Synthesis of $\text{TiO}_2/\text{SnO}_2$ core shell nanocomposite via sol-gel method

SORAIA KHOBY-SHENDY

*Materials and Energy Research Center,
Karaj, Iran
Soraia_kh@yahoo.com*

MOHAMMAD REZA VAEZI

*Materials and Energy Research Center,
Karaj, Iran
Vaezi9016@yahoo.com*

TORAJ EBADZADEH

*Materials and Energy Research Center,
Karaj, Iran
t-ebadzadeh@merc.ac.ir*

The particles of TiO_2 core/ SnO_2 shell nanocomposite were prepared by hydrolysis of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in the presence of titania nanoparticle after drying and calcinations treatments. TiO_2 particle were produced from titanium isopropoxide sol by hydrothermal processing. X-ray diffraction (XRD), Fourier transformed infrared (FTIR), and transmission electron microscopy (TEM) were used to characterize the $\text{TiO}_2/\text{SnO}_2$ core shell nanocomposites. The obtained results from XRD show that the SnO_2 nanoparticles coated on TiO_2 yields diffraction peaks correspond to the crystalline SnO_2 phase. Also, TEM results show that the nanocomposite particles have a spherical morphology and a narrow size distribution. The thickness of SnO_2 shell on the surface of TiO_2 particles were about 8 nm. Moreover, the results obtained from EDX analysis show that the core-shell structured nanocomposites have crystalline structure.

Keywords: Core Shell; Nanocomposite; Sol-Gel; TiO_2 ; SnO_2

1. Introduction

The particles of core-shell structured composite exhibit improved physical and chemical properties over their single-component counterpart and hence are potentially useful in a broader range of applications.¹ The structure, size and composition of these particles can be easily altered in a controllable way to tailor their magnetic, optical, mechanical, thermal, electrical and catalytic properties. Core shell materials consist of a core structural domain covered by a shell domain. The core and shell may be composed of a variety of materials including polymers, inorganic solids, and metals.²⁻⁵ core shell particles have diverse applications in coatings, impact modification, bio- separation, drug delivery systems, etc.⁶ The synthesis core shell particles typically involves tailoring the

surface properties of particles, often accomplished by coating or encapsulating them within a shell of a preferred material. The shell can alter the charge, functionally, and reactivity of the surface, and can enhance the stability of the core. Encapsulating colloids in a shell of different composition may also protect the core from extraneous chemical and physical changes.⁷

Coating is one of the methods that can be used for the formation of core shell nanoparticles. Up to now many routes have been developed to fabricate core shell materials such as sol gel process,⁸ layer by layer technique,⁹ electrodeposition method,¹⁰ and encapsulation of nanoparticles by in situ polymerization.¹¹

SnO₂ with a large band gap ($E_g = 3.6$ eV at 300K) used as an important n-type semiconductor is quite attractive because of its excellent optical and electrical properties and chemical stability and the use of these particles as a catalyst for oxidation of organic compounds and as gas sensors, rechargeable Li-batteries and optical electronic devices.^{12, 13} There were many reports on the fabrication and excellent properties of TiO₂/SnO₂ in which the composites may be in the form of solid solution,¹⁴ coupled TiO₂/SnO₂ or multilayer.^{15, 16} There were few reports on TiO₂/SnO₂ core shell and their corresponding properties.

In this paper, we reported the preparation of TiO₂/SnO₂ (which had uniform size and dimension) composite structure. TiO₂ nanoparticles were synthesized via hydrothermal method and crystalline SnO₂ nanolayers were coated on the surface of TiO₂ nanoparticles by sol gel method.

2. Experimental

All the chemical reagents are of analytical grade and used without any purification and treatment. TiO₂ nanoparticles were prepared from initial aqueous Ti⁴⁺ stock solution and hydrothermal treatment. These initial solutions were obtained by adding 5.4 ml of titanium isopropoxide (TTIP) and same amount of isopropanol to 56.6 ml of distilled water at pH 1.5 achieved by an acid. TTIP solution was obtained upon stirring at room temperature for a day. Certain amount of triethylamine (TEA) was then added drop wise to Ti solution till pH value reached 7. It has been reported that the use of amines, could act as shape controller template "See Refs. 17 for more details." The obtained solution was then placed in a Teflon recipient inside of stainless steel autoclave. Hydrothermal treatment was performed at 120°C for 12 h. TiO₂ powders were obtained by centrifugation and 3 times washing with distilled water. Thus obtained precipitates were then filtered and dried at 120°C for 12 h.

