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Synthesis and photoluminescence studies of polymer capped SnO_2 nanoparticles synthesized by chemical co-precipitation method

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ABSTRACT
In recent years many research works have been focused on the electrical and optical properties of metal oxides. In this present paper SnO_2 nanoparticles have been synthesized by chemical co-precipitation method using different capping agents like EDTA (ethylene diamine tetra acetic acid), PVP (polyvinylpyrrolidone), PVA (polyvinyl alcohol) and studied the influence of capping agent on various properties of SnO_2 nanoparticles. Structural, surface morphology, chemical analysis and luminescence properties of prepared SnO_2 nanoparticles were studied by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) attached with energy dispersive analysis of X-rays (EDAX) and photoluminescence studies (PL). X-ray diffraction study reveals the nano-size particle distribution of the prepared samples with tetragonal rutile structure in the range of 3 to 9 nm. FTIR spectra show the structural confirmation of SnO_2 nanoparticles. Various PL signals were observed in the visible region around 375 nm to 600 nm due to oxygen vacancies and interfacial Sn vacancies present in the prepared nanosamples.

Keywords: Chemical co-precipitation, Nano-size distribution, X-ray diffraction, scanning electron microscopy, Photoluminescence

I. INTRODUCTION

Semiconducting metal oxides have immense technological applications in the field of science and technology. Among them, SnO_2 is considered to be one of the important and wide band gap (Eg = 3.6 eV) [1] semiconductors with n-type conduction due to the existence of intrinsic defects and due to its high transparency, conductivity and thermal properties, it is suitable for modern technologies such as catalysts, gas sensors, solar cells, liquid crystal display, gas discharge display, lithium-ion batteries, etc [2 - 9]. Due to large surface to volume ratio and quantum effect, nanoparticals influences the electrical, optical and magnetic properties. The crystallite size of nanoparticles changes its properties when compared to bulk particles. SnO_2 nanoparticles can be prepared by various synthesis routes like spray pyrolysis, co-precipitation, pulse laser deposition, sol-gel, hydro-thermal, chemical vapour deposition, etc [10-15]. The controlled synthesis of SnO_2 nanoparticles have been possible using chemical co-precipitation method. This method is simple, inexpensive and does not require any sophisticated experimental setup. In this paper we discussed the preparation of polymer (PVP, EDTA and PVA) capped SnO_2 nanoparticles and studied the effect of capping agent on structural, morphological, compositional and photoluminescence properties of SnO_2 nanoparticles.

II. EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES:

All chemicals were of analytical reagent grade and were used without further purification. SnO_2 nanoparticles were prepared by chemical co-precipitation method using $SnCl_2.2H_2O$ as reactant material. Ethylene diamine tetra acetic acid (EDTA) was used as the capping agent. Ultrapure de-ionized water was used as the reaction medium in all the synthesis steps. In a typical synthesis, desired molar quantity of $SnCl_2.2H_2O$ was dissolved in 100 ml ultrapure de-ionized water and stirred for 30 minutes. Stirring process is carried out at a temperature of 90^0C and NaOH solution was drop wisely added to the solution to adjust the pH value 9. Stirring was continued for three hours to get fine precipitation. The obtained precipitate was washed with de-ionized water for several times. Finally, the powders were vacuum dried for 3 hours at 80^0C to obtain SnO_2 nanoparticles. The same procedure was repeated by varying various capping agents. The dried powder was characterized for structural, morphological, compositional and photoluminescence studies.

The X-ray diffraction patterns of the samples were collected on a Rigaku D X-ray diffractometer with the Cu-Kα radiation (λ=1.5406A°). FTIR studies were carried out by Fourier transform infrared spectrophotometer (FTIR-4700typeA). Surface Morphology and elemental composition of the prepared samples were analyzed using Oxford Inca Penta FeTX3 EDAX instrument attached to Carl Zeiss EVO MA 15 scanning electron microscope. Photoluminescence spectra were recorded in the wavelength range of 400–600 nm using PTI (Photon Technology International) Fluorimeter with a Xe-arc lamp of power 60 W and an excitation wavelength of 320 nm was used.

