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Photoluminescence properties of SnO_2 nanoparticles: Effect of solvents

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ABSTRACT

In the present work, tin oxide nanoparticles were synthesized using chemical co-precipitation method with stannous sulphate and sodium hydroxide as starting materials. The method is simple and quick. The synthesized particles were characterized using powder X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared spectroscopy (FTIR), UV–Vis optical absorption and fluorescence emission spectroscopy. XRD analysis reveals that the SnO_2 sample is in tetragonal structure with crystal size less than 15–20 nm estimated from Scherrer formula. The optical band gap is found to be 4.33 eV from UV–Vis absorption measurements, showing strong quantization. The effect of various solvents on absorption and fluorescence emission is studied. It is found that not only intensity of emission changes with solvent, but emission peak wavelength also changes.

1. Introduction

Metal oxide semiconductor nanomaterials such as ZnO, CuO, TiO_2 and SnO_2 have received considerable attention in recent past [1–8]. Tin oxide is a special class of semiconductor with direct band gap energy 3.6 eV is regarded as one of the promising materials for gas sensors [9–21], field effect transistor, solar cells [9–12], transparent electrodes, catalyst [13–15], anti-refractive coatings and so forth.SnO_2 being wide bandgap inorganic semiconductor is an excellent candidate for optoelectronic materials. Another important feature of SnO_2 in comparison with other metal oxide is large exciton binding energy, 130 meV [10–12]. Further, photoluminescence and optical band gap of SnO_2 is sensitive for doping and the material purity. SnO_2 nanostructures have shown a broad photoluminescence peak at around 2 eV is ascribed to oxygen related defects [12–14]. Though, gas sensing and electro-catalyst properties are well explored, however, compared to other oxide nanostructures, optical properties of SnO_2 is less studied. Hence, investigation of optical properties of SnO_2 nanoparticles should be of great signification [11–16].

SnO_2 nanoparticles have been synthesized via physical as well as chemical methods, namely, solvothermal [18,21], sol-gel [14,22], solid-state reaction method [24], hydrothermal method [25], microemulsion [26], chemical co-precipitation [23,27], combustion [28,29] and many other. Chemical precipitation method has proved to be efficient and cheap route for the synthesis of semiconductor nanoparticles. Researchers have synthesized SnO_2 nanoparticles using chemical precipitation method using tin chloride or tin nitrate as a tin source. Bhagwat et al. [30] have synthesized SnO_2 nanopowder using sol gel method by taking $SnCl_4.5H_2O$, ammonia and ethylene glycol. Ahmed et al. [31] have synthesized nanocrystalline SnO_2 powder by wet chemical route using tin metal and citric acid. Gu et al. [32] have studied photoluminescence properties of SnO_2 nanoparticles synthesized by simple

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sol gel method. Nanoboxes of SnO_2 with uniform morphology were synthesized using $SnCl_4$ by Wang et al. [33]. They have shown SnO_2 nanoboxes manifest improved capacity retention. Using polyol, chemical precipitation and microwave assisted methods Drzymal et al. [34] have synthesized SnO_2 nanoparticles and studied structural, chemical and optical properties. They made use of $SnCl_2.5H_2O$ and NH_3. Wu et al. [35] have developed a facile hydrothermal method to synthesize SnO_2 nanosheets. Porous tin dioxide nanoparticles have been synthesized by a facile and elegant methodology using green chemistry by Manjula et al. [36]. Aziz et al. [37] have produced SnO_2 nanoparticles by sol gel method using $SnCl_2$. $2H_2O$ and glycol. Chetri and Choudary [38] have been able to synthesize SnO_2 nanoparticles with sizes less than 5 nm using sol gel method using $SnCl_2.5H_2O$. Entradas et al. [39] using a swift chemical route method have synthesized Co-doped SnO_2 nanopowder and investigated structural, microstructural and optical properties. Chavan et al. [40] have synthesized SnO_2 nanoparticles by solution combustion method by using $SnCl_2.2H_2O$, NH_4NO_3 and citric acid as fuel.

