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STRUCTURAL AND LUMINENSENCE CHARACTERISTICS OF NANOCRYSTALLINE SnO_2 DOPED WITH Co^{2+}

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Our present study shows the synthesis of Cobalt doped Tin Oxide (Co-SnO_2) nanoparticles by co-precipitation method at room temperature with different concentration of Co doping as 2 %, 4% and 6% M with tin chloride. The structural, morphological and optical properties of these prepared samples were investigated using XRD, SEM, UV-Vis and PL spectroscopy. Structural analyses reveal that Co dopants are substituted into rutile SnO_2 nanoparticles. The UV-Vis absorption spectra of 2%, 4% and 6% cobalt-doped SnO_2 samples were exhibited absorption edges at 343, 337, and 327 nm corresponds to band gap energy 3.62 eV, 3.68 eV and 3.79 eV respectively. The PL emission spectra results predicted that by increasing Co concentration, the PL intensity gets decreased due to the absence of new energy levels in the band structure to produce a new combination of emission.

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Keywords: XRD, EDAX, SEM ,UV , PL and Nanoparticles

1. Inroduction

Nanotechnology involve the manipulation of materials at nanometer sizes leading to the fabrication of nanodevices for the enhance in performance (1-3). Tin oxide (SnO_2) has been recently received an enormous scientific interest because of its larger bandgap, high degree of transparency in visible spectrum, strong physical and chemical interaction with adsorbed species, low temperature and strong thermal stability in air(4-6). These emergent properties play an important role in the variety of applications in solar cell, LED, dye-sensitized solar cell and secondary lithium batteries(7). SnO_2 nanoparticles have been successfully synthesized by different methods (8). Furthermore, the addition of dopant to the structure of tin oxide can change the characteristics such as structural and optical properties(9-10). The results have shown that many additives and transition metal ions such as Fe, Cu, Co, Cr and Mn. They can lead to change the surface of the tin oxide. In the present work, the different concentrations of 2%, 4% and 6% M of Cobalt doped Tin Oxide nanoparticles were prepared and characterized for the optoelectronic applications. The structural and optical properties of Co doped SnO_2 nanoparticles were analyzed by using X-Ray Diffraction (XRD), Scanning electron microscopy (SEM) and Optical spectroscopy like UV-Vis absorbance and PL spectroscopy.

2. Experimental section

The prepared composition of the powder sample of Co doped SnO_2 was prepared by a chemical co-precipitation method. In a typical synthesis, The aqueous solution was prepared by the dopant of cobalt nitrate hexahydrate $Co(NO_3)_2 \cdot 6H_2O$ and host of tin chloride ($SnCl_2.2H_2O$). The precursors were weighted according to the stoichiometry as per the target compositions. Besides the subjective materials were dissolved in distilled water to make 0.3M solution. The aqueous ammonia (NH_3 OH) of 0.4 M was added dropwise to the above solution of $SnCl_2$ to increase the

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pH of the prepared solution under the continues stirring for about 3 hrs at ambient temperature until the fine brown colored precipitate was occurred. Finally, to get the powder form of Co doped SnO_2 nanoparticle, the sample was dried in vacuum oven at 60˚C for 8hrs. Using the same method, we have repeated the procedure for various concentration of $Co(NO_3)_2 \cdot 6H_2O$ doped with $SnCl_2.2H_2O$ of molar values 2%, 4% and 6% M respectively.

3. Results and discussion

The XRD patterns of Co doped SnO_2 (with different concentrations of Co) nanoparticles were shown in Fig. (1). The XRD peaks were observed at 26.6°, 33.8° and 51.78° reveals that a rutile tetragonal phase. These peaks assigned to the planes (110), (101) and (211) respectively (JPCPDF 41-1445). It is noteworthy that no diffraction peak corresponding to Co oxide and any impurity peak indicating Co were well dispersed within the SnO_2 lattice. Furthermore, the peak position shifts to larger angle with the increase in Co content, revealing the changes in lattice parameter values. All the doped samples have a clear peak broadening due to the smaller crystalline size of SnO_2 nanoparticles. Table 1. Shows the obtained crystallite sizes of the samples calculated by Scherrer formula(12).The lattice parameters reduced with increasing particle size. Also, surface stresses and surface defect dipoles were the phenomena governing the change in lattice parameters as the particle size gets increased. It was apparent that the specific surface area shifts towards higher values with the increase in Co concentrations.

