Synthesis, Structure And Characterization Of Zns Qds And Using It In Photocatalytic Reaction

Khalid T. Al- Rasoul, Issam M. Ibrahim, Iftikhar M. Ali, Raad M.Al-Haddad

Abstract: ZnS nanoparticles were prepared by a simple microwave irradiation method under mild condition. The starting materials for the synthesis of ZnS quantum dots were zinc acetate (R & M Chemical) as zinc source, thioacetamide as a sulfur source and ethylene glycol as a solvent. All chemicals were analytical grade products and used without further purification. The quantum dots of ZnS with cubic structure were characterized by X-ray powder diffraction (XRD), the morphology of the film is seen by scanning electron microscopy (SEM). The particle size is determined by field effect scanning electron microscopy (FESEM), UV-Visible absorption spectroscopy and XRD. UV-Visible absorption spectroscopy analysis shows that the absorption peak of the as-prepared ZnS sample (310 nm) displays a blue-shift comparing to the bulk ZnS (345 nm). Photoluminescence spectra of the samples revealed a broad peak centered at 404nm, which were related to excitonic emission. Photocatalytic degradation of Methylene Blue (MB) dye catalyzed by synthesized nanoparticles was studied under solar radiation, photocatalytic degradation increased with increasing time exposure to solar light.

Index Terms: Degradation, Photoluminescence, precipitation method, Microwave irradiation**,** nanoparticles, Quantum dots and ZnS

1 INTRODUCTION

In the last decade many efforts have been dedicated to synthesis and study the physicochemical characterization of nanometer-scale semiconductors. Nanoparticle synthesis has opened alternative ways in the design of materials with new properties. Interest in semiconductor nanoparticles is justified by the fact that fundamental physical and chemical properties of them can be very different from those of the bulk materials. Their reduced dimensions enable one to reduce the size of electronic circuitry. They are expected to have higher quantum efficiencies due to increased oscillator strengths as a result of quantum confinement[1]. Zinc sulfide, a wide direct band gap of II–VI compound, is one of the most typical and important crystalline materials for both application and research [2–7]. Photocatalysis is a process by which a semiconductor material absorbs light of energy greater than or equal to its band gap, causing excitations of valence band electrons in the conduction band. Such charge separation leads to the formation of electron-hole pairs which can further generate free radicals in the system for redox of the substrate. The resulting free-radicals such as hydroxyl (•OH) are very efficient oxidizers of organic materials and can degrade pollutants [8,9]. The present work focuses on the feasibility study of synthesizing nano ZnS by microwave processing.

- *Khalid T.Rasoul is assistant prof. in Univ. of Baghdad,colleage of science,Iraq,baghdad. E-mail: kmahdi39@yahoo.com*
- *Issam M.ibrahim assistant prof. in Univ. of Baghdad,colleage of science,Iraq,baghdad. E-mail: dr.issamiq@gmail.com*
- *Iftikhar M.Ali is a PH.D student in Baghdad univ.,colleage of science,Physics.Depart. E-mail: iftikhariq@gmail.com*
- *Raad M.Al-Haddad is a Prof.in Univ.of Baghdad,colleage of science,Physics depart.. Email: Raad_1960@yahoo.com*

Due to the inherent difference in the heating mechanism, microwave processing of the materials has many advantages over the conventional technique, if the material system is properly chosen. The reaction kinetics can be significantly enhanced by microwave heating of a material system that is fairly lossy in the microwave frequency region. Thus microwave heating has a great potential for accelerated kinetics in ZnS synthesis. Also the photocatalytic activity of the obtained nanostructures was examined using the degradation of methylene blue (MB) under solar light.

2 Experimental

2.1 Instrumentation

A microwave oven with 1100 W power (LG) was used. Powder X-ray diffraction (XRD) pattern of prepared ZnS was recorded by diffractometer (SHIMADZU-XRD 6000) using a Cu Kα radiation (λ=1.5406Å). Morphology was examined by scanning electron microscope(SEM) and Field Emission scanning electron microscope(FESEM). A Shimadzu UV-Vis spectrometer was used to record the UV-Visible absorption spectra (UV-1650PC SHIMADZU, Columbia, MD, USA). A SL174 Spectrofluorometer was used to record the photoluminescence spectra.

