



Synthesis, Characterization And Photocatalytic Activity Of Zn-Doped Tin Oxide Nanoparticles

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Abstract

Zn-doped mixed metal oxide nanoparticles have attracted significant attention owing to their enhanced physicochemical properties and superior photocatalytic efficiency under UV and visible light irradiation. In the present work, ZnO–SnO₂ nanoparticles were synthesized by a simple sol–gel assisted co-precipitation method. The prepared nanomaterials were characterized using X-ray diffraction (XRD), and scanning electron microscopy (SEM), to investigate their crystalline structure, morphology, and functional groups. XRD analysis confirmed the formation of crystalline mixed oxide phases with nanoscale crystallite size. SEM images revealed agglomerated nanoparticles with nearly spherical morphology. FT-IR spectra indicated the presence of characteristic metal–oxygen vibrations, confirming successful synthesis. The photocatalytic activity of the synthesized nanoparticles was evaluated by degradation of methylene blue dye under UV light irradiation. Zn-doping significantly enhanced the photocatalytic performance of SnO₂ due to improved charge separation and reduced electron–hole recombination. Among the prepared samples, ZnO–SnO₂ exhibited superior photocatalytic efficiency. The results suggest that ZnO–SnO₂ nanoparticles are promising materials for environmental remediation applications.

Keywords: Zn-doped nanoparticles; ZnO–SnO₂; Photocatalysis; Dye degradation Pineapple peels

1. Introduction

Nanostructured semiconductor metal oxides such as TiO₂, ZnO, and SnO₂ have been extensively studied due to their remarkable optical, electronic, and catalytic properties [1]. Among these, SnO₂ are widely used photocatalysts for the degradation of organic pollutants owing to their chemical stability, non-toxicity, and low cost [2]. However, their practical applications are limited by wide band gap energy and rapid recombination of photogenerated electron–hole pairs [3]. Doping and formation of mixed metal oxides are effective strategies to overcome these limitations by modifying the band structure and enhancing charge carrier separation [4]. ZnO is a wide band gap semiconductor with high exciton binding energy and good photocatalytic activity [5]. Incorporation of ZnO into TiO₂ or SnO₂ matrices can improve light absorption and suppress recombination processes, thereby enhancing photocatalytic efficiency [6]. Several researchers have reported improved photocatalytic performance of Zn-doped TiO₂ and Zn-doped SnO₂ nanomaterials prepared by various chemical routes [7–9]. Nevertheless, systematic studies comparing ZnO–SnO₂ nanoparticles synthesised under similar conditions are limited. Therefore, the present study aims to synthesise ZnO–SnO₂ nanoparticles using a green synthesis method using fruit peel extract of pineapple,

characterise them using XRD, SEM, and FT-IR techniques, and evaluate their photocatalytic activity toward the degradation of methylene blue dye.

2. Materials and Methods

2.1 Materials

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), sodium hydroxide (NaOH), ethanol, Pineapple fruit peel and methylene blue dye were of analytical grade and used without further purification. Double-distilled water was used throughout the experiments.

2.2 Synthesis of ZnO–SnO₂ Nanoparticles

ZnO–SnO₂ nanoparticles were prepared using a similar procedure. Zinc nitrate and stannous chloride solutions were mixed under vigorous stirring with Pineapple peel extract, followed by dropwise addition of NaOH to maintain pH ~10. The resulting precipitate was aged, filtered, washed, dried, and calcined at 500 °C for 4h to obtain ZnO–SnO₂ nanoparticles.

2.3 Characterization Techniques

X-ray diffraction (XRD) patterns were recorded using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of 20–80°. Surface morphology was examined using scanning electron microscopy (SEM).

2.4 Photocatalytic Activity Study

The photocatalytic activity of the synthesized nanoparticles was evaluated by degradation of methylene blue (MB) dye under UV light irradiation. In a typical experiment, 50 mg of photocatalyst was dispersed in 100 mL of 10 mg L⁻¹ MB solution shown in Figure 1.1. The suspension was stirred in the dark for 30 min to establish adsorption–desorption equilibrium, followed by UV irradiation. At regular time intervals, aliquots were withdrawn, centrifuged, and the absorbance was measured using a UV–Vis spectrophotometer at 664 nm.

