Photocatalytic activity, nanostructure and optical properties of 3D ZnS urchin-like via hydrothermal method

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ABSTRACT
In the present research, the fabrication and characterization of ZnS urchin-like nanoparticles (ULNPs) via simple, template free and one-step hydrothermal method are reported. Zinc acetate dihydrate, thiourea and ethylenediamine are utilized as precursors. Nanostructure characterization of three-dimension ZnS ULNPs is specified by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) and ultraviolet-visible (UV-Vis) spectroscopy. The photocatalytic activity of ZnS NPs is determined by measuring the degradation of an organic dye methylene orange (MO) under UV-irradiation. The lattice characteristics such as nanocrystallite size, strain, stress, and deformation energy density are specified using Williamson-Hall (W-H) and Halder-Wagner (H-W) analysis with different considerations about the isotropic nature of the crystal. XRD analysis reveals that ZnS NPs are hexagonal wurtzite phase. The shape and mean diameter of NPs are demonstrated by TEM and SEM techniques to be 3D urchin-like with an average size of 60 nm. N2 adsorption-desorption and UV-Vis spectroscopies are utilized to specify the optical characteristics such as mean pore diameter, total pore size, and BET special surface area. The band gap of fabrication ZnS NPs has been evaluated from the Tauc equation and absorption edge to be 3.84 eV.

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1. Introduction

In recent years, zinc supplied (ZnS) NPs have been subjected due to their extensive range applications and versatile characterizations such as large surface to volume ratio as well as quantum confident effects. Recent findings revealed various exquisite optical, physical and chemical properties of ZnS that are utilized extensively in various scopes of technology such as solar window layers, IR windows [1], flat panel display [2], electro-optics, photoconductors and electroluminescence [3], UV diodes [4]. Many researchers are devoted to expanding the novel fabrication method to synthesize nanostructure composites. ZnS is one of the II-VI compound semiconductors with a wide band gap in two known crystallite phase, cubic zink blend and hexagonal wurtzite, that reveal a large exciton binding energy about 40 meV and band gaps of 3.72 eV and 3.77 eV, respectively [5].

Various procedures have been developed to fabricate ZnS nanostructures such as electrochemical deposition [6], microemulsion [7], solvothermal [8], sol-gel [9,10], co-precipitation [11,12], combustion synthesis [13], pyrolysis [14], hydrothermal [15], laser ablation [16] and vapor deposition [17]. The hydrothermal method is versatile, high ability in controlling the process, productive, adjustable, not needing calcination and milling operation, low contamination and cost-effectiveness [18–20].

The physical and chemical properties of ZnS nanostructures drastically depend on dimension, size and morphology of V. ZnS nanostructures are fabricated by different geometrical dimension and shapes such as zero-dimensional (0D) in biological detection and labeling [21], one-dimension (1D) tube, rod, wire particles or two-dimension (2D) sheets [22–24], three-dimension (3D) arrays of 1D structures may provide many practical applications show enhanced optical-electrical properties for nanodevices [25–27].

The structure of NPs is drastically affected by crystallite size, lattice characteristics, stability, and lattice imperfection. The imperfection of crystals dimension in all directions is because of their finite size. This imperfection causes to broaden the diffraction peaks in XRD spectra that reveals two principal reasons for broadening, crystallite size and lattice strain. The crystallite size and strain closely impress the Bragg peak via peak width, intensity and shifting the position of the peak in $2\theta$. Crystallite size and strain are affected by two main factors, poly-crystallinity aggregation, and distribution of lattice constants, respectively. Lattice constants are further impressed by lattice dislocations and partly from coherency stresses, stacking faults, ad-atoms, grain boundary triple junction, etc. [28–30]. Williamson-Hall approach is applied to measure the crystallite size and strain on the basis of integral breadth, observing the peak width as a function of degree ($2\theta$). In this research, the strain, crystallite size, stress and strain energy density of ZnS ULNPs are estimated by a modification of the W-H method, namely, UDM, UDSM, UDEDM.

