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LUMINESCENCE PROPERTIES OF EG-ASSISTED SnO_2 NANOPARTICLES BY SOL-GEL PROCESS

S. GNANAM*, V. RAJENDRAN
Department of Physics, Presidency College, Chennai-600 005, Tamil nadu, India

We describe a simple approach to synthesize uniform tin oxide spherical nanoparticles with controllable size based on ethylene glycol (EG) and $SnCl_4.5H_2O$ via sol-gel process. The XRD analysis shows that well crystallized tetragonal rutile SnO_2 can be obtained and the crystal size was 15nm for the sample calcined at 400ºC for 2h. The evolution of the most important functional groups during the steps involved in this synthesis route is explained in view of the results obtained with FTIR and XRD. A spherical like morphology of the prepared EG mediated SnO_2 nanoparticles was observed in the SEM and TEM studies with size in the range of 15nm. Ethylene glycol mediated SnO_2 nanoparticles exhibit an extremely very strong emission at 392 nm, which may be ascribed to the contribution of oxygen vacancies and defects in the SnO_2 nanoparticles

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Keywords: Luminescence, EG-assisted, Nanoparticles, SnO_2, Sol-gel method

1. Introduction

Since the shape, size, and dimensionality of semiconductors are vital parameters for their properties, developing a facile method to prepare important nanomaterials with well-defined structures is of great interest and importance. Crystalline tin oxide, cassiterite structure, is a wide band gap semiconductor (~3.6 eV), which, in its as-grown state, is typically n-type. Because of its optical (transparent for visible light and reflective for IR) and electrical properties, allied to good chemical and mechanical stability. It has been widely used for various catalytic applications, gas sensing, transparent conducting electrodes and liquid crystal displays, etc., [1-5]. Their properties depend on microstructure, impurities and size effects of particles. Nanostructured SnO_2 particles have been prepared by using different chemical methods such as precipitation, hydrothermal, sol-gel, gel-combustion and spray pyrolysis [3-10]. Among various methods, Sol-gel is well suited for production of nanostructured materials, because of its relatively low processing cost and the ability to control the grain size. The sol-gel process can roughly be defined as the conversion of a precursor solution into an inorganic solid by chemical means.

Herein, we describe a simple approach to synthesize uniform tin oxide spherical nanoparticles with controllable size based on ethylene glycol and water/ethylene glycol mixtures. We investigated the samples with respect to their structural and photoluminescence (PL) characteristics.

2. Experimental Procedure

All analytical grade chemicals were used as received without further purification. In a typical procedure, tin oxide nanopowders were successfully prepared by means of dissolving 0.1 mol% of tintetrachloride pentahydrate ($SnCl_4.5H_2O$) in 50ml of water-ethylene glycol mixture (1:1) as a solvent. 0.1M of an aqueous ammonia solution was added to the above solution by drop wise under stirring. The resulting gels were filtered and dried at 80ºC for 24 hours in order to

*Corresponding author: gnanam.sambatham@gmail.com

remove water molecules. Finally, black brown colored tin oxide nanopowders were formed at 400ºC for 2h. The same procedure was followed for the preparation of brown colored SnO_2 nanoparticles using ethylene glycol as a solvent.

The obtained samples were characterized by X-ray powder diffraction (XRD) using a XPERT PRO with CuKα X ray radiation (λ=0.15406nm). XRD patterns were recorded from 20 to 80º (2θ) with a scanning step of 0.01º**.** The surface morphology of the samples was observed by Scanning Electron Microscopy (SEM, FEI FEG SIRION). TEM images were taken with Transmission Electron Microscope (TEM, JEOLJEM fx000II). The chemical structure information of the particles was collected by FT-IR spectra (Nicolet 205 spectrometer). Optical absorption spectra of the samples were taken with SHIMDZU UV-310PC, UV scanning Spectrophotometer. The room temperature photoluminescence (PL) spectra of SnO_2 were recorded with fluorescence spectrometer (FLS920) using Xe lamp as the excitation source at excitation wavelength λ_{ex}=315nm.

3. Results and discussion

Fig.1a and 1b shows the XRD pattern of tin oxide nanoparticles calcined at 400ºC by using ethylene glycol and water-ethylene glycol mixture as a solvent. The peaks can be clearly indexed to the tetragonal rutile structure of SnO_2 with lattice constants of a=4.738Å and c=3.178Å (JCPDS File No. 41-1445). No characteristic peaks of other impurities were observed, indicating that the product has high crystallinity and purity. Using Scherer's formula the average particle size of the SnO_2 nanoparticles obtained from ethylene glycol and water/ethylene glycol were found to be 15 and 17nm respectively. From the results, the EG mediated SnO_2 nanoparticles were most ultra-fine owing to best dispersing and capping ability. The particle size of the as-prepared sample was reduced greatly by 3nm instead of mixture solvents.

