EFFECT OF LIQUID ASSISTED SOLID STATE REACTION ON MORPHOLOGY OF ZINC OXIDE NANOPARTICLES

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ABSTRACT

Zinc oxide (ZnO) nanoparticles were synthesized by using liquid assisted solid state reaction method at room temperature. Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and excess of sodium hydroxide (NaOH) in molar ratio 1:3 were ground for 20 minutes at room temperature. Acetone, glycerol, and methanol mixed with water at different concentrations (%wt/wt); 10%, 20%, 30%, 40%, 100%; were used as assisted liquid. The product was washed with distilled water until its pH value of 7 and dried at 80 °C for 24 hours and then characterized by using XRD and SEM techniques. It was found that synthesized ZnO nanoparticles have rod-like morphology with 20-35 nm in width and 70-100 nm in length with hexagonal wurtzite structure.

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Chapter 1

Introduction

1.1 Motivation

Nanotechnology is a study of materials with morphological feature on the nanoscale, or nanometer (10^{-9} m) which is smaller than a one tenth of a micrometer in at least one dimension. The nanotechnology is a new approach to research and development that aim to control the fundamental structure and behavior of matter at the level of atoms and molecules. These fields open up the possibility of understanding new phenomena and producing new properties. Hence, many products have been enhanced by nanotechnology to improve our quality of life.

Zinc oxide (ZnO) is the interesting nanomaterials in now a day. ZnO is inexpensive, relatively abundant, chemically stable, high carrier mobility, transparency, wide band gap, low temperature process, non-toxic and easy to prepare. The characteristic of ZnO band gap energy of 3.37 eV at room temperature, exciton and biexciton energies of 60 meV and 15 meV respectively, which can creating ultra violet LEDs, white LEDs and solar cells. The improving of ZnO's exciton properties directly related to the optical properties in photovoltaic and displays. The other application of ZnO included medical and pharmaceutical, cosmetic, paint and pigment, adhesive and sealant, and rubber, etc.

ZnO can be synthesis by diverse method, such as sol-gel method, hydrothermal method, vapor-liquid-solid (VLS) method, vapor phase transfer method, and electrochemical method, etc. However, spray pyrolysis is typically used in industrial for ZnO production. Its major drawback of this process is consumed large energy consumption. Although solid state reaction is a conventional method for synthesis nanomaterials and it is not limit in the practical application and complicated equipments due to suitably condition. The chemical reaction in which solvents are not used, allows the reactants to chemically react without the presence of a solvent, produces more product than a normal reaction. It is also an environmental friendly because no waste to eliminate at the end of the reaction. Liquid-assisted is helpful in reducing the friction between particles during mixing. The liquid used must be inert, no hydrate and not react with the starting materials such as acetone, glycerol and methanol.

1.2 Objective

1.2.1 To synthesize zinc oxide nanoparticles by liquid assisted solid state reaction.

1.2.2 To study the effect of assisted liquid on morphology of zinc oxide nanoparticles.

1.3 Scope of study

1.3.1 To synthesize zinc oxide nanoparticles using liquid assisted solid state reaction at room temperature. Zinc acetate dihydrate and sodium hydroxide were used as starting materials in solid state reaction. Acetone, glycerol, and methanol at different concentration were used as assisted liquid.

1.3.2 To characterize the properties zinc oxide nanoparticles, the following techniques were used.

- X-ray Diffraction (XRD)
- Scanning Electron Microscopy (SEM)

1.4 Expected result

1.4.1 Obtain zinc oxide nanoparticles.

1.4.2 Obtain the appropriate condition for synthesis zinc oxide nanoparticles with desired morphology.

Chapter 2

Theoretical Background and Literature Review

2.1 Nanotechnology

Nanotechnology is a technology of controlling matters under nanoscale, can occur in one, two or three dimensions at the length scale of approximately 1 to 100 nanometers. A nanometer is equivalent to one-billionth of a regular meter or 10^{-9} of a meter [1], to create and utilize the material, structure, device or system [2]. However, nanotechnology is not merely working with matter at the nanoscale, but also research and development of materials, devices, and systems that have novel properties and functions due to their nanoscale dimensions or components [3].

