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Investigation of Photo-Catalytic Degradation of Co-doped SnO_2 annealed at Different Temperatures

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***Abstract*-- Annealing temperatures plays a very crucial role in the surface morphology, optical and photo-catalytic properties of Co doped SnO_2. $Sn_{1-x}Co_xO_2$ samples have been chemically synthesized with low Co concentration (≤1%). The X-ray diffraction (XRD), and scanning electron microscopy (SEM), are used to characterize these samples. The XRD pattern shows the tetragonal rutile structure. The crystallite size and the average particle size increases with increase in annealing temperature. The UV-Visible spectroscopy shows an interesting band type absorption for different samples. The oxygen vacancies play vital role in the optical properties. These vacancies cause shift in absorption peaks of annealed SnO_2 samples. The photo-catalytic activity of the Co doped SnO_2 nano-particles have also been studied in the degradation of methylene blue. It shows that the Co doped SnO_2 nano-particles annealed at 450˚C act as a highly suitable photo catalyst.**

***Keywords*-- Co-doped SnO_2, Diluted Magnetic Semiconductor, Co-precipitation, Photo-catalysis.**

I. INTRODUCTION

Diluted Magnetic Semiconductors (DMS) are interesting as well as promising materials for new era technological applications as spin degree of freedom of electrons in addition to their charge are accommodated into single matter and their interplay is expected to explore novel physics and new devices[1-4].

The interest in the physical and optical properties of metal oxides (SnO_2, TiO_2, ZnO) has significantly increased due to their desired applications in electronic and optical fields, especially when they are doped with magnetic components[5,6]. Among these nano-structured semiconductor materials, tin oxide (SnO_2) presents special properties, such as wide band gap of 3.6 eV, optical transparency, electrical conductivity, high carrier density, native oxygen vacancies and chemical sensitivity which makes it a very attractive material for solar cells, fabrication, catalysis, heat mirrors and gas sensing applications[7-10]. SnO_2 is one of the most important semiconductor material that has been used as photo-catalyst for degradation of dyes and organic pollutants in waste water effluents of industries. Previous studies suggested that the doping of tin oxide nano-structure with transition metal enhances their photo-catalytic activity by change in the band structure of SnO_2. Out of Mn, Fe, Co, Ni and Cu, doping with Co is considered to be the most effective for tuning the electronic, optical and photo-catalytic properties.

In this study, much attention has been focused to optimize a simple and an effective technique to synthesize very fine and uniformed particles of un-doped tin oxide and Co doped tin oxide nanoparticles. For both the doped and un-doped SnO_2 particles, the photo-catalytic activity are evaluated by examining the degradation of methylene blue under visible light exposure.

TABLE 1:
XRD Data of Co (x=0.005) Doped SnO_2 Samples and Pristine SnO_2 Sample.

Sample Name	Annealing Temp (°C)	Crystallite Size (nm)	Average Particle Size (nm)	a (°A)	c (°A)
SCO-350	350	22	25	4.743	3.156
SCO-450	450	28	29	4.740	3.178
SCO-550	550	43	47	4.709	3.163
SCO-650	650	49	53	4.711	3.175
SnO_2-450	450	35	40	4.683	3.157

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II. Experimental Method

Metal doped SnO_2 and undoped SnO_2 nano-particles were prepared by co-precipitation method. $SnCl_2.2H_2O$ and $CoCl_2.6H_2O$ in the proportion 50:1 were first dissolved in 100 ml of deoxygenated distilled water. An aqueous NH_4OH solution (50 ml) was added to the above solution, then precipitated at 80^0C and was kept at this same temperature for several hours. The resulting precipitates were collected, filtered, washed thoroughly with distilled water and then dried at 40°C. Finally, to obtain the Co doped SnO_2 powder, the samples were annealing treatment for 2 hr in air at different temperatures i.e. at 350°C, 450°C, 550°C and 650°C..

