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## Electrochemical Generation of $Zn_2SnO_4$ Photocatalyst for Degradation of Methylene Blue

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### ABSTRACT

In this paper, a simple two-step hybrid electrochemical-thermal route was developed for the synthesis of cubic shaped  $Zn_2SnO_4$  (ZTO) nanoparticles using aqueous sodium bicarbonate ( $NaHCO_3$ ) and sodium stannate ( $Na_2SnO_3$ ) as an electrolyte. The sacrificial Zinc metal was used as both anode and cathode in an undivided cell under galvanostatic mode at room temperature. The bath concentration and current density were respectively varied from 30 to 120 mmol and 0.05 to 1.5 A/dm<sup>2</sup>. The electrochemically generated precursor was calcined for an hour at different range of temperatures from 60 to 500°C. The crystallite sizes in the range of 24-53 nm were calculated based on the Debye-Scherrer equation. Scanning electron microscopy results reveal that all the particles have cubic morphology with a diameter of 40-50 nm. The as-prepared ZTO nanoparticles showed higher catalytic activity towards the degradation of methylene blue (MB) dye, and the 90% degradation was found for the sample calcined at 500 °C, which is greater than that of commercial  $TiO_2$ -P25 photocatalysts. These results indicate that the ZTO nanoparticles may be employed to remove dyes from waste water.

**Keywords:** Photocatalyst; Cubic; Methylene Blue; Electrochemical; Nanoparticle;  $Zn_2SnO_4$ .

### 1. INTRODUCTION :

Recently, ecology related problems associated with water pollution have attracted a lot of attention and it is envisaged that nanostructured semiconducting oxide materials can play a very important role in this respect too. So, the researchers are mainly focused on the development of new materials like metal oxides, metal-metal oxides and mixed oxides to improve the efficiency of degradation process in photocatalytic activity. Metal metal-oxide nanostructured materials have been attracted much attention due to their prominent properties and their potential applications in heterogeneous catalysis, optoelectronics, metallurgy, thin film coating, fine ceramic composites and photocatalysts [1]. Semiconducting oxide materials such as ZnO, CuO,  $TiO_2$ ,  $Al_2O_3$ ,  $SnO_2$ ,  $ZrO_2$  and  $WO_3$  are attractive photocatalysts because they are not only environmentally sustainable but also high catalytic efficiency in degradation of various environmental pollutants such as pesticides, detergents, dyes and volatile organic compounds [2-5].

Ternary semiconductor oxides  $Zn_2SnO_4$  (ZTO) is known for owning high-electron mobility, high-electrical conductivity, low visible absorption and attractive optical properties, which makes it suitable for applications in solar cell [6], gas sensor (detecting humidity and various combustible gases) [7, 8], photoluminescence, negative electrode for Li-ion battery [9, 10] and photocatalysis (degrading organic pollutants) [11-13]. ZTO (Zinc stannate) is a transparent semiconducting oxide material and has attracted considerable interest for its high photocatalytic activity. The decomposition reactions of benzene and water soluble dyes using ZTO as a photocatalyst were reported [11, 12, 14, 15]. Increased human population has resulted in the development of large-scale industries such as textile and paper production, whose waste products cause a major environmental hazard to aquatic biota and humans due to their toxicity [16] and the tendency to cause eutrophication [2]. Detection

and removal of these toxic chemicals is a major challenge with convention methods. Thus, there is an urgent need of eco-friendly technologies for the detection and removal of textile effluents from water. It has been shown that dyes can be easily adsorbed and catalyzed on oxide surfaces. However, to the best of our knowledge, there exist only a few reports [17-20] on the direct removal of commonly used industrial dyes and in many reports, the degradation of organic pollutants and industrial dye effluents through electrochemical, photo electrochemical and photo catalysis process.

