International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.6, No.1, pp 600-603, Jan-March 2014

Synthesis and Characterization of SnO_2 Quantum Dots

N. Saravanan[1], S. Ponnusamy[2], Shri Prasad S[1]*, V. Joseph[1]

[1]Department. of Physics, Loyola College, Chennai, India-600 034.

[2]Center for Materials Science and Nano Devices, SRM University, India-603 203.

*Corres.author: geoshri@gmail.com
Tel.: +919786224762.

Abstract: An efficient synthesis of tin oxide (SnO_2) quantum dots with a narrow size distribution 2-3 nm was achieved by simple wet chemical route without any surfactant. The powder X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM) and diffuse reflectance spectroscopy (DRS) instrumentation techniques were employed to characterize the synthesized nanoparticles. The XRD reflections indicate the formation of tetragonal cassitenite phase of SnO_2 nanocrystals and the average crystallite size was obtained as 2.5 nm. The surface morphology and the crystalline nature were discussed based on the SEM and HRTEM images. The DRS spectral analysis exhibiting a blue-shift from that of bulk form and its band gap energy was determined as 3.67 eV.
Keywords: SnO_2, Semiconductors, QDs, Nanoparticles, Wet chemical, solvothermal.

Introduction

SnO_2 is a wide band gap n-type semiconductor (Eg = 3.64 eV, 330 K) with an exciton Bohr radius of 2.7 nm[1] having a wide range of applications like solid-state gas sensors[2], transparent conducting electrodes[3] and rechargeable Li batteries[4]. Many processes have been developed to synthesize SnO_2 nanostructures, well known synthesis procedures are chemical vapour deposition[5], physical vapour deposition[6], spray pyrolysis[7], solvothermal[8], hydrothermal[9] and sol-gel[10] methods. However, solution based wet chemical synthesis routes have proved to be cost effective method without the need of complicated instruments. In order to achieve stable quantum dots, one requires a ligand that can stabilize the surface effectively. For example Liu et al[11] have used ethylenediamine as a ligand to obtain SnO_2 QDs of size 2.5-3.6 nm. However, surfactant free QDs of the metal oxide has also been achieved by utilizing organic solvents during the synthesis process. Ethanol[1], ethylene glycol[12] and water[13] have been the most common solvents to be used for the synthesis of SnO_2 QDs. In the present work, SnO_2 QDs were synthesized by solvothermal technique employing methanol as a solvent.

Materials and Methods

All the chemicals used were analytical grade without further purification. In this synthesis, 0.4 g of tin chloride (Merck) was dissolved in 50 ml of methanol under magnetic stirring for 2 h. After complete dissolution of the $SnCl_2$ source, 1 ml of NH_3 solution was added dropwise to the mother solution and the final pH of the solution was adjusted to 9. The temperature of this solution was increased and maintained at 90 °C for 3 hours. During the process tin hydroxide precipitate was formed. The precipitate was separated by centrifugation and washed repeatedly with water and ethanol to remove the byproducts. The tin oxide was obtained after the calcination of the precipitate at 400˚C for 2 hours.

Characterization techniques

The synthesized SnO_2 nanoparticles were characterized by a Thermo ARL XTRA X-ray diffractometer with Cu K_α (λ = 1.5406 Å) radiation and taken over the 2θ range 20° – 80° at the scanning rate of 0.025° per second. Optical UV-Vis DRS spectrum was taken in the range 225-800 nm using Perkin Elmer lambda 900 UV-Visible spectrophotometer. The DRS spectrum was referenced to barium sulfate ($BaSO_4$). Surface morphology of the material was obtained by field emission scanning electron microscope F E I Quanta FEG 200. Crystalline nature of the nanoparticle was verified by high resolution transmission microscopy (JEM-2100F operated at 200 kV). For HRTEM study the samples were dispersed well in ethanol and casted on a copper-grid. Mean crystal grain size is determined according to the Debye-Scherrer's equation,

$$D = k \lambda / \beta \cos\theta$$

Where, D is the average crystallite size (nm), k is shape factor which is 0.94, λ is the wave length of the X-ray (Å), β is the FWHM of diffraction peak (after eliminating the instrumental broadening effect) measured in radians and θ is the diffraction angle.

Results and Discussion

The powder XRD pattern of the SnO_2 in the Figure 1 shows broad peaks indicating the small sizes of the nanoparticles. The XRD peaks at 26.523°, 33.768°, 51.582 and 65.713° are corresponding to the crystal planes (1 1 0), (1 0 1), (2 1 1) and (3 0 1) that is the cassitenite structure of SnO_2 (JCPDS 77-0452). The obtained lattice constant a=4.759 Å and c=3.201Å indicate the nanocrystal belongs to tetragonal system. Using Debye–Scherrer's formula the average crystallite size of the QDs was calculated as 2.5 nm.

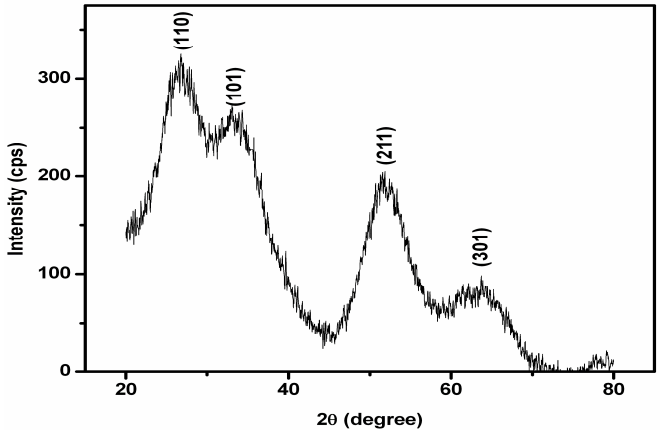

Figure 1. Powder X-ray diffraction pattern of synthesized product

The FESEM image in the Figure 2.a shows that the material has zero dimensional particle nature. The particle nature is also seen in the HRTEM image (Figure 2.b). The regular lattice fringes pattern appear in the HRTEM image (Figure 2.c), conform the nanoparticles have crystalline nature. The particles are aggloramated due to physical bonding. The interplanar spacing is 0.26 nm, which matches well with the d-spacing of (1 0 1) planes of cassitenite SnO_2.

