

# Preparation of ZnS-graphene nanocomposite and its photocatalytic behavior for dye degradation

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## ABSTRACT

In the present work, ZnS-Gaphene (ZnS-GNS) composite was prepared by microwave irradiation method. The prepared samples were characterized by X-ray diffraction (XRD), to confirm the formation of GNS by reducing Graphite as well as ZnS-GNS nanocomposite. Raman spectroscopy identified D and G photon vibration mode of GNS in the ZnS-GNS composite. X-ray photoelectrons spectra are also detected presence of graphene in ZnS. UV/VIS Spectra are studied for evaluation of photocatalytic activity. The composite is explored as photocatalysts to study dye degradation using methylene blue dye in aqueous slurry under irradiation of 663 nm wavelength. Under the same conditions the photocatalytic activity of the pure ZnS is also examined. The ZnS-GNS composite is found in enhancing the rate of photodegradation of toxic dyes as compared to pure ZnS. This Graphene based metal sulphide/oxide semiconductor nanocomposites are high potential material for Photo-degradation of toxic dyes, and act as good photocatalyst. Copyright © 2014 VBRI press.

**Keywords:** Graphene; zinc sulfide; nanocomposites; photocatalytic activity.



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reputed international journals.

## Introduction

Zinc sulfide (ZnS), is an important II-VI semiconductor with wide direct band gap (3.7 eV). The wide gap semiconductors are ideal for photo catalysts due to rapid electron-hole pair generation by photo-excitation [1, 2]. Morphology and size play very important role in these processes. These directly manipulate band gap of semiconductor with variation of surface to volume ratio, which ultimately enhance the redox potential [3]. Modification of surface of semiconductor is required to improve charge separation and reduce charge-carrier combination by doping with another semiconductor or use of composite semiconductor [4]. The nanocomposite has high surface to volume ratio, this increase the life time of charge carrier, shows catalytic activity for production of hydrogen by photo-splitting of water.

Graphene is one of the potential material exhibits outstanding mechanical, thermal, optical and electrical properties. Graphene nanosheet has very high surface to volume ratio [5]. Graphene nanosheet is highly desirable ideal candidate for use as two dimensional catalyst support [6]. Recently graphene-based semiconductor nanocomposites have attracted lot of attention as promising photocatalysts for nonselective degradation of pollutants (dyes, bacteria and volatile organic pollutant). The

photocatalytic degradation of the dyes is possible in presence of semiconductor and their composite under UV-light. ZnS has particle size 3 nm due to smaller size rapid electron hole pair generated, thus generate free radicals for dye degradation. As size of particles decreases band gap of semiconductor increases, this provides more surface to volume ratio. Ultimately this enhance redox potential. Graphene has particle size 2.5 nm and very high surface to volume ratio. This allow greater photo absorption giving formation of more hydroxyl radicals (OH). This leads to higher photodegradation efficiency towards dye degradation. There is a wide scope to exploit the potential applications of GR-based semiconductor nanocomposite. In this projected work, microwave-assisted synthesis route is used to directly synthesis ZnS-Graphene (ZnS-GNS) nanocomposite. Formation of nanocomposite is confirmed by XRD, XPS, and Raman spectroscopy. The composite is explored as photocatalysts to study dye degradation. For photodegradation commonly used methylene blue dye is used. The dye degradation in presence of pure ZnS and ZnS-GNS nanocomposites are systematically monitored by UV-VIS spectrometer. Dyes are colored ionizing, aromatic organic compound, many dyes are toxic causes serious damage to human being.

## Experimental

### Materials

Natural flake graphite used for preparing graphite oxide (GO) and GNS-ZnS, 98%  $\text{H}_2\text{SO}_4$ , 30%  $\text{H}_2\text{O}_2$ , 80% hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ),  $\text{NaNO}_3$ ,  $\text{KMnO}_4$ ,  $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ , thioacetamide (TAA), Ethylene-diamine, methylene blue (MB), ethanol. All the precursors were GR grade and procured from Merck (India) with 98% purity

### Preparation of GO and GNS

Graphite oxide (GO) were prepared by synthesis process, 3 g graphite powder and 3 g sodium nitrate were put into 150 ml concentrated  $\text{H}_2\text{SO}_4$  98% (in an ice bath). Afterward, 9 g  $\text{KMnO}_4$  was gradually added. The mixture was then transferred to a  $40^\circ\text{C}$  water bath and stirred for about 2 hrs forming a thick paste, subsequently, 150 ml de-ionized water was added gradually, causing an increase in temperature to  $98^\circ\text{C}$ . After 20 min, 30 ml 80%  $\text{H}_2\text{O}_2$  solution was added to the mixture. The mixture was stirred for another 10 min, and then diluted with 800 ml de-ionized water. The solution was then filtered and washed with de-ionized water and dried at room temperature to obtain GO solid. Graphene nanosheets (GNS) were obtained by synthesis procedure of 350 mg GO dispersed in 350 ml de-ionized water and then exfoliated to generate GONS by ultrasonication for 1 hrs using a digital sonicator. Subsequently, 5 ml 80% hydrazine hydrate was added to the solution. After heated at  $100^\circ\text{C}$  for 4 hrs, the mixture turned from a yellow-brown solution to a black suspension. The mixture was then cooled and filtered and washed several times with de-ionized water and ethanol. The product was dried at  $50^\circ\text{C}$  under vacuum overnight to obtain GNS.