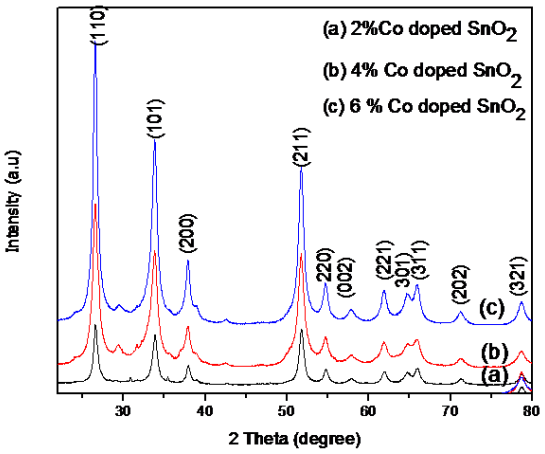

Fig. (1) XRD Pattern of (a) 2% Co Doped SnO2 (b) 4% Co Doped SnO2 (c) 6% Co Doped SnO2

It indicates that crystallite size increases with the increasing dopant concentration of Co. Thus it was implied that Co ions get substituted at the Sn site without changing the cassiterite structure in Co doped SnO_2 nanoparticles with different concentration of 2%, 4% and 6%. However, when Co doping concentration increases, a metastable or the tetragonal phase of SnO_2 arises and the crystallite size increases abruptly. Based on the XRD analysis, it was assumed that the doped Co ions were substituting for Sn in the host matrix and there were no Co metallic clusters or Co-based oxides in the Co doped SnO_2 nanoparticles.

Table 1: Strucutral parameters of (a) 2% Co Doped SnO_2(b) 4% Co Doped SnO_2 (c) 6% Co Doped SnO_2

S.No	Samples Sample	Latticeparameters(Å)		Particle Size(nm)
		a	c	
1	2% Co doped SnO_2	4.685	3.184	11
2	4% Co doped SnO_2	4.674	3.173	14
3	6% Co doped SnO_2	4.663	3.161	17

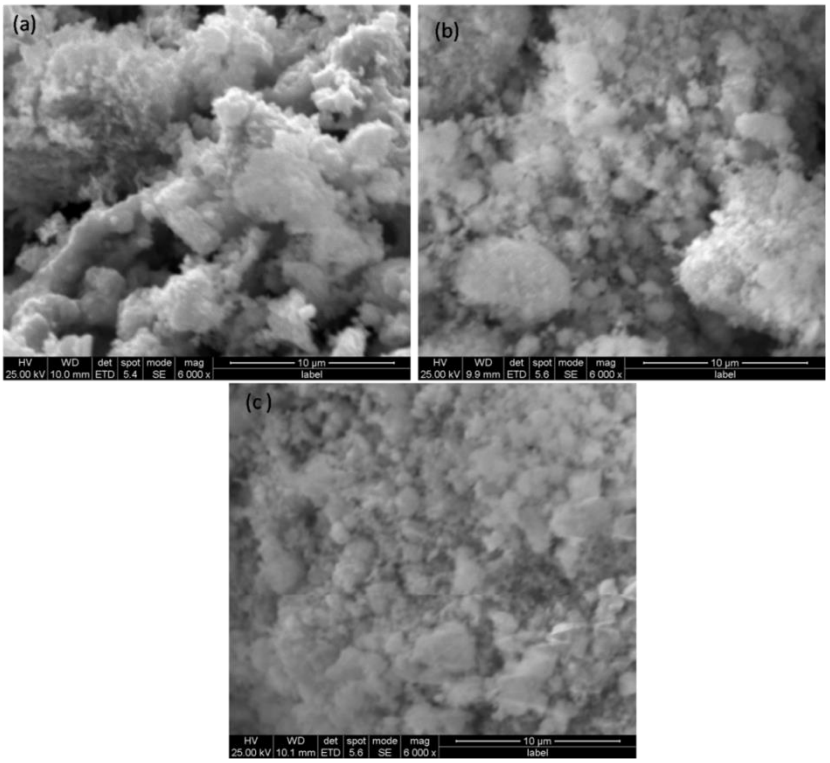

Fig.(2-a) SEM images of Co doped SnO_2, (a) 2% Co Doped SnO_2 (b) 4% Co Doped SnO_2 (c) 6% Co Doped SnO_2

