

Fabrication of ZnS:Ni²⁺ nanocrystals by reverse micelle method

Rahizana Mohd Ibrahim^{a,b,*}, Masturah Markom^b, Kamal Firdausi^a

^aDepartment of Petrochemical Engineering,

Politeknik Pagoh Johor, Hab Pendidikan Tinggi Pagoh, 84500 Muar, Johor, Malaysia

^bDepartment of Chemical and Process Engineering,

Faculty of Engineering and Built Environment,

Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia.

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ABSTRACT

In this work we synthesized Zn_{1-x}Ni_xS with x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10 nanoparticles by reverse micelle method using sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as surfactant. The effect of ion doping on the optical characterization, structure and morphology of ZnS:Ni²⁺ were investigated using ultraviolet-visible (UV-vis) spectroscopy, X-ray diffraction (XRD) and Fourier transform infrared (FT-IR). The particle size of all of samples ranged from 2 nm to 3 nm, as calculated by the Debye-Scherrer formula and Brus equation. FT-IR results confirmed the incorporation of ion dopants into ZnS crystal structure, and XRD results showed that ZnS:Ni²⁺ nanoparticles crystallized in a zinc blende structure without any impurity. Bandgap energy values ranged from 3.9 eV to 4.7 eV. Ion doping shifted the absorption edge to lower wavelengths, as shown in the obtained UV-vis spectra of samples. This blue shift is attributed to the quantum confinement effect.

1. Introduction

Research on nanosize semiconductors have grown rapidly over the past decade. This is because the optical properties of novel electronic arising from quantum confinement effect, which vary significantly in size [1]. Recombination of electron hole pairs in the semiconductor particles drastically reduced with the reduction of particle size. When semiconductor particle size reduction to the nanometer size scale, the semiconductor band gap energy increased greatly, thereby leading to the high redox potential of the system. In addition, nanoscale semiconductor particles have a higher surface to volume ratio of their peers and thus allowing greater absorption of photons at the surface of the photocatalyst [2]. Therefore, the nano-scale semiconductors are expected to have higher photocatalytic activity than the bulks.

Among the semiconductor nanoparticles, the synthesis of II-VI semiconductor nanoparticle has been extensively studied [3]. Zinc sulfide is one of an important II-VI semiconductors which direct band gap semiconductor material that has great value 3.6 eV

band gap energy. It has wide spectrum of potential applications such as in catalysis, electronics and optoelectronic nanodevice [4-6] . In recent years, considerable interest focuses on the transition metal ion doped ZnS nanosemiconductor to form a new class of materials by modification of the band structure. Recently, Nickel has been found to be a prospective doping materials in ZnS nanoparticles.

Various methods have been develop for the synthesis of nanoparticles, such as co-precipitation, soft chemical method, sol-gel ect [7-9].Among the various method for producing nanoparticles, reverse micelle method is considerable a promising technique to prepare less agglomerated and more monodisperse nanoparticles [10]. In reverse micelle synthesis, oil is used as a template to restrict H₂O nanoreactors as reaction media. Therefore, during the chemical synthesis, the excess of particle growth can be avoid when its approaches that of a H₂O nanodroplet. This technique is an established method of synthesizing and stabilizing size-controlled nanoparticles .Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) is the most commonly used surfactant in metal sulfide-nanoparticle synthesis by reverse micelle method. However, only a few studies have been reported on the formation of monodispersed nanoparticles using this method. To the best of our knowledge, there is no report on the formation of monodisperse nanoparticles of Ni²⁺ doped ZnS using reverse miceller method.

In the present study, we synthesized undop ZnS and Zn_{1-x}Ni_xS nanoparticles with x=0.00,0.02,0.04,0.06,0.08 and 0.10 by reverse micelle method using n-haptane, water and AOT as a reaction medium. The size, morphology and structure of the resulting particles were investigate. The obtained nanoparticles were characterized using UV-visible spectroscopy (UV-Vis), x-ray diffraction (XRD) Fourier transform infrared (FT-IR) and field-emission scanning electron microscopy (FESEM).