III. RESULTS AND DISCUSSION:

3.1 Structural analysis

The XRD patterns for the prepared SnO_2 nanoparticles using different capping agents are shown in Fig.1. From the fig. 1 it is obvious that the peaks are indexed as (110), (101), (200), (211), (220), (002) and (310) planes at 2θ values 26.91°, 34.11°, 38.31°, 52.17°, 54.96°, 58.22° and 62.24° that correspond to tetragonal rutile structure of polycrystalline SnO_2 which are in consistent with the JCPDS (No. 72-1147) data. The average particle size was estimated Using the Debye–Scherrer's formula, $D = 0.94\ \lambda/(\beta_{hkl}\cos\theta)$, Where, D is the average Particle size, β_{hkl} is full width at half maximum of XRD peak expressed in radians and `θ` is the position of the diffraction peak.

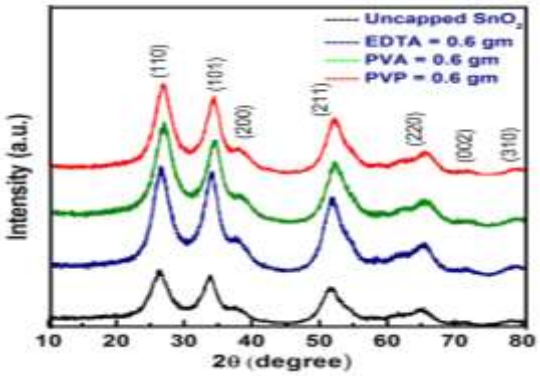


Fig.1 XRD patterns of SnO_2 nanoparticles synthesized at different capping agents EDTA, PVP & PVA.

The average particle size of the samples calculated by Debye- Scherrer's equation were tabulated in the below Table 1.

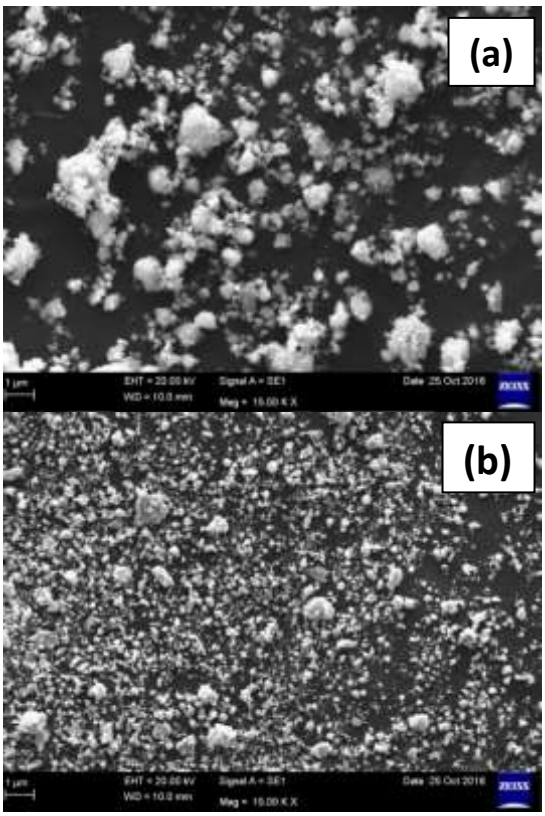
Table 1: Average Particle size of polymer capped SnO_2 nanoparticles

S.No	Capping agent concentration (at.%)	Particle size(nm)
1	Uncapped SnO_2	58
2	EDTA (0.6 gm)	3
3	PVP (0.6 gm)	8
4	PVA(0.6 gm)	9

The crystal size obtained from uncapped SnO_2 nanoparticles is bigger than the capped crystals and hence, capping agent plays an important role in tuning the various size-dependent properties of the prepared nano samples.

3.2 Morphological studies

Fig. 2 shows the surface morphology of SnO_2 nanoparticles. Fig. 2(a), 2(b), 2(c) and 2(d) show the SEM images of uncapped and capped (EDTA, PVP & PVA) SnO_2 nanoparticles respectively. From SEM images it was clearly observed that the particles were agglomerated**.** The sample prepared with EDTA capping agent exhibits slightly decreased agglomeration compared to other samples.