The coating of SnO₂ nanoparticles on TiO₂ nanoparticles was prepared at room temperature by the following process:

0.2 gr titania nanoparticles obtained by the above method were dispersed in a mixed solution of NH₄OH (25 wt% solution, 15 ml) and distilled deionized water (40 ml). When the mixing solution became homogenous, a Sn⁴⁺ solution of SnCl₄.5H₂O diluted with 25 ml distilled deionized water was introduced, producing a white slurry. After stirring 24 h, the resulting product was filtered and dried at 60°C. The as synthesized samples were

calcined as 500°C for 1 h. under the same experimental conditions, the various molar proportion of the hydrous tin chloride and titania nanoparticles were obtained. The symbols ST10, ST15 and ST20 are denoted as core shell structured nanoparticles based on the molar ratios 1:1, 1:1.5 and 1:2 of Ti to Sn^{4+} , respectively.

The XRD patterns obtained by an X ray diffractometer using $\text{CuK}\alpha$ radiation at a scan rate $0.2^\circ/\text{s}$ were used to determine the identity of crystalline phase. The crystalline domain sizes (D) had been examined from XRD peaks based on the Scherrer's equation, which has been used to roughly estimate the size of the nanoparticles:

$$D = (0.9 \lambda) / (\Delta w \cos \theta). \quad (1)$$

Where λ is the wavelength of X ray equal to 0.15406 nm for $\text{CuK}\alpha$ radiation, θ is the Bragg's diffraction angle, and Δw is the true half- peak width of the X ray diffraction lines.¹⁸

Two different acids were used to achieve low pH: Acetic Acid and Nitric Acid that were nominated as TA and TN samples, respectively. Average crystallite size of TiO_2 in TA and TN samples was obtained 8 nm and 6 nm, respectively. The result of XRD pattern shows that hydrothermal treatment at 120°C for 12 h. is proper to form the anatase phase before calcinations. The transmission electron microscope (TEM) was made with the LEO912AB transmission electron microscope operated at 120 kV. The samples for TEM were prepared by dispersing the final powders in ethanol; this dispersing was then dropped on carbon- copper grids. Fourier transformed infrared (FTIR) spectra, in the range of $3500\text{--}400\text{ cm}^{-1}$, were recorded on VECTOR 33 (Bruker) spectrophotometer.

3. Result and discussion

The XRD patterns of these powders are shown in Fig. 1. It can be shown that the diffraction peaks corresponding to TA sample in Fig.1a exhibit crystalline titanium oxide of anatase phase (peaks at $2\theta = 25.3, 37.8, 48.1, 54.0$ and 55.0). Also, Fig. 1b shows that as- synthesized TN powder consists a mixture of anatase and brookite phase by the peaks at $2\theta = 25.3$ (101) and $2\theta = 30.79$ (211), respectively.

Fig. 1. XRD patterns of TiO_2 powder produced by a) Acetic Acid and b) Nitric Acid

Fig. 2 shows that XRD patterns of the calcined samples ST10, ST15, and ST20 at 500°C for 1 h. From Fig. 2a, the peaks of $\text{TiO}_2/\text{SnO}_2$ with molar ratio 1:1 represent anatase TiO_2 , which indicates that the thickness of SnO_2 shell was not enough to make diffraction, but the samples ST15 and ST20 have all peaks of anatase TiO_2 and cassiterite SnO_2 which indicates that the local crystalline SnO_2 has been formed on the surface of titania.

Fig. 2. XRD patterns of coupled oxide $\text{TiO}_2/\text{SnO}_2$ with ratio a) 1:1, b) 1:1.5 and 1:2

The broadened diffractive peaks are probably due to the fact that the grain size is in nanometer scale. The analysis of XRD broadening line clearly reveals the nearly cassiterite (SnO_2) character of these crystallites whose size is about 6-8 nm estimated by using Scherrer's equation.

The infrared spectra of the pure TiO_2 , ST10 and ST20 are shown in Fig. 3. In all samples, the bands at around 3400 and 1630 cm^{-1} are due to the O-H vibrating mode of the absorbed water.^{13, 19-21} In the pure TiO_2 sample, the broad band (from about 800 till 400 cm^{-1}) was assigned to Ti-O and Ti-O-Ti skeletal Frequency region.^{21, 22} The peaks at 1330-1570 cm^{-1} region could be attributed to organic groups.²² The IR spectra of the ST10 and ST20 (Fig. 3) shows the new bands at around 615 cm^{-1} can be attributed to the O-Sn-O blending vibration in SnO_2 ,^{19, 23} while the band located at 1400 cm^{-1} was attributed to the vibration mode of Ti-O bond.