2. Experiment

All the chemicals used were of Analytical Reagent grade (Sigma Aldrich chemicals), without further purification. Synthesis of ZnS:Ni²⁺ nanoparticles were prepared in H₂O/AOT/n-haptane reverse micelle method using precipitation technique. The selected W [(H₂O)/(AOT)] in molar ratio values was 7 in all preparation solution. An aqueous solution of reverse micelle that separately enclosed 0.5M zinc acetate and 0.5 M nickel (II) acetate (2%) were prepared. The solution was stirrer at 60⁰ for completion of ion Ni²⁺ in the aqueous solution of zinc acetate. Another reverse micelle of AOT enclosing Na₂S solution were prepared separately. Then, an individual reverse micelles of AOT enclosing Na₂S solution was added drop by drop into the Zn²⁺ and Ni²⁺ mixture with continuous stirring until a homogeneous solution was obtained. The mixture was then allowed to stand for 1 day in the oven in constant temperature of 40⁰C for precipitation. After that, the precipitate was repeatedly washed with ultra pure water and ethanol. Finally, the precipitate was dried in the oven for one day at 40⁰C. The same procedure was followed for all ZnS:Ni ratio. The formation of Zn_{1-x}Ni_xS (x=0.00,0.02,0.04,0.06,0.08,0.10) nanoparticles was studied using The optical absorption spectra of the samples in ultrapure H₂O were measured using an AMBDA 35 ultraviolet (UV) spectrometer. Sample characterizations were performed with a NICOLET 6700 Fourier transform infrared (FT-IR) spectrometer. X-ray diffraction (XRD) patterns of the powdered samples were obtained using a D8 advance diffractometer from 20° to 80°. Crystal size was calculated using Scherrer equation $(0.9\lambda)/(\beta\cos\theta)$ at full width at half-maximum (FWHM) of the XRD peaks. Nanoparticle morphology and size particles were

determined using a field-emission scanning electron microscopy (FESEM) system (SUPRA 55 VP) and transition electron microscopy (TEM) system (CM 12). Fluorescence measurements were performed with a PL SP920 spectrophotometer for optical characterization.

3. Results and Discussion

3.1 Optical absorption and optical band gap

The room temperature UV-vis spectra of undop ZnS and doped ZnS:Ni²⁺ are shown in Figure 1 . As seen in the figure , the absorption edge of undop ZnS is observed at the 250nm and 313nm while for all sample for ion Ni²⁺ dop ZnS show absorption edge at ~250nm. The two absorption edge for undop ZnS are due to the formation of two groups size of the particles. The absorption value shift to the one absorption edge after doping with ion Nicel and become more homogeneous. The shift of absorption edge for doped ZnS was a results from incorporated of ion Ni²⁺ in the crystal structure of ZnS. However, for different percentage of ion doping in ZnS crystal structure does not shows any shifting in absorption value. This result probably was come from the effective of small percentage of dopants. However, it shows significant increase in the absorption value that indicate wide distribution of nanoparticles at corresponding absorption wavelength area. It also shows a very monodispersed nanoparticle distribution for doped ZnS.