A Nanostructure is through the control ability at atom, molecular and supermolecular level to produce a bigger structure of new molecular structure. The materials possess original physical, chemical and biological characteristics and phenomena, wherein it is mainly caused by the nano-quantum dimensional effect and surface effect, thereby changing the melting point, magnetism, heat resistance, electrical potential energy, optical properties, chemical activity, surface energy and catalysticities of matter to produce particular properties so as to trigger new applications [2].

At the very small scale, the properties of materials such as color, magnetism and the ability to conduct electricity change in unexpected ways. Nanoscale features are often incorporated into bulk materials and large surfaces.

Nanotechnology is already in many of the everyday objects around us, but this is only the start. It will allow limitations in many existing technologies to be overcome and thus has the potential to be part of every industry. New materials - Nanomaterials such as quantum dots, carbon nanotubes and fullerenes will have applications in many different sectors because of their new properties. So quantum dots can be used in solar cells, optoelectronics, and as imaging agents in medical diagnostics. Carbon nanotubes can be used in displays, as electronic connectors, as strengthening materials for polymer composites, and even as nanoscale drug dispensors. Fullerenes can be used in cosmetics, as "containers" for the delivery of drugs, in medical diagnostics, and even lubricants.

The future of nanotechnology has great potential. However, it also has the potential to change society more than the industrial revolution. It will affect everyone and so should be developed for everyone [4].

2.1.1 The structure of nanotechnology [3]

Nanotechnology is considered to be rather new, but it is by no means the only field concerned with atom and molecules. In different ways, the disciplines of physics, chemistry and biology have long dealt with atom and molecules, their behavior and their manipulation; and quantum mechanics is already firmly established the science of the absolutely small [2, 5]. The nanolevel is occurring in a variety of academic fields. More important, the most advanced research and product development increasingly requires knowledge of disciplines that, until now, operated largely independently. These areas include;

- **Physics**

The construction of specific molecules is governed by the physical forces between the individual atoms composing them. Nanotechnology will involve the continued design of novel molecules for specific purposes. However, the laws of physics will continue to govern which atoms will interact with each other and in what way. In addition, researchers need to understand how quantum physics affects the behavior of matter below a certain scale.

- **Chemistry**

The interaction of different molecules is governed by chemical forces. Nanotechnology will involve the controlled interaction of different molecules, often in solution. Understanding how different materials interact with each other is a crucial part of designing new nanomaterials to achieve a given purpose.

- **Biology**

A major focus of nanotechnology is the creation of small devices capable of processing information and performing tasks on the nanoscale. The process by which information encoded in DNA is used to build proteins, which then go on to perform complex tasks including the building of more complex structures, offers one possible template. A better understanding of how biological systems work at the lowest level may allow future scientists to use similar processes to accomplish new purposes. It is also a vital part of all research into medical applications.

- **Computer Science**

Moore's Law and its corollaries, the phenomena whereby the price performance, speed, and capacity of almost every component of the computer and communications industry has improved exponentially over the last several decades, has been accompanied by steady miniaturization. Continued decreases in transistor size face physical barriers including heat dissipation and electron tunneling that requires new technologies to get around. In addition, a major issue for the use of any nanodevices will be the need to exchange information with them. Finally, scientific advances will require the ability to manage increasingly large amounts of information collected from a large network of sensors.

- **Mechanical Engineering**

Even at the nanolevel issues such as load bearing, wear, material fatigue, and lubrication still apply. Detailed knowledge of how to actually build devices that do what we want they to do with an acceptable level of confidence will be a critical component of future research. Unfortunately, most of academia and the research community do not facilitate this type of multidisciplinary research. Work often tends to be compartmentalized into disciplines and subdisciplines with their own vocabularies. Research proposals are evaluated by experts within one area who neither understand nor appreciate developments in other fields. Young people coming into a field are usually rewarded for extending existing lines of research and take a risk if they try to look at the unexamined gaps between academic fields.

