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Ultrasonic-Assisted Wet Chemical Synthesis and Characterization of Cu doped SnO$_2$ nanoparticles

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Abstract : Nanocrystals of copper doped tin oxide have been prepared under ultrasonication using the precursors SnCl$_2$·2H$_2$O and CuCl$_2$.2H$_2$O in the ethanol solvent. The crystalline structure and grain size of Cu doped SnO$_2$ were determined from the powder X-ray diffraction (XRD) pattern. The elemental composition of SnO$_2$:Cu was analysed by Energy Dispersive X-ray (EDX) spectrum. The surface morphology and size of the synthesized nano particles were discussed through the image taken by Field Emission Scanning Electron Microscope (FESEM). The optical properties of the materials were absorbed by UV-visible and photoluminescence (PL) emissions spectroscopes.

Keywords: semiconductors, nanoparticles, ultrasonication, tin oxide, Cu doped, SnO$_2$, SnO$_2$:Cu.

Introduction

The transparent n-type compound semiconductor tin dioxide (SnO$_2$) is widely studied due to its excellent electrical, optical and electrochemical properties. This wide band gap (3.6 eV at 300 K) metal oxide offers a wide range of potential applications in dye sensitized solar cells[1], chemical gas sensors[2], optical sensors[3], light emitting diodes[4], touch sensitive screens[5], thin film transistors[6] and heat reflectors[7]. Its applications are extended by changing its physical and chemical properties under nanoscale due to large surface to volume ratio. Cu-doped SnO$_2$ nanoparticles were used as nanoscale optoelectronic devices[8]. Nanocrystalline SnO$_2$ has been prepared by various wet chemical techniques such as solvothermal[9], sol-gel[10], co-precipitation[11] etc. Here we prepared Cu doped SnO$_2$ by ultrasonic assisted solvothermal method.

Experimental Details

Synthesis

0.01 mole of tin(II) chloride dihydrate (Merck, GR) was dissolved in 50 ml absolute ethanol in a 250 ml beaker and sonicated in a bath-type ultrasonicator (157 W, 20 kHz Maxwell seller) for 10 minute. 0.0001mole of copper(II) chloride dihydrate (Sigma-Aldrich, 99.9%) was dissolved in 10 ml of ethanol and added drop by drop in the solution under sonication. 5ml of ammonia was added drop by drop in the solution and sonicated for

5 minute. The precipitate was then filtered and washed several times with ethanol. The powder was dried at 100°C for 3 hr. Then it was ground and calcinated at 400°C for 2 hr in the atmospheric condition.

Characterization

The synthesized nanopowders were characterized by a X-ray diffractometer PANalytical X'Pert powder XRD with monochromatic CuK_α ($\lambda=1.5406$ Å) radiation and taken over the 2θ range $20° - 70°$ at the scanning rate of 0.04° per second. The FESEM image of the sample was observed using Carl Zeiss, SUPRA 55 Model Scanning probe Microscope (SPM) to verify the surface morphology and its elemental composition was analyzed using EDX spectrum. Optical absorption spectra of the samples were taken with Shimadzu UV-Visible spectrophotometer for diffuse reflectance in the range of 200 to 800 nm for wave length absorbance studies. The room temperature photoluminescence (PL) spectra of SnO_2:Cu were recorded with Jobin Yvon Fluorolog-3-11SL 174 Spectroflurometer for the excitation wave length 320 nm.

Results and discussion

Fig.1 shows XRD pattern of the as prepared Cu doped SnO_2 nanoparticles. All the diffraction peaks can be indexed to the tetragonal structure of rutile SnO_2 (JCPDS 77–0447) and no characteristic peaks were observed for CuO due to low content of copper doping percentage. It has been observed that there is a slight variation in the diffraction peak positions of SnO_2 nanoparticles due to copper doping. The average crystallite size D was estimated using Scherrer's equation[12] as follows,

$$D = 0.9\, \lambda / \beta \cos\theta,$$

Where β is the full width at half maximum (FWHM) of the diffraction peak and θ is the Bragg diffraction angle. The average crystallite size of Cu doped SnO_2 nanoparticles is found to be 10.24 nm.
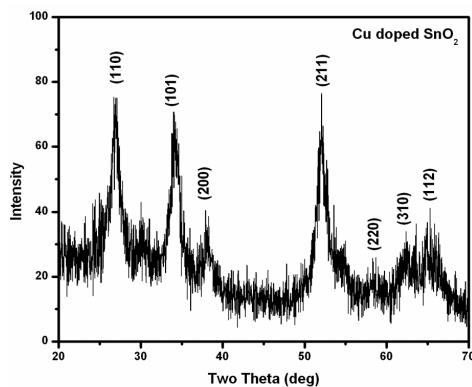

