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Influence of Co Doping on structural and Optical properties of SnO_2 Nanoparticles

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Abstract: Undoped and Co doped SnO_2 nanoparticles were synthesized by chemical co-precipitation method capped with PEG. The prepared particles were analyzed using X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-Visible spectra. XRD patterns revealed that particles are crystallized in single phase rutile type tetragonal crystal structure ($P4_2/mnm$) of SnO_2. TEM studies indicated that the particle size lie in the range of 10-15 nm. Absorption edge is blue shifted when compared to bulk is the direct evidence of quantum confinement effect. Further the bandgap narrowing is observed with the inclusion of Co in SnO_2.
Keywords: Co doped SnO_2 nanoparticles, Chemical synthesis, Structural and Optical studies.

1. Introduction and Experimental:

Among the metal oxides (ZnO, TiO_2, WO_3, CeO_2 and SnO_2etc) SnO_2 is an important n-type semiconductor with wide energy bandgap (3.6eV at 300K) observed from experimental calculations [1].Because of its optical transparency in the visible region, it has a wide range of applications in gas sensors, optoelectronic devices, dye base solar cells, secondary lithium batteries and catalysts[1,2]. A wide variety of synthesis methods such as sol-gel, co-precipitation method, mechanical alloying methodand hydrothermal method were used for the preparation of SnO_2 nanoparticles. Among these methods we have adopted chemical co-precipitation method for the synthesis of Co doped SnO_2nanoparticles because it is most effective and simple due to its capability in controlling the structural and surface properties of nanoparticles. In this paper we present a detailed study on structural and optical properties of Co doped SnO_2 nanoparticles synthesized by chemical co-precipitation method capped with PEG. The dopant Co is known to inhibit the growth of crystallite, it plays an important role in optical and magnetic properties. The ionic radius of divalent cobalt ion (0.058nm) is less than that of tetravalent Sn ion(0.069nm), Co ion is expected to substituted at Sn^{4+} site in the SnO_2 system[3, 4]. Here poly ethylene glycol (PEG) was used as a capping agent which is covalently binds to the surface atoms of nano crystallites and has the ability to control the size and shape of the growing particle through charge transfer.

Pure and Co doped SnO_2 nanoparticles were synthesized using chemical co precipitation method capped with PEG. $SnCl_4.5H_2O$ and $CoCl_2.2H_2O$ have been used as starting materials for the synthesis of $Sn_{1-x}Co_xO_2$ series. The source materials were weighed according to the stoichiometryas per the target composition (X=0.00,0.01, 0.03, 0.05 and 0.07) were dissolved in distilled water to make a 0.2M solution. In this solution NH_4OH solution was added drop wise in very controlled mannerto maintain the chemical homogeneity. The addition of NH_4OH was stopped when pH of the solution reached to 9 at room temperature and added 2ml of

surfactant (PEG) under vigorous stirring for 8 hr. The precipitate was filtered out separately and washed with de-ionized water to remove unnecessary impurities formed during the synthesis process. The obtained product was placed in oven for 14hr at 60^0C and the dried samples were annealed at 450^0C for 3hr to obtain $Sn_{1-X}Co_xO_2$ nanoparticles. The X-Ray diffraction patterns were obtained using seifert3003TT X-ray diffractometer. Transmission electron micrographs (TEM) were recorded in (JEOL-TEM 2010) with an accelerating voltage of 200 kV. The optical absorption measurements were performed in (JASCO-V-670) spectrophotometer.

2. Results and Discussions:

Structural analysis:

X-ray diffractograms were used to investigate the effect of Co doping on the structure and phase composition of the prepared nanoparticles. Fig:1 displays all XRD patterns of Co doped SnO_2 nanoparticles. They were indexed corresponding to the rutile type crystal structure ($P4_2/mnm$)of SnO_2(JCPDS file no.41-1445). No secondary phases were observed within the limit of detection of X-ray diffractometer. The crystalline size of $Sn_{1-X}Co_xO_2$ nanoparticles were determined from XRD broadening using the Debye-Scherer formula, $D=0.89\lambda/\beta\cos\theta$, where λ is the wavelength of X-ray radiation, β is the full width at half maximum of the peak at diffraction angle θ. From the XRD studies the measured average crystallite size were in the range of 8-10 nm and the crystallitesize decrease with increasing Codoping concentration it may be due to the small ionic radii of Co^{2+}(0.058nm) when compared to Sn^{4+}ion(0.069nm). SumairaMehraj et al. [3] reported similar decrease in crystalline size by doping of Co^{2+} ions in SnO_2. Fig 2(a) and 2(b) shows the TEM images taken for pure and 5% Co doped SnO_2 nanoparticles respectively. Powder samples were dispersed in ethanol and sonicated in ultrasonic bath for 15minfor TEM analysis. Particle size obtained from TEM analysis is about 10-15 nm which is slightly higher than the crystallite size calculated from XRD spectra.