In the present study, we focus on the preparation of  $Zn_2SnO_4$  (ZTO) nanoparticles with a hybrid electrochemical-thermal route without using any template or surfactant at room temperature. The effects of electrolyte, current density and reaction media on the shape, size, chemical composition of the generated product, together with the production yield were investigated. Power XRD pattern, SEM images and FT-IR absorption spectra of the products calcined at different temperatures were tested and discussed. It has been found that our method is a simple and feasible electrochemical route for the synthesis of ZTO nanoparticles on commercial scale. As well, the spectroscopic data and degradation ratio of commonly used textile dye (Methylene Blue; cationic) in aqueous solution with these ZTO nanoparticles were tested under different UV irradiation time, to characterize ZTO nanoparticles and photocatalytic properties. The optimum conditions for generation of ZTO nanoparticles were also proposed.

## 2. EXPERIMENTAL :

### 2a. Materials

High purity Zinc metal plate (99.99%), sodium bicarbonate (AR grade: 99.5%), sodium stannate (AR grade: 98.5 %) purchased from Sisco Research Laboratories, Mumbai and Methylene Blue (MB) from S. D. Fine Chemicals Ltd., India, were used as received. Millipore water (specific resistance, 15 M $\Omega$  cm at 25 °C, Millipore Elix 3 water purification system, France) was used to prepare the electrolyte solution.

### 2b. Synthesis of ZTO nanoparticles

ZTO nanoparticles were synthesized using a standard electrochemical technique mentioned in ref [21]. Prior to electrolysis, the Zn plates were activated by immersing in dilute HCl (1 M) for 30 sec followed by washing with Millipore water. The electrolyte was a 400 ml solution containing 30 mM (1.008 gm) sodium bicarbonate ( $NaHCO_3$ ) and 10 mM sodium stannate ( $Na_2SnO_3$ ). It was injected in a rectangular undivided cell ( $5.0 \times 6.0 \times 0.8$  cm<sup>3</sup>) where Zn plates were used as both cathode and anode. The electrolysis was carried out for about one hour under galvanostatic conditions, the constant current was supplied by a DC power supply (model PS 618 potentiostat/galvanostat 302/2 A supplied by Chem link, Mumbai) with constant stirring at 600 rpm. The pH of the electrolyte was recorded before and after the electrolysis. A white precipitate was formed and filtered (by whattman filter paper No.41) to isolated from the solution. The resulting wet precipitate was dried at 60 °C in hot air oven for 1 hr and then it was calcined at 300 °C and 500 °C for 1 hr.

### 2c. Characterization

The morphology, structure, crystallite size and compositional analysis of the nanoparticles were performed using powder X-ray diffraction (XRD), scanning electron microscopy and FT-IR spectroscopy. Morphology and compositional analysis were carried out in a scanning electron microscope (SEM, Philips XL 30) in the voltage range of 200-300 kV. Powder X-ray diffraction (XRD) patterns were tested for all the samples using PAN alytical X'pert Pro powder diffractometer with Cu-K $\alpha$  radiation, ( $\lambda_{Cu}=1.5418$  °A) working at 30 mA and 40 kV. The XRD patterns were recorded in the  $2\theta$  range from 10° to 90° at a scanning rate of 1°/min. Fourier transform infrared spectra (FT-IR) were obtained on KBr pellets at ambient temperature using a Bruker FT-IR spectrometer (SENSOR 27). The average crystallite sizes were calculated by using the Debye Scherrer equation  $D = K\lambda/\beta\cos\theta$  [22], where D is the diameter of the crystallite size, K is the shape factor (the typical value is 0.9),  $\lambda$  is the wavelength of incident beam,  $\beta$  is the broadening of the diffraction peak measured in radians at half of its maximum intensity (FWHM) and  $\theta$  is the Bragg's angle.