2.1.2 Example of nanotechnology morphology [6]

1. Nanopowders

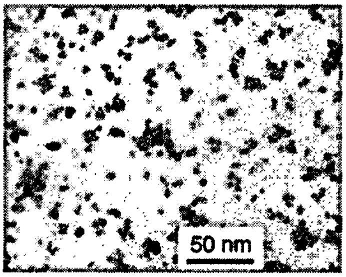


Figure 2.1: Morphology of nanopowder

Nanoparticle powders have unique properties of particles less than 100 nm give rise to a range of new and improved materials with a breadth of applications, allows to retain transparency, resistance to abrasion, improved solubility, conductivity or UV protection were found in materials.

2. Nanomembrane

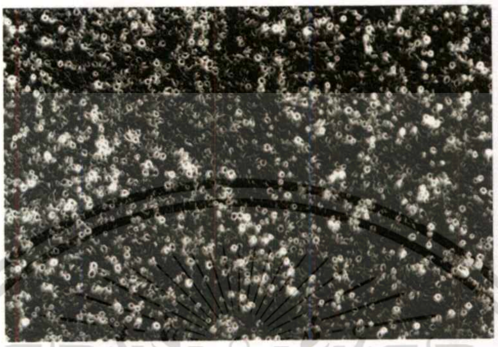


Figure 2.2: Morphology of nanomembrane

Nanomembrane filtration devices that 'clean' polluted water, sifting out bacteria, viruses, heavy metals and organic material. The key to lowering the energy demand and improving throughput for desalination is in understanding: how to selectively separate small molecules, and package these technologies for exploitation. Separation of molecules occurs efficiently in nature through membranes, such as the ion channels that remove salt from blood and the respiratory membranes that transport oxygen and carbon dioxide. In order to reduce the energy requirement for this process, nature provides large surface areas for the transport of molecules.

3. Carbon nanotubes

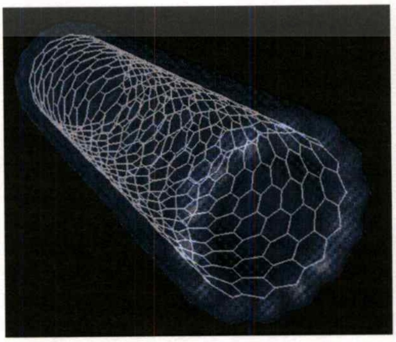


Figure 2.3: Structure of carbon nanotubes

The discovery that graphite can be rolled into a cylinder with a diameter of about one nanometer already has far-reaching consequences. Carbon nanotubes are strong but light, are being developed for a raft of uses, such as sensors, fuel cells, computers and televisions.

4. Molecular electronic "crossbar latches"

Hewlett-Packard believes that silicon computer chips will probably reach a technical dead end in about a decade, to be replaced by tiny nanodevices described as 'crossbar latches'.

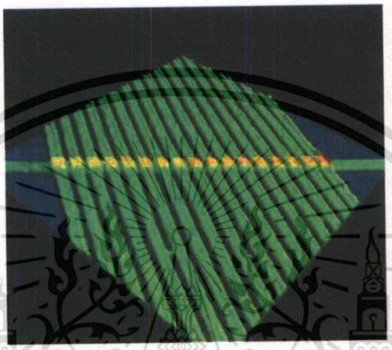


Figure 2.4: Morphology of cross bar latches

5. Quantum dots artificial atoms

Quantum dots are small devices that contain a tiny droplet of free electrons. They are fabricated in semiconductor materials and have typical dimensions between nanometers to a few microns (10^{-6}m). A quantum dot can have anything from a single electron to a collection of several thousands. The physics of quantum dots show many parallels with the behavior of naturally occurring atoms, but unlike their natural counterparts, quantum dots can be easily connected to electrodes and are therefore excellent tools to study atomic-like properties.

