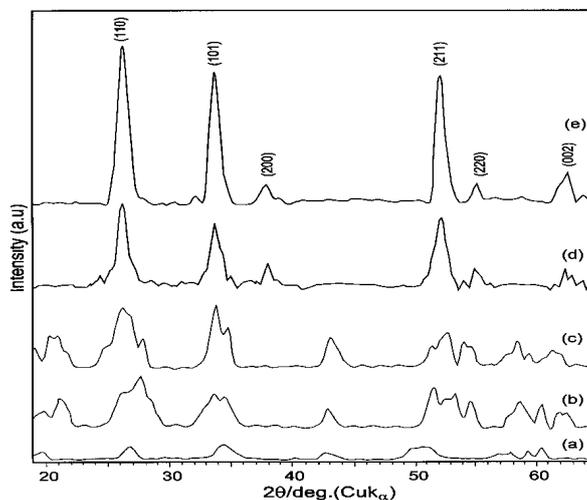


Fig. 2 – XRD patterns of SnO_2 (a) as-synthesized, calcined at (b) 400 °C (c) 500 °C (d) 600 °C (e) 700 °C

All peaks correspond to SnO_2 tetragonal structure and well match with the reported JCPDS data. The diffraction peaks became sharp with rise in calcination temperature, indicating the grain growth of SnO_2 crystallites. The crystallite size of each SnO_2 powder was calculated to be 4 - 9 nm using Scherrer's equation. Such change in crystallite size are obvious in TEM photographs shown in Fig. 4 c, indicating grain growth of SnO_2 particles, it is seen that sample calcined at 600 °C had a smaller particle size of ~ 10 nm. In accordance with these changes, the surface area decreased from $125 \text{ m}^2\text{g}^{-1}$ (for as-synthesized powder) to $36.3 \text{ m}^2\text{g}^{-1}$ (for powder calcined at 600 °C) as summarized in Table 1.

Table 1 – Structural Properties of SnO_2 at diff. Calcination temperatures (T_c)

T_c (°C)	Specific surface area (m^2g^{-1})	Pore volume ^a Dv/log d	Pore Size ^b (nm)	Crystallite Size ^c (nm)
As synthesized	125	0.81	4.2	5.3
400	121	0.79	4.5	6.3
500	61.2	0.65	8.0	6.9
600	36.3	0.45	10.0	7.9
700	35.8	0.17	19.0	7.9

^{a,b} Obtained from nitrogen adsorption.

^c Estimated from XRD peak broadening 110 plane in Fig. 2

According to Scherrer's formula the average SnO_2 crystallite size of about 5 nm in the (110) direction was derived from full width at half maximum (110) peak for as synthesized powder. The crystallite size has increased from 5 to 7.9 nm at elevated temperature (700 °C).

3.3 Pore size distribution

From the pore size distribution (Fig. 3) it is seen that the pore volume decreased and pore diameter at maximum pore volume increased with rise in

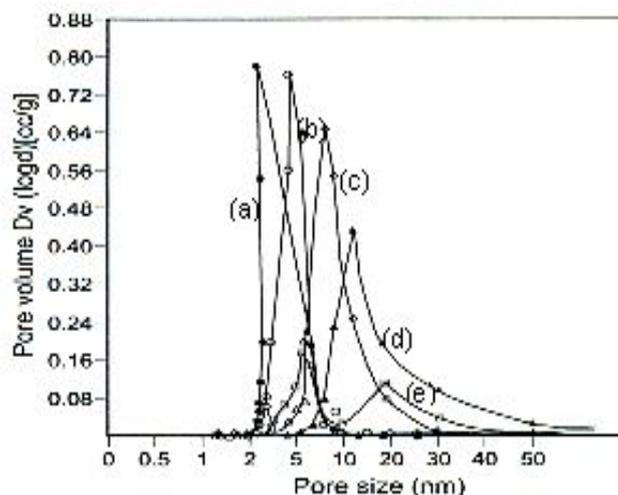


Fig. 3 – The Barret-Joyner-Halenda pore size distribution determined N_2 adsorption (a) as-synthesized, calcined at (b) 400 °C (c) 500 °C (d) 600 °C (e) 700 °C

calcination temperature. The specific surface area (SSA) was significantly high when SnO_2 powder was fired at 400 °C, the change in specific surface area and crystallite size with calcination temperature of SnO_2 powder was also determined. High surface area may result from the breakup of large agglomerates into small crystallites, exploring more surfaces. It is seen that the specific surface area decreased and simultaneously particle size increased with increase in calcination temperature (T_c).

3.4 TEM micrograph

The surface morphology and particle size of SnO_2 nanoparticles were investigated Transmission Electron Microscopy studies.

TEM analysis indicated that the calcined sample were in the nanometer range as seen from Fig. 4. It is observed that, as synthesized samples are mesoporous with particle size of ~ 5 nm, (Fig. 4a). After firing at 400 °C for 2 h the particle size still remains ~ 7 nm (Fig. 4b) with increase in temperature to 600 °C the size increased to ~ 10 nm (Fig. 4c). It is worth noting that even after calcination at 600 °C the particle size still remained small. The inset of the figure shows the SAED pattern, as synthesized sample is mesoporous and calcined samples are clearly polycrystalline.