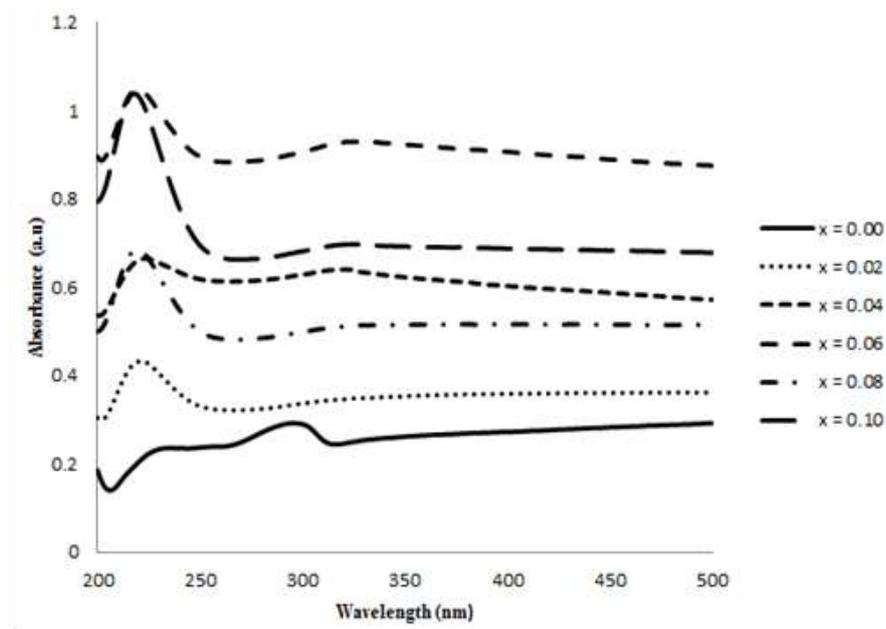


Figure 1: UV-vis absorption spectra of undop ZnS and Ni dop ZnS nanoparticles

The optical absorption spectrum probes the internal molecular orbital which corresponding to electron excitation from the valance band to conduction band . This information can be used to determine the nature value of the optical bandgap .The relation between absorption coefficients (α) and incident photon energy ($h\nu$) can be written as [11].

$$\alpha = A(h\nu - E_g)^n / h\nu \quad (1)$$

Where A is a constant and E_g is the band gap of the material and the exponent n depends on the type of the transition. For direct and allowed transition $n=1/2$, indirect transition, $n=2$ and for direct forbidden, $n = 3/2$. Then, the direct bandgap with $n=1/2$ was obtained by extrapolating the straight portion of the plot of $(\alpha h\nu)^2$ versus $h\nu$ on $h\nu$ axis at $\alpha = 0$. The calculated band gap value are between 3.9 - 4.9eV for all samples and listed in Table 1. Based on the bandgap value, the particles size were calculated using the theoretical effective mass approximation model formula [12].

$$d(E) = \frac{0.32 - 2.9 \sqrt{E - 3.49}}{3.50 - E} \quad (2)$$

where E is the bandgap (eV) and $d(E)$ is the particle diameter (nm). The calculated particles sizes are given in table I and compared with XRD results. The average particles size of the samples from this equation are agreed quite well the particles size calculated through XRD as in Table I. The grain size of doped ZnS was ~ 3 nm, which was within the quantum confinement region and the particles sizes shows almost similar . The obtained value of doped ZnS samples are higher than that of bulk value of ZnS(3.72eV). This blue shift of the bandgap takes place because of the quantum confinement effect [13].

Table 1: Absorption, bandgap and particle size of $Zn_{1-x}Ni_xS$ ($x = 0.00, 0.02, 0.04, 0.06, 0.08$ and 0.10) nanoparticle.

Sample	Absorption (nm)	Band gap (eV)	Saiz (nm)	
			UV	XRD
$Zn_{1-x}Ni_xS$				
x = 0.00	310	4.9	2.3	2.63
x = 0.02	250	4.6	2.5	2.48
x = 0.04	245	3.9	3.5	2.83

x = 0.06	240	4.3	2.9	2.63
x = 0.08	260	4.7	2.4	2.53
x = 0.10	250	4.7	2.4	2.53

3.2 FT-IR study

FT-IR spectra of the undoped ZnS and ZnS:Ni(4%) nanoparticles were recorded in the range of 3900 – 400 cm^{-1} as shown in Figure 2 below. The peak appearing at 1020, 671 and 486 cm^{-1} are due to Zn-S vibration [14]. After doped with Ni^{2+} ion, the peak at 1160 cm^{-1} appear due to Ni-S vibration. These results show that Ni^{2+} atom was partially substituted into Zn position in ZnS nanoparticles. The partial metal substitution results were consistent with XRD experiment. While the broad absorption peak in the range of 3000 – 3600 cm^{-1} corresponding to –OH group indicates the existence of water absorbed in the surface of nanoparticles [15]. The bands at 1500-1650 cm^{-1} are due to the C=O stretching modes arising from the absorption of atmospheric CO_2 on the surface of the nanoparticles. The obtained peak values are in good agreement with the literature.

