



Synthesis, characterization and photo-catalytic studies of mixed metal oxides of nano ZnO and SnO_x



K. Jeyasubramanian^{a,*}, G.S. Hikku^a, M. Sivashakthi^b

^a Centre for Nanoscience and Technology, Department of Mechanical Engineering, Mepco Schlenk Engineering College, Sivakasi, India

^b Department of Physics, Idhaya College for Women, Sivagangai, India

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ABSTRACT

Novel mixed metal oxides of Zinc and Tin (MZOTO) were synthesized by a simple co-precipitation method. The effect of blending varying compositions of SnO_x ($x=1, 2$) to ZnO has been evaluated, and it was found that the crystal structure, morphology, optical properties and photo-catalytic behavior were dependent on the percentage of SnO_x. The obtained samples were characterized using XRD, EDAX, FESEM, UV–vis spectroscopy, Photoluminescence, etc. XRD data revealed that the ZnO and SnO_x co-exist as mixture and their structures were found as hexagonal and cubic/orthorhombic respectively. FESEM image intricate about the morphology of the MZOTO prepared in 1:0.5 ratio providing nano flower structures that resemble like *Chrysanthemum* species. The band gaps of all the obtained MZOTOs were determined from UV–vis reflectance spectra using Kubelka-Munk relation. Photoluminescence emission studies revealed that the recombination of excited e[−] with the h⁺ of ZnO is greatly influenced by SnO_x nanoparticles. Visible light photo-catalytic activities of MZOTOs were followed spectrophotometrically against the degradation of crystal violet solution. MZOTO2 obtained in the ratio of 1:0.5 shows better catalytic efficiency compared to other samples, degrading crystal violet completely within 40 min. The reusability and free radical trapping experiments were performed to study the performance and mechanism of MZOTO2 as the photo-catalyst. The photo catalytic efficiency of 1:0.5 MZOTO was higher due to the presence of flower-like structures that effectively captivated more photons from the sunlight.

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1. Introduction

All over the world, the current concern of debate is to degrade the industrial pollutants that are dumped into the fresh/sea water [1]. The industrial sewage comprises of toxic organic complexes which eventually causes many environmental issues [2,3]. Dye industry plays a major role in polluting the fresh water eco-system that discharges about 15% of dyes into the environment during synthesis and processing [4–6]. The conventional methods adopted to eradicate the organic pollutants from the polluted water are flocculation, absorption, reverse osmosis, biodegradation, etc. These methods either transfer the chemicals to solid state or produce large slurries which in turn cause secondary pollution. All such draw backs could be overcome by the photo-catalytic degradation technique that promotes eco-friendly tactics, where the organic pollutants are disintegrated into smaller non-toxic molecules by UV & visible light exposure in presence of suitable catalyst. Obviously, semiconductor nano particles are being considered

as an efficient candidate for the photo-catalytic degradation process since it possess high surface to volume ratio which greatly influences the number of active sites thereby accelerating degradation process [7].

Typical photo-catalysts extensively studied in the photo-degradation processes are zinc oxide, tin oxide, titanium oxide, etc. in its pure form [8–11]. Zinc oxide and Tin oxide are semiconductor metal oxide materials which have broad range of applications such as photo-degradation, optoelectronic devices, gas sensors, etc., due to their distinctive size and shape dependent characteristics [12]. Individually, the semiconducting particles like zinc oxide and tin oxide shows lower catalytic efficiency against the degradation of organic pollutants owing to the immediate recombination of electron-hole (e[−]/h⁺) pair generated under UV–vis light exposure [13–15]. Moreover, the photo-catalytic activity of semiconducting materials can be further enhanced by blending with suitable additives that give hetero-structured arrangement which can facilitate the electronic properties thereby delaying e[−]/h⁺ pair recombination process [16,17]. Apart from these, the physical and chemical properties of the mixed oxides vary from the individual components due to the existence of many phases [18]. Rather than

* Corresponding author.

E-mail address: kjeya@mepcoeng.ac.in (K. Jeyasubramanian).

using pure ZnO as photo-catalyst for degradation of organic pollutant, SnO_x is chosen as an additive which may inhibit the instant recombination of e^-/h^+ pair during UV–vis light exposure. Such a delayed recombination of e^-/h^+ pair is vital for the decomposition of organic pollutants that will be achieved by mixing ZnO and SnO_x in varying composition.

This work details about the isolation of mixed metal oxides of zinc oxide with varying quantities of tin oxide (MZOTO) by chemical route and their structure, morphology, optical properties and photo catalytic activities has been studied extensively. Photo-catalytic activities of mixed metal oxides have been found more efficient than pure ZnO for degrading crystal violet (CV) on exposing to sunlight.

2. Materials and methods

2.1. Synthesis of ZnO nanoparticles

All the chemicals used in this work were of analytical grade, used without further purification. 0.05 M sodium hydroxide solution was added drop by drop to the 0.01 M zinc acetate solution with continuous stirring at room temperature. A white precipitate was visualized due to the formation of $\text{Zn}(\text{OH})_2$. The obtained precipitate was separated by filtration, washed with deionized water and dried at 120 °C for 5 h. The dried powder was calcinated at 700 °C for 1 h in a muffle furnace which yield ZnO nanoparticles and was stored in vacuum.