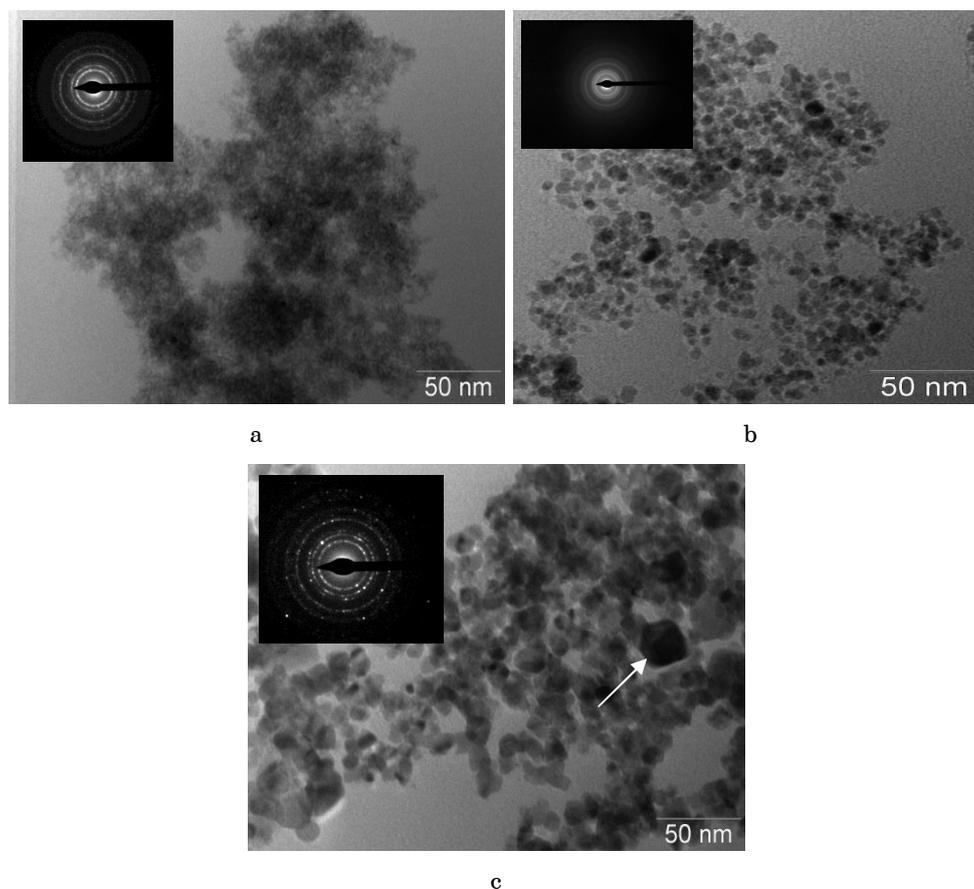


Fig. 4 – TEM micrograph of SnO₂: as synthesized 400 °C (a, b) and 600 °C (c). The inset shows the selected area electron diffraction (SAED) pattern

4. CONCLUSION

In conclusion, simple surfactant templated process has been adopted for the synthesis of SnO₂ nanosized powder, having high surface area (121 m²g⁻¹ for powder calcined at 400 °C) and small grain size (~ 7 nm). And these nanoparticles were thermally stable with tetragonal structure. EDS analysis of SnO₂ powder showed the presence of Sn and O as only detected elements.

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REFERENCES

1. A.P. Aliviastos, *Science* **271**, 933 (1996).
2. T. Huang, R.W. Murray, *J. Phys. Chem. B* **105**, 12498 (2001).

3. P.V. Kamat, *J. Phys. Chem. B* **106**, 7729 (2002).
4. C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* **359**, 710 (1992).
5. J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.h. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.* **114**,10834 (1992).
6. P. Behrens, *Angew. Chem. Int. Ed. Ehg.* **35**, 515 (1996).
7. Z.W. Pan, Z.R. Dai, Z.L. Wang, *Science* **291**, 1947 (2001).
8. (a) J. Hu, Y. Bando, Q. Liu, D. Golberg, *Adv. Func. Mater.* **13**,493 (2003).
(b) Z. Liu, D. Zhang, S. Han, C. Li, T. Tang, W. Jin, X. Liu, B. Lei, C. Zhou, *Adv. Mater.* **15**, 1754 (2003).
9. D.F. Zhang, L.D. Sun, J.L. Yin, C.H. Yan, *Adv. Mater.* **15**, 1022 (2003).
10. C.R Martin, *Science* **266**, 1961 (1994).
11. Q. Huo, D.I. Margolese, U. Ciesla, D.g. Demuth, P. Feng. T.E. Goe, P. Sieger, A. Firouzi, B.F. Chmelka, F. Schuth and G.D. Stucky, *Chem. Mater.* **6**, 1176 (1994).
12. A. Sayari and P. Liu, *Microporous Mater.* **12**, 149 (1997).
13. J.Y. Ying, C.P. Mehnert and M.S. Wong, *Angew. Chem. Int. Ed.* **38**, 56, (1996).
14. (a) M. Law, H. Kind, B. Messer, F. Kim, P.D. Yang, *Angew. Chem. Int. Ed* **41**, 2405 (2002).
(b) Y. Wang, X. Jiang, Y. Xia, *J. Am. Chem. Soc.* **125**, 16176 (2003).
15. Y.S. He, J.C. Campbell, R.C. Murphy, M.F. Arendt, J.S. Swinnea, *J. Mater. Res.* **8**, 3131 (1993).
16. (a) P.G. Harrison, M.J. Willet, *Nature* **332**, 337 (1988).
(b) S. Ferrere, A. Zaban, B.A. Gregg, *J. Phys. Chem. B* **101**, 4490 (1997).