### 2d. Photocatalytic degradation of MB dye in aqueous solution

Photocatalysis experiments were carried out with different sized (24, 35 and 53 nm) ZTO

nanoparticles (0.1g in 100 ml of dye solution) and Methylene blue (MB) dye solution (10 ppm) in Millipore water. The photochemical reactor used in this study was made of a Pyrex glass jacketed quartz tube. A high pressure mercury vapor lamp (HPML) of 125 W (Philips, India) was placed inside the jacketed quartz tube. To avoid fluctuations of the input light intensity, a supply ballast and capacitor were connected in series with the lamp. Water was circulated through the annulus of the quartz tube to avoid overheating of the solution. Synthesized ZTO nanoparticles of varying sizes were added to 100 ml dye solution (10 ppm), with continuous stirring for 2 hr for homogeneity. 100 ml of the solution (ZTO and MB) was taken in the beaker under continuous stirring to ensure the uniform suspension of the catalyst. The lamp radiated predominantly at 365 nm, corresponding to photon energy of 3.4 eV and photon flux of  $5.8 \times 10^{-6}$  mol of photons  $\text{sec}^{-1}$ . Aliquots were collected from the reaction beaker at regular time intervals, and the concentration of dye in solution and degradation ratio was plotted as a function of time by monitoring the changes of the  $\lambda_{\text{max}}$  line intensity with time.

### 3. RESULTS AND DISCUSSION :

#### 3a. Powder X-ray diffraction Studies

The phase purity and crystalline structure of synthesized powders were investigated by using powder X-ray diffraction technique. The XRD patterns for calcined compounds obtained from the electrolytic concentration of 30 mM  $\text{NaHCO}_3$ , 10 mM  $\text{Na}_2\text{SnO}_3$  and the current density of 1  $\text{A}/\text{dm}^2$  were shown in Fig. 1. It can be seen from Fig. 1 that, the thirteen peaks appeared at  $2\theta$  range of  $17.2^\circ$ ,  $29.1^\circ$ ,  $34.2^\circ$ ,  $35.9^\circ$ ,  $41.6^\circ$ ,  $45.6^\circ$ ,  $51.6^\circ$ ,  $55.1^\circ$ ,  $60.4^\circ$ ,  $63.5^\circ$ ,  $68.4^\circ$ ,  $71.3^\circ$  and  $76.0^\circ$  corresponding to cubic structure of Zinc-tin oxide ( $\text{Zn}_2\text{SnO}_4$ ) phase with standard JCPDS card no. 24-1470. The calculated crystallite size, based on XRD data was 24 nm. The XRD patterns were indexed to pure cubic structure with a lattice parameter of 8.657(6) Å and its space group: Fd3m (227). They are matching with the standard JCPDS card No. 24-1470, indicating that the Zinc-tin oxide ( $\text{Zn}_2\text{SnO}_4$ ) particles are crystalline with face centered cubic structure. No peaks related to other phases and impurities were found in XRD patterns of calcined compounds implying formation of pure Zinc-tin oxide ( $\text{Zn}_2\text{SnO}_4$ ) nanoparticles and these particles are cubic in nature having face centered Bravais lattices. From the XRD data, the average crystallite sizes were found to be 24, 35 and 53 nm, respectively. It clearly indicates that, the non crystalline  $\text{Zn}\cdot\text{Sn}(\text{OH})_6$  phase were gradually converted to cubic crystalline phase of ZTO nanoparticles.

#### 3b. SEM morphological studies

Scanning electron micrographs of as-prepared and calcined compounds of ZTO nanopowder are shown in Fig. 2. The as-prepared compound was synthesized from the bath with concentration of 30 mM  $\text{NaHCO}_3$ , 10 mM  $\text{Na}_2\text{SnO}_3$  and the current density of 1  $\text{A}/\text{dm}^2$ , and in sequence, it was calcined for 1 hr at 500 °C. The SEM images of ZTO nanoparticles show different morphologies. Figure 2(a) presents the SEM image of the starting  $\text{Zn}\cdot\text{Sn}(\text{OH})_6$  compound. It can be seen that the particles exhibit irregular, agglomerated small flower like structure, whereas calcined powder at 500 °C shows less randomly oriented cubic like morphology (Fig. 2(b)). The small flowers of the starting compound transformed to cubic like ZTO structures, starting at as-prepared compound and speeding up at 500 °C. The as-prepared sample heated at 500 °C for 1hr (Fig. 2(b)) produces uniformly oriented cubic structure due to the growth of ZTO particles. As the heat treatment temperature increases, the particles tend to grow as expected. For instance, at 500 °C, the shape of the nanoparticles is cubic in nature.