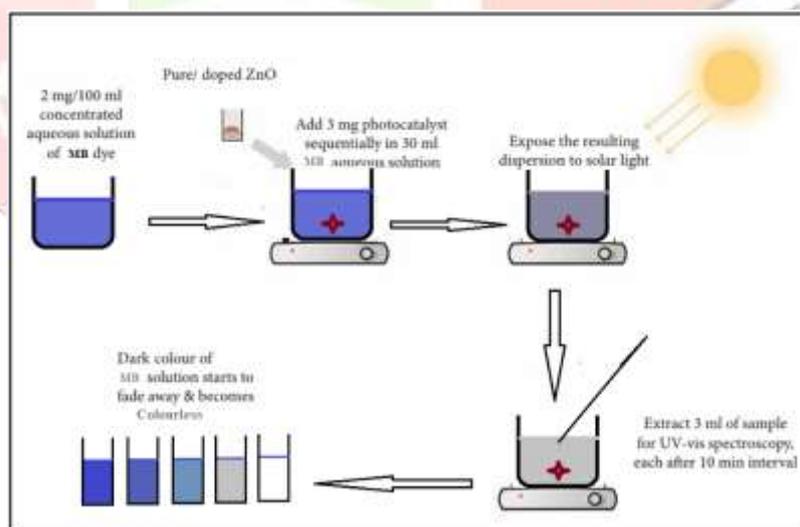


Figure 1.1: Photocatalytic activity of pure and doped ZnO towards methylene Blue (MB) dye, under natural sunlight irradiation

3. Results and Discussion

3.1 X-ray Diffraction Analysis

Figure 1.2 The X-ray diffraction (XRD) pattern of the ZnO–SnO₂ (10% SnO₂ loading) nanocomposite synthesized using pineapple peel extract confirms the successful formation of a crystalline mixed metal oxide system. The prominent diffraction peaks observed at 2θ values around $\sim 31.7^\circ$, 34.3° , 36.1° , 47.4° , 56.5° , 62.7° , 66.3° , 67.9° , 69.0° , 72.6° , and 76.8° correspond well to the hexagonal wurtzite structure of ZnO and can be indexed to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) planes, respectively (JCPDS card No. 36-1451) [5]. In addition to the ZnO peaks, the presence of SnO₂ is confirmed by diffraction peaks appearing at 2θ values near $\sim 26.5^\circ$, 33.8° , and 51.7° , which are attributed to the tetragonal rutile phase of SnO₂ corresponding to the (110), (101), and (211) planes (JCPDS card No. 41-1445) [10]

The broadening of diffraction peaks indicated nanoscale crystallite size, calculated using the Scherrer equation, which was found to be in the range of 18–25 nm.