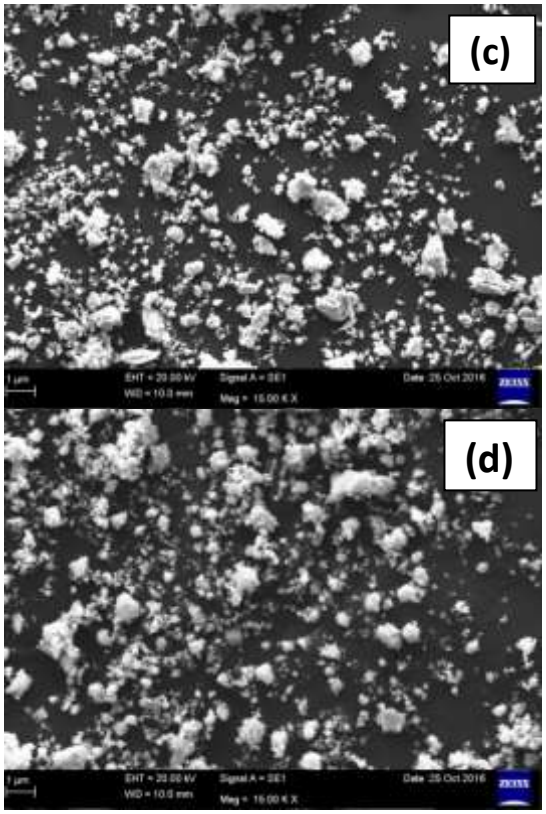
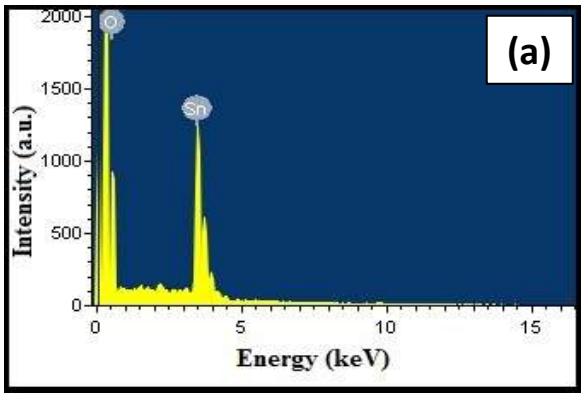
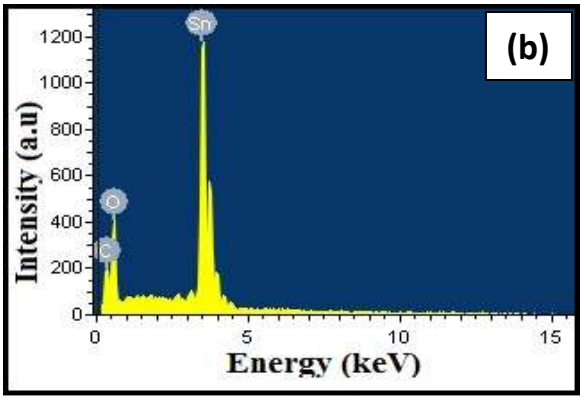


Fig.2 SEM images of (a) uncapped SnO_2 nanoparticles, (b) EDTA, (c) PVP and (d) PVA capped SnO_2 nanoparticles

3.3 Compositional analysis

The EDAX profiles of uncapped and capped SnO_2 nanoparticles are shown in Fig.3. It is evident from the EDAX Spectra that no other elemental peaks other than Sn and O are observed. This confirms the effective formation of SnO_2 nanoparticles.





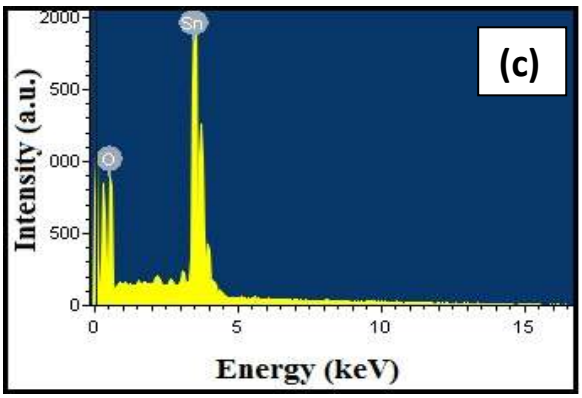


Fig.3 EDAX profile of (a) uncapped SnO_2 nanoparticles, (b) EDTA & (c) PVP capped SnO_2 nanoparticles

