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Review: Synthesis of Zinc Sulfide Nanoparticles by Various Methods

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Abstract

ZnS nanoparticles have prospects for use as diodes and sensors. These various uses caused the synthesis of ZnS nanoparticles has been widely carried out. However, sphalerite resources will be depleted, thus requiring research and development of renewable materials to meet the needs of zinc sulfide on an industrial scale. The purpose of this study was to analyze various ZnS synthesis methods. In this study, various synthesis methods of ZnS from various journals from 1982 to 2020 were discussed which include one-pot synthesis method, sol-gel, hydrothermal process, coprecipitation, ultrasonic radiation, and microwave irradiation. These methods have their advantages and disadvantages. The results of the study show that the wave irradiation method is more proper for the synthesis of ZnS, especially on an industrial scale. This is because the precursors used are commercially available, the reaction time is short, the operating temperature is low, and the products have high purity. Several raw materials have prospects for the synthesis of ZnS including, $Zn(CH_3COOH)_2.2H_2O$, CH_4N_2S, Na_2S, $ZnSO_4.7H_2O$, and ZnO. We hope this study can provide references to readers, industry, and researchers in the field of material development regarding efficient and effective synthesis methods of ZnS on a large scale.

Keywords: coprecipitation, hydrothermal process, microwave irradiation, one-pot, sol-gel, sphalerite, ultrasonic radiation, zinc sulfide (ZnS).

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1. Introduction

Nanostructure materials have dimensions of about 1-100 nm. Nanostructures can be divided into 0 dimensions/uniform), 1 dimension/lengthwise, and 2 dimensions/planar [1]. Semiconductor nanostructure materials recently attracted a lot of interest. Especially its application as optoelectronic materials [2]. Semiconductor nanostructures have a variety of different properties due to the sharing of 3-dimensional electrons and holes in volume or the fact that the number of atoms on the surface is proportional to that particles [3].

Zinc sulfide has a wide energy bandgap of 3.7 eV at 300℃and it is one of the first semiconductors to be discovered and widely used in various fields, for example in optical devices, sensors, and the environment [4,5].

ZnS applications can be found in light-emitting diodes [6], electroluminescence [7], flat panel solar cells [8], infrared windows, sensors [9], wastewater treatment [10], photocatalysis, and biological sensors [11]. The use of ZnS in optical devices is supported by its properties that have a high index of refraction and transmission in the visible light region [12].

Zinc sulfide has two common allotropes, namely, zinc blende (sphalerite) and wurtzite with a cubic structure. The cube shape has high stability at low temperatures, but at 1296K it can form polymorphs [13]. Under atomic conditions, these two allotropes have a coordination number of four forming a tetrahedral structure [14].

Sphalerite is composed of zinc and sulfur atoms that are tetrahedral coordinated and stacked in an ABCABC pattern with lattice parameters a = b = c = 5.41 Å. While wurtzite contains zinc and oxygen atoms stacked in an ABABAB pattern with lattice parameters a = b = 3.82 and c = 6.26. As a result, the electronic structures of the two allotropes are different. Wurtzite has a bandgap of 3.77 eV [15] while sphalerite is 3.72 eV [16].

Hexagon wurtzite can metastasize thermodynamically and can change the hexagonal structure into a cubic crystal structure spontaneously through reaction with organic substances [17].

ZnS was found to be more thermodynamically stable in the form of 'cubic sphalerite'. Pure sphalerite has a clear crystal form. The higher impurities such as iron, the darker the color of the sphalerite crystals [18].

ZnS nanoparticles have anomalous physical and chemical properties such as have higher surface and volume ratio, quantum size effect, surface and volume effect, macroscopic quantum tunneling effect, more optical absorption, thermal resistance, and low melting point. Table 1. presents the properties of zinc sulfide [19].

Table 1. Properties of Zinc Sulfide. This table is adopted from references [19].