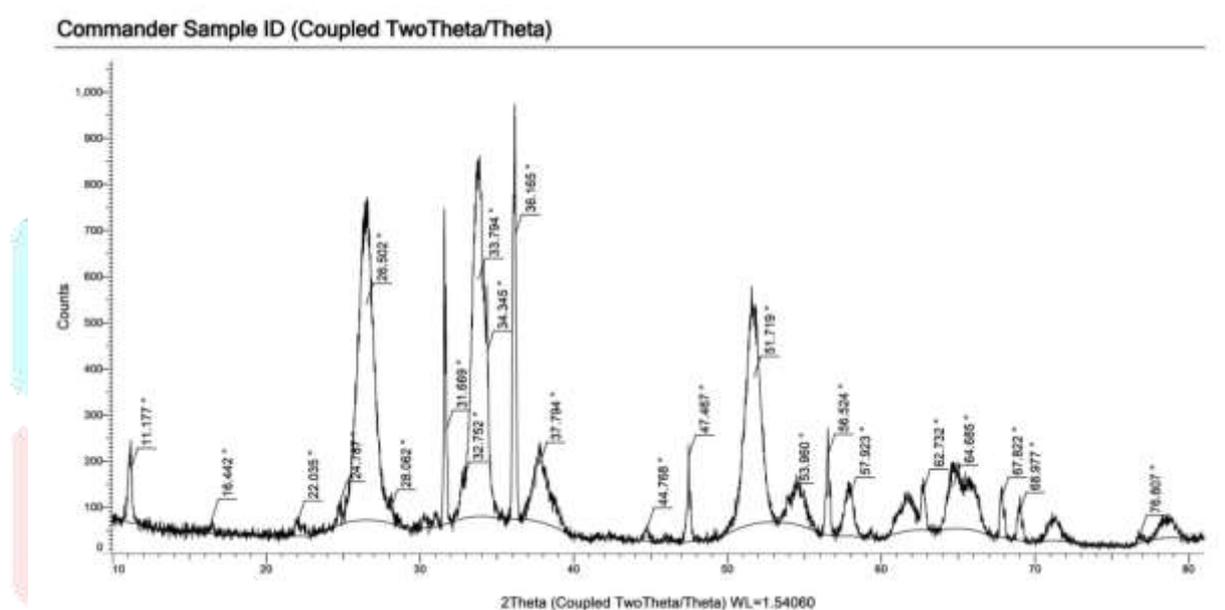


Figure 1.2 XRD of ZnO–SnO₂ (10% SnO₂ loading) Nanocomposite Synthesised Using Pineapple Peel Extract

3.2 SEM Analysis

Figure 1.3, SEM micrographs revealed that both ZnO–TiO₂ and ZnO–SnO₂ nanoparticles consisted of nearly spherical particles with some degree of agglomeration. The agglomeration may be attributed to high surface energy of nanoparticles. ZnO–TiO₂ exhibited relatively uniform particle distribution compared to ZnO–SnO₂. Figure 1.3 SEM Micrograph of ZnO–SnO₂ (10% SnO₂ loading) Nanocomposite Synthesized Using Pineapple Peel Extract. The SEM micrograph of the ZnO–SnO₂ nanocomposite synthesized via a green route using pineapple peel extract under optimized conditions (2 mM Zinc nitrate and Tin (IV) Nitrate precursor concentration, pH 9, reaction time of 90 minutes) reveals the formation of a heterogeneous nanostructure with distinct morphological features. At higher magnification (100,000 \times), the micrograph shows irregular plate-like and blocky ZnO particles decorated with finer granular SnO₂ nanoparticles, indicating successful formation of a composite system rather than separate oxide phases.