Scanning electron microscope (SEM) was used for the morphological study of as synthesized nanoparticles. Fig. (2) Shows the SEM images of Co doped SnO_2 with different concentration of 2%, 4% and 6% respectively. All the samples shows the spherical shaped SnO_2 nanoparticles, while Co doped SnO_2 show the aggregated particles. The increasing dopant concentration nanoparticles were improved. The dispersion was better than 6% Co doped SnO_2 samples. However, on the whole, it was clear that doping can inhibit the excess aggregation of SnO_2 nanoparticles. This indicates that the Co doping into SnO_2 can change the surface character of the primary nanoparticles, which was deduced to be from the effects of the diffusion of Co^{2+} into the SnO_2 lattice, and the formation of a Co–O–Sn bond on the surface of the doped samples were confirmed.

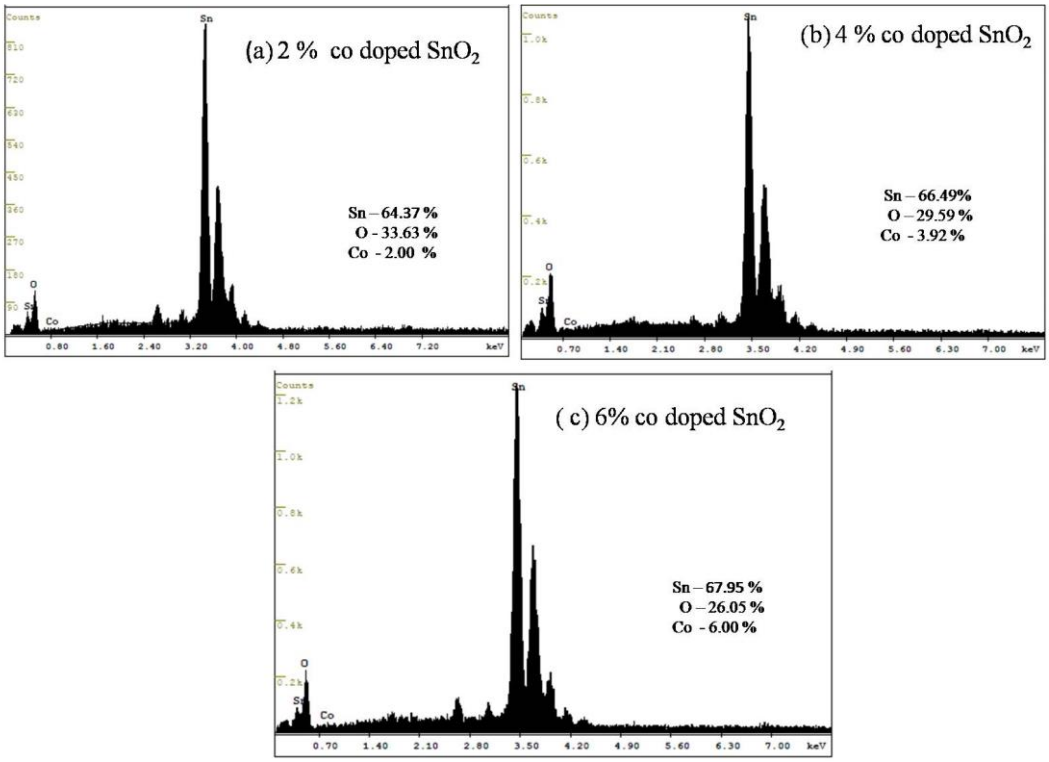

Fig.(2-b) EDAX Spectra of (a) 2% Co Doped SnO_2 (b) 4% Co Doped SnO_2 (c) 6% Co Doped SnO_2

The EDAX analyses of Co Doped SnO_2 was indicated in Fig.(2-b), which resembles that the elemental analyses of Co Doped SnO_2 nanoparticles has the components of Tin (Sn), Cobalt (Co) and oxygen (O) confirming the effectively doped Co on SnO_2 nanoparticles. While comparing every part of samples, there is no evidence for the foreign atoms which makes the material as a highly pure.