#### 3c. FT-IR spectroscopic studies

Infrared spectroscopy was used to detect the presence of functional groups adsorbed on the surface of synthesized nanoparticles during electrochemical process. Figure 3 represents the FT-IR spectra of as-prepared and calcined compounds of ZTO powder obtained from the bath concentration of 30 mM  $\text{NaHCO}_3$ , 10 mM  $\text{Na}_2\text{SnO}_3$  at the current density of 1  $\text{A}/\text{dm}^2$ . The as-prepared sample was heat treated at different temperatures of 300 and 500 °C for 1 hr. Figure 3(a) indicates a strong and broad absorption peaks in the range of 3100-3600  $\text{cm}^{-1}$  centered at 3447  $\text{cm}^{-1}$ , corresponding to the stretching vibration of hydrogen bond (O-H) of surface adsorbed crystalline water and higher amount of hydroxyl group. These vibrations are the evidence for the existence of water in the as-prepared compound. These peaks gradually disappear under increasing calcinations temperature, indicating the removal of water. It is interesting to note that there is one band centered at 1522  $\text{cm}^{-1}$  are ascribed to

the vibration of absorptive water (M-OH-M groups). The weak band at  $1040\text{ cm}^{-1}$  appearing in IR spectrum of as-prepared compound may be attributed to the vibrations of M-OH or M-OH-M groups for  $\text{Zn}\cdot\text{Sn}(\text{OH})_6$ , and the absorption peak at  $502\text{ cm}^{-1}$  is due to the vibration of M-O or M-O-M groups for ZTO nanoparticles. This indicates that the presence of ZTO nanoparticles in as-prepared and calcined compounds. The metal oxygen frequencies observed for the respective metal oxides are in accordance with literature values for  $\text{Zn}\cdot\text{Sn}(\text{OH})_6$  and ZTO [23].

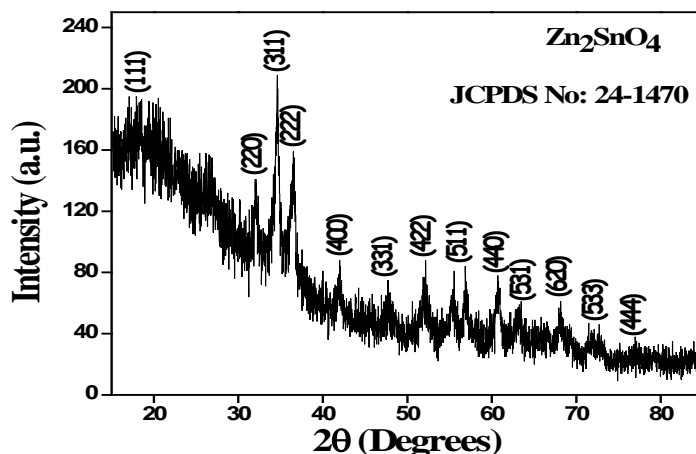


Fig. 1 : XRD patterns of ZTO Nanoparticles obtained from 30 mM  $\text{NaHCO}_3$ , 0.01 M  $\text{Na}_2\text{SnO}_3$  at  $1\text{ A/dm}^2$ .

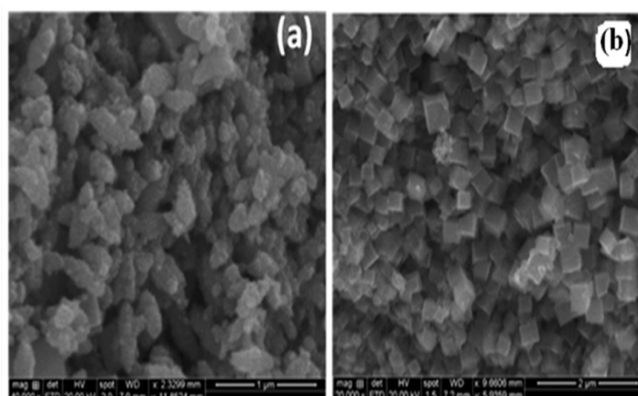


Fig. 2 : SEM images of (a) ZTO precursor, (b) calcined at  $500\text{ }^\circ\text{C}$ .