### Synthesis of zinc sulfide- graphene nanosheets nanocomposite (ZnS-GNS)

In a typical experiment, about 300 mg GO was dispersed in 300 ml de-ionized water. Subsequently, 0.04 mol  $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$  dispersed in 100 ml de-ionized water was added to the aqueous dispersion, followed by ultrasonication for 10 min. Then added 0.06 mol TAA to the mixture. The Mixture was placed in microwave oven with a refluxing system outside, and then irradiated by microwave (400 W) at  $85^\circ\text{C}$  for 20 min. The mixture cooled to room temperature, the suspension was filtered and repeatedly washed with de-ionized water and ethanol to remove impurities. The obtained ZnS-GNS nanocomposites were dried in vacuum oven at  $60^\circ\text{C}$  as a black solid.

### Characterization

The dried sample were characterized by X-ray power diffraction, (XRD) patterns were obtained on a X-ray diffractometer (XPRT-PRO at IITB Mumbai) with Cu- $\alpha$  radiation ( $\lambda=1.5406\text{\AA}$ ). A Raman spectrum was recorded on a Laser Raman spectroscopy (BRUKER RFS 27 at IITM Chennai) with 632.8 nm He-Ne laser excitation. A UV (Perkin-Elmer) Spectrometer with Hg Laser excitation was used to record the UV-VIS spectra of various samples.

### Photocatalytic activity measurement

Photocatalytic experiments were conducted to photocatalytically degrade methylene blue in water. In a typical experiment, different Percentage of ZnS-GNS nanocomposites was added to 3.5 ml of 0.00016 mg methylene blue solution. Subsequently, the mixture was exposed to UV irradiation by a high-pressure Hg lamp (500 W) at room temperature. The samples were collected by centrifugation at different time intervals. The UV-VIS spectrum (300-800 nm) of each sample was recorded and the characteristic absorption peak of MB solution at 663 nm was chosen as the monitored parameter for the photocatalytic degradation process. Compare the photocatalytic activity with that of ZnS-GNS nanocomposites under the same experimental conditions.

## Results and discussion

### X-ray diffraction

Crystallinity of samples was studied by using an X-ray diffractometer, **Fig. 1** shows XRD pattern of ZnS, GNS and ZnS-GNS. It confirmed the formation of GNS by reducing GO during reaction but no signal for any other phases. For pure ZnS, highly crystalline structure and phase identification carried out with help of standard JCPDS data base the three different peaks  $29.0^\circ$ ,  $48.1^\circ$  and  $57.0^\circ$  corresponded to (111), (220) and (311) planes of cubic crystalline ZnS, respectively, which indicates that the prepared nano crystals belongs to the Cubic zinc blend structure. The broadening of peak of nano crystal is due to their small size. The average size of ZnS and ZnS-GNS particle calculated by Debye Scherrer formula is 3 and 2.4 nm, respectively. Position of diffraction peaks almost matched with standard JCPDS No. 05-0566. The lattice

parameter computed as  $5.33\text{\AA}^0$  which is very close to standard value ( $5.42\text{\AA}^0$ ) [7].

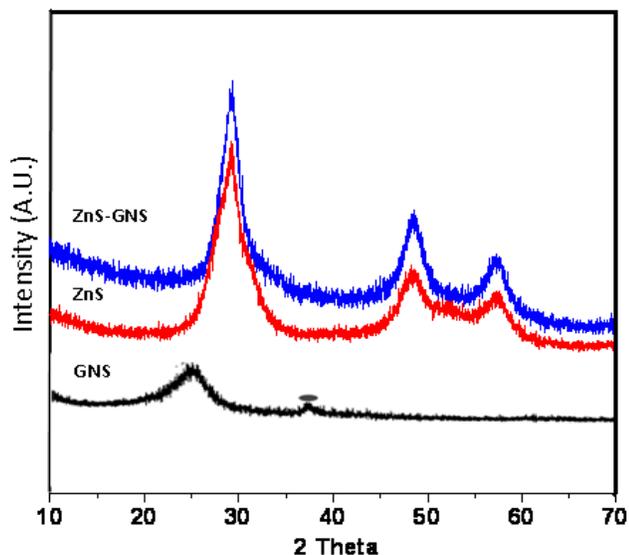


Fig. 1. XRD patterns of GNS, ZnS and ZnS-GNS.

