Facile one-pot solvothermal technique to synthesis ZnS / graphene nanoplatelets (0.2) nanocomposites

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ABSTRACT

In this work, we report the fabrication of ZnS / graphene nanoplatelets (0.2) nanocomposites (ZnS/G(0.2)) by a simple step solvothermal manner. The nanocomposite with weight ratio (0.2) of graphene nanoplatelets was prepared and characterized by several techniques. X-Ray diffraction measurements have shown three sharp peaks at (111), (220), (311) Miller indices, which referred to Sphalerite and Wurtzite phases of the cubic face. The average crystal sizes of 11.03 nm to 14.41 nm for ZnS nanoparticles. The graphene nanoplatelets enhanced crystallinity properties of prepared nanocomposites. Fourier-transform infrared and Raman spectrums confirm formation of ZnS nanoparticles and ZnS/G(0.2) nanocomposites. Furthermore, FESEM was performed to study morphology and structure of nanocomposites. BET isotherm, and the BJH method have given information consistent with Type V with the H₃ hysteresis loops. Moreover, the results have supported the effective change in the surface area, pore-volume, pore diameter, and external surface area values.

Keywords: ZnS nanoparticles, nanocomposites, Raman spectrum, and BET-BJH

Introduction

Zinc sulfide (ZnS) is one of the primary inorganic compounds that commonly studied as a photocatalyst[1]. It has a high negative reduction potential value for the excited electrons with higher generation "electron-hole pairs" under sunlight irradiation[2–5]. It is well known the rapid combination of the electron-hole pairs it is constrained for just the practical applications[6]. ZnS is an essential semiconductor material as it contains an energy gap whose value in the phase of the cubic blends is 3.72 eV as for the hexagonal wurtzite phase about 3.76 eV and it enters in many applications one of these as catalysts[7]. Among these applications, photocatalytic water splitting that was discovered by the Honda and Fujishima in 1972 on titanium dioxide material under the ultraviolet light. Later on, such discovery facilitated the use of semiconductors to produce hydrogen from the water by the photocatalytic water splitting and has received intense attention in the practical and
theoretical research field, due to its critical application to convert sunlight energy into chemical energy[8,9]. In other words, the photocatalytic water splitting to produce the hydrogen and oxygen gases offers an up-and-coming technique for the clean, non-expensive, and environmentally friendly transformation of solar energy to another state[10,11]. Several researchers have focused on the photocatalysts evolution that responds to visible light to use the available visible light that occupies about 43% of the solar energy[12–14]. Thus, more of the attempts have introduced via several scientific articles to improve the photocatalytic hydrogen production performance when utilizing a zinc sulfide[15–17]. For that, co-catalysts are commonly used in the photocatalysts based on graphene[18–20]. It is a single layer of graphite that possesses excellent electron-transport property and a high specific surface area. Numerous studies have been displayed to combine semiconductors with graphene sheets for improving their photocatalytic performance[16,21,22]. This work demonstrates that the one-pot solvothermal technique can be used as one of the effective co-catalysts to synthesis ZnS graphene nanoplatelets (0.2) nanocomposites.

**Experimental part**

**Materials:** The all materials were used in this research without further purification. Zinc acetate dehydrate ((CH₃COO)₂Zn.2H₂O) Sodium sulfide hydrate (Na₂S.7H₂O)and ethylene glycol (C₂H₆O₂) were supplied from the Aldrich LTD.Com. The adsolute ethanol was purchased from the Merck company. The graphene nanoplatelets was supplied from the supermarket company.

**Characterization:** The instrumentals were used in the present work, (X-Ray diffraction (6000 XRD), FT.I.R Spectrophotometer (Bruker 8400), Field-Emission Scanning electron, DRS Spectroscopy (Quantachrome Instruments, USA), BET-BJH Surface Area Analyzer (Quantachrome Instruments, USA).

**Preparation ZnS/Graphene (0.2)**

In a typical reaction procedure, 0.8 mmol of zinc acetate dehydrate was dissolved in 30 mL of ethylene glycol. Then 0.2 g of graphene nanoplatelets was added into the solution. The ultrasonication mixed the solution for one hour; the colour of the solution became a light brown (solution A). In the next step, 0.8 mmol of Sodium sulfide hydrate was dissolved in 30 mL of ethylene glycol (solution B), the following sonication for one hour and then added into the solution A. Again the ultrasonic vibration exposed the mixture for two hours. Finally, the mix of the solution was transferred into a 100 mL solvo-thermal reactor and heated to 160°C for 15 h. The reactor was cooled down at lab temperature[23]. The precipitate was filtered and washed with deionized water and absolute ethanol several times. The yield product dried in the oven at 500°C for 24 h.