2.2 Preparation of ZnS Quantum Dots

The starting materials for the synthesis of ZnS QDs were zinc acetate (R & M Chemical) as zinc source, thioacetamide as a sulfur source and ethylene glycol as a solvent. In a typical synthesis, 5 mM of zinc source and 6 mM of sulfur source were added in a glass beaker of 100 mL containing 20 mL of solvent. The solution was stirred for 30 min. The beaker was placed in a high power microwave oven (1100 W) operated using a pulse regime with 20% power for 25 min irradiation time. The formed precipitates were centrifuged (4000 rpm, 10 min) and the residue was washed several times with distilled water and absolute ethanol. The products were dried in air at 60°C for 24 h under control environment and can be stored for extended period of time.

3 Result and discussion

3.1 Structural properties

3.1.1 XRD analysis

The XRD pattern of ZnS QDs is displayed in Figure1. It can be identified as the cubic zinc blende structure with a comparison to the standard card (JCPDS, no. 05-0566).

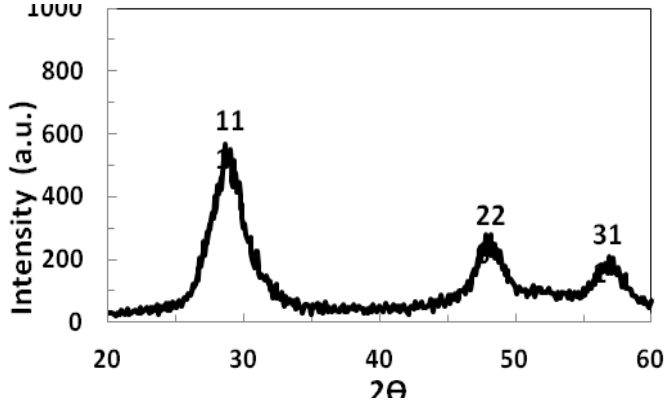


Fig. 1. The XRD pattern of ZnS Quantum Dots.

The three main peaks can be indexed with (111), (220) and (311) planes. The broadened peaks indicate the small particle size of the sample. The d-spacing is calculated using the relation $d_{hkl} = n\lambda / 2\sin\theta$ where λ is the X-ray wavelength (here λ = 1.54060 Å). The average crystallite size of the powder calculated by Scherrer's formula is estimated to be 2.19 nm through the Scherrer equation after constructing the broadening due to instrumentation and strain $D=0.9\lambda/(\beta\cos\theta)$, where β is the full width at half maximum (FWHM) and θ is the diffraction angle. Also the dislocation density (δ) which represents the amount of defects in the sample is calculated using the relation[10] $\delta = 1/D^2$, where D is the average crystallite size. The lattice constant is estimated from the intercept of the Nelson-Riley plot which is a graph of the calculated values of lattice constant for different planes versus the error function given by[11]:

$$f(\theta) = \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right) \qquad (1)$$

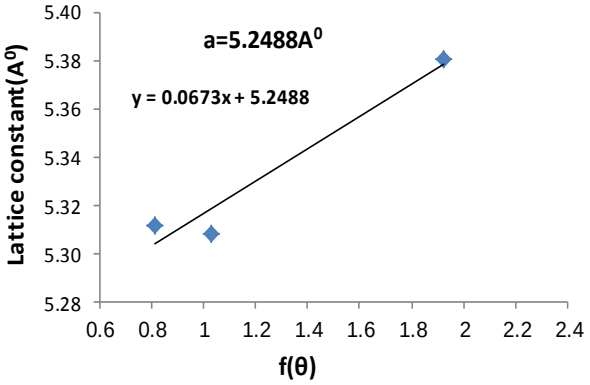


Fig. 2. Nelson-Riley plot of nanocrystalline ZnS sample

The value obtained from N-R plot is more or less free from systematic errors. The calculated structural parameters are given in table-1.