The advanced oxidation processes (AOPs) show more impress than conventional methods to remove the complex organic pollutions and industrial contaminations [31,32]. Among semiconducting nanomaterials, ZnS nontoxic NPs are well-known as excellent photocatalyst because of its unique optical properties such as band gap energy, retention time, the high light absorption, electron-hole recombination time, high negative reduction-oxidation potential of excited electrons and ability of generation the plenty of electron-hole pairs [33,34]. Photocatalytic performance is intensely related to nanostructure characteristics. Enormous attempts have been devoted to enhancing the photocatalytic efficiency of ZnS NPs by altering the nanostructure features via diverse methods and procedures [35–37].
This research accounts for the fabrication of ZnS ULNPs by the hydrothermal method. Besides, modification W-H models have been applied to investigate the nanostructure and lattice strain.

2. Experimental procedure and details

In order to synthesize the ZnS three-dimensional ULNPs, zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, ≥ 98% ≥ 99%, Merck co.), thiosemicarbazide (NH₂CSNHNH₂, ≥ 98% ≥ 98%, Merck co.), ethylenediamine (C₂H₈N₂, ≥ 98% ≥ 99%, Merck Co.) and deionized water are used as precursors without further impurity and purification. Thiosemicarbazide and zinc acetate dihydrate salts are applied as ligand and metallic source, respectively. Firstly, a solvent of ethylenediamine and deionized water are provided in the volume ratio of 1:1. Then, zinc acetate dihydrate and thiosemicarbazide are dissolved with 1:2 molar ratio in the above solvent under vigorous magnetic stirring for 15 min and afterward, dispersed in the ultrasound bath for 10 min (model: Sono Swiss, 45 kHz) at room temperature. The obtained solution is inserted inside a thick-walled stainless-steel autoclave equipped with Teflon-walled container with 80 mL inner capacity to endure high pressure, corrosion, and temperature. The chemical reaction is carried out at 200°C for 10 h, and then the container is cooled down in an ice-bath abruptly to prevent the formation of ZnS.0.5 complex at 200°C. Formation of pure-phase ZnS.0.5 complex indicates ≥ 90% product yield, then ethylenediamine is applied as the reactive solvent according to following reversible reaction which occurs at 200°C in the pressure of ethylenediamine (EN):

\[
\text{ZnS.0.5 + (EN) } \leftrightarrow \text{ ZnS + 0.5 (EN)}
\]

Where as the autoclave is quenched to room temperature by ice-bath, the reversible reaction is prevented and the pure hexagonal ZnS could be obtained. Afterward, a white gel product is gathered by centrifuge at 5000 rpm from the Teflon container and washed several times by deionized water and ethanol to eliminate the impurities and pollutions. Finally, the product is dried in a vacuum chamber for 6 h at 60°C. The crystalline structure and phases of 3D ZnS ULNPs are specified by XRD analysis (model: GBC-MMA) using Cu Ka radiation (λ = 0.15406 nm, 0.02° step size and 10 deg/min radiation speed) equipped with Nickel filter over the range of 10–80 degrees (2θ). The morphology of the samples is investigated by SEM (model: Hitachi S-4160) equipped with EDX and TEM (model: Philips CM120). The photocatalytic activity of fabricated NPs is determined by the photodegradation of MO under UV light (Philips, 253.70 nm) using UV-spectrophotometer (model: Varian 50 scan). The chemical binding of the product is characterized by FT-IR spectra recorded on (model: Perkin-Elmer Pyris) in the range of 400–4000 cm⁻¹ using KBr pellets. The optical absorption and transmission of ZnS NPs are evaluated in the range of 190–800 nm by using a UV-Vis spectrophotometer (model: Shimadzu UV-2550-8030) with slit width of 0.5 nm and light source wavelength of 360 nm at room temperature.