Molecular Weight	97.46 g/mol
group	Zinc-12
	Sulfur-16
Crystal structure	Cube
Density	4.079 g/cm3
Melting point	1185°C
Boiling point	1850°C
Dielectric constant	8.9
Band Gap	3.54 ev
Electron mobility	180 cm2/Vs
formation energy	477 kJ/mol
Thermal expansion coefficient	6.36 µm/m°C
Heat capacity	0.472 J/g°C

This article aims to present information about the source of the material and the synthesis method of zinc sulfide nanoparticles, which is equipped with information about the advantages and disadvantages of each synthesis method. The synthesis methods of ZnS nanoparticles presented include the one-pot method, sol-gel formation, hydrothermal processes [4], coprecipitation [20], ultrasonic radiation [21], and microwave radiation [22]. Information about the ZnO synthesis method is summarized in Table 2.

2. Synthesis of ZnS Nanoparticles

The synthesis of ZnS nanoparticles consists of two methods, namely the physical method and the chemical method. The chemical method includes thermal decomposition methods, micro-emulsions, sol-gels, and others. These methods require high reaction temperatures, lots of organic solvents, high operating and equipment costs, and complex process controls. Even in many cases, the particles produced by this method have not good particle size and easily clump [38].

The synthesis of ZnS nanoparticles also can be done by a dopping method. ZnS nanoparticles doped with optical luminescence centers can create many new physics and applications. Some materials apply to luminescence devices, phosphors, optical sensor light emitters, and others [39]. Zinc sources from sphalerite can use as salts such as zinc acetate and zinc chloride, which reacted with thiourea to obtain ZnS nanoparticles [40].

Table 2. Materials, Methods, Advantages, and Disadvantages of Synthesis of ZnS.

Materials	Method	Advantages	Disanvantages	Reference
$Zn(MA)_2$	One-Pot	• Precursors are non-toxic, inexpensive, and readily available. • The morphological structure and electrochemical properties of the product can be controlled by preparative parameters such as temperature, solution pH, and precursor concentration.	• The experimental setup is tricky. • If the temperature is too high, structural damage can occur and reduce the safety of the preparation process.	[23, 24, 25]
$Zn(CH_3COO)_2 \cdot 2H_2O$	Sol-Gel	The product has high purity in terms of physical properties, morphology, and chemical properties.	• Preparations of large quantities of precursors are difficult to prepare without cracking. • The reaction time is too long due to slow drying to avoid cracking. • Conditions must be controlled well.	[26,27,24]
$Zn(CH_3COO)_2$, CH_4N_2S, Na_2S, oleic acid, $Eu(CH_3COO)_3$ $6H_2O$.	Hydrothermal	• Easy and high yielded products. • The product crystal has high purity, good dispersion, and high stability. • The precursor is non-toxic and inexpensive. • Environmentally friendly. • The method can be carried out in various combinations of aqueous and solvent mixture-based systems.	• The reaction time is long so it consumes a lot of energy. • This method requires an expensive stainless-steel autoclave and Teflon. • Reactions are difficult to study because they are closed systems.	[17, 28, 29, 30, 31]

Table 2. (continued) Materials, Methods, Advantages, and Disadvantages of Synthesis of ZnS.

$ZnSO_4.7H_2O$ and CH_4N_2S.	Coprecipitation	• Affordable cost. • Simple working method. • Produce high quantities of products. • The method can be used for large-scale production.	• The time to make the product is fairly long.	[20, 32, 33, 34, 35]
ZnO and Na_2S	Ultrasonic Radiation	• It does not take much time because of the large temperature and pressure and extreme cooling. • High reaction yield. • Enhance organic transformation.	The radiation source only relies on ultrasonic radiation.	[28, 36, 21]
$Zn(CH_3COOH)$ $2.2H_2O$ and CH_3CSNH_2.	Microwave Irradiation	• Precursors are commercially available. • Short reaction time. • Low operating temperature. • The method was carried out under ambient atmospheric conditions. • The resulting product has high purity.	• The control method on the size and morphology of the results is less accurate.	[22, 37, 12]

2.1 One-Pot

This process uses one reaction. The purpose of this process focused on ZnS materials. The reactions used in this process are reactions with easy steps, a fast process, and high product yields [41].