TABLE 1
STRUCTURAL PARAMETERS OF ZNS QDS

2θ(degree)	Plane(hkl)	Interplaner Spacing d(A⁰)	Lattice Constant a(A⁰)	FWHM(rad)	Average Crystallite Size D(nm)	Dislocation Density δ(lines/m²)	Average Strain(ε_{str})
28.7158	(111)	3.10632		0.043			
48.4664	(220)	1.87671	5.25	0.026	2.19	20.7×10^{16}	58×10^{-3}
57.5002	(311)	1.60149		0.017			

3.1.2 SEM & FESEM analysis

The SEM images for powder as seen in Figure 3a indicates that nano-sized particles seem to be homogenous. FESEM image illustrates that the radius of nanoparticles is less than 2.5nm which is smaller than Bohr radius as shown in Figure 3b.

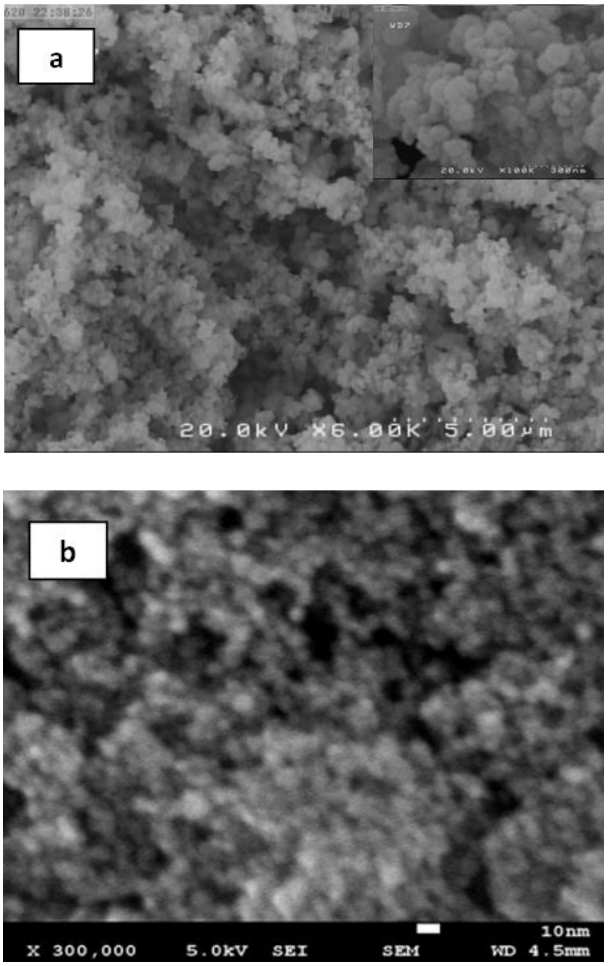


Fig. 3. (a) SEM & (b) FESEM images of ZnS QDs.

3.1.3 EDAX Study:

The EDAX pattern shown in Figure 4 confirms the presence of Zinc and Sulphur. Other signals including Si, In and O are recorded possibly due to the elements present in the substrate (InO conductive glass).

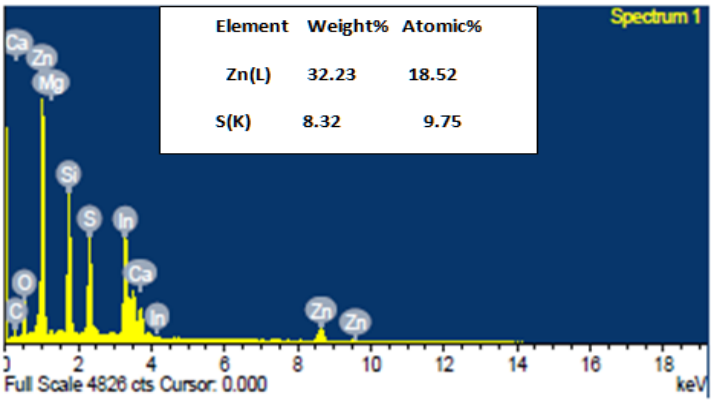


Fig. 4. EDAX of ZnS QDs.