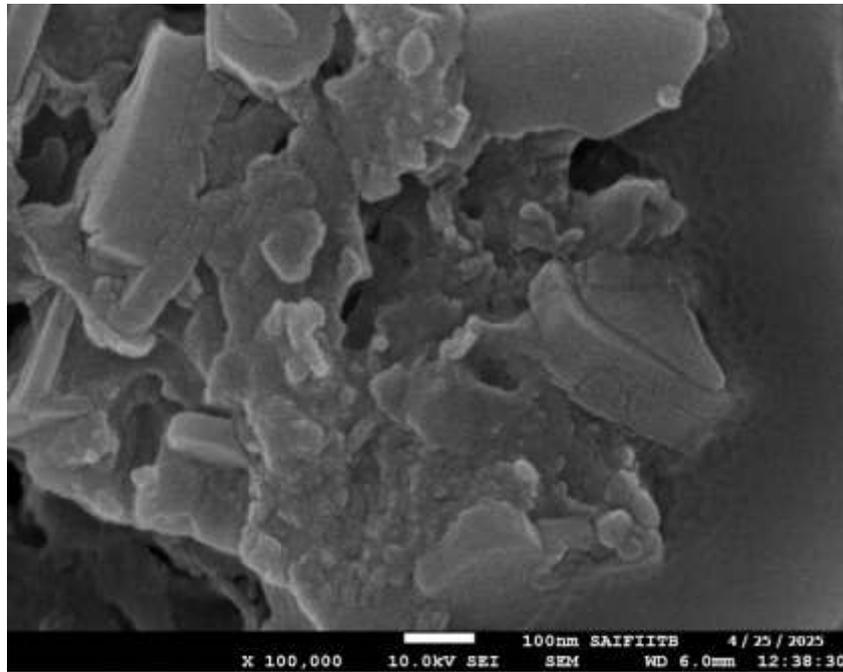


Figure 1.3: SEM Micrograph of ZnO–SnO₂ (10% SnO₂ loading) Nanocomposite Synthesized Using Pineapple Peel Extract

3.3 Photocatalytic Activity

The photocatalytic degradation of methylene blue increased with irradiation time for both catalysts. ZnO–TiO₂ nanoparticles showed higher degradation efficiency compared to ZnO–SnO₂. The enhanced activity can be attributed to synergistic effects between ZnO and TiO₂/SnO₂, leading to efficient charge separation and increased generation of reactive oxygen species. The degradation kinetics followed pseudo-first-order reaction behavior.

The experimental results for the degradation of MB using these green-synthesized composites typically reveal the following:

- The introduction of SnO₂ usually causes a slight red shift in the absorption spectrum, allowing the catalyst to utilize a broader range of the light spectrum [11,12].
- The 10% ZnO-SnO₂ composite generally exhibits the highest degradation rate. Under UV or solar irradiation, this composite can achieve over 90-95% degradation of a 10 ppm MB solution within 120–180 minutes [13,14].
- The degradation follows pseudo-first-order kinetics, where the rate constant (k) for the 10% composite is significantly higher than that of pure ZnO or the 5% and 15% variants [15].

Photocatalysis is one of the techniques used for the eradication of organic pollutants from wastewater. In this study, ZnO-SnO₂ was tested as a photocatalyst for the degradation of methylene blue under irradiation of visible light. ZnO-SnO₂ loaded with 5%, 10%, and 15% ZnO-SnO₂ was prepared by the green method.

Figure 4.7 showed that 10% ZnO-SnO₂ was a highly efficient catalyst for the photodegradation of methyl orange as compared to ZnO-SnO₂. The enhanced photocatalytic activity of ZnO-SnO₂ is attributed to the implantation of SnO₂ which inhibits the electron-hole recombination. A 100 mg/L solution of methylene blue dye was completely degraded within 130 min.