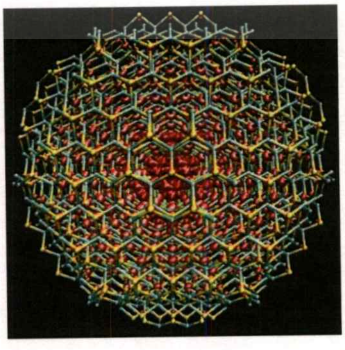


Figure 2.5: Structure of quantum dots

Since nanotechnology is classified by the size of the materials being developed and used, the products of this engineering can have little in common with each. At this level, Characterization tools used to be able to examine and see the nanostructures or the building blocks of nanomaterials, characterization tools such as X-ray diffraction, Synchrotron, Scanning and Transmission Electron Microscopy and Scanning Tunnelingunified. Nanoscale science unified the properties of materials change in unexpected ways at the nanoscale, the science of understanding the behavior of molecules at this scale is critical to the rational design and control of nanostructures for all product applications. Molecular level computations unified computation technologies such as quantum mechanical calculations, molecular simulations and statistical mechanics are essential to the understanding of all nanoscale phenomena and molecular interactions. Most important, Fabrication and processing technology unified processing techniques such as sol-gel, chemical vapor deposition, hydrothermal treatment, and milling are common techniques.

2.1.3 A Brief History of Nanotechnology [3]

Nanoparticles of gold and silver have been found in Ming dynasty pottery and stained glass windows in medieval churches. However, the origins of nanotechnology did not occur until 1959, when Richard Feynman, US physicist and Nobel Prize winner, presented a talk to the American Physical Society annual meeting entitled There's Plenty of Room at the Bottom 7. In his talk, Feynman presented ideas for creating nanoscale machines to manipulate, control and image matter at the atomic scale.

In 1974, Norio Taniguchi introduced the term 'nanotechnology' to represent extra-high precision and ultra-fine dimensions, and also predicted improvements in integrated circuits, optoelectronic devices, mechanical devices and computer memory devices8. This is the so called 'top-down approach' of carving small things from large structures.

In 1986, K. Eric Drexler in his book Engines of Creation discussed the future of nanotechnology, particularly the creation of larger objects from their atomic and molecular components, the so called 'bottom-up approach'. He proposed ideas for 'molecular nanotechnology' which is the self assembly of molecules into an ordered and functional structure.

The invention of the scanning tunneling microscope by Gerd Binnig and Heinrich Rohrer in 1981 (IBM Zurich Laboratories), provided the real breakthrough and the opportunity to manipulate and image structures at the nanoscale. Subsequently, the atomic force microscope was invented in 1986, allowing imaging of structures at the atomic scale.

Another major breakthrough in the field of nanotechnology occurred in 1985 when Harry Kroto, Robert Curl and Richard Smalley invented a new form of carbon called fullerenes ('buckyballs'), a single molecule of 60 carbon atoms arranged in the shape of a soccer ball. This led to a Nobel Prize in Chemistry in 1996. Since that time, nanotechnology has evolved into one of the most promising fields of science, with multi-billion dollar investments from the public and private sectors and the potential to create multi-trillion dollar industries in the coming decade.

2.2 Zinc oxide

Figure 2.6: Zinc oxide particles

2.2.1 General properties of zinc oxide

Zinc oxide (ZnO) is an inorganic compound come from earth's crush as zincite mineral. It is a white powder known as zinc white or calamine that is insoluble in water. The ZnO power is used as additive in various productions such as cosmetic, ceramic, rubber, glass, paint, pigment, adhesive, sealant, etc. However, most ZnO to be used in commercial is produced synthetically [7]. Hence, it can be widely used since it is inexpensive, relative abundant, chemically stable, easy to prepare and non-toxic [8].

2.2.2 Mechanical properties [9]

The micro- and nanoindentation methods have been widely used to determine the hardness of ZnO over a wide range of size scales and temperatures. ZnO is a relatively soft material with approximate hardness of 4.5 on the Mohs scale. Its elastic constants and bulk modulus are smaller than those of group III nitrides semiconductors such as GaN. Ultrasonic experiments on single-crystal specimens of the wurtzite ZnO have shown that this material becomes softer against shear-type acoustic distortions under pressure.

Among the tetrahedrally bonded semiconductors, it has been stated that ZnO has the highest piezoelectric tensor when compared to that of GaN. This property makes it a technologically important material for many piezoelectrical applications, which require a large electromechanical coupling. ZnO also have high heat capacity, heat conductivity, low thermal expansion, and high melting temperature.