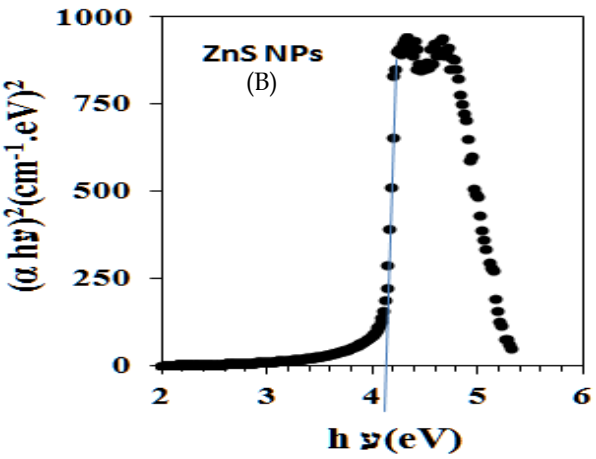


Fig. 5. (A**)**Optical absorption spectra (B)Tauc Plot of as-prepared ZnS QDs

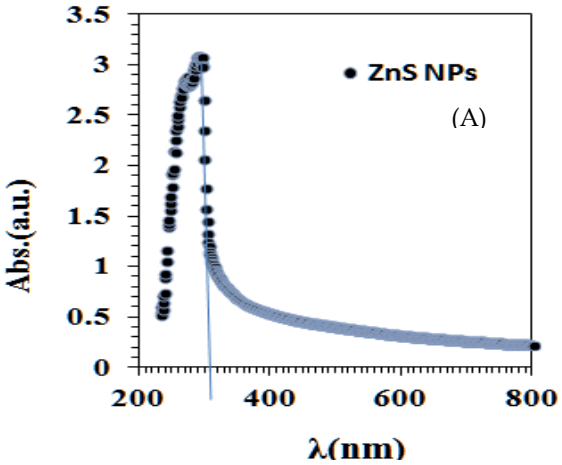
3.2 Optical Properties

3.2.1 UV–Vis absorption

Figure 5a shows that the UV–Vis absorption spectra of ZnS nanoparticles obtained in microwave irradiation. The absorption edge (λ_e being obtained from the intersection of the sharply decreasing region of the spectrum with the baseline,310nm) of the ZnS nanoparticles was at a shorter wavelength than 345 nm for bulk ZnS[12]. The blue shift of the absorption edge can be attributed to the quantum confinement of the ZnS nanoparticles. Figure 5b represents Tauc plots for determination of band gap. Tauc developed the following equation to obtain band gap energy:

$$(\alpha h\nu)^n = B(h\nu - E_g) \qquad (2)$$

where, α is the absorption coefficient, $h\upsilon$ is the incident photon energy, B is a constant and E_g is the band gap energy of the material. The exponent n depends on the type of the transition. Here, the transitions are direct so we take n=2. The band gap energy is calculated by extrapolating the linear portions of the $(\alpha h\upsilon)^2$ vs $h\upsilon$ graph on the $h\upsilon$ axis to α =0.



The obtained band gap energy value is given in table-2. From the band gap value of nanoparticle and bulk, the particle size is calculated using the equation below[13]:

$$\Delta E = \frac{h^2}{|8r^2}\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right)-\frac{1.8e^2}{4\pi\varepsilon_0\varepsilon_r} \qquad (3)$$

Where, ΔE is the blue shift of the band gap, m_e* is the effective mass of electron, m_h* is the effective mass of hole, r is the radius of the particle , ε_r is the dielectric constant and ε_o is the permittivity of free space. The first term indicates the confinement effect and the second term is the coulomb term. In the present case, the second term is small due to the strong confinement and can be neglected. The calculated particle size is given in Table-2. The obtained particle size is smaller than Bohr radius a_B, where Bohr radius for ZnS is 2.5nm[14].

TABLE 2
OPTICAL GAP, BLUE SHIFT AND PARTICLE SIZE OF THE ZnS QDS

Optical band gap(eV)	Blue Shift ΔE(eV)	Particle Size from(nm)		
		UV-Vis	XRD	FESEM
4.12	0.52	2.92	2.19	< 2.5

3.2.2 Photoluminescence

Because our synthesized ZnS nanoparticles were all quantum-sized semiconductor nanoparticles, the photoluminescence (PL) spectra is measured. Figure 6 displays the room temperature PL spectra of this nanostructure. The strongest PL emission centered at 404 nm with excitation wavelength at 250 nm, indicating that our synthesized nanoparticles are wide-bandgap semiconductor exhibiting blue emission properties. Appearance of the broad peak centred at 404nm is due to the zinc vacancies present near the valance band[15].