The structural characterization i.e. the grain size and the crystalline phase of Co-doped and undoped SnO_2 was studied by X-ray diffraction (XRD) using Cu Kα radiation (λ=1.5406Å). Morphological study was done through Scanning Electron Microscopy (SEM). The optical measurements were carried over by UV-vis spectrometer. The photo-catalytic degradation of Methylene Blue with Co-doped SnO_2 powder was done by exposing the samples to a Xenon light of 1000W.

III. Results And Discussion

Structural Investigations

At room temperature, the structures of the Co-doped SnO_2 nano-particles are examined by XRD as shown in Fig.(1) at four different annealing temperatures (350°C, 450°C, 550°C and 650°C respectively). All the peaks index well to the tetragonal rutile structure. Within the sensitivity of XRD measurements, there is no evidence of extra secondary phases. But some metallic Co or other SnO or CoO based phases are observed. The crystallite size and the lattice parameters are calculated from XRD data of doped and undoped SnO_2. The average crystallite size (D) has been determined using the diffraction peaks (110) and (101) using Scherer's formula

$$D = \frac{k\lambda}{\beta\cos\theta}$$

where K is a constant whose value is taken as 0.89, λ is the wavelength of CuK radiation and β is the corrected full width at half maximum (FWHM) of the diffraction peak.

It is interesting to note that with increase in annealing temperature, the cassiterite SnO_2 phase decreases while the relative concentration of the ortho-rhombic phase gradually increases.

The variation of both the lattice parameters (Table 1) is not systematic. At higher annealing temperatures there might be diffusion of randomly distributed Co ions toward the surface leading to grain growth during the annealing

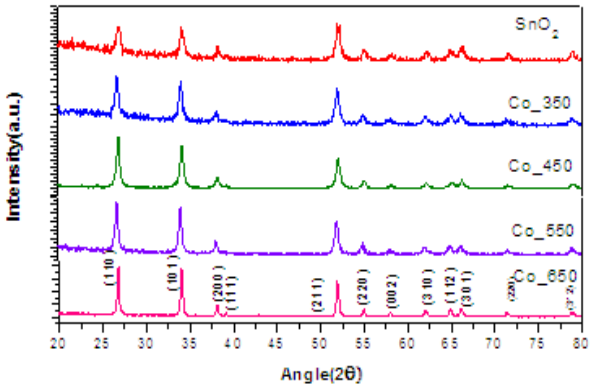

Fig.(1) XRD patterns of Co doped SnO_2 (x=0.005) annealed between 350°C to 650°C

The SEM images of Co doped SnO_2 nanoparticles are shown in Fig.(2). Using SEM techniques, the surface morphology of undoped and Co doped SnO_2 were studied. In case of pristine SnO_2 the particles are found to be larger compared to the doped ones. The results revealed that undoped SnO_2 appeared as a spherical shaped. It is seen that the crystallite size of the samples is in good agreement with the size calculated from Scherrer's formula. It also indicates that with the increasing annealing temperature, the particles are found to aggregate and may be attributed to a lesser number of nucleation centres leading to surface redistribution of grains. During the annealing process, the number of surface defects also increases with the increasing annealing temperature. The high magnification SEM images in Fig.(2) reveals that the average particle sizes are in range of 25-53 nm.