Preparation of ZnS use chemical reagents such as $ZnCl_2$ and $ZnSO_4$ with a sulfur source from Na_2S [42]. Sources of sulfur contain thiosulfate because thiosulfate hydrolyzed to S^{2-} [43]. It also contains organic solvents such as methanol, ethanol, ethylene glycol, and a small amount of acid or base to catalyze. In this method, it is necessary to control physical properties such as surface area, pore size, and pore volume. So organic stabilizers are uses [44]. Although the one-pot synthesis process has been using successfully to prepare ZnS particles with high product purity, this process is still limited to the use of high temperatures. So, organic stabilizers and solvent media can remove by the calcination process [45]. The S^{2-} ion will bind to Zn^{2+} then become ZnS in the form of a precipitate. [42]

$$S_2O_3^{2-} + H_2O \rightarrow SO_4^{2-} + H_2S \ (1)$$

$$H_2S + Zn^{2+} \rightarrow ZnS + 2H^{+} \ (2)$$

In general, the reaction used is shown in Figure 1. The product of this process is shown in Figure 2.

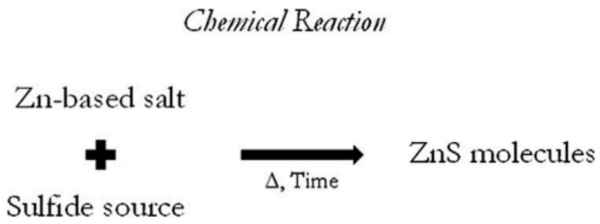

Figure 1. The chemical reaction of the One-Pot process for the formation of ZnS. Figure was adopted from Ummartyotin and Infahsaeng [46].

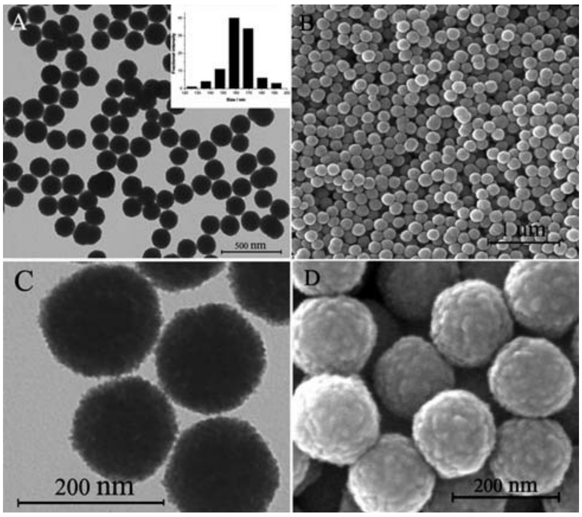

Figure 1. ZnS nanoparticles. The results of the One-Pot method with various characterizations. The figure was adopted from Li, et al. [47].

2.2 Sol-Gel

The sol-gel formation is a method that produces solid materials from nanoparticles. This method involves the conversion of monomers into colloidal solutions. The reagents used are metal-based alkoxides. In the formation of sol-gel, there are different categories, namely sol and gel [48]. The factors that influence this method are gel formation reaction time, solvent and pH conditions, chemical reagents, and temperature during calcination [49]. This process requires a stabilizer to protect the particles from particle enlargement. The thing to note in this method is to use a clean surface [3].

The size and shape of ZnS are controlled by adjusting the molecular weight of the stabilizer. For example, polyvinylpyrrolidone, polyethylene glycol, and polyacrylic acid with various molecular weight sizes from 500-100,000 are used as stabilizers. So that different sizes of ZnS are produced [46].

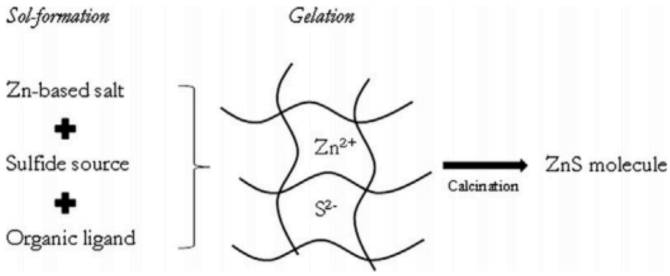

Figure 3. Schematic of the Sol-Gel process for the formation of ZnS. Figure adopted from Ummartyotin and Infahsaeng [46].