**RESULTS AND DISCUSSION**

The X-ray patterns were shown in Fig.1 for the ZnS nanoparticles and its nanocomposite. It can be seen the peak intensity of ZnS nanoparticles wurtzite increases with width at 2θ = 28.59° that corresponding with (1 1 1) plane of wurtzite phase. Others peaks at (33.12°, 47.56°, 56.41°, 69.50°, 76.75°) are Identical to Miller indexes (200, 220, 311, 400, 331), respectively which corresponding with spectrum standard peaks (file no. 5-566 JCPDS). This indicates that no other peaks are reporting the presence of impurities. ZnS/GNPs nanocomposite appeared in the same diffraction peaks of ZnS nanoparticle. However, no
characteristic peaks of graphene nanoplatelets was observed for the ZnS nanocomposite, which may be owing to the fact that the content of the graphene nanoplatelets was low; this result was consistent with Junli Xu et al. [24]. It is essential to apply Debye-Scherer and Bragg [25] equations were utilized to determine the particles sizes and d-spacing of energy levels, as displayed in Table 1. The results were shown the range of particles size from 11.03 to 14.41 nm.

![Fig.1: XRD pattern of ZnS and ZnS/GNPs(0.2) nanocomposite](image)

**Table 1:** XRD intensity peaks, 2-theta, crystal size, displacing, and Miller index values for the zinc sulfide-nanoplatelets nanocomposite.

| 2θ(deg) | FWHM   | crystal size(nm) | Intensity | d-spacing(nm) | Miller index |
|---------|--------|------------------|-----------|---------------|--------------|
| 28.6154 | 0.40900 | 10.23            | 848       | 0.311699      | (111)        |
| 33.1230 | 0.44670 | 9.47             | 58        | 0.270239      | (200)        |
| 47.5605 | 0.41920 | 10.57            | 488       | 0.191032      | (220)        |
| 56.4152 | 0.41270 | 11.15            | 300       | 0.162969      | (311)        |
| 69.5014 | 0.50000 | 9.87             | 46        | 0.135139      | (400)        |
| 76.7591 | 0.42340 | 12.22            | 90        | 0.124068      | (331)        |

The structural data of the zinc sulfide and its nanocomposite were also investigated by the Raman. As mentioned in XRD information, the ZnS nanoparticle have a wurtzite structure, for that the space group of the ZnS $C_{6v}$ [1]. The references were reported the zone-center optical phonons as irreducible representation: $\Gamma_{opt} = A_1 + E_1 + 2E_2 + 2B_1$. $B_1$ modes are silent.
modes, $E_1$, and $A_1$ modes for the polar modes. These modes are active in infrared and Raman spectrum\[26\]. However, the $E_2$ is a active in Raman only that has a nonpolar property. Fig. 2 depicts the Raman spectrum of the ZnS and ZnS/GNPs as-prepared. The intense peak at 342 cm$^{-1}$ that refers to scattering peak of ZnS. This is indicates to the LO phonon mode of zinc sulfide. The a weak peak in 274 cm$^{-1}$, which consists to the TO phonon mode of zinc sulfide.

![Fig. 2: Spectrum of Raman spectroscopy of ZnS and ZnS/GNPs.](image)

The Raman spectra for the ZnS/GNPs(0.2) shows the characteristic peaks of G and D peaks at 1574 and 1407 cm$^{-1}$, respectively. As it known the G-band is a consequence of the first order scattering (E$_{2g}$) mode for sp$^2$-carbon domains\[23,27\]. Furthermore, D-band is related with the dis-ordered of graphene edges. Thus, these results have confirmed the formation of the ZnS and ZnS/GNPs.
To study the change of the photocatalytic activity mostly evidently. The relative characterization of the zinc sulfide-based catalyst was carried out with its graphene nanoplatelets. **Fig. 3** illustrated the Nitrogen adsorption-desorption isotherms with pore diameter information of nanoparticles as-prepared. It was cleared in **Fig.3**, the isotherms belonged to standard of IUPAC recommendation type IV isotherms to display a multilayer adsorption on the zinc sulfide and its nanocomposite with H3 hysteresis loops[28]. This is pronounced and was affirmed the presence of mesoporous – structure form the Brunauer–Emmett–Teller (BET) data with specific surface area of 37.48 and 26.50 m²/g for ZnS and ZnS/GNPs(0.2), respectively. The Barrett-Joyner-Halenda (BJH) results was shown the pore volume and pore diameter are 0.195 cm³/g and 15.72 nm for ZnS; 0.136 cm³/g and 1.71 nm of zinc sulfide – graphene nanoplatelets, respectively, which confirmed the presence of mesoporous – structure for the ZnS nanomaterials (the average between 2-50 nm ). in contrast, the pore diameter in ZnS nanocomposite is related to the microporous under super-micropores type (1.4 to 2 nm). The results of BET and BJH were offered the dramatic change when added the nanoplatelets. The effectiveness of the structure of nanomaterial which may modify the properties when utilising in Hydrogen generation *via* photoelectrocatalytic water splitting applications.
Fig. 4: DRS plots of for ZnS and ZnS/GNPs

