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Research Report

PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE UNDER VISIBLE LIGHT USING PVP-CAPPED UNDOPED AND Ni DOPED ZnS NANOCRYSTALLINE POWDER

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ABSTRACT

Ni doped and undoped ZnS nanocrystalline powders were synthesized by a Wet Chemical Synthesis method. The synthesized products were characterized by X-ray diffraction, scanning electron microscope, field emission electron microscope and ultraviolet–visible spectrometer. The X-ray diffraction and field emission electron microscope studies show that the size of crystallites is in the range of 1–3 nm. Photocatalytic activities of undoped and Ni doped ZnS were evaluated by decolorization of Methylene Blue in aqueous solution under visible light irradiation. It was found that the Ni doped ZnS bleaches Methylene Blue much faster than the undoped ZnS upon its exposure to the visible light.

INTRODUCTION

Today the entire world is facing a major problem of water pollution, which is caused in different manners. Dyes from different textile, dyeing and printing industries are one type of pollutant as these industries discharge their effluent into adjacent natural water resources without any treatment. Dyes are used by industries on a vast scale. These dyes are released in the environment causing severe pollution. Photocatalysis has received considerable attention in recent years as an alternate for treating water polluted with heavy metal ions, dyes and other pollutants. Photocatalysis has large capability for the water treatment and so an attempt is made to remove these dyes through photocatalysis. Various semiconductors have been used as photocatalysts for the removal of different dyes from their aqueous solutions. Photocatalytic and oxidative degradation of wastewater pollutants in the presence of TiO2 was observed by [Das *et al, 1994*]. Zinc sulfide (ZnS) is a promising material for the use in various application devices such as nano sized sensors, photodiode and photocatalyst for the degradation of organic dyes [X. Fang *et al*, 2011]. Nano scale semiconductor particles possess higher surface area-to-volume ratio than their bulk counterparts, and thus allow for greater photon absorption on the photocatalyst surface (Hoffimann *et al*., 1995). Moreover, recombination of the electron-hole pair within the semiconductor particle is drastically reduced as particle size decreases (Oldroyd *et al*., 1998). When particle size of semiconductor decreased to nanometer-size scale, the band-gap energy greatly increased, which in turn led to higher redox potentials in the system. Therefore, the nano-scale semiconductor is expected to have higher photocatalytic activity than its bulk. An attempt is made to remove the dyes using Ni doped and undoped ZnS nanocrystalline powders presence of solar energy which may provide an efficient and cheaper way for removal of dyes. Wet chemical synthesis involving colloids is the most energy efficient ‘bottom -up’ technique for the synthesis of nanoparticles. The chemical synthesis has the advantages of producing size-controlled, un-agglomerated nanoparticles.

MATERIALS AND METHODS

ZnMnS nanocrystals have been synthesized using wet chemical co-precipitation method already opted by (Singh *et al*, 2009). All synthesis was carried out at room temperature under ambient conditions in aqueous media for its inherent advantages of being simple and environment friendly. Analytical reagent grade chemicals: zinc acetate (C4H6O4Zn 2H2O), nickel acetate (Ni(OCOCH3)2.4H2O), sodium sulphide (Na2S.H2O), and polyvinyl pyrrolidone (PVP) [(C6H9NO)n] were used without further purification. Solutions of 0.3 M zinc acetate, 0.6 M sodium sulphide, and 0.01 M nickel acetate were prepared in separate beakers. Then zinc and nickel precursor solutions were mixed in the stoichiometric proportion under vigorous stirring, 4 ml of 2% PVP solution

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was added to total 50 ml volume, before drop - wise addition of sulfur precursor. PVP will act as the capping agent to avoid the agglomeration of nanocrystals. The resulting precipitates were centrifuged and dried in oven for 6 h continuously.

The photo-catalytic activity of undoped and Ni doped ZnS was studied by monitoring the degradation of Methylene blue (MB) (C16H18ClN3S. 2H2O) dye in an aqueous suspension containing undoped and Ni doped ZnS nanocrystalline powder under the visible sunlight. Following the visible sunlight exposure, 5 ml sample of aqueous suspension was taken out after every 10-min interval for the total 50 mins of the visible sunlight exposure to record UV-visible absorption spectra.

RESULTS AND DISCUSSION

X-ray Diffraction: It has been reported that ZnS may have either cubic or hexagonal structure, depending on the synthesis conditions such as deposition temperature and precursor concentration [J.A. Ruffiner *et.al*, 1989]. The phase purity and crystal structure of these samples were analyzed by using CuKα radiations source in the range of 10^{o} to 80^{o} with 0.050 step size using XPERT – PRO diffractometer. Figure 1 shows the XRD Pattern of the undoped and Ni doped ZnS nanocrystalline powder.

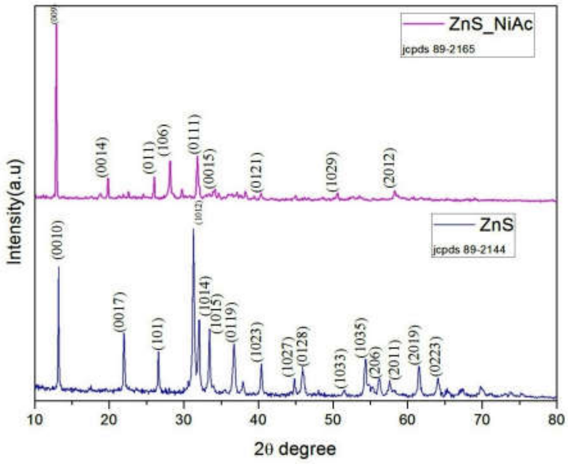

Figure 1 XRD pattern of undoped and Ni doped ZnS.