The results of ZnS nanoparticles are shown in Figure 4.

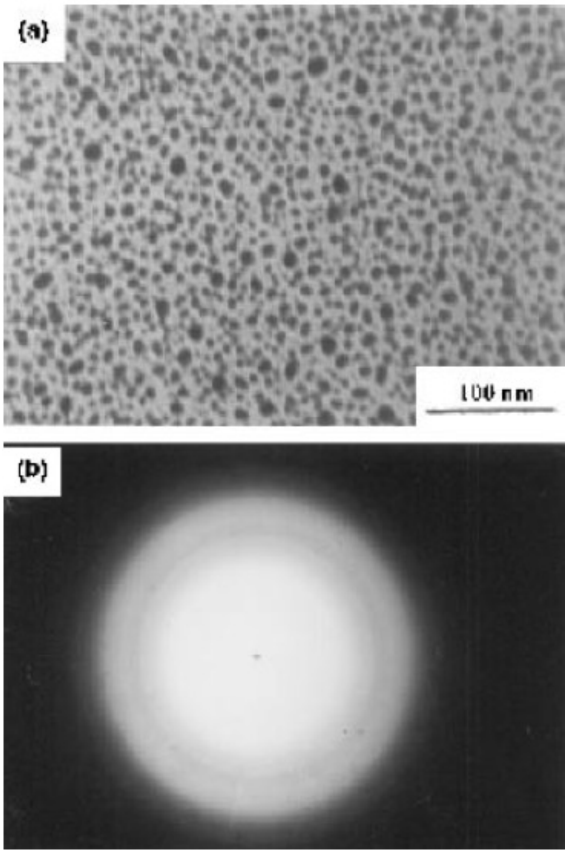

Figure 4a. Transmission of electrons in the form of a micrograph. Figure adopted from Bhattacharjee, et al. [51].

Figure 4b. ZnS film. Sol-gel method results. Figure adopted from Bhattacharjee, et al. [51].

2.3 Hydrothermal Process

There are methods of preparation ZnS, namely the oil phase method and the water phase method. The hydrothermal method belongs to the water phase method, which is environmentally friendly because it uses water as a solvent and inorganic salts as reaction precursors. Therefore, the operation is simple, the reagent is non-toxic and inexpensive. This method is widely used, and the crystals obtained have high purity and good dispersion. The advantages of this method are its high stability and fast process requiring only a low thermal supply [30].

The hydrothermal technique is one of the effective methods for the preparation of ZnS particles. This technique involves the crystallization of aqueous solution materials from high temperatures at high vapor pressure. Theoretically, it is defined as the synthesis of single crystals that depend on the solubility of minerals in hot water under high pressure. The apparatus consists of a pressurized steel container called an autoclave. The container contains nutrients supplied along with water [46].

This method uses autoclaves made of steel cylinders with tight covers. It is used for holding high temperatures and pressures inside for a long time [51].

The hydrothermal method is also effective for the preparation of inorganic nanomaterials such as oxides, sulfides, phosphates, zeolites, and diamonds. The particle size and distribution, phase homogeneity, and morphology of the material are controlled well in this method [52]. The result of the hydrothermal process is shown in Figure 5.