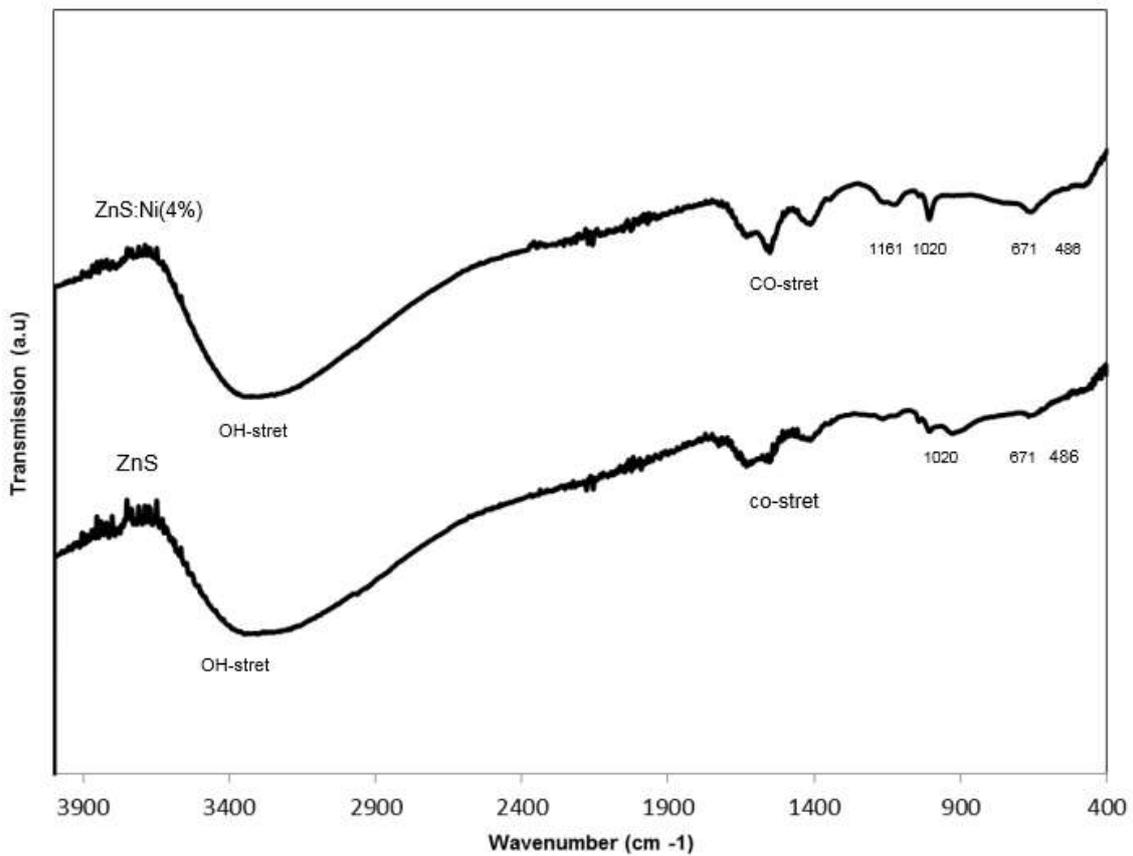


Figure. 2: FTIR spectra of Ni doped ZnS and undoped ZnS

3.3 X-ray diffraction

XRD pattern for prepared samples are showed in Figure 2 . From this figure, the X-ray powder diffraction of nanoparticles ZnS and ZnS:Ni revealed that both nanoparticles have zinc blende structure with plane at (1 1 1), (2 2 0) and (3 1 1) . The broadening of the XRD pattern of the prepared samples were due to nano crystalline nature of particles. From the XRD results, the average crystallize size is calculated using the Debye Scherer formula (10).

