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Synthesis, Structural and Optical Properties of Al-doped ZnO (AZO) Nanoparticles

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KEYWORDS

Nanoparticles, Sol-gel method, Photocatalysis, UV-vis spectra

ABSTRACT:

For the environmental remediation and degradation of pollutants the study of advanced materials is rapidly increasing due to large varieties of application. Zinc oxide (ZnO) is a semiconductor with a direct band gap between 3.28-3.30 eV and has a wide range of applications in environmental remediation and degradation of pollutants as a photocatalyst material. The energy band gap of ZnO can be minimized and light absorption increased through doping. Pure and Al-doped ZnO nanoparticles are prepared using the sol-gel method with high-purity $Zn(NO_3)_2.6H_2O$, $Al(NO_3)_2.9H_2O$, and Propylene glycol, with varying Al : Zn ratios (1%, 2%, 3%, 4%, and 5%). The prepared samples are characterized by using Fourier Transform Infrared spectroscopy (FTIR), X-ray Diffraction (XRD), X-ray photoelectron Spectroscopy (XPS) and UV-Vis spectroscopy. The XRD pattern confirms the formation of phase pure Pure and Al-doped ZnO nanoparticles at calcination temperature of 500 °C. The optical band gap of Pure ZnO is found to be 3.2 eV which decreases to 2.7 eV on increasing the doping concentration of Al in ZnO matrix.

1. Introduction:

Zinc oxide (ZnO) is a semiconductor with a direct band gap, which means it has potential applications in electronics, optoelectronics, and sensors. The energy band gap of monocrystalline ZnO is between 3.1-3.3 eV at room temperature and 3.44 eV at Kelvin, while that of polycrystalline ZnO nanoparticles is 3.28-3.30 eV. ZnO is also known for its optical, acoustic, and electrical properties. It is a stable, non-toxic, and low-cost material that is widely abundant in nature. However, to improve its photocatalytic efficiency, the energy band gap needs to be minimized and light absorption increased through doping with materials such as Gallium (Ga), Fluorine (F), Indium (In), Manganese (Mn), and Aluminum (Al). Aluminum is a particularly effective dopant because it has high conductivity, transparency, and low resistivity, and it helps to increase the surface area and photocatalytic activity of ZnO.

The Sol-gel method is a simple and low-cost chemical method for synthesizing Al-doped ZnO (AZO). The study of temperature effects on crystallization of ZnO and AZO is done by calcining the samples at 500°C. The effect of Al dopant on structural characteristics and physical properties is determined by synthesizing AZO samples with different doping concentrations of Al, such as 0%, 1%, 2%, 3%, 4%, and 5% [1].

2. Experimental Method:

2.1 Materials and Method:

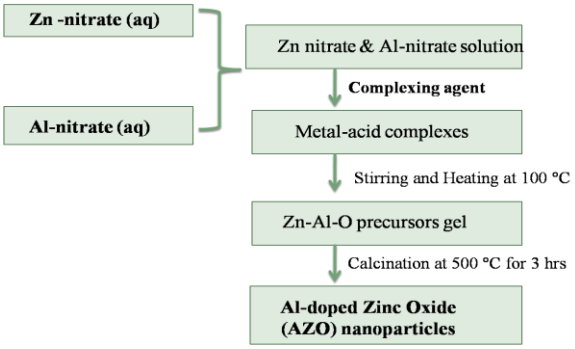

Fig-1: Flow diagram for the synthesis of Al-doped nanoparticles

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2.2 Synthesis of Catalyst Sol-gel method :

2.2.1 Synthesis of Al doped ZnO nanoparticles doping with Al:

Synthesis of Al-doped ZnO (AZO) nanoparticles ($Zn_{1-x}Al_x$) is prepared by the Sol-gel method by using stoichiometric amounts of reagents of high level purified Zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$, Aluminium nitrate $Al(NO_3)2.9H_2O$ and Propylene glycol ($C_3H_8O_2$) (all from Sigma-Aldrich, USA).