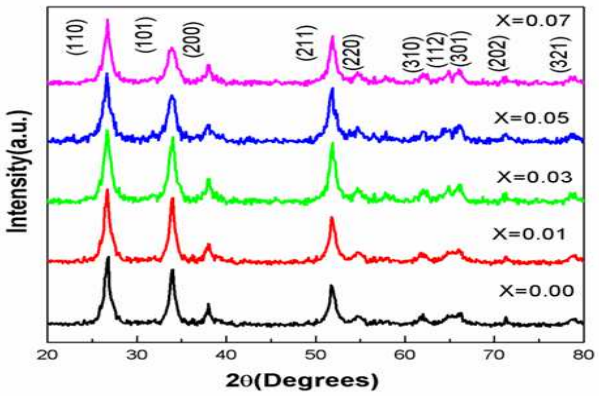

Fig.1 XRD patterns of $Sn_{1-X}Co_xO_2$ (x=0.00, 0.01,0.03,0.05 and 0.07) nanoparticles.

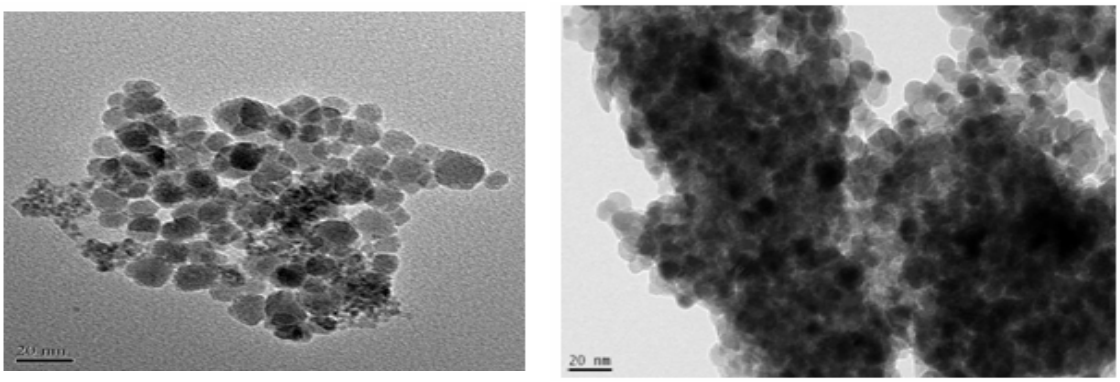

Fig. 2 (a) and (b) TEM images of pure and 5% Co doped SnO_2 nanoparticles.

Optical properties

Optical absorption spectra of pure and Co doped SnO_2 nanoparticles are shown in Fig 3. Absorption spectra shows an ultraviolet cut-off wavelength around 250-340nm, which can be attributed to the photo-excitation of electrons from valance band to conduction band. The energy bandgap of the prepared samples

were calculated using Tauc's relation (not shown in manuscript).The measured bandgap was found to be 4.82 eV for undoped SnO_2, it is higher than the reported value of bulk SnO_2(3.6eV)[1]. This can be attributed to the strong quantum confinement effect of the nanoparticles. On doping with Co, the bandgap energy is decreases from 4.82 to 3.62 eV even though the particle size decreases. This is in contrast to the normal phenomenon of quantum confinement effect, however the decrease in the bandgap with increasing the doping concentration due to sp-d exchange interaction between the band electrons and localized d electrons of the Co^{2+} ions substituting Sn^{4+} ions or Co substitution in Sn site may create two holes because of lower vacancy of Co^{2+}ion as compared to Sn^{4+} ion. Creation of additional holes likely to decrease the bandgap [4].

In summary, we have studied the effect of Co doping on the structural and optical properties of SnO_2 nanoparticles. Structural studies revealed that particles are crystallized in single phase rutile type tetragonal crystal structure ($P4_2/mnm$) of SnO_2. Optical absorption spectra suggests that absorption edge is blue shifted when compared to bulk is the direct evidence of quantum confinement effect. Further the band gap narrowing is observed with inclusion of Co in SnO_2.

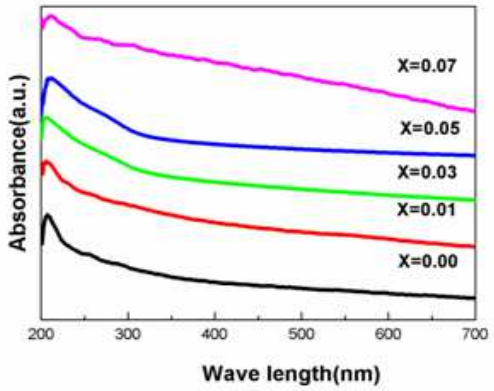

Fig. 3 Optical absorption spectra of $Sn_{1-X}Co_xO_2$ (x=0.00, 0.01,0.03,0.05 and 0.07) nanoparticles.

3. References:

1. BouaineA.,BrihiN., SchmerberG., UlhahqC.,Colis S., Dinia A., Structural, Opticaland Magnetic Properties of Co-doped SnO_2Powders Synthesized by the Co precipitation Technique, J. Phys. Chem. C.,2007, 111,2924 - 2928.
2. Yu A.S. andFrech. R., Coating of multi-walled carbon nanotube with SnO_2 films controlled Thickness and its application for Li-ion battery, J. Power Sources., 2002, 104, 97-102.
3. MehrajS., ShahnawazeA. M.,Alimuddin.,Rutile-type Co doped SnO_2Dilutedmagnetic semi conductor nanoparticles: Structural,dielectricandferromagneticbehavior,Phys.B.,2013, 430, 106–113.
4. ShendongZ., XiaoyongX., Pang Y., Jingguo H., Variation in structural,optical and magnetic properties with Co-doping in $Sn_{1-x}Co_xO_2$ nanoparticles., J.Magn. Magn.Mater., 2013,327, 24–27.

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