Here, in this article we present the synthesis and optical properties of SnO_2 nanoparticles. We have used stannous sulphate and sodium hydroxide as starting materials. To the best of our knowledge, there have been no reports of the synthesis of SnO_2 using stannous sulphate as a tin source. To characterize the SnO_2 nanoparticles, we have used XRD, FESEM and FTIR. The optical absorbance and photo luminescence are studied in various solvents.

2. Experimental section

2.1. Synthesis of SnO2 nanoparticles

The chemicals used are of analytical grade (SD fine chemicals) without further purification. In an optimized synthesis procedure, 2.156 g (0.01 mol) of $SnSO_4$ powder was dissolved in 50 ml of deionized water and subjected to stirring at the rate 500 RPM using a magnetic stirrer at room temperature. The solution of sodium hydroxide prepared by dissolving 0.8 g (0.02 mol) of NaOH pellets in 20 ml deionised water. After15 min of stirring of $SnSO_4$ solution, sodium hydroxide solution was added drop wise under constant stirring. This process is continued for about an hour. During the process colorless solution turns into a dark brown precipitate. The resulting precipitate was separated from solution by filtration. Then the precipitate was washed many times with deionized water and absolute alcohol (ethanol) to remove byproducts if any. Thereafter the precipitate was heated at 80 °C for one hour in hot air oven. Finally, the powder was calcinated at 400 °C for 2 h in muffle furnace to obtain SnO_2 powder.

The reaction mechanism is given below:

$$SnSO_4 + 2NaOH \rightarrow Sn(OH)_2 + Na_2SO_4$$

$$Sn(OH)_2 \xrightarrow[400°C]{\text{Heating for2h/Oxidation}} SnO_2 + H_2O$$

2.2. Characterization techniques

The calcinated sample is characterized by XRD, FESEM, FTIR and optical absorption and photoluminescence properties are investigated. The phase identification and the crystallinity of the SnO_2 particles were recorded by using X-ray diffractometer (Bruker AXS analytical instrument, Model: D2 PHASER)in the 2θ range of 20°–80° with CuKα radiation of wavelength 1.5406 Å. The surface morphologies of nanoparticles were characterized by using field emission scanning electron microscopy (FESEM MIRA 3 LMH TESCAN). The chemical composition and the occurrence functional group in SnO_2 nanoparticles is investigated by using FTIR spectrophotometer(Nicolet-6900, Model:912A0637) in the wave number region between 4000–400 cm^{-1}. The UV–vis absorbance spectra of the samples were measured by UV–vis spectrophotometer (JASCO, V-670) in the range 200–700 nm. The fluorescence emission spectra were recorded using spectrofluorometer (HORIBA, Fluromax-4) at room temperature with optimized excitation wavelength.

3. Results and discussion

3.1. XRD analysis

Fig. 1 depicts the XRD pattern of SnO_2 nanoparticles. All the diffraction peaks of sample confirm the formation of the SnO_2 nanoparticles in tetragonal rutile structures and is in agreement with the joint committee on powder diffraction standards (JCPDS) No 14-1445. The diffraction peaks located at 2θ are 26.67°, 33.94°, 37.98°, 39.03°, 51.86°, 54.85°, 57.91°, 62.0°, 64.82°, 66.10°, 71.32° and 78.71° corresponding to the (110), (101), (200),(111), (211), (220),(002),(310), (112),(301),(202) and (321) lattice planes respectively [41,42]. High intense with narrow peaks indicates the long range of crystallinity of SnO_2 nanoparticles. The average crystalline size was estimated by the Scherrer equation given by $\mathbf{D = K\lambda/\beta Cos\theta}$, where D is the crystallite size, K is the shape factor, being taken as 0.9, λ is the X-ray wavelength, β is the full width at half maximum of the diffraction peak, and θ is the Bragg diffraction angle in degree. The average crystallite size of the nanoparticles is found to be 15–20 nm.