2.2.3 Electronic properties [9]

Typically, ZnO is represented II-VI, n-type semiconductor with a direct wide band gap of 3.37 eV and large exciton binding energy of 60 meV. So it requires high breakdown voltages to maintain large electric fields, lower electronic noise, high-temperature and high-power operation. The n-type doping is easily substituting Zn with group-III elements such as Al, Ga, and In or by substituting oxygen with group-VII elements such as chlorine and iodine. The p-type doping is substituting group-I elements such as Li, Na, K with Zn and group-V elements such as N, P and As with O. The limitation of ZnO semiconductor is the difficulty of unstable p-type doping of GaN. However, this p-doping limitation does not change electronic and optoelectronic property of ZnO. The application of ZnO as electronic and optoelectronic devices such as transistors, solar cells, dye-sensitized solar cells (DSSC), light-emitting diodes (LED), and some other sensors devices.

2.2.4 Crystal structure [9]

The crystal structures of ZnO are hexagonal wurtzite, cubic zincblende, and cubic rocksalt are shown in Figure 2.7. Wurtzite and zincblende ZnO are tetrahedral geometry where each oxygen anion is surrounded by four zinc cations. The wurtzite symmetry is the most common and thermodynamically stable under ambient conditions. The zincblende structure can be stabilized by growth on cubic substrates, and the cubic rocksalt may be obtained at relatively high pressure.

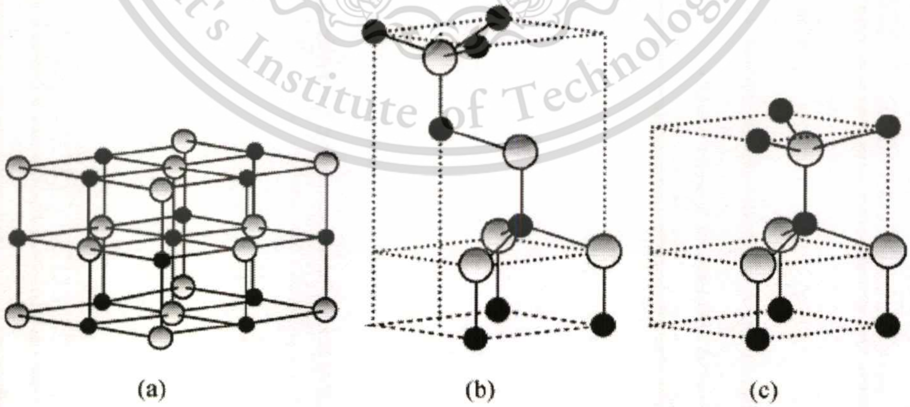


Figure 2.7: ZnO crystal structure (grey and black spheres represent Zn and O respectively)

a) Cubic rocksalt
b) Cubic zincblende
c) Hexagonal wurtzite

2.2.5 Example of zinc oxide morphology

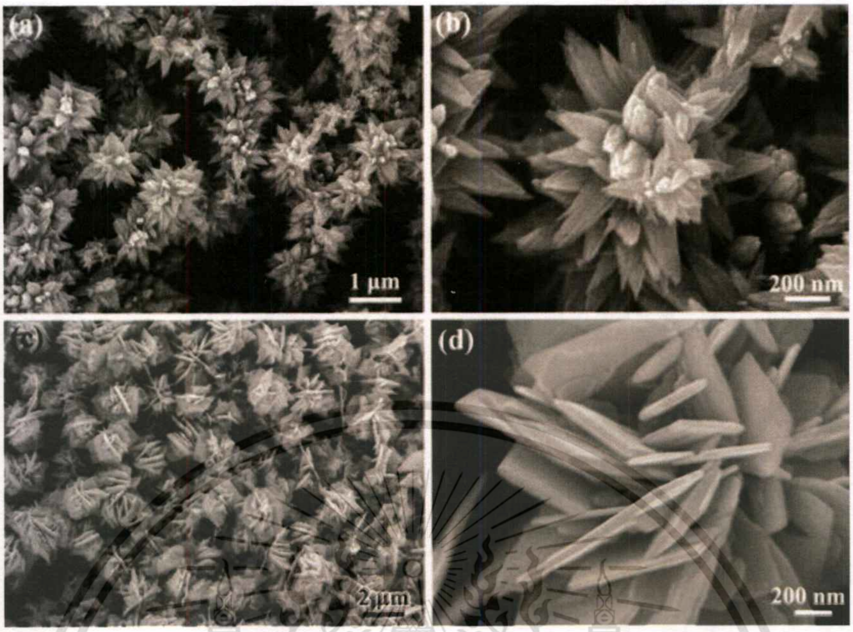


Figure 2.8: Morphology of ZnO nanoflowers (from nanoflakes) [10]