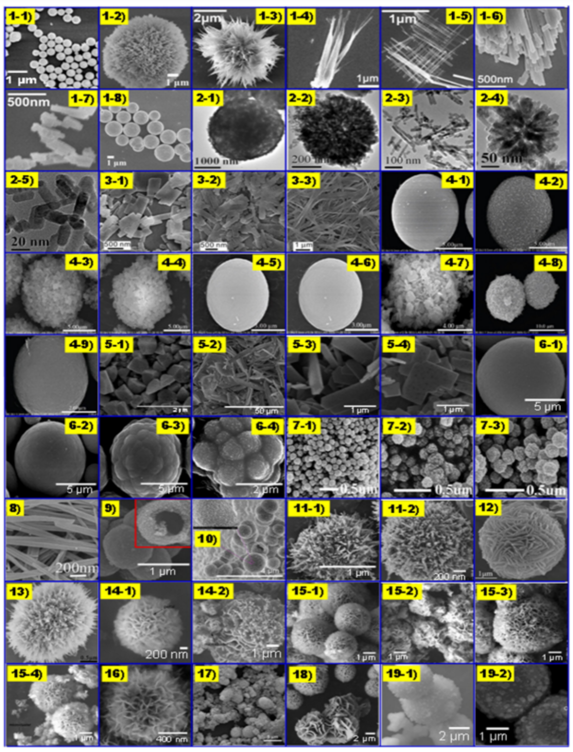

Figure 5. ZnS Nanoparticles. The result of the Hydrothermal process with a variety of solvents and reaction conditions. Figure adopted from Lee [28].

The synthesized ZnS nanoparticles were analyzed by X-Ray Diffraction D-8 Advance Bruker Germany equipped with graphite for Cu Kα (λ = 2,54056 Å) radiation monochromator. This is to determine the structural properties of ZnS nanoparticles [35]. The results of the ZnS analysis using XRD are shown in Figure 6.

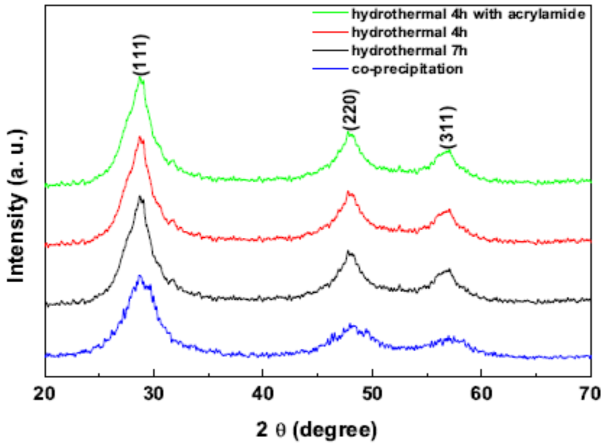

Figure 6. Results of XRD Analysis of ZnS Nanoparticles with Hydrothermal and Coprecipitation Methods. Figure adopted from Master, et al. [35]

From the figure, it can be concluded that each reflection pattern of (111), (220), and (311) shows the structure of ZnS nanoparticles is zinc blende or sphalerite.

2.4 Coprecipitation

Coprecipitation and deposition synthesis methods with spin coating are considered cost-effective methods [20]. In addition, this method is a simple technique, high product yield, and can use for large-scale production. [32][34]. In his research, Harvey used $ZnSO_4.7H_2O$, ammonium sulfate, and thiourea reagents with a molar ratio of 1:1.5:1.5 [33]. $ZnSO_4.7H_2O$ and ammonium sulfate mixed with 50 mL of distilled water. Then ammonia was added to the mixture until a clear metal complex formed (pH maintained at 9.5). Thiourea dissolved in the previous solution. The sample solution was washed with distilled water and methanol to remove impurities [33]. The ZnS nanoparticles synthesized by the coprecipitation method are shown in Figure 7.

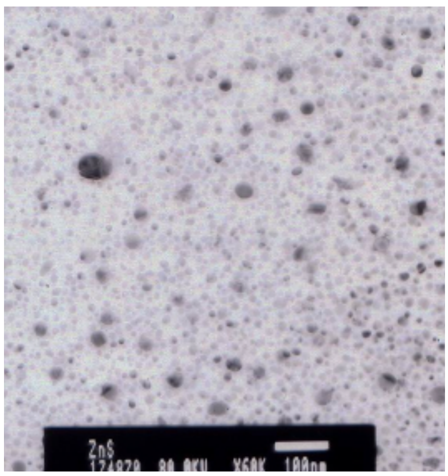

Figure 7. ZnS Nanoparticles by coprecipitation method. Figure adopted from Vazquez., et al. [12].

The results of the synthesis of ZnS nanoparticles are characterized by XRD Rigaku Mini using Cu Kα radiation (λ = 0.1541 nm). The diffractogram was recorded in the range of 10-80°. The results of the XRD analysis of ZnS nanoparticles are shown in Figure.5 [53]. The average ZnS particle size was calculated by the Debye formula and it found that the particle size was 4.9 nm [53]. Bahmani conducted a similar experiment and obtained data that ZnS nanoparticles tend to show a zinc blende or sphalerite crystal structure [54].