Extensive UV-Vis absorption spectroscopy has been carried out to understand the optical properties and electronic interaction of doped nanoparticles. In order to confirm the substitution of Sn^{4+} by Co^{2+} ions, the optical absorption spectra for Co doped SnO_2 nanoparticles were measured at room-temperature. The absorption spectrum of pristine SnO_2 shows the sharp absorption peak at 332 nm (3.7eV) which corresponds to the band gap (Eg) of bulk tetragonal SnO_2 (3.6eV) (13). The increase in band gap is mainly due to the incorporation of Co atoms in SnO_2. The UV-Vis absorption spectra of Co Doped SnO_2 in various concentration of 2%, 4% and 6% cobalt-doped SnO_2 samples were shown in Fig.(3), which exhibited a fundamental absorption edges at 343, 337, and 327 nm corresponds 3.62 eV, 3.68 eV and 3.79 eV respectively. The resultant values confirm that the well blue shift was occurred by increasing the dopant concentration due to the high incorporation of Co within SnO_2, which makes the material as a vastly doped Co-SnO_2 nanocomposite.

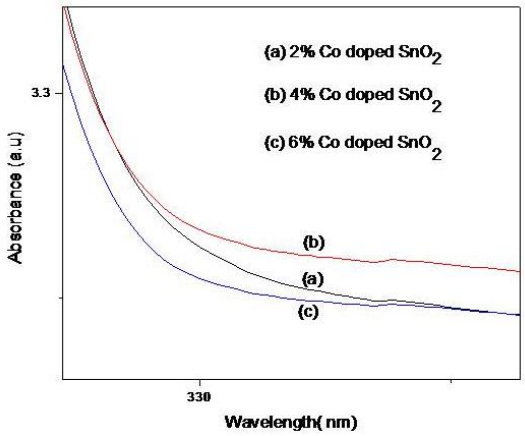

Fig. (3) Absorption spectra of (a) 2% Co Doped SnO_2 (b) 4% Co Doped SnO_2 (c) 6% Co Doped SnO_2

Table 1: Strucutral parameters of (a) 2% Co Doped SnO_2(b) 4% Co Doped SnO_2 (c) 6% Co Doped SnO_2

S. No.	Concentration	Absorption Wavelength (nm)	Band gap (eV)
1	2% Co doped SnO_2	343.05	3.62
2	4% Co doped SnO_2	337.27	3.68
3	6% Co doped SnO_2	327.16	3.79

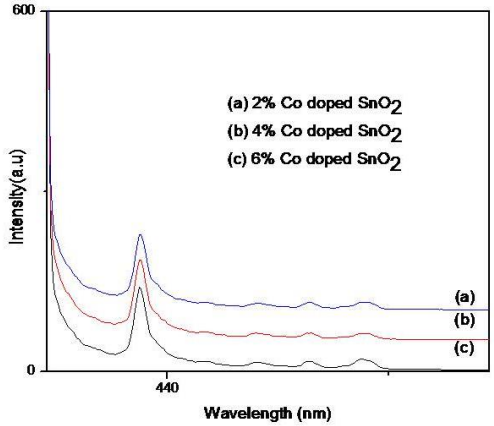

Fig. (4) Emission spectra of (a) 2% Co Doped SnO_2 (b) 4% Co Doped SnO_2 (c) 6% Co Doped SnO_2

To further explore the optical properties of Co-doped SnO_2 nanoparticles, PL characterization was carried out. Fig. (4) represents the PL spectra of the prepared samples (with different concentrations of Co) under the excitation wavelength of 385 nm. The spectrum shows the considerably broad PL emission at 430 nm, which was confirmed by previously reported values [14]. Thus the results predicted that by increasing Co concentration, the PL intensity gets decreased which clearly mention that the doping does not bring about new energy levels in the

band structure to produce a new combination of emission (15). In addition, which indicates that the Co^{2+} ions substitute for Sn^{4+} ions without formation of other additional energy levels in the host material.

3. Conclusion

Co doped SnO_2 nanoparticles have been effectively synthesized under the co-precipitation method at ambient temperature. Co substitution in the SnO_2 lattice confirmed the rutile tetragonal structure from the XRD pattern. The absorption spectra of Co doped SnO_2 sample shows the optical band gap values are higher than the bulk value of SnO_2 which reveals the formation of nanoparticles. An extremely strong emission at 430 nm, which may be ascribed to the contribution of oxygen vacancies and defects in the SnO_2 lattice. We anticipate that our strategy will offered a new path for deign of low cost functional materials containing a nanoparticles with controllable morphologies, structures and compositions as well as promising optoelectronic applications.

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