Synthesis, Characterization, and Photocatalytic Activity of ZnO Nanoparticles Co-doped with Tin and Ferric Chloride for Environmental Remediation Applications

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ABSTRACT

Sn and Ferric chloride doped ZnO can be synthesized by the co-precipitation methods. X-ray diffractometer (XRD) has been used to study the structural properties of the nano materials which confirmed orthorhombic structure with space group Pbcn. Scherer formula are used to calculate the crystalline size of nanomaterials. William hall plots confirm tensile strain in the unit cell of the crystalline material. Scanning electron microscopy (SEM) has been used to study the morphology of the prepared nanomaterials which confirm that gains are unequal in size and randomly oriented in the materials. Archimedes principle has been used to study the density of materials which observed to be increase with Fe doping. Thermo gravimetric analysis confirmed the weight loss of the materials at low temperature and materials become stable at higher temperature. Vibrating sample magnetometer (VSM) confirmed the Ferromagnetic behavior of the material. Impedance analyzer has been used to study the dielectric and electric properties of the nanomaterials. Dielectric constant of the materials is high at low frequency and decrease at high frequency confirms the polarization loss inside the materials at value of frequency.

Keyword: *Zinc oxide (Zno) nanoparticles, photocatalytic performance*

I. Introduction

ZnO nanoparticles are extensively researched for their remarkable photocatalytic properties, making them highly effective in environmental remediation applications, particularly for degrading organic pollutants like dyes, pesticides, and pharmaceuticals. Their wide bandgap (~3.37 eV), high exciton binding energy (60 meV), and strong oxidation ability enable ZnO nanoparticles to efficiently generate reactive oxygen species (ROS) under UV light irradiation, which break down complex organic molecules into less harmful compounds. These attributes render ZnO a promising candidate for wastewater treatment and air purification technologies.

However, pure ZnO nanoparticles face significant limitations, primarily due to the high recombination rates of photogenerated electron-hole pairs. When ZnO absorbs UV light, electrons are excited from the valence band to the conduction band, leaving behind holes. These charge carriers can either participate in redox reactions with surface-adsorbed species or recombine, which results in energy loss and reduced photocatalytic efficiency. The rapid recombination of these electron-hole pairs restricts the availability of charge carriers for ROS generation, thus diminishing the overall photocatalytic performance.

To address this issue, strategies such as doping with metal ions like tin (Sn) and ferric chloride ($FeCl_3$) have been explored. Co-doping introduces impurity levels within the ZnO bandgap, which can trap charge carriers, thereby reducing recombination rates and extending light absorption into the visible range. This enhancement in charge separation and light absorption significantly improves the photocatalytic efficiency of ZnO nanoparticles, making them more effective for environmental remediation.

II. Methodology

Synthesis of Co-doped ZnO Nanoparticles:

Precursor Preparation: Zinc acetate, tin chloride, and ferric chloride will be used as precursors. Zinc acetate provides the zinc source, while tin chloride and ferric chloride introduce Sn and Fe dopants, respectively. These materials are chosen for their solubility and reactivity, facilitating the uniform incorporation of dopants into the ZnO matrix.

Synthesis Method: A sol-gel or hydrothermal synthesis method will be employed. In the sol-gel method, zinc acetate is dissolved in distilled water, followed by the addition of tin chloride and ferric chloride solutions under constant stirring. The pH is adjusted to 7-8 using ammonia, forming a gel. This gel is aged, dried at 100°C, and calcined at 400-500°C to produce nanoparticles. The hydrothermal method involves mixing the precursors in water, transferring the solution to an autoclave, and heating at 180-200°C for 12-24 hours. The resulting product is cooled, washed, dried, and calcined.

Doping Concentrations: Various molar ratios of Sn and Fe will be used to optimize doping levels. These ratios will be systematically varied to determine their effects on the structural and photocatalytic properties of the ZnO nanoparticles.

Characterization:

X-ray Diffraction (XRD): XRD will be utilized to determine the crystalline structure and phase purity of the synthesized nanoparticles, providing information on the crystallite size and any possible phase impurities.

Scanning Electron Microscopy (SEM): SEM will be employed to examine the morphology and size distribution of the nanoparticles, revealing surface texture and particle uniformity.

Transmission Electron Microscopy (TEM): TEM will provide detailed structural information at the nanoscale, including particle size, shape, and the distribution of dopants within the ZnO matrix.

