

STRUCTURAL ANALYSIS OF ZINC SULPHIDE NANOPARTICLES SYNTHESIZED VIA WET CHEMICAL ROUTE

Nur Shafiza A. Sharif, Nur Shafinaz Ridhuan, Zainal A. Ahmad, Sabar D. Hutagalung

*School of Materials and Mineral Resources Engineering,
Universiti Sains Malaysia, 14300, Nibong Tebal, Pulau Pinang, Malaysia.*

ABSTRACT

Nanocrystalline of zinc sulphide (ZnS) were synthesized by using wet chemical route with the addition of capping agent. The main objective is to find out the optimum parameters of the wet chemical synthesized ZnS nanophosphor which are including pH, capping agent concentration and refluxing time of the synthesis. The main sources of zinc acetate, natrium sulphide and the capping agent PVP or PVA were prepared in the certain ratio and mixed together inside the three neck flask. The pH of solution was adjusted by the drop wise addition of natrium hydroxide that expected contribute to the formation of nanoparticles. The preparation of sample was done at room temperature, where the natrium sulphide is mix slowly into the solution under vigorous stirring. Effect of refluxing time and capping agent composition were studied. The final product of ZnS nanoparticles were characterized by XRD analysis to obtain the structure phases, SEM and EDX analysis to obtain the microstructures and elemental composition inside the samples. From the XRD results was calculated the crystallite size of ZnS nanoparticles which is in the range of 5.92 to 6.78 nm.

INTRODUCTION

The nanocrystalline II-VI semiconductors, which show significant quantum confinement effects, have attracted extensive research interest because of their shape, size dependent electronic band gap energies, melting temperatures, solid-solid phase transition temperatures and pressure. These properties of nanocrystals make them an interesting category of materials for optoelectronics applications [1]. ZnS is an II-VI material that can find future applications such as window layers of solar cells, coatings sensitive to UV light, data storage and data transfer. ZnS nanoparticles are also often used as phosphors for display devices. In a bulk state, ZnS has a direct large bandgap of 3.66eV at 300 K [2, 3]. It exists both in a natural and synthetic crystalline form possessing cubic (Zinc blende) or hexagonal (Wurtzite) lattice structures. At room temperature, hexagonal wurtzite and cubic sphalerite has a wide band gap around 3.5–3.8 eV [4].

There are numerous techniques available for preparing semiconductor nanoparticles which basically divided into 2 major routes which are physical [1] and chemical methods [2]. In this paper, wet chemical methods using suitable capping agent/surfactant have been used to synthesize the nanocrystalline ZnS. The wet chemical synthesis method is a simple and also has the advantages of producing size-

controlled and un-agglomerated nanoparticles [5].

Moreover, the polymers or capping agent/surfactant were used as stabilizer during the preparation of semiconductor nanoparticles. The main objectives using the capping agent/surfactant is to study the effect of polyvinyl alcohol (PVA) and polyvinyl pyrrolidin (PVP) matrix as well as Zn:S ion ratio on the particle size of ZnS nanoparticles, and also to monitor the variation of size through the absorption and photoluminescence measurements. The ZnS nanoparticles would be characterized through the X-ray diffraction (XRD) measurement to confirm it's crystalline and purity [6].

EXPERIMENTAL

ZnS nanocrystals were synthesized by a wet chemical method at room temperature using sodium sulphide, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (32-38%, Merck) used as the source as S^{2-} ions, zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) (100%, Merck) the source for Zn^{2+} , solvent Polyvinyl Alcohol (PVA) (95%, AppliChem GmbH) and Polyvinyl Pyrrolidin (PVP) (100% EMD Chemicals) as starting materials.

The main sources of Zn^{2+} and the capping agent PVA or PVP were prepared in the same ratio of moles and mixed together inside three neck flasks. The pH of this solution was adjusted by adding a few drops of sodium hydroxide solution. At the same time, sodium sulphide $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was added into the solution under vigorous stirring⁷. Different refluxing times are varied within 1-15 hours range. The white precipitation product was centrifuged and washed several times by using deionized water and acetone to remove other soluble salts before measurement [6]. Then, vacuum dried at 60-70°C for 6 hours. In this project, the parameters that have been study are including pH and refluxing time for the synthesis. Table 1 shows the parameters for the sample that have been synthesis using wet chemical method. The final product of ZnS nanoparticles were characterized by XRD analysis to obtain the structure phases.