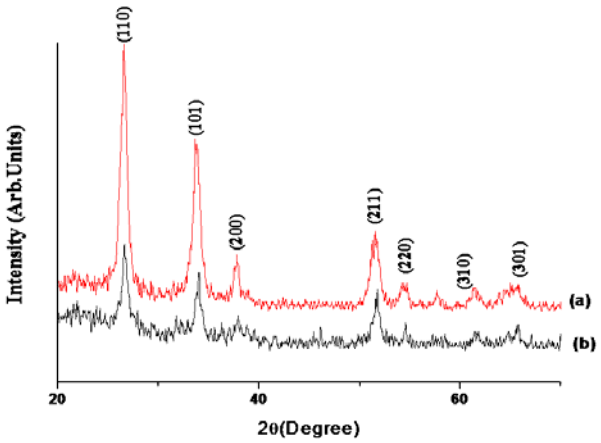


Fig.1 XRD pattern of tin oxide nanoparticles calcined at 400ºC by using (a) ethylene glycol (b) water-ethylene glycol mixture as a solvent.

Fig.2a and 2b shows the FTIR spectra of tin oxide nanoparticles calcined at 400ºC by using ethylene glycol and water-ethylene glycol mixture as a solvent. As-prepared SnO_2 powders exhibit an intense, very broad peak ranging from ca. 3600 to 2400 cm^{-1}, with two maximum at ca. 3380 and 3050 cm^{-1}, which may be due to the adsorbed water and NH_3. After calcination, the peak at 3380cm^{-1} shifts to higher wave numbers, while the peak at 3050cm^{-1} disappears. The band centered at ca. 1626cm^{-1} may also be related to water. Increasing the calcination temperature results in the decrease in the intensity of the water band, and after heating at 400ºC, the band attributed to NH_3 at around 3050cm^{-1} disappears. The low wave number region exhibits a strong vibration around 615 cm^{-1}, which can be assigned to ν(Sn–O–Sn) of the tin oxide framework [11].

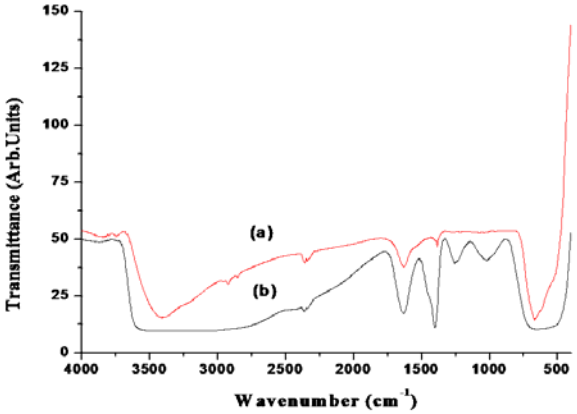
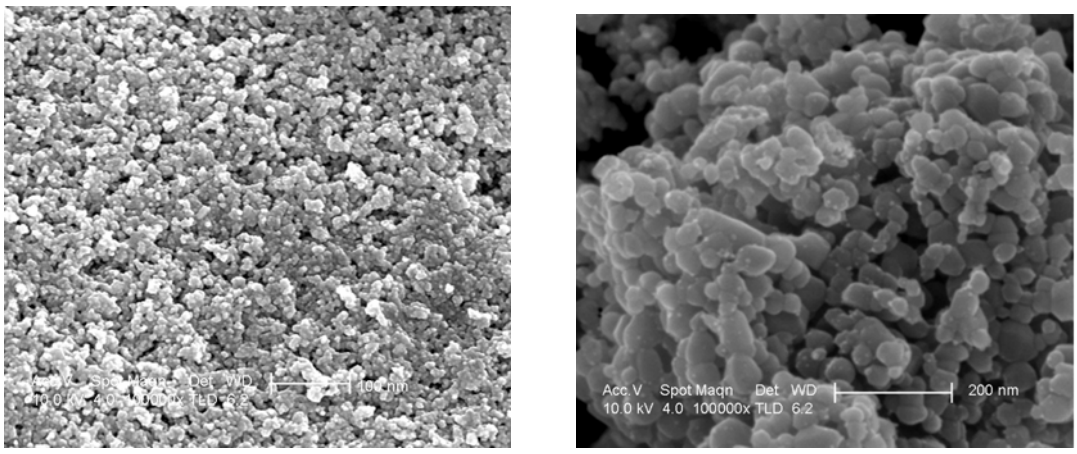


Fig.2 FTIR spectra of tin oxide nanoparticles heat-treated at 80°C (a) ethylene glycol (b) water-ethylene glycol mixture as a solvent.