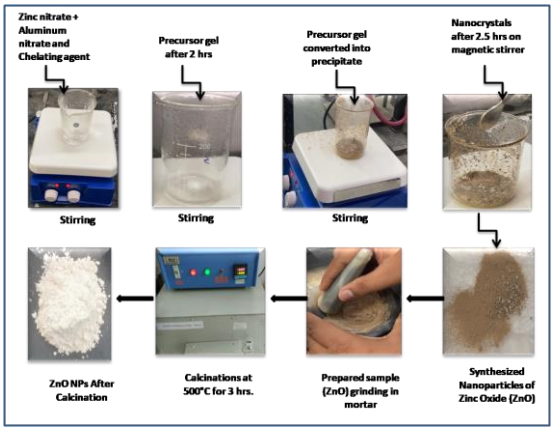

Fig-2. Schematic representation of synthesis of Al doped ZnO (AZO) nanoparticles

First, the precursor solution was prepared by mixing 50 ml of 2 millimolar solution of Zn(NO3)2.6H2O in dil. HNO3 and 50 ml of 2 millimolar solution of Al(NO3)2.9H2O in distilled water. Subsequently, a complexing agent was added to the aforementioned solution in 1:1 mol ratio with respect to metal nitrates. After that, the mixture was heated continuously to about 90°C while being stirred constantly to remove any excess water. Gel formation occurs as a result evaporation of water and an increase in the viscosity of the solution. Subsequently, a fluffy brown powder was obtained with the evolution of brown fumes resulting from the decomposition of nitrate ions. Then, the obtained brown powder was scratched out from the beaker and ground into a fine powder and AZO precursor was obtained. Finally, the resulting fine powder obtained was calcined at 500 °C for 3 hrs. to obtain well-crystallized AZO NPs. The change in color from brownish to white after the sample has been calcined (heated at high temperatures) is likely due to the removal of impurities or the formation of a new compound during the calcinations process. The white powder that remains is then used for characterization, which could include analyzing its composition, structure, or properties. The various steps involved in the synthesis process of BFO NPs are illustrated schematically in Figure 2.

3. Results and discussion:

3.1 Characterization:

The structure of the crystal was analyzed using X-ray diffraction (XRD) on an X'Pert Pro machine from PANalytical (Netherlands). This was done with copper Kα radiation (wavelength of 1.5406 Å), under 40 kV and 40 mA. To fine-tune the lattice parameters, the Rietveld refinement technique was applied using FullProf software. The thermal stability of the sample was studied through thermogravimetric analysis (TGA) on a Mettler Toledo Star System, where the sample was heated in air up to 850°C at a rate of 10°C per minute. The Fourier transform infrared (FT-IR) spectrum was recorded on a Bruker Vertex–70 spectrometer using KBr pellets, covering a range of 400 to 4000 cm^{-1}.

A transmission electron microscope (TEM) (FEI Technai G2 U-Twin) was used to observe the morphology and crystallinity of the sample at an accelerating voltage of 200 kV. To identify the elemental composition, energy dispersive X-ray spectroscopy (EDX) attached to the TEM was employed. The surface area was calculated using a surface area analyzer (Autosorb 1C system, Quantachrome, USA) based on the Brunauer–Emmett–Teller (BET) method. Raman spectroscopy was performed at room temperature using a WITec spectrometer in the range of 100 to 800 cm^{-1}, with a laser excitation wavelength of 514.5 nm.

Ferroelectric properties were measured using a ferroelectric tester (automated P-E loop tracer, Marine India Electronics Pvt. Ltd.), allowing for the observation of polarization-electric field (P-E) hysteresis loops at room temperature. Magnetic characteristics were examined with a SQUID magnetometer (Quantum Design). UV–vis diffuse reflectance spectra (DRS) of the ZnO nanoparticles

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were obtained using a Varian Cary-100 spectrometer. Lastly, the photocatalytic degradation of dyes, such as methylene blue (MB) and rhodamine B (RhB), was studied using a UV–visible spectrophotometer.