3. Results and discussion

XRD patterns of ZnS NPs are utilized to estimate peak broadening, crystallite phase, crystallite size, and lattice strain. As shown in Figure1, the intensity of narrow peaks
indicates high sharpness, fine grain size, and well crystallization in the hexagonal wurtzite phase, while there are not extra diffraction peaks associated with other irrelevant phases and impurities. All preferred diffraction peaks truly correspond to the Joint Committee on Powder Diffraction Standards (JCPDS) card No. 1314-98-3, as well as located at 2θ values of 26.80°, 28.60°, 30.60°, 47.50°, 51.90°, 56.50°, 62.40°, and 73.30° correspond to Miller indices (hkl): (100), (002), (101), (110), (103), (112), (202) and (203) of wurtzite crystallite phase, respectively. The interplanar space values (d-space) and Miller indices can be calculated via the Bragg equation ($nλ = 2d \sin θ$). The cell constants and unit cell volume of the wurtzite crystallite phase of ZnS NPs are obtained from the Lattice Geometry equation as indicated below [38] and summarized in Table 1.

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + k^2 + l^2}{a^2} \right) + \frac{l^2}{c^2}
\]

\[
V = \frac{\sqrt{3}a^2c}{2}
\]

3.1. Crystallite size and strain
Dislocation affects on the crystallite size and lattice strain ($ε$) by broadening the diffraction peaks [39]. The crystallite size and lattice strain of ZnS NPs are calculated by the breadth of the Bragg peak using the Scherrer equation:

\[
L = \frac{kλ}{βD\cosθ}
\]
Table 1. Structure data and geometric parameters of the wurtzite crystalline phase of ZnS NPs.

| 2θ deg | d Bagg (nm) | d_o Bagg (nm) | d_{Bragg} (nm) | E_{rel} (GPa) | D UDM (nm) | D USDM (nm) | D UDEDM (nm) | D SSP (nm) | ε_{SSP} x 10^{-4} | σ_{SSP} MPa | u (X/y) |
|--------|-------------|---------------|----------------|----------------|------------|------------|------------|------------|----------------|-------------|--------|
| 26.8   | 100         | 33.0          | 32.2           | 87.87          | 50.41      | 5.649      | 45.16      | 4.344      | 38.59          | 44.00       | 10.89  |
| 28.6   | 002         | 31.20         | 30.60          | 122.85         | 45.15      | 4.95       | 45.15      | 4.95       | 44.00          | 10.89       | 11.96  |
| 30.6   | 101         | 29.20         | 28.70          | 80.79          | 47.5       | 5.19       | 46.10      | 5.19       | 43.12          | 5.19        | 11.96  |
| 47.5   | 110         | 19.10         | 18.70          | 87.87          | 51.9       | 9.03       | 51.9       | 9.03       | 46.10          | 11.96       | 11.96  |
| 51.9   | 103         | 17.60         | 17.30          | 90.31          | 56.5       | 16.00      | 56.5       | 16.00      | 80.159         | 16.00       | 80.159 |
| 56.5   | 112         | 16.30         | 16.00          | 80.159         | 62.4       | 14.40      | 62.4       | 14.40      | 80.799         | 14.40       | 80.799 |
| 62.4   | 202         | 14.60         | 14.40          | 80.799         | 73.3       | 12.70      | 73.3       | 12.70      | 80.03          | 12.70       | 80.03  |

Additional data:
- a = 0.382 nm
- c = 0.625 nm
- c/a = 1.63
- V = 0.0789 nm³
where \( L \) is the crystallite size, \( \lambda \) is the wavelength of the X-ray radiation (0.154056 nm), \( k \) is a Scherrer’s shape factor equal to 0.9, \( \beta_D \) is the peak width at the half-maximum intensity and \( \theta \) is the peak position in half diffraction angle (Bragg’s angle).