UV-Vis Spectroscopy: UV-Vis spectroscopy will be used to analyze the optical properties and bandgap energy, crucial for understanding the light absorption capabilities of the doped nanoparticles.

Photoluminescence (PL) Spectroscopy: PL spectroscopy will assess the recombination rate of electron-hole pairs, indicating the efficiency of charge separation, which is critical for photocatalytic activity.

Photocatalytic Activity Testing:

Model Pollutant: An organic dye such as methylene blue or rhodamine B will be used as a model pollutant to evaluate the photocatalytic activity of the nanoparticles.

Photocatalytic Degradation Setup: Degradation experiments will be conducted under both UV and visible light irradiation to assess the photocatalytic performance of the doped ZnO nanoparticles.

Kinetic Studies: The degradation kinetics will be studied to determine the rate constants and efficiency, providing insight into the effectiveness of the photocatalysts and the optimal doping concentrations for maximum performance.

This structured approach aims to synthesize and optimize Sn and Fe co-doped ZnO nanoparticles, thoroughly characterize their properties, and evaluate their potential for environmental remediation through photocatalytic degradation of organic pollutants.

III Result and Discussion

1. X-rays diffraction technique (XRD)

X-ray diffraction (XRD) is a powerful analytical technique used to determine the crystalline structure of materials. When X-rays are directed at a crystalline substance, they are diffracted in specific directions based on the atomic arrangement within the crystal.

By measuring the angles and intensities of these diffracted beams, XRD provides detailed information about the crystal lattice, including unit cell dimensions, phase identification, crystallite size, and strain. This technique is essential for characterizing the structural properties of nanomaterials, such as co-doped ZnO nanoparticles, ensuring their phase purity and confirming the successful incorporation of dopants.

X-ray diffraction patterns of prepared Sn doped ZnO nano powders at different doping concentrations and different n annealing temperature as shown in figure no.1, pattern shows that the 1% Sn doped ZnO have a sharp peaks and show the crystalline behaviour of zinc oxide. In pure ZnO the annealing temperature is rising in 101°c.

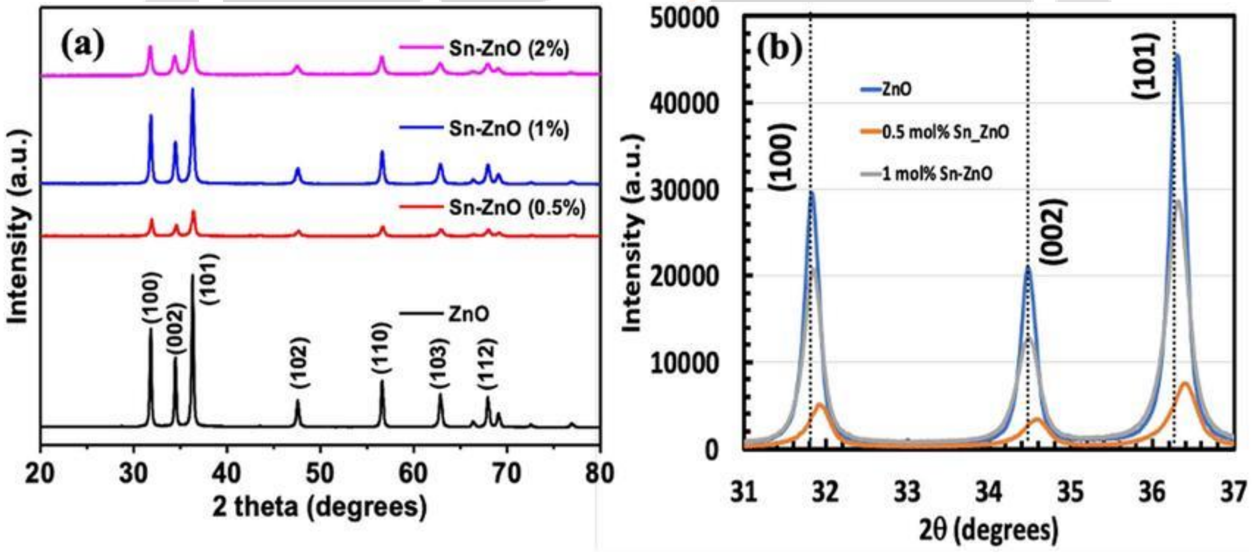

Figure no.1 X-ray diffraction patterns of 0.5%Sn doped ZnO, 1%Sn doped ZnO and 2%Sn doped ZnO.