As a ZnS and ZnS/GNPs semiconductor, to additional known the band gap, Diffuse reflectance spectroscopy (DRS) was recorded for the materials as-prepared (Fig.4). Clearly, the light absorption of ZnS/GNPs increased in visible region owing to the black color of graphene nanoplatelets. Moreover, the apparent red shift in the absorption edge of zinc sulfide nanocomposite shows increasing the light harvesting ability of the ZnS/GNPs semiconductor. For that, the energy of band gap of ZnS/GNPs nanocomposite decrease in comparison with ZnS nanoparticles from the 3.58 eV for the zinc sulfide nanoparticles to about 3.27 eV for the ZnS/GNPs nanocomposite (Fig.4). The energy of band gaps were estimated from the Tauc's relation[5,29], that is, a plot of photon energy ($h\nu$) versus ($\alpha h\nu)^{1/2}$
Fig. 5: FE-SEM images of ZnS nanoparticles (a) and ZnS/graphene nanoplatelets (b), with the EDS spectrums.
By the field emission electron spectroscopy (FE-SEM), as shown in Fig. 5 a,b. It can be cleared the ZnS nanoparticles the particles have a semi-spherical shape and aggregations with high order due to the high temperature of the calcination process is effected to a uniform of the nanoparticles and the range crystal size from 38 to 58 nm. The FE-SEM image (Fig. 5.b) of ZnS/GNPs nanocomposite was demonstrated as the graphene adhered to zinc sulfide particles to reduce the crystal size to be in a range (31-44) nm. Furthermore, the energy-dispersive X-ray spectrometer (EDS) spectra's results displayed the high dispersion of elements in the ZnS with its nanocomposite. For that, the composition of elements for the ZnS/ GNPs included the Zinc, sulfide, and carbon. Furthermore, the ratio of the S/Zn is 0.54 for the ZnS nanoparticles, while the ratio of elements to be about 0.94. this is good indicates for the synthesis of zinc nanocomposite change in the ration value , as a result to add the graphene nanoplatelets. Obviously, the layers sheets were recognized that decorated with the ZnS nanoparticles.

![Fig. 5: FE-SEM images of (a) ZnS nanoparticles and (b) ZnS/GNPs nanocomposite.](image_url)

The ZnS nanoparticles and its nanocomposite was further affirmed from the FTIR analysis as shown in Fig. 6.a,b. The characteristic FTIR features of ZnS nanoparticles indicated the presence of broadband concentrated at 612 cm\(^{-1}\) attributed to the vibrations of Zn-S in the inorganic crystal lattice. Moreover, the other two bands at 851 cm\(^{-1}\) due to the OH bending. The broadband in 3450 cm\(^{-1}\) indicates OH stretching that results from the interaction between the surface of ZnS nanoparticles and adsorbed the water molecules (OH- group) on surface zinc sulfide nanoparticles. The spectra has also displayed the presence of a weak bands at 2921, 2847,2353,1634, and 1409 cm\(^{-1}\) that are related to zinc sulfide nanoparticles. In the ZnS/ graphene nanoplatelets observed peak at 1130 cm\(^{-1}\) was assigned to the C-H bending band and at 1414 cm\(^{-1}\) is attributed to bending vibration of the C=C bond. Also, it was seen a
peak at 1638 cm\(^{-1}\) that is related to the C=O vibration bond as well as the peaks at 670, 503, and 3400 cm\(^{-1}\) were assigned to the Zinc – sulfur bond and hydroxyl group vibrations, respectively.

CONCLUSION

In the present work, ZnS and ZnS/graphene (0.2) were successfully prepared by one-step solvothermal. The XRD results confirmed the formation wurtzite phase with high purity. The peak of graphene sheets has disappeared clearly in (002) Miller index due to the content of the graphene nanoplatelets may be minimal. But, the FE-SM, Raman, and FTIR results have used to characterize the zinc sulfide and its nanocomposite. The graphene sheets changed the ZnS properties, that be cleared via enhancement the energy of bandgap value to become about 3.27 eV for the ZnS/GNPs(0.2), which indicates to use in photoelectrocatalytic applications for water splitting to produce hydrogen gas.

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