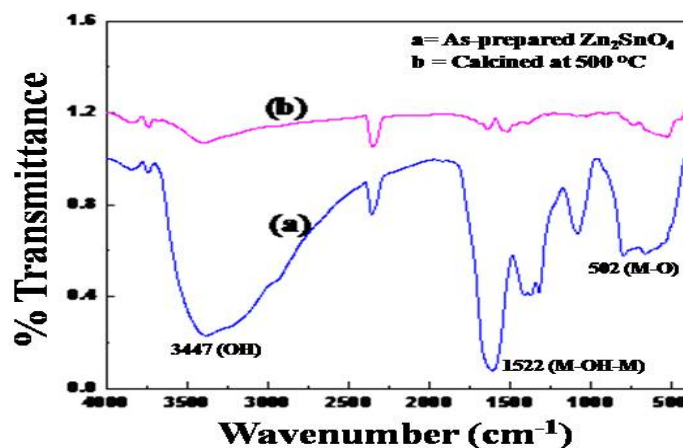
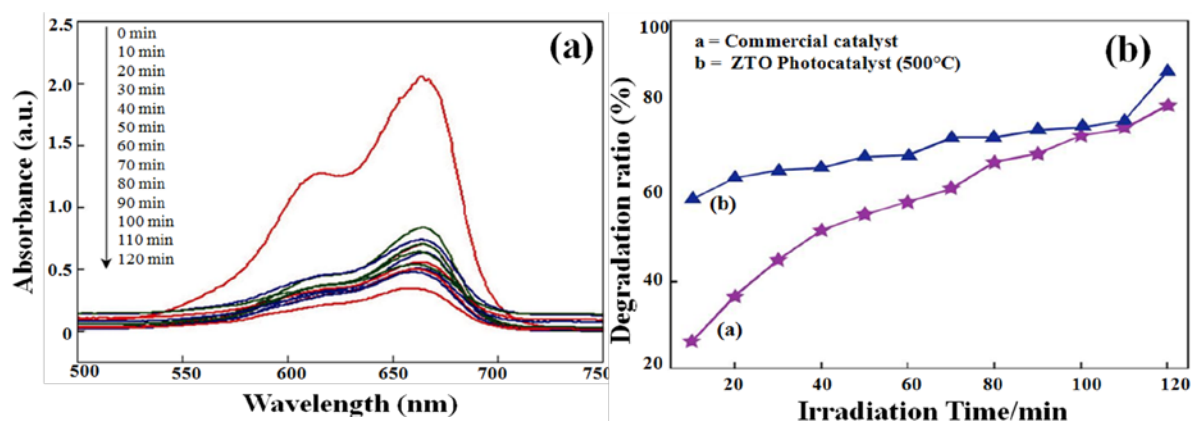


Fig. 3 : FT-IR spectra of (a) ZTO precursor, (b) calcined at  $500\text{ }^\circ\text{C}$ .

### 3d. Photocatalytic performance of ZTO with MB dye

The successful synthesis of ZTO nanoparticles offers an opportunity to examine their photocatalytic activity. The as-prepared and calcined ZTO nanoparticles were selected for the evaluation of photocatalytic activity with MB dye under the illumination of UV light. In order to study the effect of UV light on degradation of MB dye, a blank experiment was performed under UV light without the addition of photocatalysts (ZTO). The results indicated that MB dye of 10 mg/L was photolyzed up to 5% in 2 hr. This degradation efficiency was negligible when the different sized (24, 35 and 53 nm) nanoparticles were added to the solution under illumination. When there was no UV light, the concentration of MB dye with the addition of ZTO photocatalysts remains unchanged for 2 hr. From these blank experiments, it can be concluded that UV light and photocatalysts are the necessary factors in the photocatalytic process. MB dye absorbs light in the visible region (550-700 nm) with the absorption maxima at 664 nm. A series of experiments were carried out with different sizes (24, 35 and 53 nm) ZTO nanoparticles in MB dye solution.