This pattern is repeated for all different concentration of Sn doped ZnO. The sample did not show any diffraction peaks of tin or tin compound, which suggest the formation of an tin -zinc solid solution, where the tin ion has been incorporated in to the ZnO crystal structure substitutionally, due to similar ionic radii.

2. Scanning electron microscopy analysis

Scanning Electron Microscopy (SEM) is used to analyze the surface morphology and microstructure of materials. In this technique, a focused electron beam scans the sample surface, generating secondary and backscattered electrons that provide detailed images. For co-doped ZnO nanoparticles, SEM reveals the shape, size, and distribution of particles, as well as surface texture. This analysis helps in understanding the effects of Sn and Fe doping on the nanoparticles. Additionally, Energy Dispersive X-ray Spectroscopy (EDS) attached to SEM can confirm the presence and distribution of dopants, ensuring the synthesis process's effectiveness and uniformity.

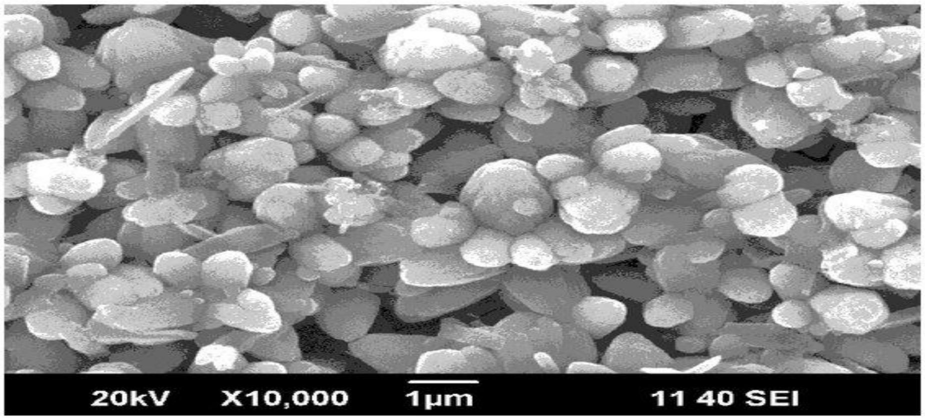

Figure no 2 (a) SEM image for ZnO

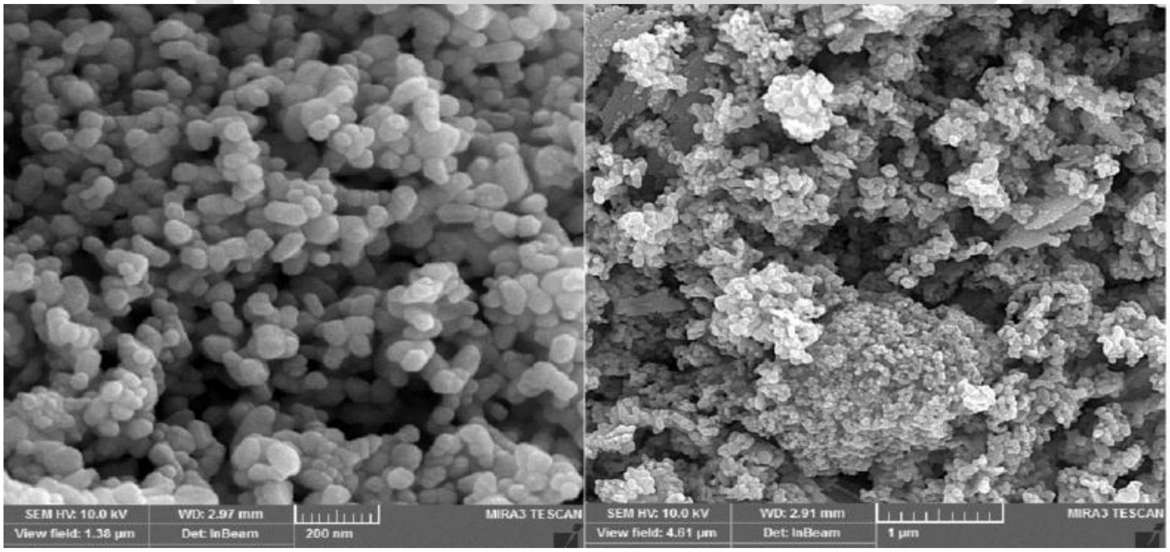

Figure no 2 (b) SEM image for Sn doped ZnO

3. VIBRATING SAMPLE MAGNETOMETER (VSM)

A Vibrating Sample Magnetometer (VSM) is an instrument used to measure the magnetic properties of materials. In VSM, a sample is placed in a uniform magnetic field and vibrated sinusoidally. The vibration induces a magnetic dipole moment in the sample, which generates an alternating magnetic flux. This flux is detected by pick-up coils and converted into a voltage signal proportional to the magnetic moment of the sample.