2.2. Synthesis of MZOTO mixed metal oxides

50 ml separate solutions comprising 0.0025, 0.005, 0.0075 and 0.01 M tin (II) chloride dissolved in distilled water were mixed individually with 50 ml 0.01 M zinc acetate solution at room temperature. To this, 50 ml solution containing 0.05 M NaOH was added drop wise with vigorous stirring. The resultant samples were named as MZOTO1, MZOTO2, MZOTO3 and MZOTO4 respectively, collectively referred as MZOTOs. The above mixture was stirred till a white precipitate was formed. The obtained precipitate was filtered and washed many times with deionized water followed by ethanol several times to remove the excessive ions. The precipitate was dried at 120 °C for 5 h, and it was calcinated at 700 °C in a muffle furnace for 1 h and was stored in vacuum. Flow chart describing the process involved in the isolation of mixed metal oxides is given in Fig. 1.

2.3. Photo catalytic studies

Photo catalytic degradation studies of CV was examined by mixing 0.1 g of MZOTO powder in 100 ml of water containing 1 mg of CV. The contents were then sonicated using SONICS, 750 W, USA

(for getting evenly distributed nano particles in the CV solution) and the mixture was exposed to sunlight. Periodically, once in 5 min the contents present in the reaction mixture exposed to sunlight were drawn and the change in absorbance of the solution was followed spectroscopically (Pekin Elmer, Lambda 25, USA) using UV–vis spectrometer at $\lambda_{\text{max}}=579$ nm. Since CV shows its characteristic absorption at 579 nm, the spectrophotometry was followed at that specific wavelength.

3. Results and discussion

3.1. XRD characterization of MZOTOs

The phase and structural investigation of MZOTOs were done from the powder XRD pattern recorded in the range of $2\theta=10^\circ$ to 80° using Siefert X-ray diffractometer. Different sets of diffraction peaks were visualized from the XRD pattern of MZOTOs. The diffraction peaks observed at $2\theta=31.8^\circ$, 34.4° , 36.2° , 47.5° , 56.6° , 62.9° , 66.4° , 67.9° , and 69.06° corresponds to the hexagonal ZnO structure resembled the JCPDS file no. 89-1397 [19]. The diffraction peaks corresponding to $2\theta=31.8^\circ$, 36.2° , 39.42° and 51.09° are attributed to the cubic structure of SnO_2 matched with the JCPDS No. 33-1374 [20]. Besides, low intensity diffraction peaks found at $2\theta=16.2^\circ$, 32.9° , 45.46° and 58.03° are attributable to SnO that exist along with SnO_2 nano particles in trace amount having orthorhombic phase corresponding to the JCPDS No. 77-2296. The XRD patterns of all the mixed oxides are depicted in Fig. 2. The crystalline nature of ZnO nanoparticles can be inferred from the XRD pattern showing sharp peaks. While on increasing the molar concentration of SnO_x , the diffraction peak becomes broadened and the peak sharpness gets reduced. Apart from the peak sharpness, another noteworthy feature was noticed while looking the XRD of MZOTOs from MZOTO1 to MZOTO4. The characteristic peaks of ZnO at $2\theta=31.7^\circ$ and 36.2° (from JCPDS file No. 89-1397) are very close to the major reflections of SnO_2 found at $2\theta=31.5^\circ$ and 36.4° (from JCPDS file No. 33-1374) respectively. So, in the mixed state, the peaks are merged together and appeared as a single peak with higher intensity. Also, from the XRD data it is noticed that when the molar concentration of SnO_2 increases, the preferential orientation peak at $2\theta=31.8^\circ$ increases gradually. The increase in composition of tin oxide also modifies the crystalline nature of MZOTOs into amorphous type, which is further visualized from FESEM images given in Section 3.2.

3.2. FESEM and EDAX analysis

The morphology of ZnO and MZOTOs were analyzed from the FESEM micrograph obtained using Carl Zeiss, Neon 40, is represented in Fig. 3(a, c, e, g, i). From Fig. 3(a), the morphology of ZnO was visualized as near spherical shaped particles of size ranges from 150 to

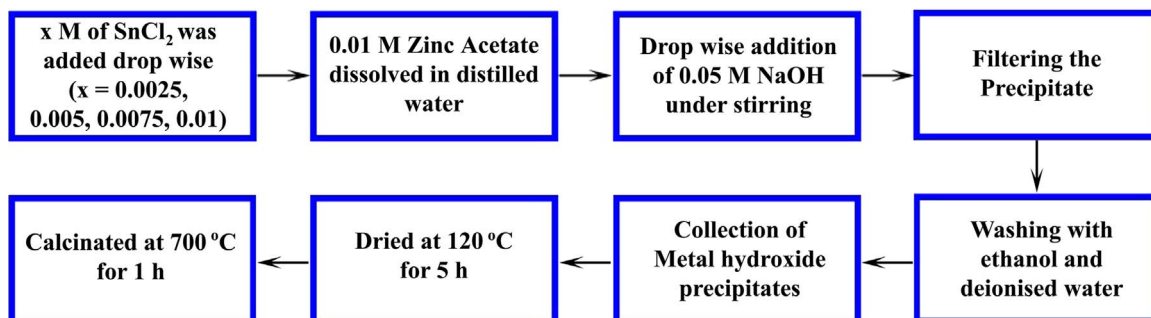


Fig. 1. Flow chart for the synthesis of MZOTO mixed metal oxide.

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