For ZnS-GNS composite no phases of GO or GNS are detected. This may be due high content and good crystallinity of ZnS in the composite cover the diffraction of carbon sheet.

#### Raman spectroscopy

To explore the componential and structural characteristics, a Raman spectroscopy technique used. Fig. 2 shows the Raman spectra of ZnS-GNS and ZnS, respectively.

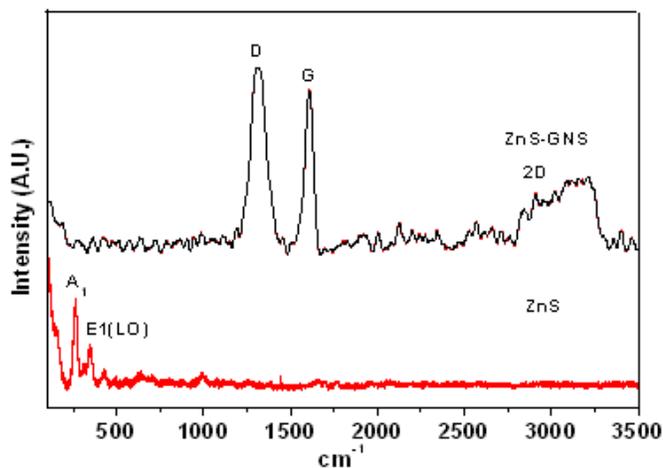


Fig. 2. Raman Spectra of ZnS and ZnS-GNS composites.

The excitation laser of 632.8 nm was used. The raman peak of ZnS was found at  $265\text{ cm}^{-1}$  and  $348\text{ cm}^{-1}$  correspond to the TO and LO modes respectively. The peak at  $1610\text{ cm}^{-1}$  (G band) correspond the  $E_{2g}$  phonon vibration of  $sp^2$ -bonded carbon atoms in a 2D hexagonal lattice. The peak at  $1318\text{ cm}^{-1}$  (D band) is associated with vibration of carbon atoms with dangling bonds in plane terminations of disordered [8]. The G band indicates presence of number of graphene layers. As number of layer increases G band

position shifted to lower frequencies and there is no significant change in spectral shape. D band is known as disorder band, This is peak due to lattice motion away from center of the Brillouin zone. The peak intensity ratio of D and G band,  $I(D)/I(G) = 1.13$ .

#### X-ray photoelectron spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is surface analytical techniques used to investigate the chemistry at the surface of a sample. In the present study it was used to confirm presence of graphene in ZnS. XPS spectra of ZnS-GNS display (Fig. 3) the four peaks located at 285.5, 290.6, 293 and 295.3 eV observed from  $C_{1s}$  deconvolution spectrum correspond to the C-C, C-OH and C-O and O-C=O (-COO) groups, respectively.

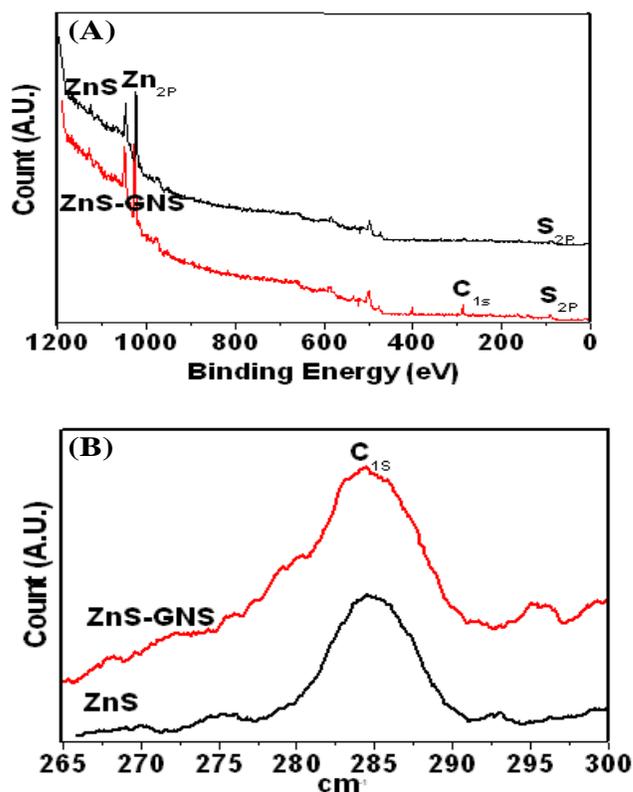


Fig. 3. XPS spectra of ZnS and ZnS-GNS composite (A) survey scan (B) Slow scan.