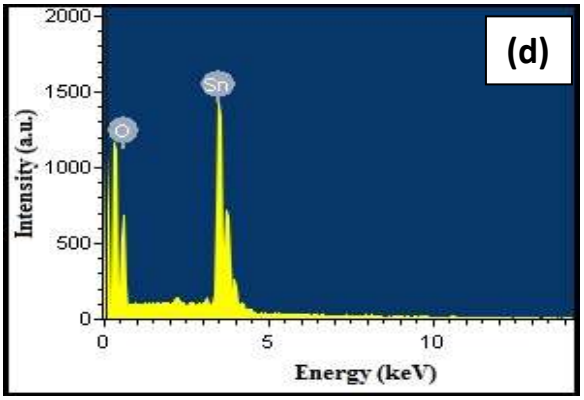


Fig.3 EDAX profile of (d) PVA capped SnO_2 nanoparticles

3.4 Photo Luminescence studies

Fig. 4 shows the Photoluminescence spectra of SnO_2 nanoparticles excited at 230 nm at room temperature. The PL spectra are recorded in the range of 250- 700 nm. As seen in Fig.4, all the samples showed multiple PL emission bands at 3.31 eV (375 nm), 3.16 eV (392 nm), 2.83 eV (438 nm), 2.72 eV(456 nm), 2.23 eV (557 eV), 2.07 eV (598 nm) and a strong peak has been observed at 375 nm and weak peaks attributed the defect levels in the band gap such as surface oxygen vacancies of SnO_2 nano samples [16]. No impurity peaks were observed in all the samples.

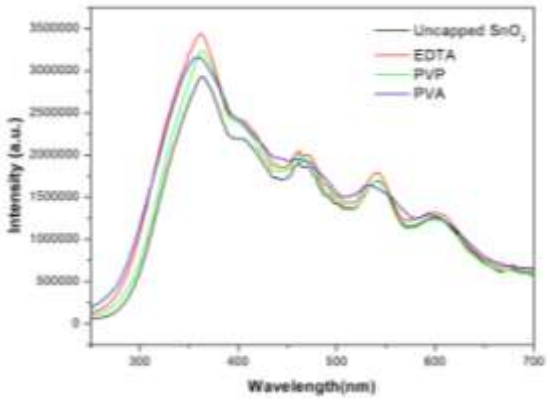


Fig.4 PL spectra of uncapped and capped (EDTA, PVP and PVA) SnO_2 nanoparticles

The emission peaks observed in the UV - Visible regions are may be due to a recombination of free excitons and defects in energy levels originated due to oxygen vacancies present in the band gap of the SnO_2 nanosamples. These oxygen vacancies are present in three different charge states v_o^0, v_o^+ and v_o^{2+} and acts as radiative centers [17]. Compared to other samples, EDTA capped SnO_2 nanosample exhibited enhanced luminescence intensity and this may be due smaller particle size of the nanosample.

3.5 FTIR studies

FTIR spectra of prepared nanosamples with different capping agents are shown in fig.5. The FTIR band observed around 659 cm^{-1} due to asymmetric stretched mode of O–Sn–O bridge functional group which clearly indicates the formation of SnO_2 phase [18-19]. A new peak is present at 1098 cm^{-1} which is due to the vibrations of c–c bond in the ion radical stabilized on the sn^{2+}. Sn-O-Sn band indicates the excited states of O^{2-} in the SnO_2 host material.

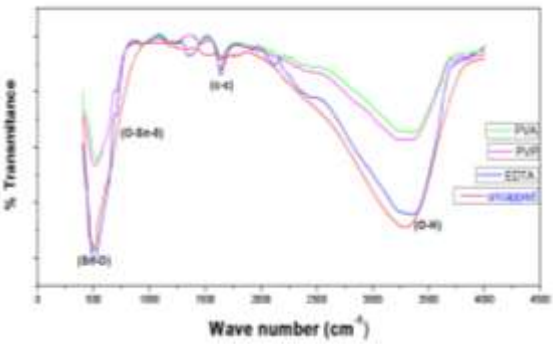


Fig.5 FTIR spectra of uncapped and capped (EDTA, PVP and PVA) SnO_2 nanoparticles

The bands 1047 cm^{-1} and 1400 cm^{-1} may be attributed to the bending of vibrations present in the sample. The FTIR band observed at 1635 cm^{-1} can be attributed to the overtones of Sn-O-Sn mode and the band at 3415 cm^{-1} indicates the presence of O-H oscillators [19- 21].

IV. CONCLUSIONS

SnO_2 nanoparticles were successfully prepared by chemical co-precipitation method using different capping agents (EDTA, PVP & PVA). XRD and FTIR studies revealed the tetragonal rutile structure of polycrystalline SnO_2 nanoparticles. From SEM micrographs, it is observed that EDTA capped SnO_2 nanosample shows decreased agglomeration compared to other samples and EDAX studies confirms the effective composition of the samples. Compared to other samples, EDTA capped SnO_2 nanoparticles exhibits increased luminescence intensity when compared to other capping agents and hence finds luminescence applications.

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