3.2 X-Ray Diffraction (XRD):

The XRD results suggest that aluminum atoms have successfully substituted for zinc atoms in the crystal lattice of ZnO without changing the hexagonal crystal structure. The absence of impurity peaks indicates that the nanoparticles formed are pure. The crystallite size of the aluminum-doped ZnO samples has also been estimated using Sherrer's equation. Sherrer's equation is a widely used method to estimate the average crystallite size of nanoparticles from the XRD data. The equation relates the broadening of the diffraction peaks to the crystallite size and is given by:

$D = K\lambda / (\beta \cos\theta)$

where D is the average crystallite size, K is the Scherrer constant (typically taken as 0.9), λ is the X-ray wavelength (usually 1.54 Å for Cu Kα), β is the full-width at half-maximum (FWHM) of the diffraction peak, and θ is the diffraction angle.

By using this equation and the FWHM values obtained from the XRD pattern, the average crystallite size of the aluminum-doped ZnO samples can be estimated. It is important to note that the estimated crystallite size is an average size and there may be a distribution of sizes present in the sample [2, 3]. Crystallite sizes of AZO (aluminum-doped zinc oxide) particles decrease as the Al concentration increases Shown in Fig.-3. This is because, during the formation of Al-doped ZnO, some of the Zn ions are replaced by smaller Al ions, which causes a lattice mismatch and strain within the crystal structure. This strain can lead to a lower degree of crystallinity, resulting in smaller crystallite sizes. The decrease in crystallite size is often accompanied by a broadening of the diffraction peaks observed in XRD (X-ray diffraction) analysis and slit diffraction. This broadening is due to the presence of a larger number of small crystallites with different orientations and lattice parameters, as compared to a sample with larger and more well-defined crystallites. The range of 12-23 nm for the crystallite size of AZO particles is within the typical size range reported in the literature for Al-doped ZnO materials. However, it is worth noting that the exact size and distribution of crystallites can depend on various factors such as the synthesis method, reaction conditions, and post-treatment processes [4, 5].

Effect of Al doping on ZnO:

The XRD pattern of Al doped ZnO with concentration addition of Al 1%, 2%, 3%, 4% and 5% respectively. Al doping in ZnO can have a significant effect on its crystallinity. As the concentration of Al dopant increases, the peak width in the XRD pattern broadens, indicating a decrease in crystallinity. The highest crystallinity of AZO is typically obtained at Al dopant concentrations of 2% and 3%. At higher concentrations of dopant, the difference in ion size between Zn and Al can cause stresses and the formation of aluminum at the grain boundaries, further decreasing crystallinity.

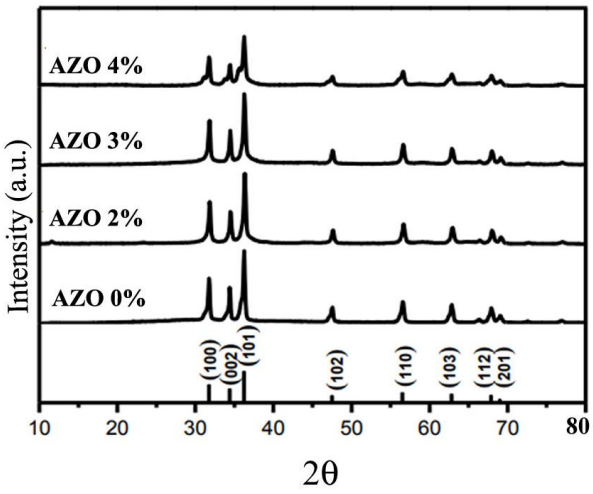

Fig.3: XRD patterns of Al doped ZnO (AZO) nanoparticle

3.3 Scanning Electron Microscopy (SEM):

SEM is a powerful technique for investigating the morphology and structure of materials at the nanoscale. It uses an electron beam to scan the surface of a sample and generate images with high resolution and magnification. By analyzing these images, researchers can gain insight into the size, shape, and arrangement of particles in a material, as well as other structural features. The study of morphology and structure were done by SEM technology and it has been investigated that For the pure zinc oxide sample (0% Al or AZO), the particle morphology was described as

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broken, irregular, and round in shape shown in Fig.4. However, when dopant concentrations of 1%, 2%, 3%, 4%, and 5% were added, the AZO particles ranged in shape from round to flat with a smooth surface.