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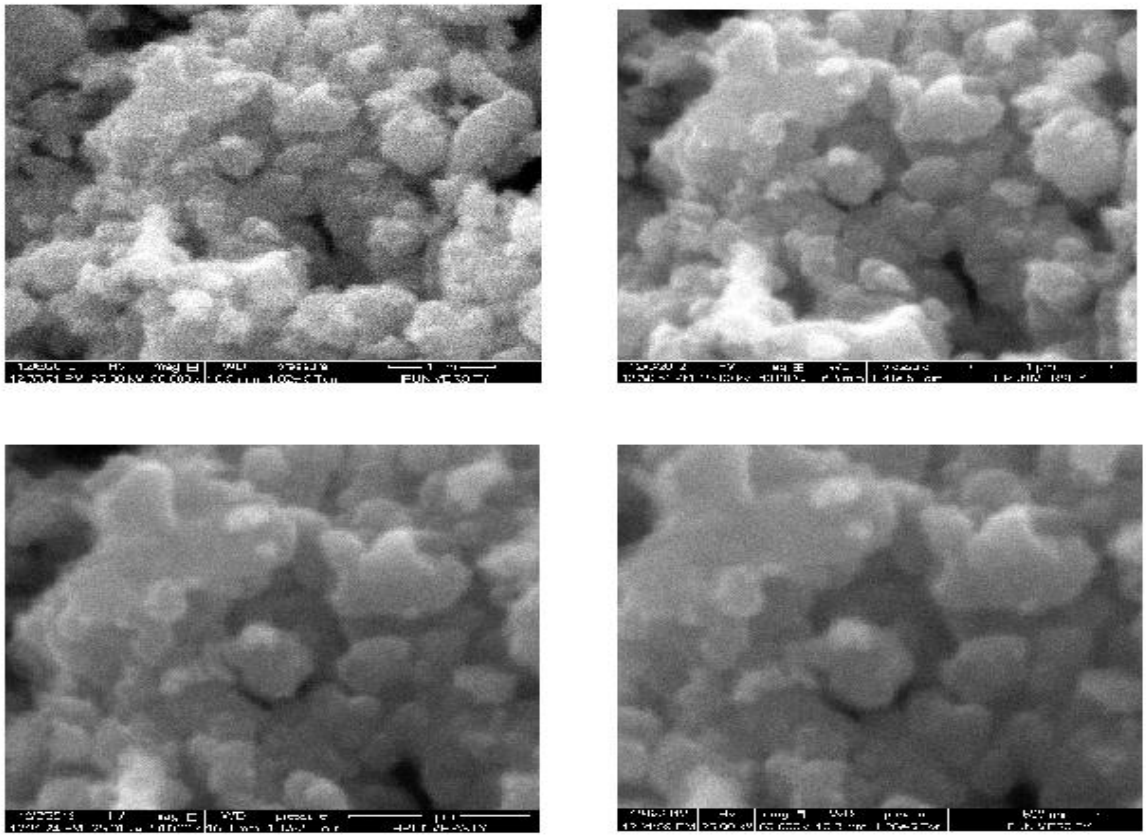

Fig.(2) SEM morphology images for nano-crystalline Co doped SnO_2 powders annealed at (a) 350°C, (b)450°C, (c) 550°C, (d) 650°C

IV. Optical Investigations

To study the influence of Co doping level, the absorption spectra were recorded with the help of UV-visible diffused reflectance spectrometer (UV-DRS) for Co doped SnO_2 prepared at different temperatures i.e. 350 °C, 450°C, 550°C and 650°C as shown inFfig.(3). Probably due to Co d states the Co doped samples exhibit absorbance edge which extends into the band gap region resulting from the overlapping of orbitals. With increase in annealing temperatures, there is a slight blue shift in the band gap values of Co doped SnO_2 as compared with pristine SnO_2. As the annealing temperature increases, the particle size also increases but the band gap is found to decrease. This indicates a blue shift in the absorption edge.