Instrument and sample-dependent broadening affect on the total breadth. In order to separate these portions, it is incumbent to obtain the instrumental broadening by including diffraction patterns of standard material (e.g., silicon). The correction of instrumental broadening (\( \beta_D \)) associated with the diffraction peak of wurtzite ZnS NPs is calculated by using the following relation:

\[
\beta_D = \left( \frac{(\beta)_{\text{measured}}^2 - (\beta)_{\text{instrumental}}^2}{C_{138}} \right)^{1/2}
\]  

Therefore, in Scherrer equation \( \beta_D \) is substituted by the instrumental corrected integral breadth of the reflection (in radians).

In order to determine the nanocrystallite size, the term \( \cos \theta \) is plotted with respect to \( \frac{1}{\beta} \) for the preferred orientation peaks of ZnS with the wurtzite phase considered between 10°-80°. Accordingly, the crystallite size \( L \) is extracted from the slope of the fitted line to be 50.41 nm (Figure 2(a)), while applying Equation (1) for the most intensive diffraction peak (200) located at \( 2\theta = 28.6^\circ \), the average grain size obtained is 43.32 nm. The total broadening of diffraction peaks is ascribed to the microstrain induced and size induced broadening. The extent of coherently diffracting domains determines the crystallite size. Strain-induced broadening is attributed to crystallite imperfections and lattice distortions, determined by:

\[
\varepsilon = \frac{\beta_L}{\tan \theta}
\]  

As indicated in Equations (1) and (5), the dependency of the peak width and lattice strain on diffraction angle (\( \theta \)) are obviously different. In Equation (1), the peak width relates to \( \cos \theta \), whereas, in Equation (5) the lattice strain varies as \( \tan \theta \). This remarkable difference develops an approach to separate the microstrain and size broadening in total reflection.

Figure 2. XRD patterns and modified models of Williamson-Hall analysis of the wurtzite crystalline phase of ZnS NPs.
broadening by obtaining a mathematical function of $2\theta$ (Bragg’s angle). The explicit dependency of both factors establishes a method to separate the mentioned portions in the Williamson-Hall equation [40]. A combination of the Equations (1) and (5) results in the following equations. Whereas $\beta_{hkl}$ is the total integral breadth of Bragg peak, $\beta_D$ is the instrumental-corrected broadening arising from causes-small crystallite size, $\beta_{hkl}$ is the microstrain broadening arising from crystallite imperfection and distortion.

$$\beta_{hkl} = \beta_D + \beta_S$$  

(6)

$$\beta_{hkl} = \left( \frac{k\lambda}{L \cos \theta} \right) + 4\varepsilon \tan \theta$$  

(7)

$$\beta_{hkl}\cos \theta = \frac{k\lambda}{L} + 4\varepsilon \sin \theta$$  

(8)

The above approach introduces Uniform Deformation Model (UDM), whilst the strain is considered to be uniform in all crystallographic directions. This consideration supposes that material characterizations are independent of measured directions so that the nature of crystal is assumed to be isotropic. A plot is drawn with $(\beta_{hkl}\cos \theta)$ on the x-axis and $(4\sin \theta)$ along the y-axis for the preferred orientation peaks of ZnS wurtzite crystallite phase. The strain and crystallite size could be determined from the slope and y-intercept of the fit line, respectively (Figure 2(b)).

In the Uniform Stress Deformation Method (USDM), the principal assumption is anisotropic nature of the crystal and the linear proportionality between lattice stress ($\sigma$) and strain ($\varepsilon$) according to the generalized Hook’s law $\varepsilon = \frac{\sigma}{E_{hkl}}$, where $E_{hkl}$ is introduced as Young’s modulus in the direction perpendicular to the set of lattice planes (hkl) corresponding to the preferred peaks and $\sigma$ is the lattice stress. The acceptance of this model depends on the small size of the strain so that with a further increase in the strain size the linear proportionality between lattice strain and stress deviates. Therefore, in this model, the Williamson-Hall equation (Equation 8), is modified as: The Young’s modulus and the relation between elastic compliances $S_{ij}$ for hexagonal crystallite phase are given by the following equation:

$$\beta_{hkl}\cos \theta = \frac{k\lambda}{L} + 4\varepsilon \sin \frac{\theta}{E_{hkl}}$$  

