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PHOTOCATALYTIC POTENTIAL OF CO-PRECIPITATION DERIVED ZNS NANOPARTICLES FOR EFFICIENT DEGRADATION OF METHYLENE BLUE DYE

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ABSTRACT

***In this study, pure ZnS nanoparticles are prepared using a simple co-precipitation method.* X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FE-SEM), Energy Dispersive X-ray Analysis (EDAX), UV-visible spectroscopy, and photoluminescence studies were employed to evaluate the synthesized nanoparticles. UV-visible absorption spectrum issued to calculate the optical band gap energy, and its value is approximately 4.27 eV. On examining the XRD pattern, it depicts that the particle size of the nanoparticles is about 44 nm, their capacity to perform better across a range of applications. The EDAX analysis confirms that the synthesized nanoparticles are pure. The catalysis of MB dye by synthesized ZnS nanoparticles exhibits pseudo-first order kinetics with observed rate constants.**

KEY WORDS : Co-precipitation method, Zinc sulfide, Characterization, Photocatalysis, Methylene Blue dye

INTRODUCTION

Nanoparticles of binary semiconductors of group II-VI like ZnS, ZnSe, CdS, and CdSe exhibit unusual structural, optical, and electronic properties than bulk materials (Jagdeep *et al.*, 2015 and Carley *et al.*, 2009). Recently, there has been extensive research focused on these materials. The semiconductor photocatalyst zinc sulphide (ZnS) is widely recognized for its peculiar features, broad bandgap energy, and high UV activity. Among the group II-VI semiconductor nanomaterials, ZnS exhibits enhanced optical and magnetic properties when doped with one or more transition metals. Due to its excellent properties at the nanoscale, ZnS has versatile applications in sensors, solar cells, and photocatalysis. ZnS is an important type of semiconductor with direct and wide bandgap of 3.66 eV (Anindita *et al.*, 2007, Breen *et al.*, 2001, Pan *et al.*, 2010 and Zewei *et al.*, 2007). These nanoparticles are more technologically effective, less hazardous, and more chemically stable than other semiconductors of group II-VI compounds. ZnS nanoparticles could be used as good photocatalysts due to rapid generation of electron-hole pairs by photo-excitation and highly negative reduction potentials of excited electrons; considering ZnS has a higher conduction band position in aqueous solution than other semiconductors for example TiO2 and ZnO (Liao *et al.*, 2005). Since, a larger ratio of surface to volume of a catalyst would facilitate a better catalytic activity (Li *et al.*, 2008 and Haifeng *et al.*, 2009) the size-controlled synthesis of ZnS nanostructures to produce a larger ratio of surface to volume is of great importance. The enhanced surface-to-volume ratio result in surface states to rise, changing the behaviour of electrons and holes and modifying chemical reaction kinetics. The size quantization increases the band gap of photo catalysts to enhance the redox potential of conduction band electrons and valence band holes (Hoffman *et al.*, 1992). In this study, ZnS nanoparticles were prepared by using co-precipitation method without employing any capping agent. The absence of a capping agent in the synthesis process may influence the morphology and photocatalytic potential of the resulting particle. Characterizations such as XRD, FESEM, EDAX, FTIR, UV, and PL were carried out to examine the structure, morphology and composition of the synthesized nanoparticles. Using Methylene Blue as the model dye, the produced nanoparticles' photocatalytic activity was assessed.

MATERIALS AND METHODS

Materials

Zinc chloride ($ZnCl_2$)and Sodium sulphide (Na_2S) were used as precursor materials to synthesize Zinc sulphide (ZnS) for the co-precipitation method. All the reactants were of high analytical grade, ensuring optimal purity without the need for any further purification steps. For the synthesis process, we utilized pristine distilled water, which served as a pure medium for combining the ingredients. Ethanol was employed to thoroughly wash the precipitate, ensuring that no impurities remained and leaving behind a refined product ready for the next phase of experimentation.