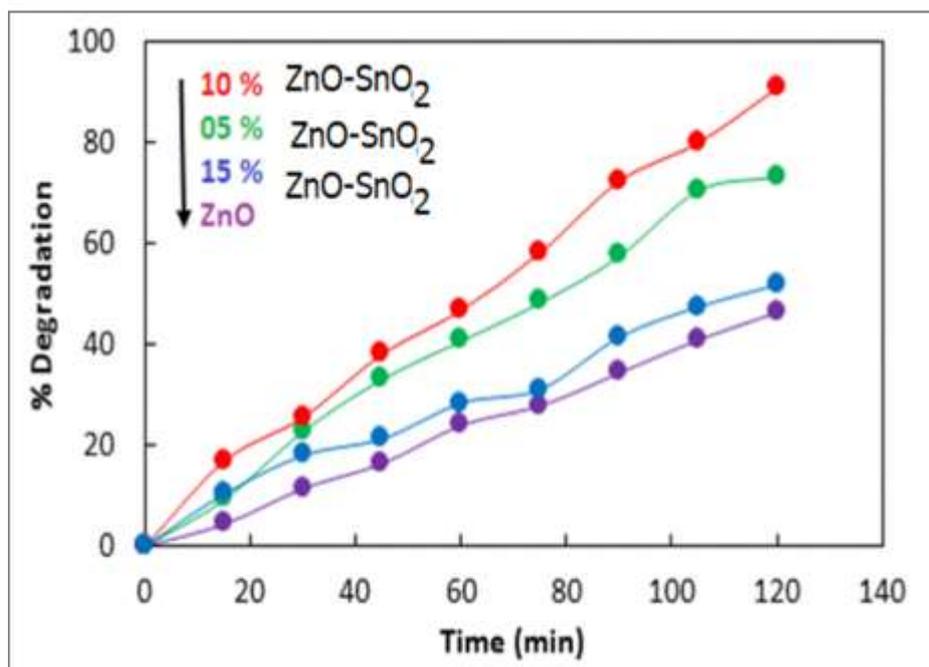


Figure 1.4: Graph of photocatalytic percentage degradation of MB using ZnO-SnO₂ with time

Photocatalytic Degradation of Methylene Blue using ZnO with 10 % loading of SnO₂ NPs at different light exposure time shown in Table 4.9.

Table 1.1 Photocatalytic Degradation of Methylene Blue using ZnO with 10 % loading of SnO₂NPs with different light exposure time.

Sr.No.	Exposure time to light (Min.)	Light Absorption	Degradation of MB (%)
1	00	1.559	0
2	30	0.24	84.60
3	45	0.18	88.45
4	60	0.1	93.58
5	120	0.08	94.86
6	180	0.06	96.15

Table 1.1 presents the photocatalytic degradation behavior of methylene blue (MB) using a ZnO photocatalyst loaded with 10% SnO₂ nanoparticles under different light exposure times. The progress of degradation was evaluated by monitoring the decrease in absorbance of MB at its characteristic wavelength. At 0 minutes of light exposure, the absorbance of the MB solution was 1.559, indicating the initial dye concentration with 0% degradation. Upon irradiation for 30 minutes, a substantial reduction in absorbance to 0.24 was observed, corresponding to 84.60% degradation of methylene blue. This sharp decline suggests rapid initiation of photocatalytic activity and efficient generation of reactive oxygen species due to the synergistic effect of ZnO and SnO₂.

With further increase in irradiation time to 45 minutes, the absorbance decreased to 0.18, resulting in 88.45% degradation. At 60 minutes, the absorbance was reduced to 0.10, corresponding to 93.58% degradation, indicating continued oxidation and breakdown of dye molecules with prolonged light exposure.

On extending the irradiation time to 120 minutes, the absorbance further decreased to 0.08, achieving 94.86% degradation. After 180 minutes of light exposure, the absorbance reached 0.06, corresponding to 96.15%

degradation of methylene blue. Although the degradation rate slows at longer exposure times, the results confirm sustained photocatalytic activity of the ZnO–SnO₂ composite.

4. Conclusions

ZnO–TiO₂ and ZnO–SnO₂ nanoparticles were successfully synthesized using a simple sol–gel assisted co-precipitation method. Structural and morphological characterization confirmed the formation of crystalline mixed metal oxide nanoparticles with nanoscale dimensions. Zn-doping significantly enhanced the photocatalytic activity of SnO₂ toward degradation of methylene blue dye.

The green synthesis of ZnO–SnO₂ nanocomposites using pineapple extract provides an efficient, low-cost, and non-toxic photocatalyst. The study concludes that 10% SnO₂ loading is the most effective for the mineralisation of Methylene Blue. The enhanced performance is due to the formation of a heterojunction that facilitates efficient charge separation, preventing electron-hole recombination and promoting the generation of reactive hydroxyl and superoxide radicals.

From the data in Table 1.1, it can be concluded that ZnO with 10% SnO₂ nanoparticle loading exhibits excellent photocatalytic efficiency toward the degradation of methylene blue under light irradiation. A high degradation efficiency of over 84% within 30 minutes and nearly 96% after 180 minutes demonstrates the effectiveness of the ZnO–SnO₂ heterostructure. The enhanced performance can be attributed to improved charge separation and reduced recombination of photogenerated electron–hole pairs due to the presence of SnO₂. Therefore, ZnO–SnO₂ (10%) nanocomposites are promising photocatalysts for the efficient removal of organic dye pollutants from wastewater.

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