(9)

$$E_{hkl} = \frac{\frac{h^2 + (h+2k)^2}{3} + \frac{\frac{h^2 + (h+2k)^2}{3} + \frac{(h+2k)^2}{3}}}{S_{11}\left(\frac{h^2 + (h+2k)^2}{3}\right)^2 + S_{33}\left(\frac{h^2 + (h+2k)^2}{3}\right)^4 + (2S_{13} + S_{44})(h^2 + \frac{(h+2k)^2}{3})(\frac{\theta}{E_{hkl}})^2}$$  

(10)

where $S_{11}, S_{13}, S_{33}, S_{44}$ are the elastic compliances of ZnS wurtzite hexagonal crystallite phase and their values are $11.38 \times 10^{-12}, -2.24 \times 10^{-12}, 8.14 \times 10^{-12}, 33.98 \times 10^{-12} m^2/N$, respectively [41].

According to this model, the uniform lattice stress ($\sigma$) and crystallite size ($L$) could be determined from the slope line and y-intercept of linear fitted line plotted between $\frac{4\sin \theta}{E_{hkl}}$ and $\beta_{hkl}\cos \theta$, respectively (Figure 2(c)). Average Young’s modulus ($E_{hkl}$) for hexagonal ZnS NPs is estimated as 88.83 GPa. The mentioned models indicate the homogenous nature of crystals, whilst this assumption is not confirmed generally. The deformation energy density
(u) could be determined by considering the Hook law in the elastic lattice. This assumption is enough to regard the relation between the strain energy density \( u \) (energy per unit volume) and strain as a function of \( u = \frac{E_{hkl} \varepsilon^2}{2} \). Therefore, Equation (9) can be adjusted to the form:

\[
\beta_{hkl} \cos \theta = \frac{k\lambda}{L} + 4 \sin \theta \left( \frac{2u}{E_{hkl}} \right)^{1/2}
\]

(11)

Figure 2(d) indicates the plot of \( \beta_{hkl} \cos \theta \) versus \( 4 \sin \theta \left( \frac{2u}{E_{hkl}} \right)^{1/2} \). The deformation energy density \( u \) and crystallite size \( L \) are calculated from Uniform Deformation Energy Density Model (UDEDM) by determining the slope and y-intercept of the linear fit, respectively. Due to the existence of micro-strain portion and isotropic diffraction domains, the Williamson-Hall plots include the isotropic broadening. By including the strain energy density, the proportionality constants in strain-stress correlation are dependent.

In the condition of isotropic line broadening, a suitable assessment is carried out, so that the symmetric Voigt function gives the size-strain parameters by considering an average size-strain plot (ssp), which shows more benefit. According to the Halder-Wanger model, the crystallite size and strain profiles are characterized by the Lorentzian and the Gaussian function, respectively [42]. By this method, the data for reflections at low and mid-angles are considered more significant and more weight than those at higher angles where the accuracy is generally lower. The SSP method can be written according to the size and strain relation:

\[
(\beta_{hkl}d_{hkl}\cos \theta)^2 = \frac{K}{L} \left( d^2_{hkl}\beta_{hkl}\cos \theta \right) + \left( \frac{\varepsilon}{2} \right)^2
\]

where \( K \) is a shape constant that for spherical it is considered as \( 4/3 \). As shown in Figure 2(e), \( (\beta_{hkl}d_{hkl}\cos \theta)^2 \) versus \( (d^2_{hkl}\beta_{hkl}\cos \theta) \) for the all orientation peaks of wurtzite ZnS NPs is plotted. The mean value of the strain and crystallite size are determined by the y-intercept and slope of linear fitted data, respectively.