Synthesis of ZnS nano paricles

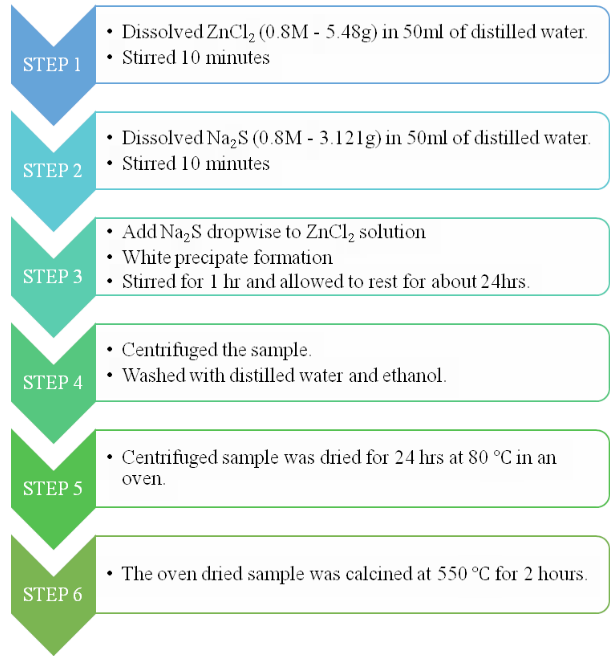
Using 50 ml of distilled water, 0.8M solutions of $ZnCl_2$ and Na_2S were made individually. The solutions were stirred using a magnetic stirrer for about 10 minutes. The Na_2S solution was added dropwise to the $ZnCl_2$ solution with a dropper while stirring continuously until a white precipitate formed. The synthesis took place at room temperature, and the solution was left to settle for approximately 24 hours.

The precipitate has been centrifuged and cleansed with ethanol and distilled water once it had settled. The sample was then air-dried at 80 °C for 2 hours, followed by calcination at 550 °C for 2 hours.

$$ZnCl_2 + Na_2S \xrightarrow{\text{White precipitate}} ZnS! + 2NaCl$$

Characterization

The X-Ray Diffraction (XRD) patterns were



examined using monochromatic Cu-Kα radiation in the 2θ range of 10° to 80° using an X' Pert PRO Diffractometer (PANalytical, Netherlands) that operates in continuous scanning mode in steps of 0.050 to identify the phase purity and crystal structure of the synthesized pure ZnS nanoparticles. (Deng *et al.*, 2007, Borah *et al.*, 2008 and Caifeng *et al.*, 2009). The morphology of the ZnS nanoparticles were micrographed using a JEOL-Scanning Electron Microscopy (SEM) (Model JSM- 6390, Made in Japan). Shimadzu spectrophotometer in the range of 4000-400 cm^{-1} using KBr pellet technique has been used to record the FTIR spectra of the prepared sample. Optical absorption studies were carried out using a UV-Visible Spectrometer (JASCO V- 570, CANADA Make) about 200 - 1200 nm (Hong *et al.*, 2011). The photoluminescence (PL) study was carried out at room temperature using a Hitachi F-7000 FL spectrometer with a 450W xenon lamp as excitation source.

Photocatalytic studies

The photocatalytic performance of the ZnS was evaluated by measuring the degradation rate of methylene blue dye when exposed to UVA light. To conduct this investigation, stock solution was prepared by dissolving 0.001 mole of MB in 100ml of distilled water and stirred using a magnetic stirrer. 0.5 ml of stock solution was then mixed in 50 ml of distilled water (mother solution) for which absorbance peak observed at 665 nm. 0.05 g of synthesized ZnS was dissolved in methylene blue solution and stirred vigorously for about 20 minutes using a magnetic stirrer. The solution was kept in a dark box for 30 minutes. After that UV light was turned on and degradation has been studied for every 10 minutes for about 1 hour.

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD)

Fig. 1. shows the XRD pattern of the prepared ZnS nanoparticle which has been measured in the scan range 10^0 to 80^0.From the diffraction pattern it is observed that main peaks were obtained at 2è values of 28.51^0,33.04^0, 47.61^0 and 56.46^0. The peaks represent the (111), (200), (220), and (311) planes of the ZnS cubic phase and the data matches well with JCPDS card No.80-0020. Previous studies confirms that cubic phase is highly active towards the photocatalytic applications than the hexagonal phase (Jagdeep *et al.*, 2015).