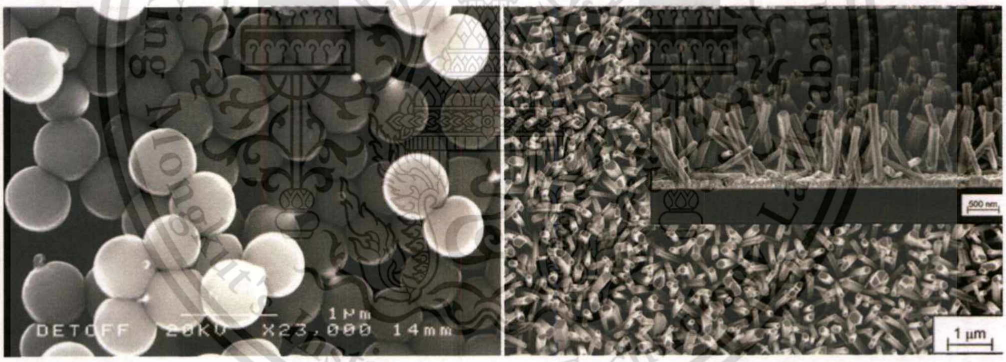


Figure 2.9: Morphology of ZnO nanopowders [11] and nanorods [12]

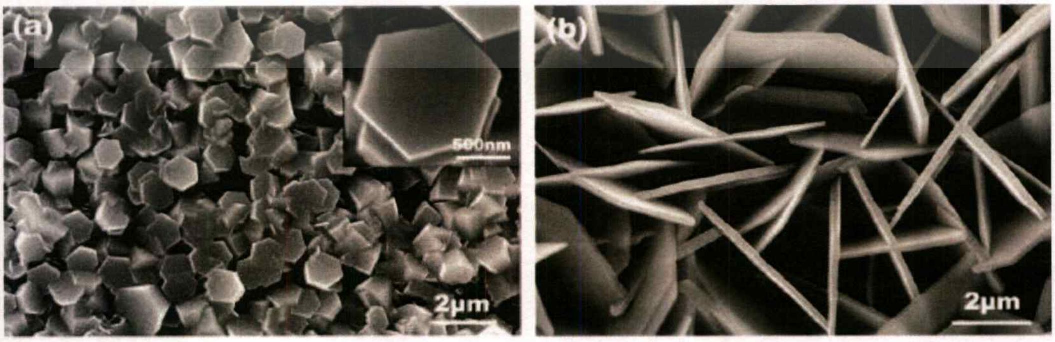


Figure 2.10: Morphology of ZnO nanodisks (from hexagonal plates) [13]

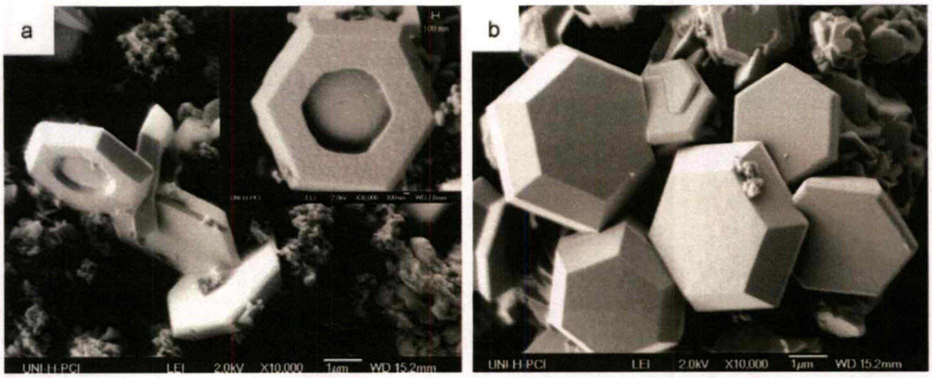


Figure 2.11: Morphology of ZnO grooved hexagonal disks [14]