In order to estimate the proper portion of the residual or applied stresses in a polycrystalline patterns, the root-mean-square lattice strain \( \varepsilon_{RMS} = \sqrt{\frac{2}{\pi} \frac{d_{hkl} - d_{0hkl}}{d_{0hkl}}} \) is presented. For this purpose, it is required to take into account only those grains which are correctly oriented according to the x-ray incident beam. Here, \( d_{hkl} \) and \( d_{0hkl} \) denote the observed and ideal interplanar spacing of the ZnS wurtzite crystallite phase. Consequently, elastic compliances \( S_{ij} \) of ZnS wurtzite phase connecting the \( \varepsilon_{RMS} \) estimated from UDEDM for the specific set of planes. Substantially, if there is a slight scattering of the data points around a straight line making an angle of 45° with the x-axis, there is an acceptable agreement between strains derived from the root-mean-square \( \varepsilon_{RMS} \) and UDEDM. This linear variation theoretically suggests that there is no variance on the nature of nanocrystallite of hkl planes and strain may be caused by dislocation as well as the excess growth of grain boundaries [43].

Various values of lattice deformation parameters may be inferred corresponding to different Williamson-Hall models. Among the mentioned models, SSP is the most appropriate model reveals the most compatibility to the experimental results. By comparing the data of three lattice deformation models, one can see the data scattering away from a linear relation for model SSP is less than the rest.

The wurtzite crystallite phase shows two types of the nearest-neighbor, associated with the first-nearest distance (bond length) between closely anion-cation adjacent. Bond
strength depends on band distance that is estimated by the bond theory. The first-bond length for one bond ($L_{1b}$) and three bonds ($L_{3b}$) of Zn-S could be calculated by these following equations, respectively.

$$L_{1b} = uc$$  \hspace{1cm} (13)

$$L_{3b} = \left[ \frac{a^2}{3} + \left( \frac{1}{2} - u \right)^2 c^2 \right]^{\frac{1}{2}}$$  \hspace{1cm} (14)

where $a$ and $c$ denote the lattice constants, while $u$ denotes the positional parameter, it also presents the cell-internal ratio by measuring the distance of each atom where located associate with the next atom along the $c$ axis [44]. $u$ could be measured by the following relation:

$$u = \frac{1}{3} \left( \frac{a}{c} \right)^2 + 0.25$$  \hspace{1cm} (15)

The values of $L_{1b}$, $L_{3b}$ and $u$ are calculated as 1.430 Å, 2.341Å and 0.3744, respectively. Figure 3 reveals the morphology of 3D ZnS ULNPs n prepared by hydrothermal method. As shown, a large number of microspheres particles with an average size of 60–70 nm that is composed of enormous packed tiny nanorods. The perpendicular growth of nanorods on the micro-spheres surface and make up an urchin-like structure is due to attaining a stable condition with low total particles energy. This morphology of NPs is approved and investigated by TEM. It is thoroughly observed the formation of urchin-like spheres with an average diameter of 60 nm, in different magnifications. As seen in Figure 5, the surface of spheres is made of thin needle rods. N nano-clusters made up of nanorods within the hydrothermal process, based on liquid-solid transformation. According to Figure 4, the energy dispersive of 3D ZnS ULNPs reveals the presence of Zn and S atoms in the nanostructure without the further impurity or unwanted elements.

Figure 3. SEM images of 3D ZnS ULNPs, (a) ZnS microspheres (b) surface of ZnS microspheres.
It is worth noting that the nanocrystallite size calculated from above-mentioned deformation models is consistent with the TEM and SEM results.

In order to investigate the optical absorption characteristic of the NPs, the prepared NPs were dispersed in deionized water by ultrasound at 45 kHz for 5 min. The shoulder of the absorption peak associated with the absorption edge could be utilized to measure the band gap of nanomaterials. Figure 6(a) reveals a UV-Vis absorption spectrum of ZnS NPs. As seen, the shoulder of the absorption curve corresponding to the exciton energy lies at 266 nm which shows blue-shifted compared with the bulk samples (340 nm) due to the
quantum size effect. The measurement of the absorption edge indicates that the band gap of ZnS NPs 4.67 eV (306 nm) is more than the bulk samples.