In pure ZnS,  $C_{1s}$  peak is also observed with deconvolution spectrum, which may arise due to carbon contamination on the surface. All other peaks are corrected accordingly. The two peaks at 1032.55 and 72.5eV correspond to  $Zn_{2p}$  and  $S_{2p}$  the peak area of Zn and S cores are measured and yield ratio of Zn to S shows that the surface of the products are a little rich in Zinc. [9].

#### UV- spectroscopy

To demonstrate the effect of the photocatalytic activity, the photocatalytic performance of GNS-ZnS nanocomposites was studied for the degradation of methylene blue in water. The characteristic absorption peak of methylene blue

solution at 663 nm was chosen as the monitored parameter to detect the concentration of methylene blue.

Fig. 4 shows absorption spectra of methylene blue in the presence of ZnS-GNS nanocomposites. It clearly shows that the intensity of the adsorption peaks corresponding to methylene blue decreases slowly with increasing percentage of ZnS-GNS. No new absorption peaks appear in the visible and ultraviolet regions, indicating the complete degradation of methylene blue.

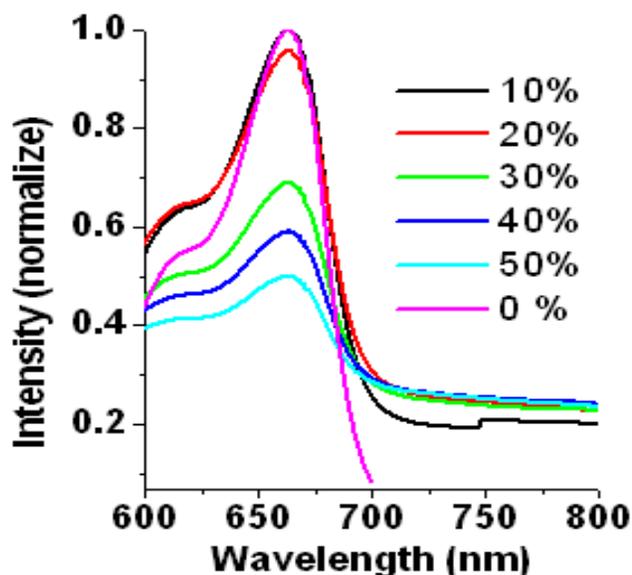


Fig. 4. Variation of UV-VIS absorption spectrum of ZnS-GNS with different percentage in methylene blue.

Rate of photodegradation of methylene blue (Fig. 5) was observed to be more in presence of ZnS-GNS compared to pure ZnS. It provides clear evidence to demonstrate that ZnS-GNS enhance the rate photodegradation of toxic dyes compared to pure ZnS.

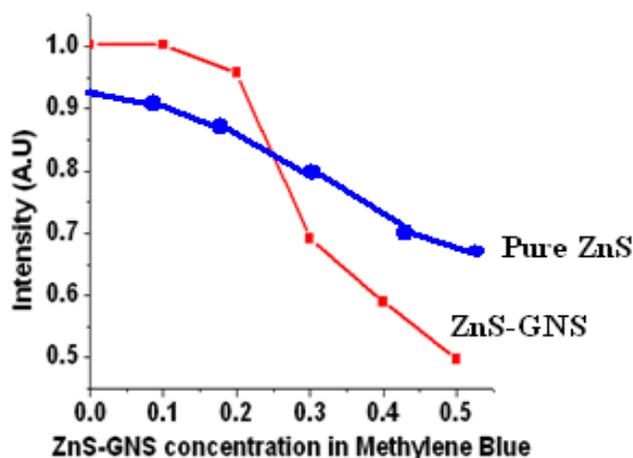


Fig. 5. Photodegradation rate with methylene blue (a) pure ZnS and (b) ZnS-GNS.

ZnS-GNS is potential nanocomposite photocatalyst. There are several Classical methods for degradation of dyes,

but end products of these techniques need to be processed further for complete dye degradation however these are much costly. The method used in the present work of photodegradation of methylene blue by ZnS and ZnS-GNS composite is inexpensive and efficient. The microwave-refluxing synthesis assembly used for the directly synthesis of ZnS-GNS composite method is very fast and high potential to commercially synthesis of metal oxide/sulphide-GNS nanocomposites. According to our knowledge this is the first attempt to develop the composite system by microwave-assisted route.

## Conclusion

In summary, microwave-refluxing synthesis assembly was used to directly synthesis ZnS-Graphene (ZnS-GNS) nanocomposite. XRD confirmed the formation of GNS by reducing graphite as well as ZnS-GNS nanocomposite. XPS ensure the presence of graphene on the surface of ZnS-GNS composite. Raman spectroscopy study identified D and G photon vibration mode of GNS in the ZnS-GNS composite. The composite is explored as photocatalysts to study dye degradation. For photodegradation methylene blue dye is used as dye degradation in presence of pure ZnS and ZnS-GNS nanocomposites are systematically monitored by UV-VIS spectrometer.

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