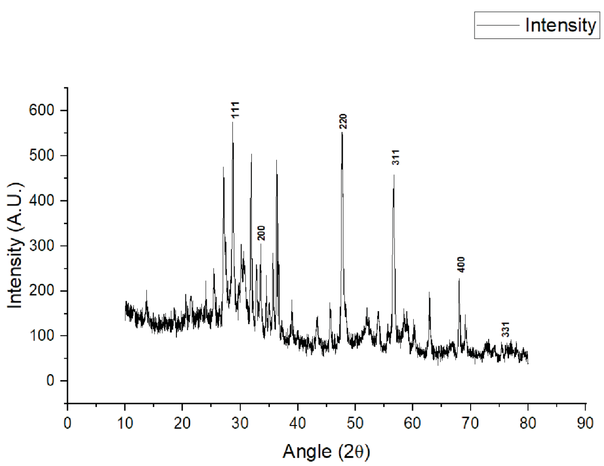


Fig. 1. X-ray Diffraction pattern of the synthesized zinc sulfide nanoparticle

Average crystallite size of pure ZnS nanoparticles is calculated using the Debye-Scherer's equation

$$D = K \lambda / \beta \cos \theta \qquad .. (1)$$

where, D is the mean grain size, K is constant, λ is the X-ray wavelength (1.5406 Å), β is the full width at half maximum and θ is the Bragg diffraction angle. The average crystalline size of the synthesized pure ZnS nanoparticle was 44.55 nm, which confirms the formation of nanoscale crystalline domains.

Field Emission Scanning Electron Microscopy (SEM)

Fig. 2 shows the SEM image of the ZnS NPs. The

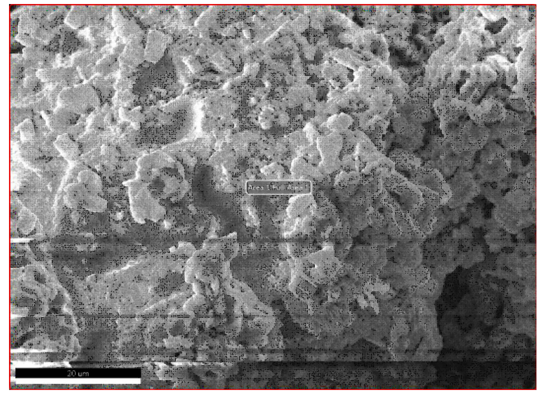


Fig. 2. Field Emission Scanning Electron Microscopy of the synthesized zinc sulfide nanoparticle

micrograph of ZnS nanoparticles shows significant amounts of agglomeration, which may occur during the synthesis and calcination at 550 ^{0}C, along with uneven and sparsely spherical particle morphologies in the nanosized range.

Particle clustering may be encouraged by this thermal treatment because it increases surface energy and inter-particle interactions. Furthermore, the observed morphology shows that the nanoparticles are irregularly shaped, with just a small percentage displaying roughly spherical, sparsely scattered shapes. The particles are still within the nanoscale size range in spite of their morphological abnormalities. Capping agents function as stabilizing or binding molecules that play a crucial role in preventing nanoparticle agglomeration by providing steric and electrostatic hindrance (Amanpreet *et al.*, 2022). They also influence the surface chemistry and biological activity of the nanoparticles, thereby enhancing their stability and dispersion within the preparation medium. In the present synthesis, the absence of capping agents may have contributed significantly to the observed agglomeration, as the nanoparticles lacked the necessary surface stabilization to remain discrete and uniformly dispersed.

Energy Dispersive Analysis of X-rays (EDAX)

Pure ZnS nanoparticles' elemental composition was studied and EDAX was used to identify the distinctive elements. To ascertain the proportion of zinc and sulphur in the synthesized ZnS sample, the Energy Dispersive X-ray (EDAX) study was employed. Energy dispersive X-ray analysis provides quantitative and qualitative data regarding the materials' elemental composition [Liao *et al.*, 2005]. From the EDAX spectra, Fig.3, the sample do not contain any other components and contaminants. The electron dispersive X-ray spectrum of the prepared ZnS nanoparticles shows the presence of Zn and S elements as expected in the prepared sample. The presence of impurities like Na, C, O and Cl in EDAX spectra of ZnS can be caused by several factors such as the materials used to coat the samples during SEM/EDAX analysis, glass substrate or unreacted precursor materials. From this it is evident that the as prepared ZnS nanoparticles are highly pure.