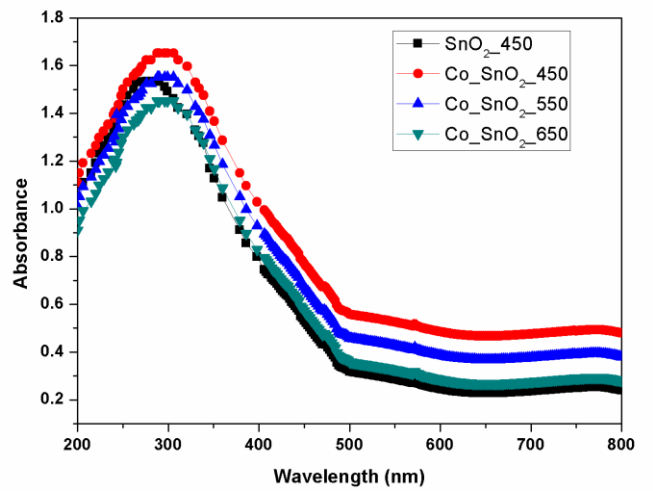

Fig.(3) Absorption Spectra of pristine & Co doped SnO_2 annealed between 450°C to 650°C

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V. Photocatalytic Investigations

The photo-catalytic activity of Co doped SnO_2 annealed at different temperatures i.e. 450°C, 550°C and 650°C have been studied for exposure time interval from 0-120 min. Fig (4) shows the degradation of Methylene Blue solution under visible light exposure, for the undoped and doped SnO_2. Addition of photo-catalyst exhibits decrease in absorption band. It It is also noticed that by increasing the irradiation time, the maximum absorption band at 654 nm steadily decreases. The homogeneous and uniform morphology of the samples facilitates the photo-catalytic degradation as it can lead to a better transfer of both electrons and holes generated in the lattice system. In the present case, the Co addition leads to an upward shift in the Fermi level of the doped system and thereby increases the band gap. The increase in band gap is evidenced by the blue shift in the absorption edge of the spectrum. The photo-catalytic degradation efficiencies of the synthesized samples were evaluated from the formula,

$$\% \text{ of Degradation} = Ao - A/ Ao * 100$$

Where Ao and A are initial absorbance of the dye and the actual absorbance at particular time respectively.

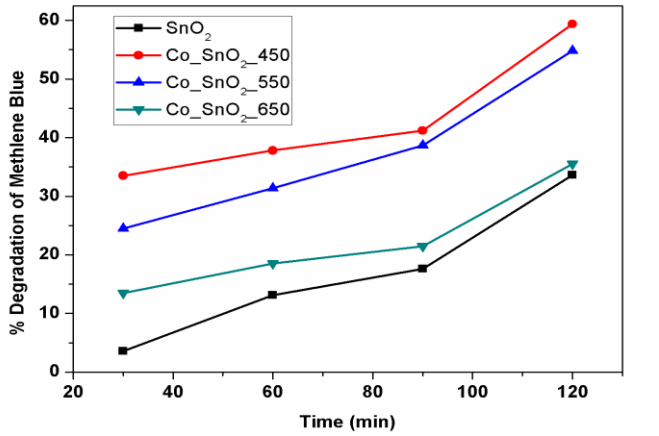

Fig.(4) Degradation % of Methylene Blue for pristine & Co doped SnO_2 annealed between 450°C to 650°C

The presence of cobalt in tin oxide matrix accelerates the photo-catalytic process. The Co doped SnO_2 particles have highly efficient photo-catalytic activity for degradation of Methylene Blue. It clearly indicates that the samples annealed at 450°C shows highest photo-catalytic activity of Co doped SnO_2 which may be attributed to the sample with good crystallization and higher surface area.

The photo-catalytic activity of the samples decreases with increasing annealing temperatures due to weak crystallization and decrease in surface area .

VI. Conclusions

To summarize, SnO_2 and Co doped SnO_2 nano-particles have been successfully prepared by using co-precipitation method. In the presence of visible light, both doped and un-doped SnO_2 nano-particles are found to be an excellent photo-catalyst for the degradation of MB. With the increasing annealing temperature, it is observed that the photo-catalytic activity of samples decreases due to decrease in surface area and weak crystallization. It shows that the doped samples annealed at 450°C show better photo-catalytic activity for MB dye degradation compared to pristine SnO_2 sample. Through the optical measurements, we came to know that the nano-metric size of the materials influences the energy band gap values with a slight shift in the absorbance bands.

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