VSM provides precise measurements of magnetization, magnetic hysteresis, and other magnetic parameters, making it essential for characterizing magnetic materials, including co-doped ZnO nanoparticles with potential magnetic properties due to doping with elements like Sn and Fe.

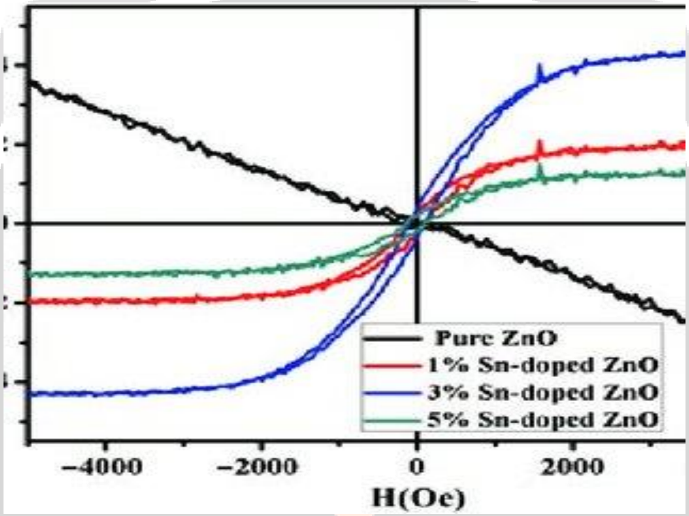

Figure no 3 VSM graph for Sn doped ZnO

4. FTIR ANALYSIS

Fourier Transform Infrared (FTIR) Spectroscopy is a technique used to identify and analyze the molecular composition and chemical bonds in a material. In FTIR, an infrared light beam is passed through a sample, and the absorbed wavelengths are measured.

These absorption peaks correspond to specific vibrational modes of the molecular bonds. For co-doped ZnO nanoparticles, FTIR analysis can confirm the presence of functional groups, identify bonding interactions between ZnO and dopants (Sn and Fe), and detect any impurities or organic residues from the synthesis process.

This information is crucial for understanding the chemical environment and ensuring the quality of the synthesized nanoparticles.