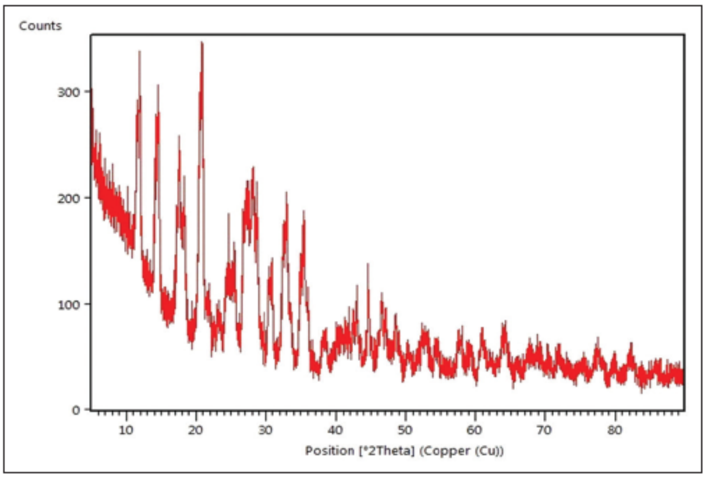

Figure 8. Results of XRD Analysis of ZnS Nanoparticles with Coprecipitation Method. Figure adopted from Othman, et al. [53]

2.5 Ultrasonic Radiation

Ultrasonic waves are widely used to produce new materials with unusual properties and can induce the formation of particles in smaller sizes with a larger surface area compared to other methods [63].

ZnS nanoparticles can be prepared using the method without the use of any stabilizer. ZnO as a source of Zn mixed with a solution of Na_2S as a source of S under ultrasonic radiation in a water bath for 2 hours. After reacted, the resulting product was washed and dried under reduced pressure [21].

The use of ultrasonic irradiation for the production of nanomaterials has become a very interesting research topic. This is due to the simplicity of the sonochemical method, the low cost of the equipment, and in most cases, the prepared material obtained in the crystalline phase. The chemical effects of ultrasonic irradiation come from non-linear acoustic phenomena, especially acoustic cavitation which is divided into three distinct stages namely formation, growth, and bursting of bubbles [55].

Ultrasonic is a unique interaction between energy and matter due to the chemical effects of ultrasound arising from the acoustic membrane, including the formation, growth, oscillation, and fall of gas bubbles in an adsorbed form under the right conditions. The collapse of the gas bubbles is caused by cavitation which results in intense local heating, high pressure, and a short life span. Acoustic cavitation serves as a means to concentrate dead sound energy. In an extreme environment, it can accelerate the condensation or hydrolysis reaction [56]. During cavitation, falling bubbles generate intense transient hot spots, high pressures, and short service life, consequently promote high-energy chemical reactions. A series of ultrasonic applications increase chemical reactivity [61]. The chemical effects of ultrasonic radiation cause many unique properties in irradiated solutions. With these extreme conditions, ultrasonic radiation methods are used to prepare nanoscale metals, metal oxides, metal sulfides, and others [57].

Ultrasonics are widely used in organic synthesis over the past few years. Compared with the traditional method, this method is better used and the reaction can be carried out with higher yields, shorter reaction times, and lighter conditions under ultrasonic radiation [58].

ZnS nanoparticles will be prepared using an inert-gas evaporation technique with induction heating. Furthermore, ZnS nanoparticles mixed with Na_2S solution under ultrasonic radiation. The product obtained was washed and separated by centrifugation and followed by drying. The synthesis product of ZnS using the ultrasonic radiation method with various solvents and reaction conditions is shown in Figure 9.