The diffraction peaks for the sample can be indexed to hexagonal phase of ZnS with lattice constants of a = 3.823A˚ and c = 68.728A˚ which are in agreement with the standard literature data (JCPDS card number: 89-2144) for undoped ZnS. Similarly for Ni doped Zns the sample can be indexed to hexagonal phase with lattice constants of a = 3.823 A˚ and c = 62.48 A˚ (JCPDS card number: 89-2165). Average crystallite size has been calculated from the line broadening of the X-ray diffraction (XRD) diffractogram using Scherrer formula and its of 1.8 nm and 1.7 nm respectively for undoped and Ni doped ZnS.

FE – SEM

Photographs of the undoped and Ni doped ZnS nanocrystalline powder were taken with (ZEISS) FESEM and shown in Figure 2. The FESEM images of undoped and Ni doped ZnS nanocrystalline powder shows that the dopant has a vital function in controlling surface morphology. The FESEM analysis indicates that grain sizes of Ni doped ZnS were regular. The FESEM photograph clearly indicates the formation of sub - micrometer crystallites and it shows the morphology of near rod in nature. The average diameter of Ni – doped ZnS is in a rod shape and its diameter is about 2.45 µm, which is in proximity to the average crystallite size determined by XRD. So, all the synthesized particles are single nanocrystals.

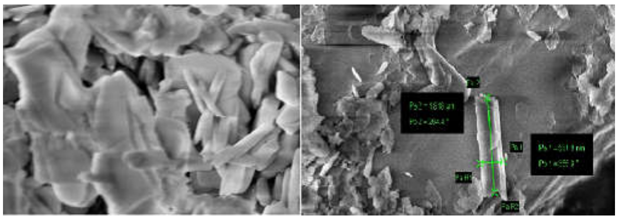

Figure 2 FE-SEM images of undoped and Ni doped ZnS.

UV–Visible optical absorbance and band gap

The UV–Visible optical absorption spectrum of the samples recorded in room temperature is shown in Figure. 3. UV–Visible absorbance spectrum indicates that undoped ZnS having an absorption peak at 208 nm while Ni doped ZnS is having an absorption peak at 228 nm. Undoped and Ni – doped ZnS have very good absorption extended up to 800 nm. The as prepared samples show a wide range of absorption from UV to NIR which indicates that the prepared material is good for sun light absorption. The optical band gap of undoped Zns is 3.6 eV and for Ni – doped ZnS is 5.6 eV, from its evident that doping of Transition Metal increase the optical band gap. The bandgap values were found to increase due to reduced particle size showing strong quantum confinement effects which is higher than bulk values.

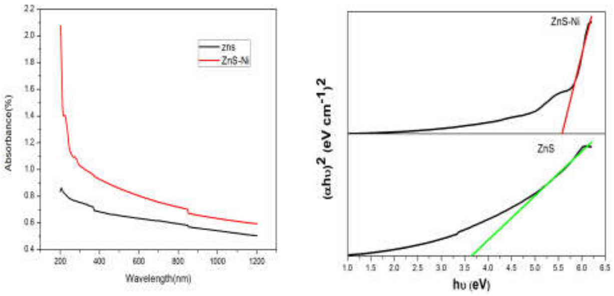

Figure 3 UV – Visible Spectrum and optical bandgap of Undoped and Ni – doped ZnS

Photocatalytic Dye Degradation Study

ZnS has been used as a semiconductor-type photocatalyst for the photoreductive dehalogenation of halogenated benzene derivatives, photocatalytic degradation of water pollutants, and photocatalytic reduction of toxic metal ions. [H. Fujiwara *et al*, 1998]. In the present undoped and Ni doped ZnS nanocrystalline powder we investigated their photocatalytic activity. In order to study the effect of dopant on degradation efficiency, photodegradation experiments were carried out in presence of doped/undoped catalyst for 50 minutes/60 minutes sunlight irradiation. The results obtained are shown in figure 4. The degradation efficiency for undoped ZnS is 82% and for Ni doped Zns is 92%. Doping ions is a way to trap electrons and/or holes on the surface or during interface charge transfer because of the different positions of the dopant in the host lattice.

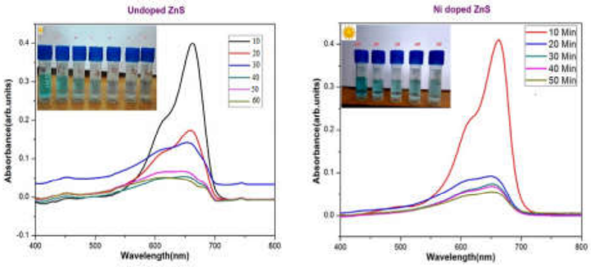

Figure 4 Absorption spectrum of sunlight radiation of Undoped and Ni – doped ZnS

CONCLUSION

Undoped and Ni – doped ZnS nanocrystalline powder have been successfully synthesized in aqueous media using a simple wet chemical synthesis technique. Crystallographic and morphological studies reveal the zinc blende nanostructures having average crystallite size approx. 2 nm. Energy resolved luminescence spectra report for Undoped and Ni – doped ZnS nanocrystalline powder is 662 nm and 663 nm respectively. This mechanistic information of photo-catalytic activity dependence on dopant concentration and luminescence quantum yield will significantly contribute to enhance the understanding of photo - initiated processes in semiconductor nanocrystal such nanocrystal exhibit good photocatalytic activity for degradation of water - soluble dyes.

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