Fig. 1 XRD pattern of SnO$_2$:Cu

The fig. 2 shows Field Emission SEM image of the Cu-doped SnO_2 sample. The synthesized material is appeared as zero dimensional crystalline particle nature in the micrograph. The particles are agglomerated due to increase of physical bond among the particles in the nano scale. The fig. 3 shows the EDX spectrum of the Cu-doped SnO_2 nanoparticles and the peaks corresponding to Cu observed in the EDX spectrum of the doped samples confirms the incorporation of Cu ions into SnO_2 lattice network.
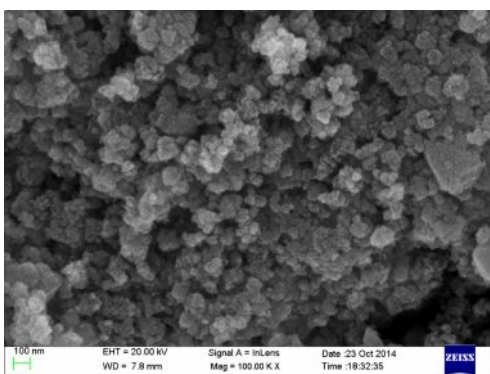
Fig. 2 FESEM image of SnO$_2$:Cu
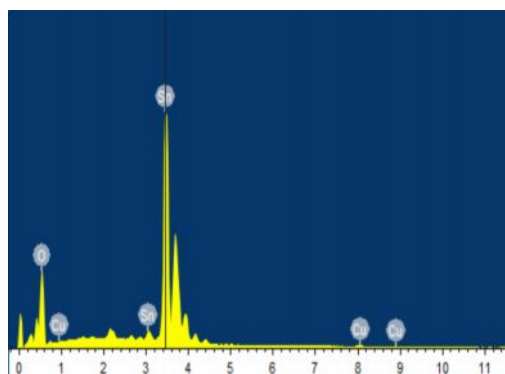
Fig. 3 EDX spectrum of SnO$_2$:Cu

The optical property of Cu doped SnO_2 was studied using Diffusion Reflections Spectroscopy (DRS). The absorbance is given by

$$F(R) = (1 - R)^2 / 2R$$

The variation of absorbance with wavelength is given in fig. 4. The band gap is calculated using Kubelka-Munk equation[13], where $(\alpha hv)^2$ is plotted against incident photon energy (hv) and the extra plotted line at $(\alpha hv)^2 = 0$ gives the band gap 3.8 eV as shown in fig. 5 which is slightly greater than its bulk value 3.6 eV due to distortion effect. This distortion effect may arise due to two reasons either Cu is creating levels nearby conduction band or incorporation of Cu producing oxygen vacancies which are making levels nearby conduction band[14]. The fig. 6 shows the room temperature photoluminescence spectra of the as-synthesized Cu-doped SnO_2 nanoparticles.

Ultrasound generates cavitations that produce local pressure and high temperature[15]. This disperses the molecules and enhances the formation of nano hydroxide. During the calcinations, the metal hydroxide is converted into corresponding metal oxide under the atmosphere. The emissions observed at 405 and 470 nm are due to the formation of doubly ionized oxygen vacancies and the green peak at 520 nm and yellow peak at 557 nm are attributed due to the different luminescent centers such as defect energy levels arising due to tin interstitials or levels formed by copper within the system[16].
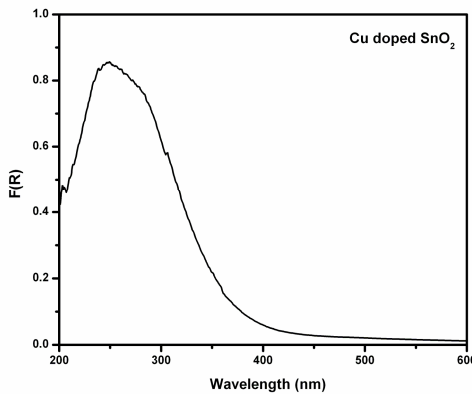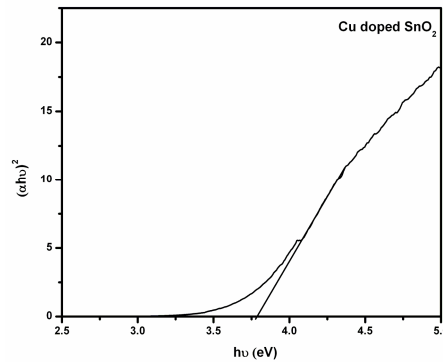

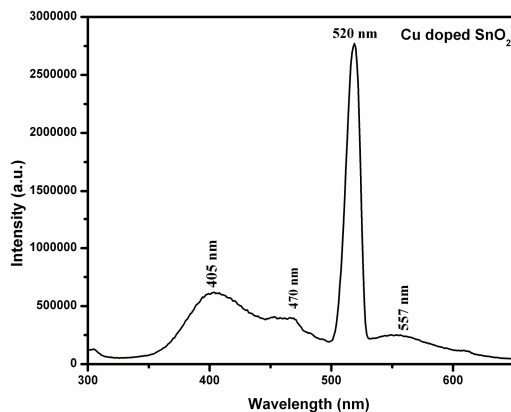**Fig. 4 UV-Vis absorption of SnO₂:Cu**   **Fig. 5 Band gap determination of SnO₂:Cu**

Fig. 6 PL spectrum of SnO₂:Cu

Conclusion

Cu-doped SnO_2 nanoparticles of size 10.24 nm were synthesized successfully by ultrasonic assisted solvothermal method using ethanol as a solvent. The XRD pattern revealed that the synthesized material has tetragonal rutile phase. The particle nature of the synthesized material is conformed in the FESEM image. The availability of the doped Cu in the SnO_2 lattice also conformed from the elemental composition of the material in the EDX spectrum. Reason for various photoluminescence emission peaks were discussed through the PL spectrum.

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