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Synthesis and Characterization of Ultrafine SnO_2 Nanoparticles via Solvothermal Process

***J. Gajendiran and V. Rajendran**

Department of Physics, Presidency College, Chennai-600 005, Tamilnadu, India.
**Corresponding author E-mail: gaja1986msc@yahoo.co.in*

Abstract

Well-dispersed ultrafine tin oxide (SnO_2) nanoparticles were synthesized by solvothermal process, using low-cost tin chloride as the starting material. The crystal structure, particle size and optical properties of the products were investigated by X-ray diffraction (XRD), Transmission electron microscopy (TEM), UV-Vis absorption and Photo luminescence (PL) spectrum. The XRD pattern revealed that the tetragonal rutile phase and the average crystallites size were calculated to be 5 nm for the SnO_2 nanoparticles. PL exhibit enhanced UV emission at 394 nm and could be used as optoelectronic devices.

Keywords: Semiconductor; nanoparticles; SnO_2; solvothermal process; optical property

Introduction

Nanoscale materials have attracted significantly scientific and industrial interests because they demonstrate a variety of chemical, physical and functional properties different from the corresponding bulk materials. Metal oxide semiconductors are low cost and effective gas–sensing materials [1]. Tetragonal SnO_2 is an n-type semiconductor with a wide band gap of 3.6eV. SnO_2 a well-known wide direct band gap semiconductor has been considered as the most promising functional material due to their highly sensitive gas sensing and excellent optical properties. It has attracted many interests as an excellent candidate for gas sensor [2, 3], transparent conducting electrode [4], solar cells [5, 6].The conductivity and optical properties of SnO_2 are largely dependent on the particle size and shape of the nanocrystallites [7]. Increasing the surface/ bulk ratio and the crystallinity is crucial to achieving high-sensitivity gas sensors [1]. Hence, the synthesis of SnO_2 nanoparticles (less than twice of the depletion layer depth of 3nm) and improved crystallinity (making the crystallite size as close as possible to the particle size) are of important scientific and technological

significance [1]. Many methods have been developed to synthesize SnO_2 nanocrystallites, including sol-gel [8], chemical vapor deposition (CVD) [9], laser ablation [10], mechanochemical reaction [11], solvothermal process [12], and so on. Among the methods, solvothermal process is simple and cost effective. In solvothermal synthesis, the solvent acts as a reaction medium and has been proved to play a crucial role during the growth process of nanocrystalline materials [13]. Ethanol has always been good candidate solvent because of the easier proton releasing capability, limiting particle growth, prohibiting agglomeration and low boiling point.

We have achieved a smaller particle size of well-dispersed ultrafine SnO_2 nanoparticles about 5nm. To best of our knowledge the easy and effective method for the preparation of well -dispersed SnO_2 nanoparticles with both small particle size and high crystalline could be used for gas sensing applications and its photolumescence exhibit enhanced UV emission at 394 nm and could be used as optoelectronic devices.

Experimental procedure

All chemicals were of the highest purity (A.R grade) available and were used as received without further purifications. In a typical experimental procedure, 0.045g (0.002mol) of $SnCl_2.2H_2O$ was dissolved in 40ml of absolute alcohol under vigorous stirring at room temperature and then it was followed by the addition of 0.1mol% of NaOH solution and it was put into a Teflon-lined stainless steel autoclave of 100ml capacity. It was sealed and maintained at 200˚C for 16h, then cooled to room temperature naturally. A black precipitate was collected and washed with absolute alcohol and distilled water in sequence. Finally, black colored tin oxide nanoparticles were obtained, when it was dried in vaccum at 60ºC for 4h.

The synthesized sample was characterized by X-ray powder diffraction (XRD) using Schimadzu model; XRD 6000 with CuKα radiation λ= 1.5417 Å, at scanning rate of $0.02s^{-1}$ was applied to record the patterns in the 2θ range 20 to 80º. UV-Vis absorption spectrum of the sample was recorded at room temperature by using Varian cary5E spectrophotometer. High resolution transmission electron microscope (HR-TEM) analysis was carried out for the sample on a JEOL- JEM - 3010 TEM using an accelerating voltage of 300kV. Photoluminescence (PL) measurements were carried out on a Fluoromax-4 spectrofluorometer with a Xe lamp as the excitation light source.