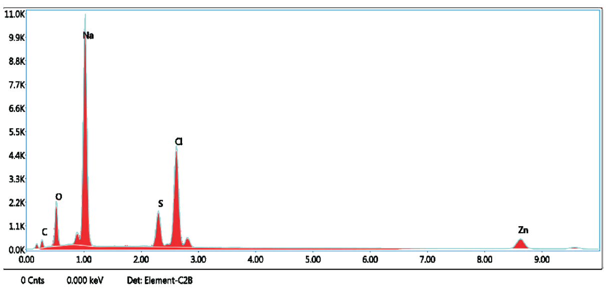


Fig. 3. Energy dispersive X-Ray image of the prepared zinc sulfide nanoparticle

Fourier transforms infrared spectroscopy (FTIR)

The FTIR spectrum of ZnS nanoparticles analysis is shown in Fig. 4. The peaks were produced due to different vibrational modes. Spectrum analysis of the ZnS shows that despite the successive washes with absolute ethanol, traces of solvent still exist (Khalid*et al.*, 2013). This is confirmed by the presence of a broad and intense band exhibited from 3263.5 cm^{-1} and 3441 cm^{-1} to the vibrations of the valence of the O-H mode in the H_2O molecules. This

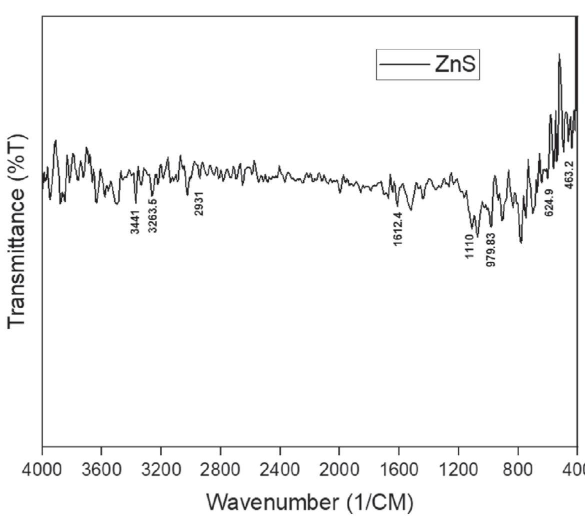


Fig. 4. Fourier Transform Infrared spectrum of the synthesized zinc sulfide nanoparticle

peak may be due to water present in the sample. The vibration of the ZnS bond is confirmed by the presence of medium and strong bands located around 1110 cm^{-1} and 624.9 cm^{-1} bands are assigned to the stretching modes of Zn-S. Whereas the vibration bands observed at 1550 cm^{-1} is the typical vibration band of C = O. The vibrational band at 1203.5 is probably attributed C-H stretching band at 979.83 assigned to C-H bending. The weak bands at 2931.8 cm^{-1} and 2962.6 cm^{-1} are probably attributed to C-O stretching. The peak at 480 cm^{-1} is assigned to NH_2 symmetric stretching vibration (Li *et al.*, 2008).

UV-Vis Spectroscopy

Fig. 5 represents the UV-Vis absorption spectrum of the synthesized ZnS nanoparticles. The absorption spectrum has been recorded to measure their band-gap. From the spectrum it is observed that the absorption edge of the synthesized nanoparticles lies at 290 nm. This sharp peak exhibits a phenomenal blue shift relative to its bulk equivalent (340 nm). From the UV- Vis spectrum, the band gap of the synthesized ZnS NPs has been calculated using the following equation;