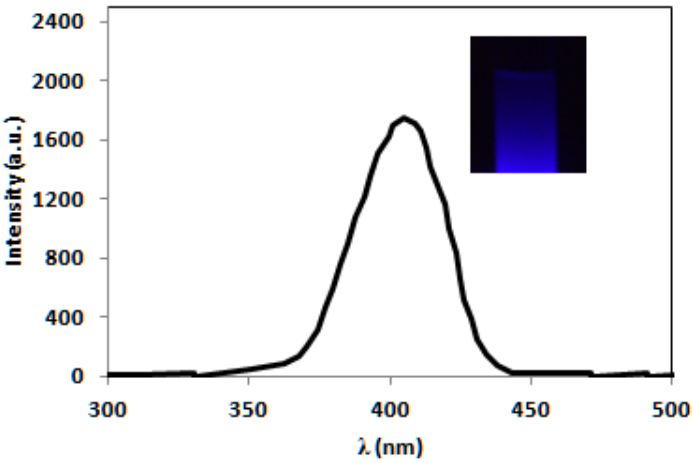


Fig. 6. The luminescence spectra of water soluble ZnS QDs. The exciton emission at 404 nm was excited by 250 nm.

3.3 Photocatalytic Degradation of Methyl Blue(MB) dye under solar radiation by ZnS QDs

A 1*10^{-5} M solution of (MB) was prepared as a stock solution. The optical density of the MB solution was determined using a spectro-photometer at λ_{max} = 661 nm. Zinc sulphide, with a band gap is 4.12 eV, was used as a photocatalyst in the present investigation. Its dispersion was quite stable during illumination, the ZnS powder neither degrading nor dissolving under the employed experimental conditions. First, the feasibility of using the semiconductor zinc sulphide as a photocatalyst was confirmed. Thus, four sample solutions were made. using 100 mL of 1×10^{-5} M (MB) dye in four beakers. The first and second solutions contained only MB; the first solution was kept in the dark while the second was exposed to light. The third and fourth samples contained in addition to MB, 0.025 g zinc sulphide; the third sample was kept in dark, while the fourth was exposed to light. After 3.5 h, the optical densities of the four solutions were measured using a spectrophotometer. It was found that the optical densities of solutions 1–3 remained almost constant, while that of the fourth solution had decreased from its initial value. From these observations, it was clear that this reaction requires presence of both light and ZnS NPs, i.e., it was a photocatalytic reaction. A solution of 1x10^{-5} M of MB was prepared in distilled water and 0.025 g of zinc sulphide was added to it. The pH of the reaction mixture was adjusted to 8, then the solution was exposed to solar light(240-320)mW/cm^2. An aliquot of 4.0 mL was taken out from the reaction mixture and its optical density was observed at 661 nm at regular time intervals (30min). It was observed from Figure 7 that the optical density of MB dye solution decreased with increasing time of exposure and that the degradation of MB was almost completed after 210 min of illumination. This was confirmed experimentally in additional experiments.

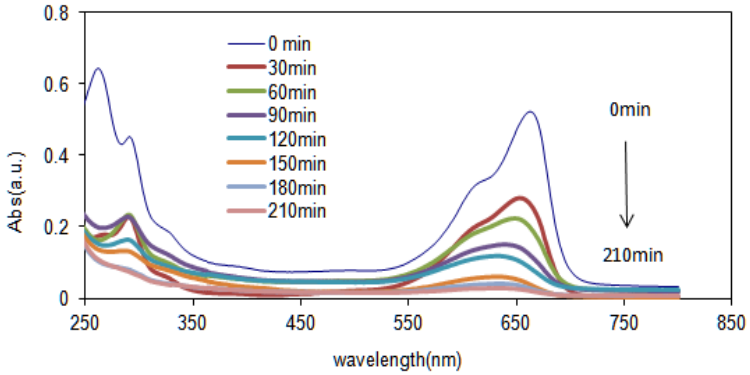


Fig. 6. Absorption spectral changes and photodegradation of methylene blue (MB) aqueous solution degraded by ZnS QDs under solar light.