Results and discussion

Fig.1 shows the XRD pattern of as-prepared SnO_2 nanoparticles by using solvothermal process. All the diffraction peaks have been identified. The peak position fits well with the tetragonal rutile structure of SnO_2, which is consistent with the standard data file (JCPDS file No.41-1445).No other phases can be detected. From the XRD pattern, we can evaluate the SnO_2 average size of particles is to be 5nm by using the scherers formula.

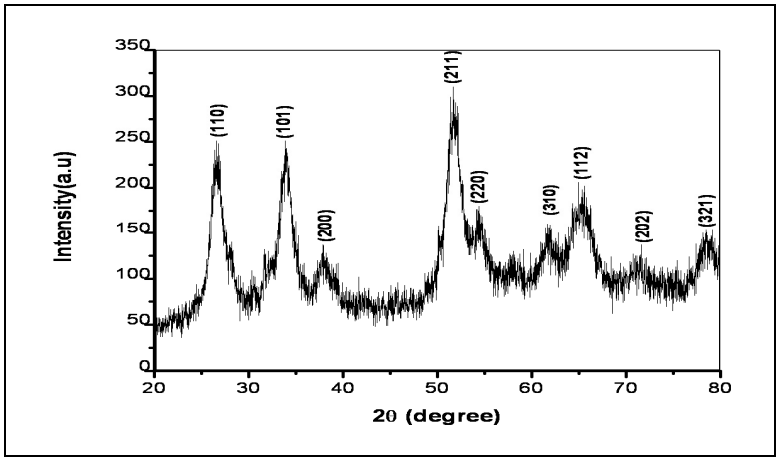
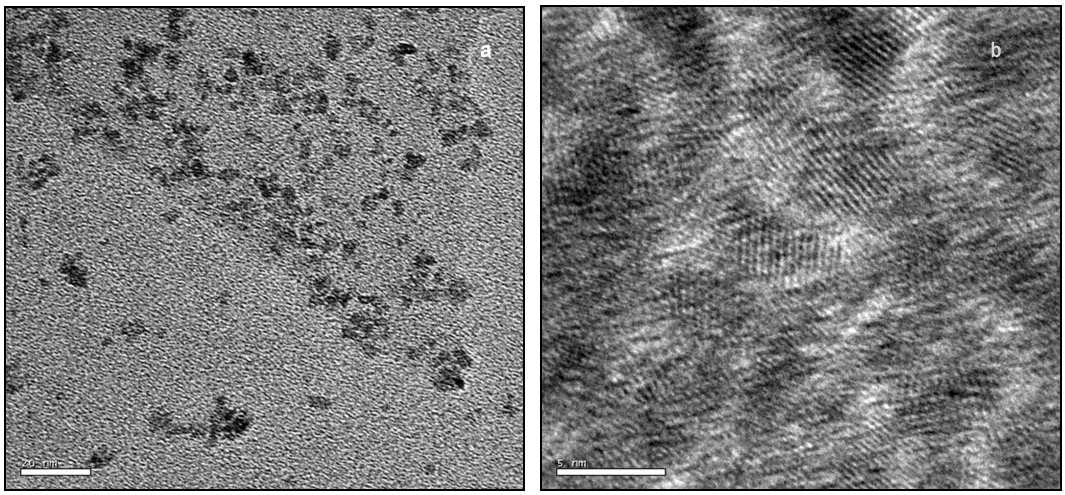


Fig.1 X-ray powder diffraction pattern of the as-prepared sample SnO_2 nanoparticles.

Fig.2a shows the TEM image of the as-prepared sample consists of ultra fine particles with average size of about 4-5nm, which is consistent with the value obtained from XRD analysis. Fig.2b shows the High-resolution TEM image of the as-synthesized SnO_2 nanocrystallites, which shows clear lattice fringes, indicating that the polycrystalline nature of SnO_2 nanoparticles. The distribution of particles obtained from the TEM image is given in figure.2c. The average diameter of the particles is approximately identical with the calculated value of d_{XRD} from broadened diffraction lines and the statistical value of d_{TEM} according to TEM images. The average grain size (d) of the SnO_2 nanoparticles was calculated from the formula $d= (6x10^4)/\rho.S$ where ρ is the theoretical density of the material and S is the specific surface area of the powder [14]. The specific surface area of SnO_2 sample can be roughly calculated to be 169 m^2g^{-1}.