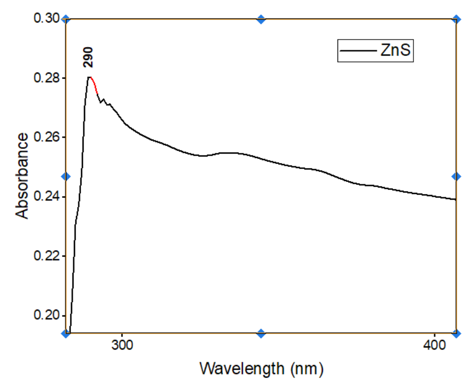


Fig. 5. Absorption spectra of synthesized Zinc sulfide nanoparticles

E_g = hc/ë$_p$ where E_g is the bandgap energy,h is the Plank's constant (6.626 x 10^{-3} Js), c is the velocity of light (3 x 10^8 m/s) and ë$_p$ is the peak value.A strong photoluminescence emission peak is observed at 421nm and the calculated bandgap value is about 4.3 eV. On comparing with bulk particles, the bandgap energy has increased as a consequence of quantum confinement. The quantum confinement of the excitons existing in the sample causes the blue shift in the absorption edge, therefore producing a more distinct energy spectrum of the individual nanoparticles. The effect of the quantum confinement on impurity depends upon the size of the host crystal (Mahesh *et al*., 2017).

Photoluminescence Spectroscopy (PL)

The photoluminescence (PL) spectrum of the chemically synthesized ZnS has been recorded to study its luminescence features. Fig. 6 shows the PL spectrum of as synthesized ZnS. At 421nm, a strong emission peak can be observed from the spectrum. This is the exciton emission peak. At about 460 nm, a broad band can be seen. This may be the trapped emission peak. Usually for semiconductor nanocrystals, two emission peaks can be observed- the exciton and the trapped luminescence (Nell *et al*., 1990). The exciton emission peak is sharp and (Omar *et al*., 2019 and Peng *et al*., 2006). The PL peak at 421nm is known to be due to the trapped emission is broad recombination between sulphur vacancy related donor and valence band. The luminescence around 460 nm is due to the trap states emission of ZnS (Peng *et al*., 2006). Previous studies reported that these peaks remain unaltered with change of Cu concentration.

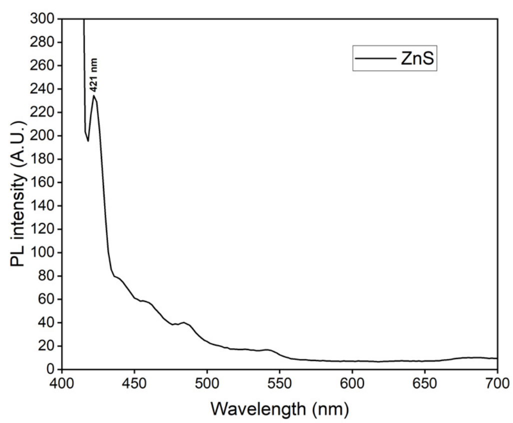


Fig. 6. Room temperature photoluminescence spectra of synthesized Zinc sulfide nanoparticles

Photocatalytic Activity

ZnS nanoparticles' photocatalytic characteristics can be utilized to break down biological pollutants like dyes and phenolic compounds that are frequently detected in wastewater. When exposed to UV or high-energy visible light, ZnS, a semiconductor featuring a wide band gap (~3.6 eV), can result in reactive oxygen species (ROS), which are imperative for the advanced oxidation processes (AOPs) which break down pollutants and the possible mechanism is presented in Fig. 7.

ZnS nanoparticles exhibit photoexcitation when

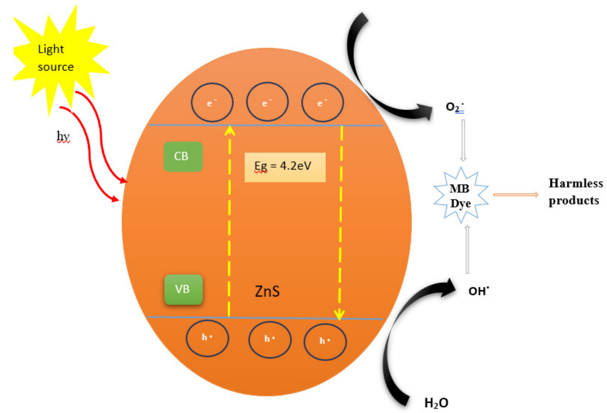


Fig.7. Photocatalytic mechanism of ZnS nanoparticles with Methylene Blue dye

exposed to UV light, triggering the valence band (VB) to gain positive holes as electrons in the VB absorb energy and navigate to the conduction band (CB):