Fig. 3. FTIR spectra of TiO_2 , ST10 and ST20 samples

The TEM micrographs of typically $\text{TiO}_2/\text{SnO}_2$ nanoparticles are shown in Fig. 4. From the micrographs, it can be clearly seen that a SnO_2 coating is on the TiO_2 surface forming core shell structured $\text{TiO}_2/\text{SnO}_2$ nanoparticles, and TiO_2 particle is encapsulated by a thin layer of SnO_2 .

Fig. 4. The micrograph of a) ST10 and ST20 core shell nanocomposites

Also, it can be seen that in the sample ST10, ratio of core to shell (dark particle) is higher than to sample the ST20. ED pattern (Fig. 4a) shows diffuse rings, indicating the formed $\text{TiO}_2/\text{SnO}_2$ are polycrystalline.

References

1. W. Fu, H. Yang, M. Li, L. Chang, Q. Yu, J. Xu, G. Zou, *Mater. Lett.* 60, 2723 (2006)
2. D.S. Jacob, I. Genish, L. Klein, A. Gedanken, *J. Phys. Chem. B*, 110, 17711 (2006)
3. S. Tavenner-kruger, Y. S. Park, M. Loneragan, U. Woggon, H. Wang, *Nano lett.* 6, 2154 (2006)
4. Y. Yang, O. Chen, A. Angerhofer, Y. C. Cao *J. Am. Chem. Soc.* 128, 12428 (2006)
5. O. Iglesias, X. Battle, A. Labarta, *Phys. Rev. B*, 72, 212401 (2005)
6. Q. Wang, L. Liu, W. Yang, *Polymer*, 48, 6581 (2007)
7. Z. Gang, Z. Kia, Y. Yi, Y. Bia, *Core/Shell Nanospheres, Hollow Capsules and Butties*, in *Dekker Encyclopedia of nanoscience and nanotechnology*, ed J. A. Schwarz, C.I. Contescu, K. Putyera (Taylor & Francis, 2004), p. 865.
8. G.Z. Li, M. Yu, Z. L. Wang, J. Lin, R. S. Wang, J. Fang, *J. Nanosci. Nanotechnol.* 6, 1416 (2006)
9. G. Schneider, G. Decher, *Nano Lett.* 4, 1833 (2004)
10. S. Tang, Y. Tang, S. Zhu, H. Lu, X. Meng, *J. Solid State Chem.* 180, 2871 (2007)
11. X. Liu, H. Wu, F. Ren, G. Qiu, M. Tang, *J. mater. Chem. phys.* 109, 5 (2008)
12. Y. Wang, J.Y. Lee, T.C. Deivaraj, *J. Mater. Chem.* 14, 362 (2004)
13. Y.D. Wang, C. L. Ma, H. D. Li, S. Zhang, *J. mater. chem. phys.* 107, 248 (2008)
14. M.C. Carotta, S. Gherardi, V. Guidi, C. Malagu', G. Martinelli, B. Vendemiati, M. Sacerdoti, G. Ghiotti, S. Morandi, A. Bismuto, P. Maddalena, A. Setaro, *Sensors and Actuators B*, 130, 38 (2007)
15. H.C. Lee, W. S. Hwang, *Appl. Surf. Sci.* 253, 1889 (2006)
16. K. Zakrzewska, M. Radecka, *Thin Solid Films*, 515, 8332 (2007)
17. M.C. Hidalgo, M. Aguilar, M. Maicu, J.A. Navío, G. Colón, *Catal. Today*, 129, 50 (2007)
18. N. Venkatachalam, M. Palanichamy, V. Murugesan, *Mater. Chem. Phys.* 104, 454 (2007)
19. L. Xi, D. Qian, X. Tang, C. Chen, *Mater. Chem. Phys.* 108, 232 (2008)
20. R. Wei, H. Yang, K. Du, W. Fu, Q. Yu, D. Xu, L. Zhang, G. Zou, *J. Alloy. Comp.* 461, 1 (2008)
21. M.R. Mohammadi, D.J. Fray, A. Mohammadi, *Micropo. Mesopo. Mater.* 112, 392, (2008)
22. G.S. Guo, C.N. He, Z.H. Wang, F.B. Gu, D.M. Han, *Talanta*, 72, 1687 (2007)
23. M.H. Liao, C. H. Hsu, D. H. Chen, *J. Solid State Chem.* 179, 2020 (2006)