In order to investigate the optical band gap, firstly the optical absorption coefficient $\alpha(\lambda)$ is derived from the evaluated spectral extinction coefficient $k(\lambda)$ by utilizing the following equation [45]:

$$\alpha(\lambda) = 4\pi k(\lambda)$$  \hfil (16)

where $\lambda$ is the wavelength of the incident photon energy. The optical direct and indirect band gap, $E_g$ for ZnS NPs are measured by fitting the reflection data to applying the Tauc expression [46,47]:

$$\alpha h\nu = A(h\nu - E_g)^n$$  \hfil (17)

where $\alpha$ is the optical absorption coefficient, $h\nu$ is the incident photon energy, $A$ is the relation constant and $E_g$ is the direct and indirect band gap depends on $n$ values of 0.5 and 2 corresponding to direct and indirect allowed transition, respectively. The value of $n$ is chosen 0.5, which is the case of ZnS NPs. The optical band gap $E_g$ of ZnS NPs can be estimated by extrapolating the linear portion of the absorption plot of $(\alpha h\nu)^n$ against the $h\nu$ to the energy axis (Figure 6(b)). The measured direct optical band gap $E_g$ for ZnS NPs is 3.43 eV, which is smaller than the band gap of the bulk ZnS (3.6 eV). This evaluation is in line with the similar previous investigations [46].

The generation of electron-hole pairs after absorbing high energy photons is subjected to the photocatalytic performance of photocatalyst nanomaterials. Superoxide and hydroxyl high reactive radicals ($O_2^-$, $OH$) attack to the complex organic compounds and degrade them to simple and harmless components.

Photocatalytic activity and potential applicability of ZnS nanostructure are evaluated by the photodegradation of methylene Orange dye. For this purpose, a stock solution is prepared by adding 70 mg of ZnS nanopowder into 100 mL of 3.75 ppm MO solution at pH = 5.5 and kept in a dark place. The experimental results exhibit that visible light exposure is of no effect on the photodegradation of MO. Before irradiation under UV light, every 10 min a certain amount

![Figure 6](image-url). (a) Optical absorbance spectra versus wavelength, (b) The band gap of the evaluation from the curve of $(\alpha h\nu)^2$ versus incident photon energy ($h\nu$).
(10 mL) of reaction suspension of stock solution is taken and sonicated at 40 kHz for 5 min in a dark place in order to make a uniform dispersion and absorption-desorption equilibrium. Thereinafter, at periodic intervals (10, 20, 30, 40, 50 and 60 min), the taken reaction solution is irradiated under two UV-c lamps (Philips, 253.7 nm, 33.6 μW cm⁻²), then centrifuged at 5000 rpm for 2 min and immediately filtered through a 0.1 Millipore membrane to settle and eliminate the NPs suspended. Ultimately, the absorption of the filtered solution is determined by the UV-Vis spectrophotometer at 503 nm as shown in Figure 7. Figure 8 indicates the time-dependent absorption spectra of MO that focused at 503 nm. The intensity of absorption curves gradually reduce with increasing the time irradiation due to photodegradation and decoloration of MO. This graph reveals the curve of $\frac{C}{C_0}$ versus the time irradiation and shows the photodegradation is about 80% after 60 min.

The photocatalytic performance of ZnS ULNPs can be measured by calculating the photodegradation rate of the aqueous solution of MO influenced by ZnS NPs under UV irradiation specified as comparative expression:

\[
\text{Photodegradation rate\%} = \frac{100}{\ln \left( \frac{C_0 - C}{C} \right)}
\]

where $C_0$ and $C$ are the initial and equilibrium contamination (MO) concentration, respectively. Kinetical calculation of photodegradation of ZnS NPs can be explained by the pseudo-first kinetic model proposed by Langmuir-Hinshelwood:

\[
\ln \left( \frac{C_0}{C} \right) = kt
\]

Figure 7. UV-Vis absorption spectrum of MO aqueous solution in the presence of 3D ZnS ULNPs.
where \( k \) denotes photodegradation rate constant \( (\frac{1}{\text{min}}) \). The variation of comparative concentration of MO in the logarithmic scale against UV-irradiation time is plotted in Figure 9. The photodegradation rate of ZnS NPs is evaluated 0.0315 \( \frac{1}{\text{min}} \) from the slope of the logarithmic plot.