ZnS+ hv $e_{CB} + h_{vB}$

These photogenerated electrons and holes take part in redox processes on the ZnS nanoparticles' surface. Superoxide radicals ($\bullet O_2^-$) are generated when the conduction band electrons decrease dissolved oxygen molecules, while hydroxyl radicals ($\bullet$OH), which are highly reactive oxidizing agents, evolved when the valence band holes oxidize water or hydroxide ions:

$$O_2 + e^- \rightarrow \bullet O_2^-$$

$$H_2O + h^+ \rightarrow \bullet OH + H^+$$

These ROS attack and degrade organic pollutants into less harmful or mineralized products such as CO and HO:

$$\text{Pollutant} + \bullet OH \,/\, \bullet O_2^- \rightarrow \text{Degraded products}$$

The UV absorption spectra (Fig. 8a) of the methylene blue solution, catalysed by the synthesized ZnS sample showed a decrease in absorption intensity with increasing reaction time (Zewei Quan *et al*., 2007). Fig. 8b shows the plot of the pseudo-first order kinetics at 0.05g catalyst concentration. This photocatalytic reaction has pseudo-first-order degradation kinetics.

CONCLUSION

Pure ZnS nanoparticle was synthesized by chemical co-precipitation method without the incorporation of any capping agents.It can be perceived from the SEM image that the nanoparticles have an asymmetrical form. The particle morphology can be

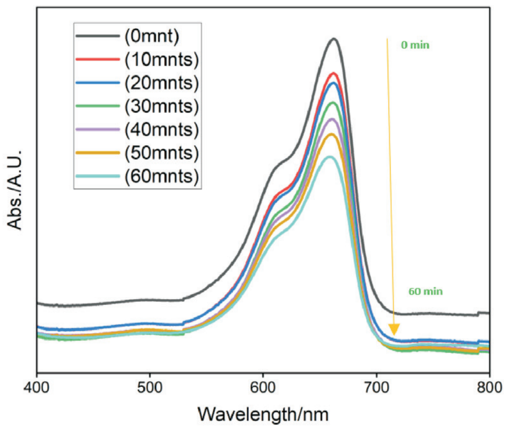


Fig. 8a. Time dependent photocatalytic degradation of MB dye containing synthesized ZnS.

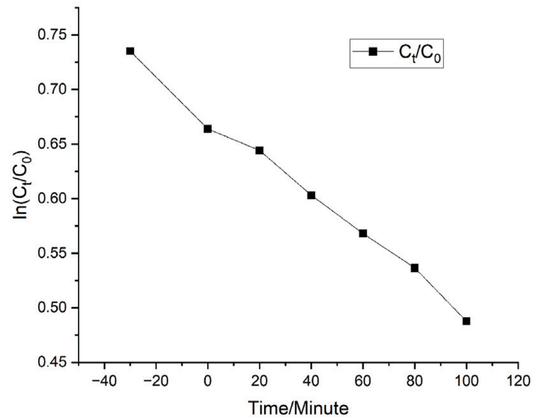


Fig. 8b. Plot of $\ln(C_t/C_0)$ versus time showing pseudo first order kinetics.

tailored by incorporating an appropriate capping agent during the synthesis process, which can guide the growth of nanoparticles and promote uniform shape and size distribution. Under UV illumination, the synthesized ZnS sample shows good degradation property. It could effectively breakdown MB dye dissolved in water. Although the synthesized nanoparticles did not exhibit a well-defined shape or uniform structural morphology-likely due to the absence of a capping agent and the conditions of the synthesis process- they successfully achieved nanoscale dimensions. In spite of their uneven shape, the synthesized ZnS nanoparticles demonstrated significant photocatalytic efficiency, suggesting that particle homogeneity is not the only factor which influences their functional performance. This implies that factors such as high surface area, crystallinity, and surface imperfections may have contributed positively to their photocatalytic activity. From previous studies it is analyzed that doping of pure ZnS can improve its degradation efficiency. As synthesized ZnS sample can be doped with possible dopants and the efficiency can be compared in future studies.

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Conflicts of Interest

The authors declare no conflicts of interest.

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