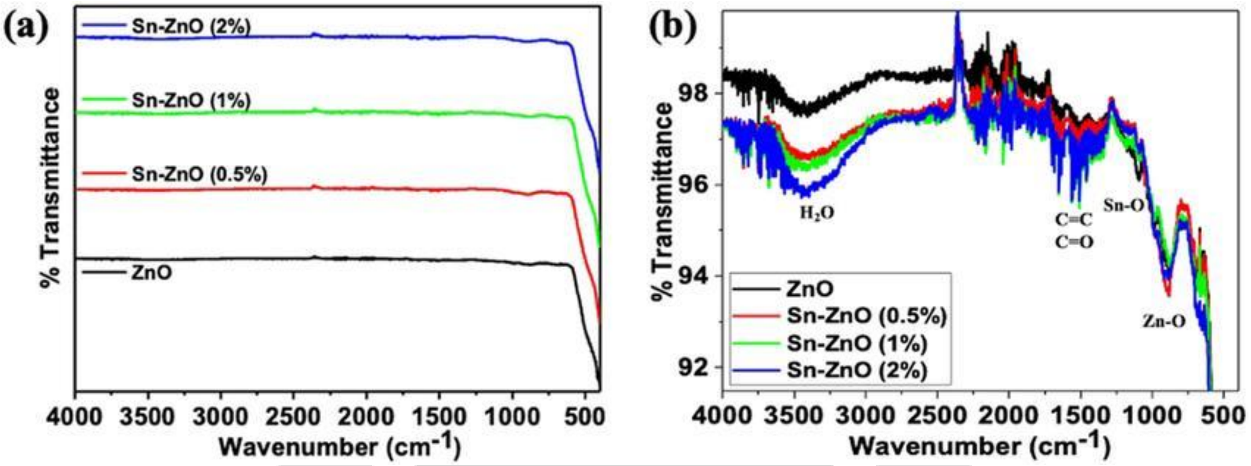

Figure no. 4 FTIR graph of Sn doped ZnO

IV CONCLUSION

1. **Successful Synthesis**: Pure ZnO and Sn doped ZnO nanoparticles (NPs) were effectively synthesized through physical methods, demonstrating the feasibility of the synthesis approach.
2. **Crystallinity Analysis**: The analysis revealed varying average crystalline sizes for both pure ZnO and Sn doped ZnO NPs, indicating successful synthesis and the influence of Sn doping on crystal growth.
3. **Morphological Observations**: Both pure ZnO and Sn doped ZnO NPs exhibited flake-like structures with aggregation. However, Sn doping resulted in the formation of micron-sized crystallites, indicating alterations in morphology due to doping.
4. **Optical Properties**: The band gap values of pure ZnO NPs were determined to be 3.37 eV, while those of Sn doped ZnO NPs ranged from 3.14 to 3.18 eV. This slight reduction in band gap suggests changes in electronic structure induced by Sn doping, potentially enhancing the photocatalytic activity of the nanoparticles.
5. **Magnetic Properties**: The magnetic moment of Sn doped ZnO nanoparticles increased with suitable doping levels, as determined by Vibrating Sample Magnetometer (VSM) analysis. This enhancement in magnetic properties signifies the successful incorporation of Sn and its influence on the magnetic characteristics of ZnO NPs.

In summary, the synthesis and comprehensive characterization of pure ZnO and Sn doped ZnO nanoparticles provide valuable insights into their structural, optical, and magnetic properties. These findings contribute to the understanding of the effects of Sn doping on ZnO nanoparticles, highlighting their potential applications in various fields, including photocatalysis and magnetic devices.

REFERENCE

[1] M. Vert, Y. Hellwich, M. Hodge, P. Kubisa, "Terminology for biorelated polymers and applications", Pure and Applied chemistry. Doi: 10-12-2004.

[2] Hasscllov, R. Martin, W. James, F. Tiede, "Nano particle Analysis and characterization methodologies in environmental risk assessment of engineered nanoparticle", Ecotoxicology. Doi: 10.1007/s.

[3] P. Kevin, W. Palazuelos, M. Maria, Brij, M. Stephen, "Characterization of the size, shape, and state of dispersion of nanoparticles for toxicological studies", Nanotoxicology, doi: 10.1080.

[4] Tiede, K. Buxall, Alistar, P. Lewis, "Detection and Characterization of engineered nanoparticles in food and the environment", Food Additives and Contaminants, doi: 10-10-1980.

[5] Linsinger, P.J.Thomos, G. Roebben, S. Coinxita, "Reference materials for measuring the size of nanoparticles", Trends in Analytical chemistry, doi: 10.1016/j.trac 2010.09.005.

[6] Burke, A. Ding, X. Singh, "Nanoparticles for Biomedical Applications", doi: 10.1073/pnas.0905195106.

[7] Tajabadi, Mahdis, "Application of carbon Nanotubes in Breast Cancer Therapy". Drug Research. Doi: 10.1055/a-0945-1469.

[8] Raza, Hassa, "Nanoelectronics Fundamentals: Materials, Devices and System". Springer nature. Doi: 2019-11-26.

[9] Pelz, Beatriz, A.Christoph, C. Bosi, "Diverse Application of Nanomedicine", ASCNANO doi: 2017-03-28.

[10] Serrano, E. Rus, Javier, "Nanotechnology for sustainable energy"' Renewable and sustainable Energy Reviews, doi: 2009-12-01.

[11] Maria, Sarmo, "Nanotechnology in energy storage the supercapacitor", studies in surface science and catalysis, doi: 2021-01-01 Complexity, doi: 10.1002/cplx.21427.

[12] Saini, Rajiv, S. Santosh, S. Sugandha, "Nanotechnology: The Future Medicine", Journal of Cutaneous and Aesthetic Surgery, doi: 10.4103/0974-2077.63301.

[13] Belkin (2015), "Self-Assembled Wiggling Nano-Structure and the Principle of Maximum Entropy Production", doi: 10.1038/srep08323.

[14] Buzea, C. Pacheco, I. Robbie (2007), "Nanomaterials and nanoparticles: Sources and toxicity", Biointerphase, doi: 10.1116/1.2815690.