In order to study the available chemical bonds on fabricated ZnS NPs, the FTIR spectra in the range of 400–4000 cm\(^{-1}\) are investigated in the as-prepared and the product that was preheated at vacuum oven at 200°C for 2 h. Figure 10 shows characteristic peaks at 3442, 1627, 659 and 1012 cm\(^{-1}\). As seen, the peak at 3442 cm\(^{-1}\) is associated with anti-symmetrical and symmetrical \( \nu(\text{OH}) \) bonding stretching vibrational modes. The band 1627 cm\(^{-1}\) is attributed to the bending vibration of hydroxyl groups. By increasing the temperature for the heated product, the intensity of 3442 and 1627 cm\(^{-1}\) peaks decreases due to the vaporization of the liquid. The weak bands located at 657 and 1012 cm\(^{-1}\) are assigned to the Zn-S vibration bond [48].

The Brunauer-Emmet-Teller (BET) isotherm investigates the physical surface and porosity of ZnS NPs by measuring the adsorption versus relative pressure in static equilibrium. To this purpose, the N\(_2\) adsorption-desorption isotherm is carried out at 77 K. According to International Union of Pure and Applied Chemistry (IUPAC) classification, Figure 11 illustrates the N\(_2\) physisorption isotherm is assigned to the type VI, while the hysteresis loop is similar to H2, over the range of 0.39 < \( \frac{P}{P_0} < 0.88 \). This isotherm indicates capillary condensation in meso and macropores, while closure at about \( \frac{P}{P_0} \sim 0.4 \) predicates on the presence of small mesopores. Additional porosity parameters including Burret-Joyner-Halenda (BJH) pore size distribution, the BET specific surface area (\( S_{\text{BET}} \)) and total pore volume are calculated and tabulated in Table 2, whilst, \( r_{p,\text{peak}} \) and \( r_m \) indicate the peak of the size and mean pore diameter in pore size distribution. According to the adsorption-desorption profile (Figure 11 (a)), about 90% of porosity belongs to mesopores.
Figure 9. The kinetic linear relation between Ln(C₀/C) and UV irradiation time.

Figure 10. FTIR spectra for (a) as-prepared and (b) preheated ZnS NPs.
4. Conclusions

In summary, 3D ZnS ULNPs have been successfully fabricated by the hydrothermal method, while the shape, size, and structure were homogeneous and controllable. XRD analysis demonstrated that the fabricated NPs possess a wurtzite structure. The broadening of XRD peaks is independently associated with strain and size effects, while investigated by four models, i.e., UDM, UDSM, UDEDM, and SSP. These models are carried out to determine the lattice strain, stress and deformation energy values depending on the isotropic and homogenous nature of the materials. The results have shown that the SSP is the most appropriate model to determine the size and strain. SEM and TEM images show the morphology and size of ZnS NPs to be urchin-like and about 60 nm, respectively. Mean pore diameter, total pore size, and BET special surface area were calculated by the N₂ adsorption-desorption. Methylene orange was utilized as an organic contaminant dye to determine the photocatalytic activity of ZnS NPs by photodegradation of it under UV irradiation. The photocatalytic activity rate was calculated to be $0.0315 \frac{1}{\text{min}}$. FTIR transmission spectrum was carried out to investigate the existing chemical bonds as well as vibration modes. The optical band gap of fabricated ZnS NPs was calculated to be 3.43 eV.

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Disclosure statement

No potential conflict of interest was reported by the authors.
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