Table 1: Parameters for the sample that have been synthesis using wet chemical method

Sample	Zinc Acetate (ml)	Natrium Sulphide (ml)	PVA (ml)	PVP (ml)	pH	Refluxing time (hours)
S1	100	100	20	-	6.6	4
S2	100	100	20	-	6.65	4
S3	100	100	-	5	9.0	5
S4	100	100	20	-	6.4	3

RESULTS AND DISCUSSION

The reaction between Zn and S ions in the PVA or PVP medium has a great effect on crystallization as well as the size of the formed ZnS nanoparticles [6]. Figure 1 shows the XRD patterns of prepared ZnS nanoparticles. The results show four strong peaks that match with the standard cubic ZnS according to reference data of JCP No.5-566 [9].

Furthermore, the all of the peaks are plane-indexed with Miller indices (hkl), which are (111), (200), (220) and (311). The XRD peaks of the cubic crystallite ZnS nanoparticles proved to be broad due to small grain size [8]. Based on the observed full width at half maximum (FWHM) value of the (111) peak and the use of Debye-Scherrer formula the average particle size were calculated to be 6.43 nm.

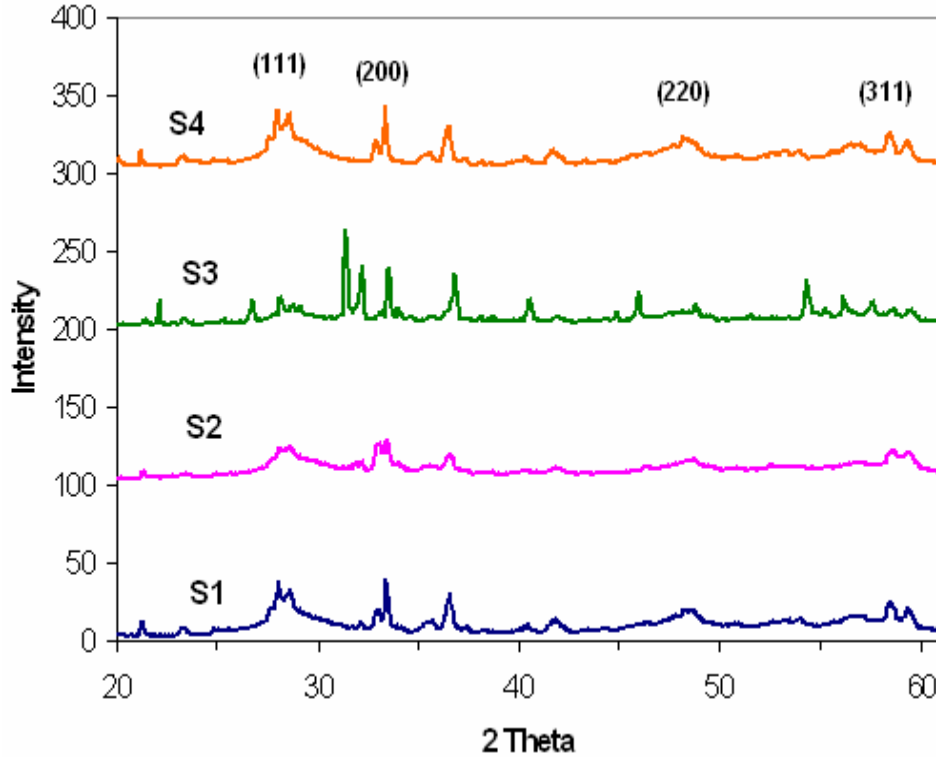


Figure 1: The XRD analysis results of ZnS samples.