Figure 4(a) represents the large degradation efficiency was observed in ZTO nanoparticles calcined at 500 °C. In the initial 20 min, the degradation efficiency reached the highest value of 60%. Afterward, the absorbance curve decreases and the efficiency of degradation ascend tardily up to almost 90%. The crucial degradation efficiency after 80 min illumination has changed a little compared with the efficiency obtained after the initial illumination for 20 min. The increase of particle size with increased calcination temperature to 500 °C. (Fig. 4(a)) is helpful to increase the photocatalytic activity. However, a higher catalytic activity is observed for calcined ZTO sample only in the early stage of reaction (30 min), the percentage of activity is little increased for longer time degradation.



**Fig. 4 :** Time-dependent absorption spectra of MB dye during UV light irradiation in presence of ZTO (a) calcined at 500 °C and (b) degradation rate of two different catalysts.

Figure 4(b) shows the degradation ratio of calcined (500 °C) ZTO photocatalysts compared with that of commercially available TiO<sub>2</sub>-P25 photocatalysts, which was evaluated by the degradation of MB dye in aqueous solution. The performance of degradation process was defined as % Degradation =  $(A_0 - A) / A_0 \times 100\%$ , where  $A_0$  is the initial absorbance and  $A$  is the final absorbance. The degradation of dye molecules by self-direct photolysis was negligible. The activity of ZTO photocatalysts is slightly greater but it is almost equal to commercial TiO<sub>2</sub>-P25 photocatalysts, which is attributed to its high surface area (41.8 m<sup>2</sup>/g), higher crystallinity and smaller particle size ( $\approx$  19 nm). The catalytic performance on degradation is a complex function involving several parameters such as morphology, charge density, dye adsorption capacity, and is related to the BET surface area and pore size distribution. Lou et al. [11] observed that ZTO nanocrystals exhibited high photocatalytic activity to various reactive dyes such as K-NR, B-RN and B-GFF because of their large surface area ( $\approx$  62 m<sup>2</sup>/g). Zhang et al. [24] observed that oxide coupled ZnO-SnO<sub>2</sub> nanocrystals had equally excellent photocatalytic activity for the degradation of methyl orange when compared to TiO<sub>2</sub>-P25. The degradation efficiency of ZTO nanoparticles calcined at different temperature reduced in the order of 500 °C > 300 °C > 60 °C. The above results recommend that the photogenerated holes are the main oxidative centers of ZTO system. This suggests that calcined ZTO nanoparticles are highly efficient

photocatalysts when compared to commercially available TiO<sub>2</sub>-P25 photocatalysts for the degradation of MB dye.

#### 4. CONCLUSION :

- Nanosized ZTO particles were successfully synthesized by hybrid electrochemical thermal method using NaHCO<sub>3</sub> and Na<sub>2</sub>SnO<sub>3</sub> electrolyte, without zinc salts, templates or surfactants. The particle size range of the generated ZTO powder was 24-53 nm.
- The FT-IR spectrum shows the existence of OH<sup>-</sup>, M-OH-M and M-O-M groups in uncalcined sample. After calcinations, the particles morphology was cubic like and is well crystallized in the nanosize of 40-50 on nanometer scale. The method could be effectively used to synthesize ZTO on large scale.
- The as-prepared ZTO exhibited an efficient catalytic activity in degrading MB dye, and the calcined ZTO has higher photocatalytic activity compared to TiO<sub>2</sub>-P25 under UV light irradiation.
- The higher photocatalytic property was probably caused by larger crystallinity and smaller particle size.
- Thus, synthesized by the simple, fast and eco-friendly electrochemical method, the nano ZTO is a promising candidate for the photodegradation of dyes from waste waters.

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