TABLE 3
A typical run; [MB] = 1x10^{-5} M, m(ZnS) = 0.025 g, light intensity = 292mW cm^{-2}, pH= 8.

t(min)	0	30	60	90	120	150	180	210
Abs.	0.5224	0.2819	0.2241	0.1514	0.119	0.0623	0.0392	0.0299

4 Conclusions

In summary, ZnS quantum dots have been successfully synthesized via a simple microwave-assisted heating process. The size of ZnS NPs is smaller than Bohr radius so that, there is strong quantum confinement. Photocatalytic degradation of MB dye was performed in the presence of the nanosemiconductor zinc sulphide and solar light. The degradation increased with increasing time exposure.

5 References

[1] A. Van Dijken, A.H. Janssen, M.H. P. Smitsmans, D. Vanmaekelbergh and A. Meijerink" Size-selective photoe-tching of nanocrystalline semiconductor particles" Chem. Mater. 10(1998) 3513-3522.

[2] O. Tetsuichiro, K. Kenichi, T. Tsunemasa, "Growth of high-quality cubic ZnS crystals and their application to MIS blue light-emitting diodes" J. Cryst. Growth 99 (1990) 737.

[3] P.I. Ekwo, C.E. Okeke," Thermoelectric properties of the PbS/ZnS alloy semiconductor and its application to solar energy conversion" Energy Convers. Manage. 33 (1992) 159-164.

[4] L.P. Colletti, R. Slaughter, J.L. Stickney," Luminescence properties of Br-doped ZnS nanoparticles synthesized by a low temperature solid-state reaction method" J. Ceramics International,39,5(2013)5521-5525.

[5] V elumani, J.A. Ascencio," "Formation of ZnS nanorods by simple evaporation technique", Appl. Phys. A 79 (2004) 153.

[6] Huaming Yang, Chenghuan Huang, Xiaohui Su, Aidong Tang,"Microwave-assisted synthesis and luminescent properties of pure and doped ZnS nanoparticles", Journal of Alloys and Compounds,

402(2005) 274–277.

[7] J.F. Chen, Y.L. Li, Y.J. Yun, "Preparation and Characterization of Zinc Sulfate Nanoparticles Under High-gravity Environmental" , Mater. Res. Bull. 39, 185(2004).

[8] Torres-Martínez, C.L.; Kho, R.; Mian, O.I.; Mehra, R.K ," Efficient Photocatalytic Degradation of Environmental Pollutants with Mass-Produced ZnS Nanocrystals", J. Colloid Interface Sci.240, (2001) 525–532.

[9] Hamidi Raza,Omid khani, Mojtaba Shamsipur,Vahid Vatanpour,"High-performance pure and Fe3+-ion doped ZnS quantum dots as green nanophotocatalysts for the removal of malachite green under UV-light irradiation",J. Hazard. Mater. (2013) 250-251.

[10] Senapati U.S, Jha D.K and Sarkar D"Green Synthesis and Characterization of ZnS nanoparticles" Research Journal of Physical Sciences, 7(2013) 1-6.

[11] Sarma K., Sarma R. and Das H.L.,"STRUCTURAL CHARACTERIZATION OF THERMALLY EVAPORATED CdSe THIN FILMS" Chalcogenide Letters, 5, (2008) 153-163.

[12] Ramasamy V., Praba K. and Murugadoss G., " Study of optical and thermal properties in nickel doped ZnS nanoparticles using surfactants" Superlattices and Microstructures , 51, (2012) 699-714.

[13] Brus L.E., " Electron–electron and electronhole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state "J.Chem.Phys, 80, (1984) 4403-4409.

[14] J. Sinclair and Dr. Dagotto, "An Introduction to Quantum Dots: Confinement, Synthesis, Artificial Atoms and Applications"Solid State II Lecture Notes, University of Tennessee, Knoxville, 2009.

[15] Denzler D., Olschewski M. and Sattler K, " Luminescence studies of localized gap states in colloidal ZnS nanocrystals", Journal of Applied Physics, 84, (1998)2841.