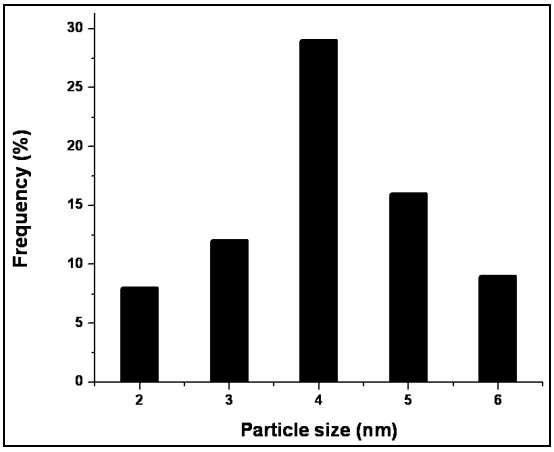


Fig.2 (a) The TEM image of SnO_2 nanoparticles, (b) HR-TEM image of SnO_2 nanoparticles and (c) particle distribution obtained from TEM image.

When the size of SnO_2 nanocrystallites is smaller or comparable to the exciton Bohr radius, the quantum confinement effect would occur and a blue shift in energy is observed. The band gap is found to be particle size dependent and increases with decreasing particle size.Fig.3 shows the UV-Vis absorption spectrum of SnO_2 nanoparticles. The absorption band edge is observed at 295 nm, which clearly indicates a blue shift from the bulk SnO_2 (340nm). The corresponding band gap energy (Eg) can be calculated to be 4.2eV, which is larger than that of the bulk SnO_2 (3.6eV) [7]. This showed a marked blue shift from the bulk value due to the quantum confinement effect.

Fig.4 shows the emission spectrum for the SnO_2 nanoparticles taken at room temperature. The PL spectrum have strong UV emission band peaking around 394nm [15].

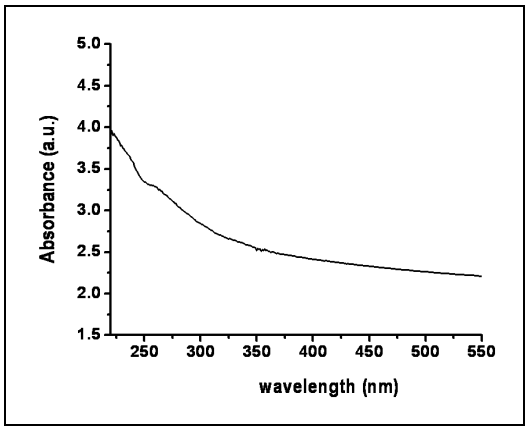


Fig.3 UV-absorption spectrum of SnO_2 nanoparticles.

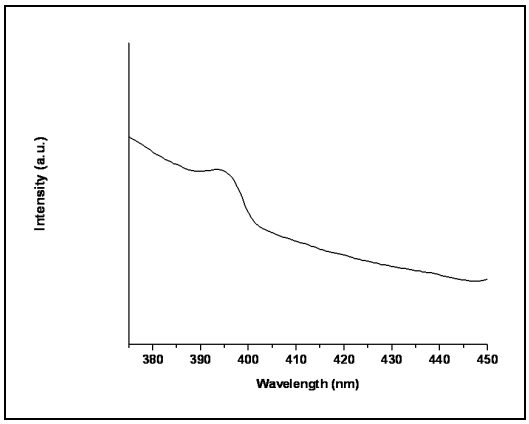


Fig.4 Emission spectrum of SnO_2 nanoparticles.

The emission in the UV region is called the near band-edge emission, generated by the free-exciton recombination. The UV emission is originated from excitonic recombination corresponding to the near-band-edge emission of SnO_2. However, the absence of green-yellow and orange-red emissions in the sample indicates the potential to produce a low concentration of oxygen defects and high optical quality of crystalline SnO_2. We believe that the as-synthesized SnO_2 nanoparticles are promising materials for nanoscale optoelectronic devices due to their excellent UV emission properties.

Conclusion

In summary, SnO_2 nanoparticles were synthesized successfully by solvothermal route using ethanol as a solvent. The XRD pattern showed that the product was tetragonal rutile phase. The average size of about 5nm was estimated using the Scherrer's equation, which was in good agreement with the TEM analysis. The absorption band edge was observed at 295 nm, which clearly indicates a blue shift from the bulk SnO_2. Further, PL emission spectrum was discussed simply. From the results, it was concluded that the solvothermal method is simple and cost effective to produce SnO_2 nanoparticles. Moreover, the ultra-fine SnO_2 nanoparticles would be promised in the applications of sensors, solar cell and optical electronic devises.

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