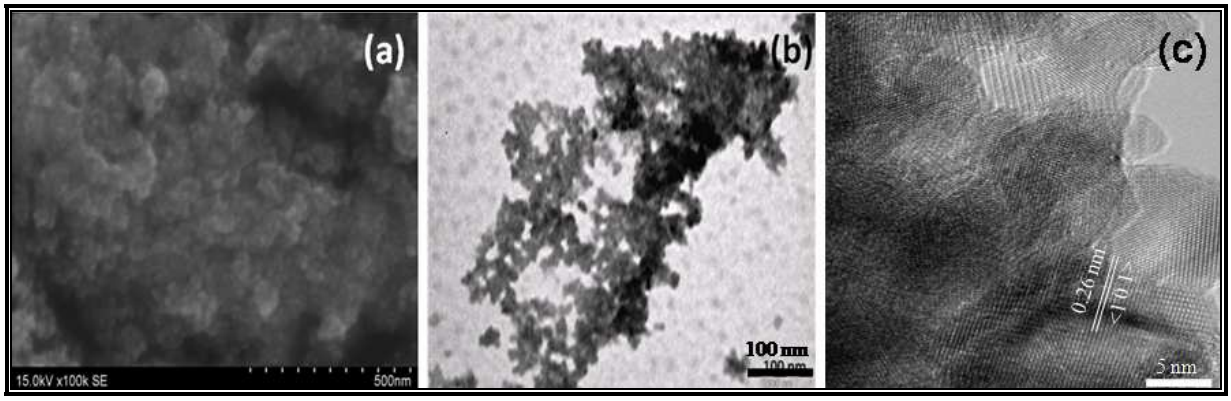

Figure 2.a. FESEM, 2.b. & 2.c. TEM image of SnO_2 QDs

The quantum confinement effect is expected for ultrafine semiconducting nanoparticles and the absorption edge will be shifted to a higher energy when the particle size decreases. In the Figure 3.a., UV-Vis DRS spectrum shows that the synthesized particles reflect most of the visible spectrum and absorption starts below 300 nm. Furthermore, the Kubelka–Munk function, $F(R) = (1 - R)2/2R$ is used to determine the band gap energy by analyzing the DRS results, where R is reflection intensity of the DRS spectrum . The plot of *F(R)* versus wavelength is shown in the Figure 3.b. The band gap is defined by extrapolation of the rising part of the plot to the *X*-axis. The band gap energy of the SnO_2 QDs is obtained at 3.67 eV which is greater than of its bulk form.

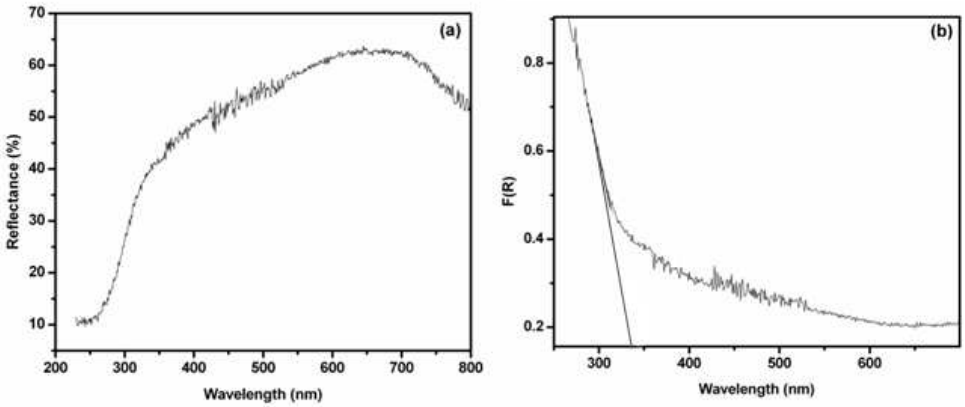

Figure 3.a. DRS spectrum of the SnO_2 QDs., Figure 3.b. Plots of *F(R)* versus wavelength

The possible reaction mechanism to synthesis SnO_2 QDs can be depicted as:

$SnCl_2 + 2CH_3OH \rightarrow Sn(OH)_2 \downarrow + 2\ CH_3Cl$

$Sn(OH)_2 \rightarrow SnO + 2H_2O$

$2SnO + O_2 \dashrightarrow 2SnO_2$

The maintained pH value and the methanol solvent are suitable for nanoparticles formation. The growth rate of the nanocrystals is dependent on the polarity of the solvent[14]. The radius (1.25 nm) of the obtained particle is less than the exciton Bohr radius of SnO_2 (2.7 nm) that is favourable for strong quantum confinement. The band gap shift to the higher value and blue shift in the DRS spectrum conform the strong quantum confinement effect.

Conclusion

SnO_2 QDs were successfully synthesized by a cost effective wet chemical method without using any capping agent at room temperature. The structural, surface morphology, lattice parameters optical and electronic properties studies are reveals that the synthesized particles are quantum dots.

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