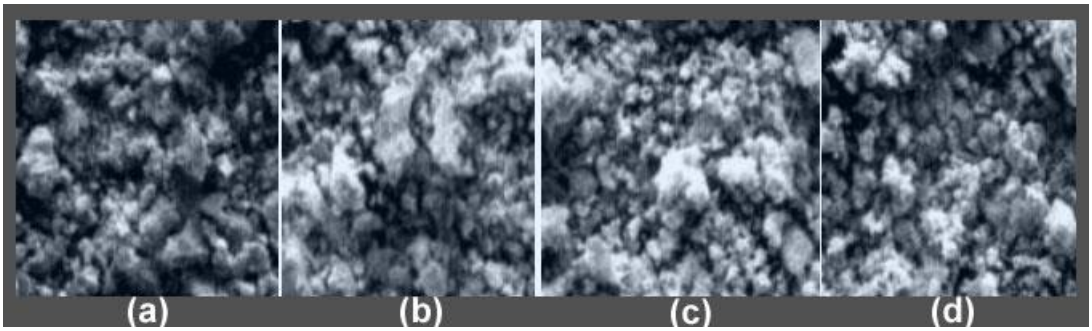

Fig.4: Image of SEM for Al doped ZnO (a) 0% (b) 2% (c) 3% (d) 4%

3.4 UV-Visible spectroscopy:

The UV-Vis spectrum showed absorption band at 324 nm. The band-gap energy obtained was 3.32 eV [6].

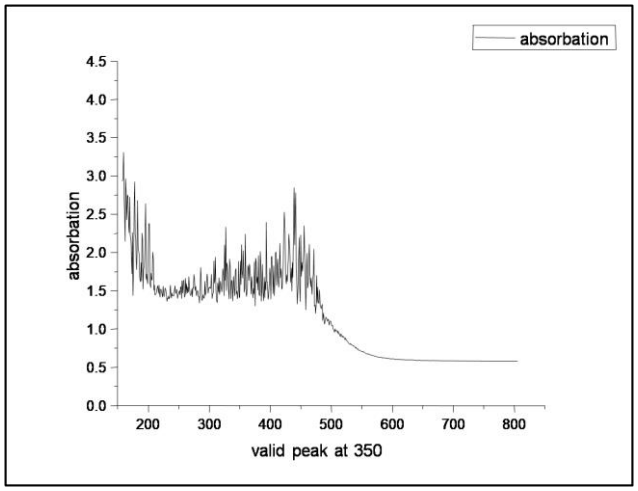

Fig.5: UV-visible spectroscopy of ZnO nanoparticles

Precaution and Observation:

In the synthesis of ZnO, it is observed that at the initial stage, the solution is transparent. After one hour, the color remains white and transparent. After two hours, the solution minimizes to 5 ml and the color becomes a light brown, giving off ashes. The color of the ashes is a brown or muddy color and is also volatile, causing a significant amount of the sample to be wasted, with only 70% of the sample being saved. To avoid this loss, in the final stage of the synthesis process, when only 5 ml of sample remains in the beaker, the beaker should be covered to prevent the ashes from flying out.

Properties and Application of Al-doped ZnO:

Aluminum-doped Zinc Oxide (AZO) nanoparticles are nanoscale materials that are widely used in various applications due to their unique properties. Some of the important properties of Al-doped Zinc Oxide nanoparticles are:

Optical Properties: AZO nanoparticles have high transparency in the visible region and a wide band gap, making them suitable for use as transparent conductive electrodes in optoelectronic devices.

Electrical Properties: Al-doping significantly improves the electrical conductivity of Zinc Oxide, making AZO nanoparticles a promising material for use in electronic devices such as thin-film transistors and solar cells.