The morphology and particle size was further investigated by SEM and TEM studies. From the SEM studies, EG and mixture solvents mediated tin oxide nanoparticles are spherical and ellipsoidal morphology and the diameter of the nanoparticles was ca. 15 and 17nm (Shown in Fig.3a and 3b). Moreover, some of the particles were aggregated. In this preparation method, the gel structure was maintained during the rutile SnO_2 nanoparticles formation process. Fig.4 shows the TEM image of ethylene glycol mediated tin oxide nanoparticles. It shows that homogeneous and well-dispersed spherical nanoparticles and some of them partially aggregated in the form of irregular shaped tin oxide nanoparticles. The average particle size is about 15nm. Moreover, the particle size of EG mediated tin oxide nanoparticles obtained from TEM patterns quite similar to those calculated from Scherer's equation. The presence of spherically elongate crystals indicates that the growth of the SnO_2 crystal is followed the grain rotation induced grain coalescence mechanism. Comparing the TEM patterns, we can clearly observe the anisotropic growth trend of the spherical and some aggregated SnO_2 nanoparticles with the presence of EG in the precursor, which are well consistent with those of XRD. Moreover, the particle sizes of all the samples obtained from TEM patterns quite similar to those calculated from Scherer's equation.



a b

Fig.3 SEM morphology of tin oxide nanoparticles calcined at 400°C by using (a) ethylene glycol (b) water-ethylene glycol mixture as a solvent.

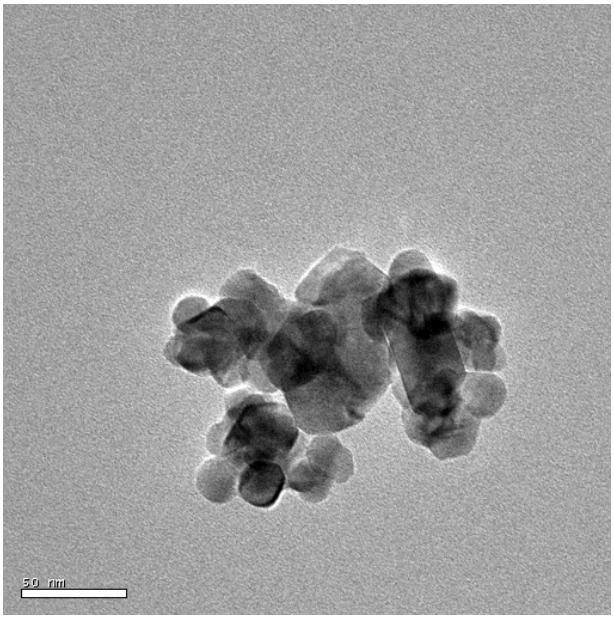


Fig.4 TEM image of ethylene glycol mediated tin oxide nanoparticles calcined at 400°C.

Fig.5a and 5b shows the optical absorbance spectra of the EG and mixture solvents mediated SnO_2 nanoparticles with photon wavelength in the range of 200–800 nm. The sharp rise of the spectrum at the absorption edge demonstrates high crystalline nanocrystals with less surface defects. As the sizes of the nanocrystals decrease, the higher surface to volume ratio incorporates various surface related defects in the nanocrystals. This causes a broadening of the absorption spectra at the absorption edge. Therefore, the sharp rise in the spectra can help us to conclude that in the nanocrystals, the surface related defects are less and the nanocrystals are homogeneously distributed. The corresponding band gap energy can be calculated to be 3.93 and 3.82 eV and are larger than the bulk SnO_2 (3.6eV). The band gap is found to be particle size dependent and increases with decreasing particle size.