$$D = 0.89\lambda/(\beta\cos\theta) \quad (3)$$

Where λ is the wavelength of incident X-ray (1.54 Å) and θ is the Bragg's angle. From the calculation, the average diameter of the particles are 2.46 nm for undop ZnS and 2.51 nm for Ni dop ZnS. The substitution of higher radius Ni^{2+} ions ($r_{\text{Ni}^{2+}} = 0.78 \text{ \AA}$) to parts of Zn^{2+} ion ($r_{\text{Zn}^{2+}} = 0.74 \text{ \AA}$) in the ZnS structure leads to slightly increase in nano particles size of ZnS. This increase of particles size equivalent with the decreasing in the lattice parameter of ZnS as shown at the most intense peak (1 1 1) plane in Figure 3. The average crystallite sizes (D) was calculated to range from 2.0 nm to 3.0 nm as shown in Table I. The decreasing of particles size is due to a very small amount of ion doped into ZnS lattice which gives the strong evidence for the incorporation of ion dopan.

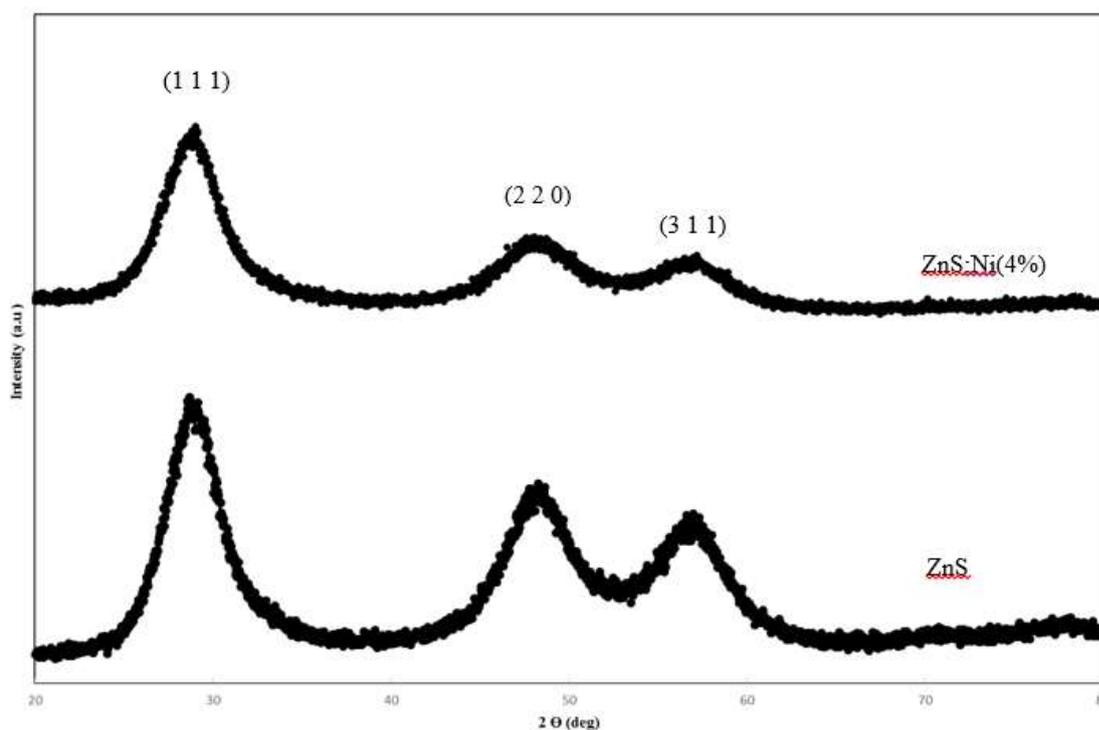


Figure 3 : XRD pattern of Ni doped ZnS and undoped ZnS

4. Conclusions

Ni²⁺ doped ZnS nanoparticles have been successfully synthesis by reverse micelles method using precipitation technique. It has zinc blende structure, as observe by X-ray diffraction and incorporated of ion Nickel as shown in FT-IR results analysis. The average size lies in the range of 2.0 ~ 3.0nm for all samples and band gap values increase greatly from the bulk value which indicated strong quantum-size effect. Ni doped ZnS nanoparticles exhibit a uniform size distribution using reverse micelle method.

ZnS

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6. References

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