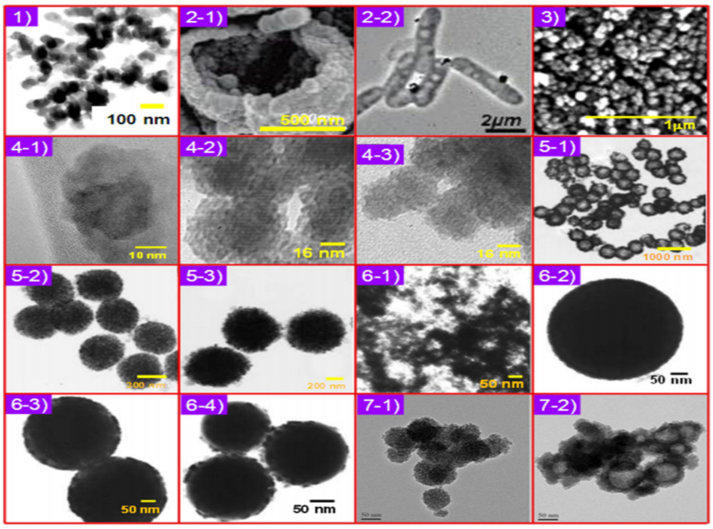

Figure 9. ZnS Nanoparticles. The results of the synthesis by ultrasonic radiation method with a variety of solvents and reaction conditions. Figure adopted from Lee [28].

The product obtained by ultrasonic radiation method tested with XRD, TEM, UV-VIS spectrophotometer, and photoelectron spectrophotometer [3].

2.6 Microwave Irradiation

Synthesis of ZnS nanoparticles can be done by the microwave irradiation method. The advantages of this method are using commercially available precursors, shorter reaction times, lower operating temperatures, carried out under ambient atmospheric conditions, and the product has a high purity [22].

Microwaves have lower quantum energy than the ionization energy of compounds, which is about 1.24 × 10-6 -1.24 × 10-3eV. Microwaves produce a dielectric heating effect [59].

The heat is caused by the interaction of the molecular dipole moment with high-frequency electromagnetic radiation, which is 2.45GHz. Water has a high dipole moment so it is widely used as a solvent in reactions with microwaves [62].

The precursors used in the microwave irradiation method included zinc salts, such as zinc acetate and thioacetamide [37]. The stages of ZnS synthesis using the microwave irradiation method are as follows:

- Zinc acetate solution ($Zn(CH_3COOH)_2.2H_2O$) and thioacetamide solution (CH_3CSNH_2) were prepared and combined stoichiometrically.
- The solution was diluted to 400 mL with the addition of distilled water.
- The solution is stored in a magnetic stirrer for one hour at a speed of 840 rpm to make a homogeneous solution.
- The solution was placed in a microwave oven (LG make) with a power of 900W for 12 minutes.
- A white precipitate was obtained and it was washed with distilled water and dried in an oven at 60° for 6 hours [37].

The representation of zinc sulfide nanoparticles in the form of a micrograph is shown in Figure 10.

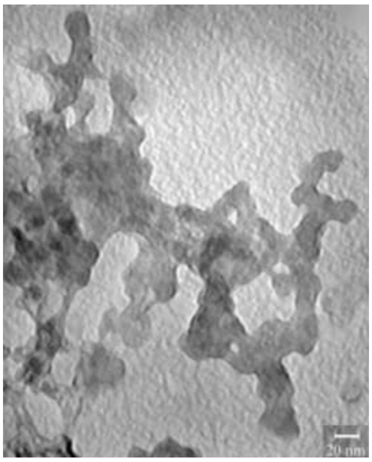

Figure 10. ZnS micrograph form. The result of the synthesis by microwave irradiation method. Figure adopted from Vazquez., et al. [12].

Conclusion

Semiconductor nanostructure materials recently attracted a lot of interest. One of them is zinc sulfide. This is because zinc sulfide has very diverse and useful applications. Its abundant source in the form of sphalerite is also one of the factors that zinc sulfide is easy to obtain.

Several ZnS nanoparticles synthesis methods can be carried out, including the one-pot process, sol-gel formation, hydrothermal process, coprecipitation, ultrasonic radiation, and microwave irradiation. Some of these methods have advantages and disadvantages. In terms of material availability, time efficiency, and quality of results, the microwave irradiation method has advantages over other methods and it is more proper, especially on an industrial scale. The results of the XRD analysis of ZnS nanoparticles showed that ZnS has a Zinc Blende (Sphalerite) structure.

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