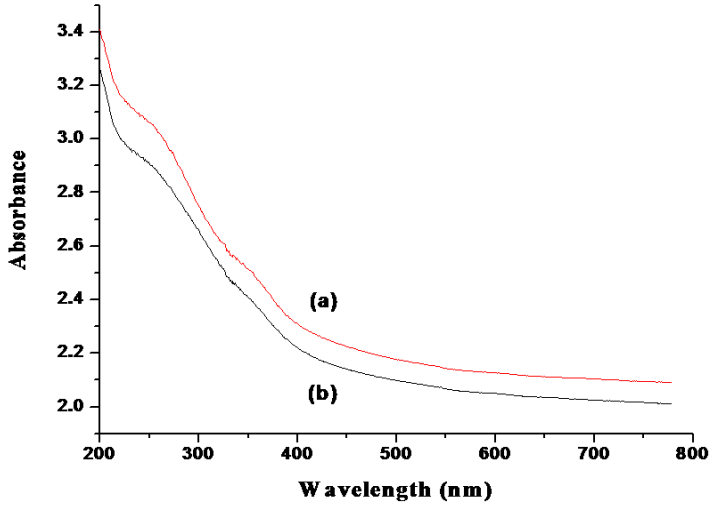


Fig.5 UV-Vis absorption spectra of tin oxide nanoparticles calcined at 400°C by using (a) ethylene glycol (b) water-ethylene glycol mixture as a solvent.

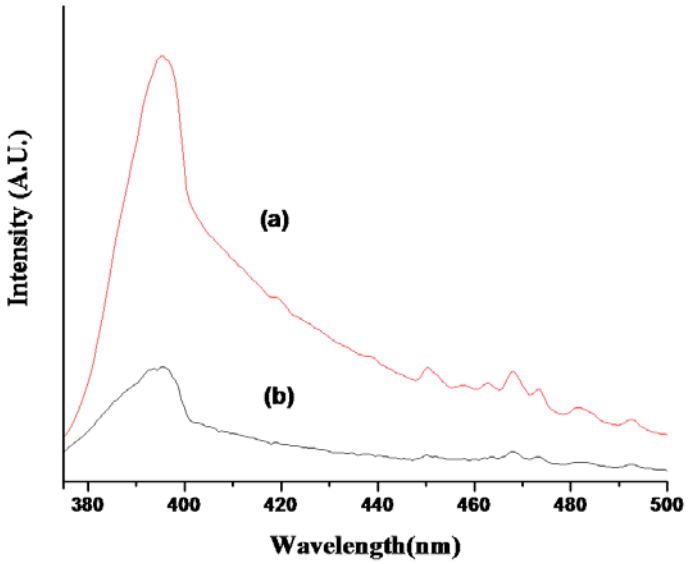


Fig.6 PL emission spectra of tin oxide nanoparticles calcined at 400°C by using (a) ethylene glycol (b) water-ethylene glycol mixture as a solvent.

Fig.6 shows PL emission spectra of SnO_2 nanoparticles prepared by using ethylene glycol and water-ethylene glycol mixture at 315nm excitation. As can be seen from Fig.6a ethylene glycol mediated SnO_2 nanoparticles exhibit an extremely very strong emission at 392 nm, which may be ascribed to the contribution of oxygen vacancies and defects in the SnO_2 nanoparticles [12-13]. However, in the case of mixture solvents exhibit a narrow broad emission at that same position (Fig.6b). As well as, EG mediated tin oxide nanoparticles exhibited two strong visible emission range located at 450 and 471nm than the mixture solvents. These emissions are different with other PL patterns of SnO_2 nanostructures. As we know that oxygen vacancies usually act as radiative centers in the luminescence process [14]. It reveals that the ethylene glycol mediated tin oxide nanoparticles exhibited high luminescence property than the mixture solvents.

4. Conclusions

Tin oxide nanoparticles were synthesized successfully by the Polymerizing sol-gel method. The XRD analysis shows that well crystallized tetragonal rutile SnO_2 can be obtained and the crystal size was 15nm for the sample calcined at 400ºC for 2h. Although the organic species strongly influence the structural, compositional, and morphological characteristics of the inorganic product and thus offer a versatile tool for tailoring particle size, shape, composition, and surface properties. Considering these results, the most suitable annealing temperature for preparation of SnO_2 nanopowder is 400°C, and the sol-gel method is very efficient for the preparation of homogeneous SnO_2 nanoparticles. The ethylene glycol mediated sample exhibited high luminescence property than the mixture solvents. Ethylene glycol mediated SnO_2 nanoparticles exhibit an extremely very strong emission at 392 nm, which may be ascribed to the contribution of oxygen vacancies and defects in the SnO_2 nanoparticles.

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