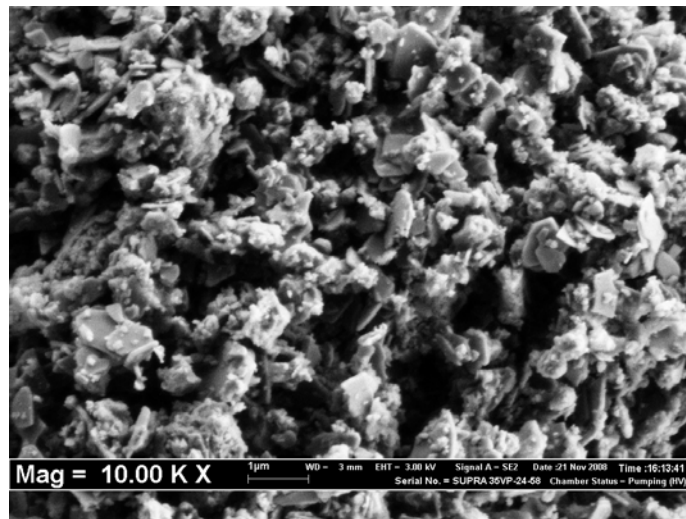
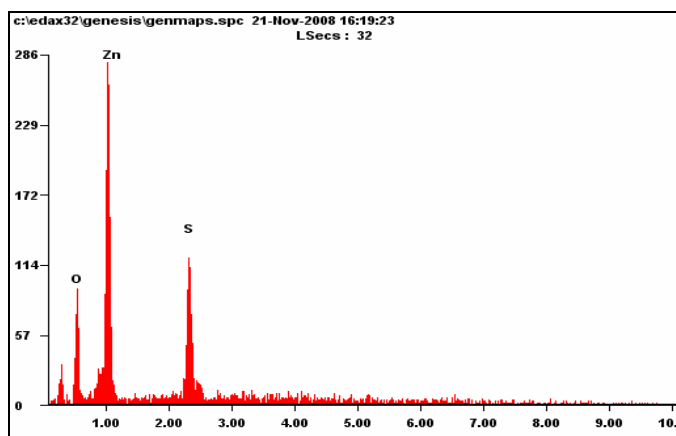


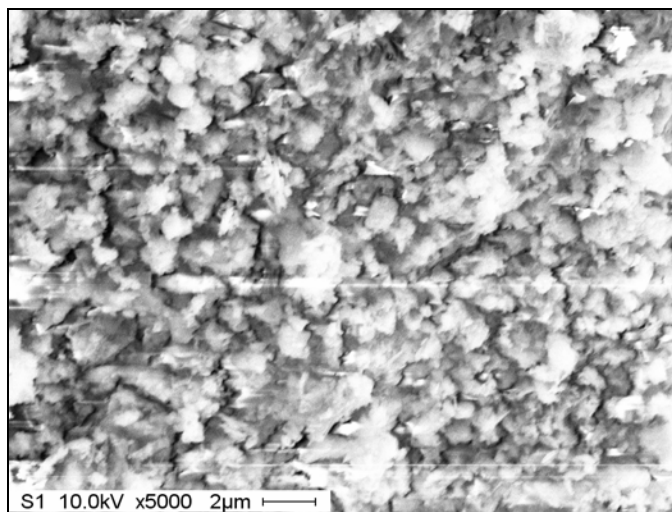
Figure 2: The microstructure image of a selected sample (sample S1).

The microstructure of ZnS nanoparticles was studied by using a scanning electron microscope (SEM). Figure 2 shows the SEM image as prepared a selected samples (sample S1). It was found that the final product is made up of agglomerated nanoparticles forming microspheres. The concentration of PVA and PVP effects the nanoparticle size formed.

The energy dispersive analysis of X-rays (EDAX) was performed to the sample S1. The counted chemical composition is shown in Figure 3. The EDAX analysis gave elemental composition of 34.90 at% of Zn, 32.44 at% of S and 32.66 at% of O in the sample. The presence of oxygen in ZnS nanoparticles is expected because of the oxidation during synthesis ZnS nanoprticles process and might be also it come from the capping agent itself.



(a)



(b)

Figure 3: The EDAX spectrum (a) on the whole surface (b) of a selected sample S1.

CONCLUSION

The ZnS nanostructures have been successfully synthesized by a wet chemical process using suitable capping agent which are PVA and PVP. The X-ray diffraction studies revealed that the synthesized particles have cubic zinc blende structure. Beside, from the obtained results found the most suitable parameters are the capping agent of PVA at room temperature processing, pH within 6-7 range and the refluxing time of 3-4 hours. The size of produced nanoparticles is in the range of 5.92-6.78 nm, however some of the nanoparticles still agglomerated and form bigger size particles.

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