Chemical Stability: AZO nanoparticles have high chemical stability and resistance to corrosion, making them suitable for use in harsh environments.

Photocatalytic Activity: AZO nanoparticles exhibit excellent photocatalytic activity and can be used in water purification, air purification, and degradation of organic pollutants.

Antimicrobial Properties: AZO nanoparticles have been found to have antimicrobial properties, making them potentially useful in the development of antimicrobial materials and coatings.

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It is important that the properties of AZO nanoparticles can vary depending on the synthesis method, doping concentration, and particle size. Further research is needed to fully understand the properties and potential applications of these materials.

4. Conclusions:

The sol-gel process, employing propylene glycol as a complexing agent, successfully produces pure ZnO nanocrystallites. XRD confirms that the Al-doped ZnO nanoparticles retain the wurtzite hexagonal crystal structure, which is characteristic of pure ZnO. This indicates that the aluminum doping does not significantly alter the basic crystal structure of ZnO formed after heat treatment at 500°C for 3 hours. XRD can reveal slight shifts in the diffraction peaks due to the incorporation of Al^{3+} into the ZnO lattice. Since Al^{3+} has a smaller ionic radius than Zn^{2+}, the substitution of Zn^{2+} with Al^{3+} ions may lead to a reduction in the lattice constants. The presence of aluminum in the ZnO lattice can be inferred from peak shifts in the XRD pattern. A shift toward higher angles is usually observed due to the smaller ionic size of Al^{3+} compared to Zn^{2+}. The intensity of the peaks can also be affected by the level of doping. The sharpness and intensity of the XRD peaks indicate the crystallinity of the Al-doped ZnO nanoparticles. Well-defined peaks suggest high crystallinity, while broader or less intense peaks suggest lower crystallinity. XRD confirms the successful formation of Al-doped ZnO nanoparticles with a wurtzite structure, provides information on changes in lattice parameters due to doping,

High-resolution TEM (HRTEM) can reveal the lattice fringes of the AZO nanoparticles, providing detailed insights into the atomic arrangement within the particles. This helps to confirm the wurtzite crystal structure of AZO and any possible distortions caused by aluminum doping. The optical band gap of AZO is measured to be 3.32 eV, confirming that the synthesized AZO nanoparticles act as efficient photocatalysts for the degradation of organic pollutants under sunlight.

The UV-Vis peak at **334 nm** confirms both the reduction of metal ions (Zn^{2+}) and the formation of ZnO or AZO nanoparticles, as well as indicating their nanoscale size, likely smaller than that of bulk ZnO.

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Reference:

1. Munawaroh H., Wahyuningsih S., Ramelan A., Synthesis and Characterization of Al doped ZnO (AZO) by Sol-gel Method, Materials Science and Engineering **176** (2017) 012049, doi:10.1088/1757-899X/176/1/012049.
2. N. T. Kaniz, R. Rosaleena, S. Afrina, S. B. Muhammad and M. H. Zahid, "Electrical, optical and structural properties of transparent conducting Al doped ZnO (AZO) deposited by Sol-gel Spin Coating", AIP Advances 8, 065307 (2018); https://doi.org/10.1063/1.5023020.
3. Musat V., Teixeira B. Fortunato E., Monteiro R.C.C., Vilarinho P., "Al-doped ZnO thin films by sol-gel method", Surface and Coating Technology 180-181 (2004) 659-662, doi:10.1016/j.surfcoat.2003.10.112.
4. Bhattacharyya S. R., Majumder S., "Synthesis of Al doped ZnO films by Sol-gel Technique", World Scientific Publishing Company, Vol. 3, 2 (2010) 111-114, DOI: 10.1142/S1793604710001111.
5. Sahay P P and Nath R K 2008 Sensors and Actuator B 133 p 222-227.
6. Sharada S., Pusarla S., "Synthesis of Zinc Nanoparticles and its Application in Treatment of Municipal Water of Anantapur", International Journal of Science and research, ISSN (online):2319-7064 Vol. 7 (2017).