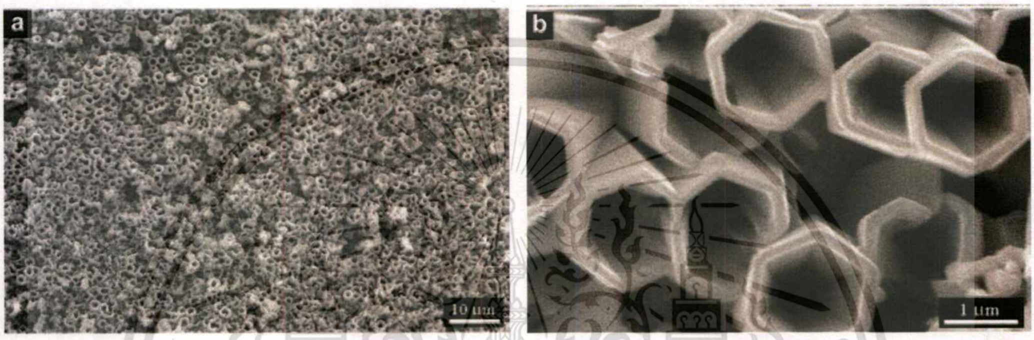


Figure 2.12: Morphology of ZnO tube arrays [15]

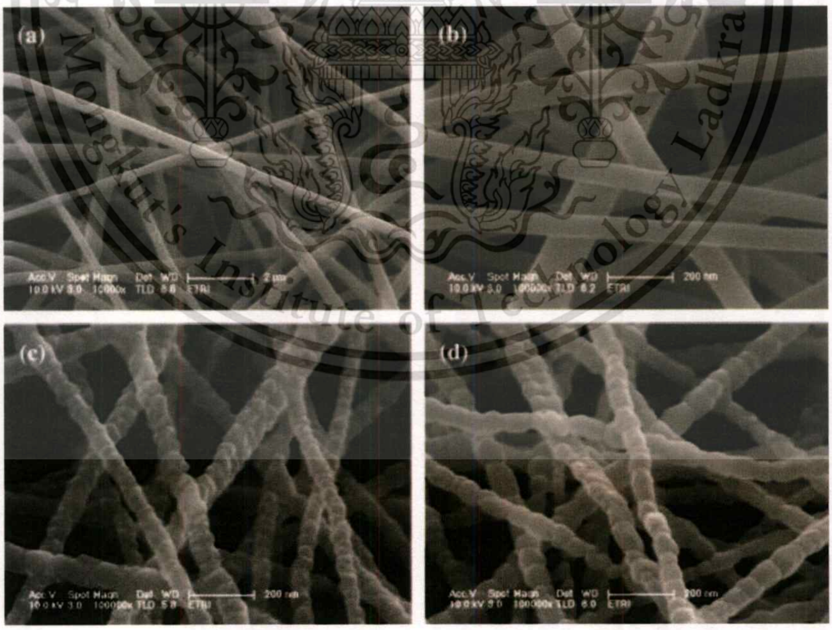


Figure 2.13: Morphology of ZnO nanofibers [16]

2.3 Application of zinc oxide [17]

- **Adhesive and sealant**

Figure 2.14: Zinc oxide adhesive plaster

ZnO has long been a major constituent of surgical and industrial tapes based on natural or synthetics rubber as it is outstanding in retention of tack during shelf–aging.

Neoprene adhesives are improved by the addition of both phenolic resins and zinc compounds (including ZnO), the reaction products imparting special properties such as high heat resistance, high bond strength, improved peel and shear-stress resistance, and stability to settling of neoprene solution adhesives.

- **Batteries, fuel cells, and photocells industry**

Figure 2.15: Energizer zinc air prismatic battery

ZnO is used in zinc-carbon dry cells, zinc-silver oxide batteries, nickle oxide-cadmium batteries and even in secondary batteries. In fuel cells, ZnO is used as electrode material, cathodic material and as a fuel element. And in solar energy cells, it can act as a photocatalyst. Purification of motorcar exhaust gases is currently the subject of extensive research, and ZnO is already demonstrating its catalytic properties in some of those programs.

- **Ceramics industry**

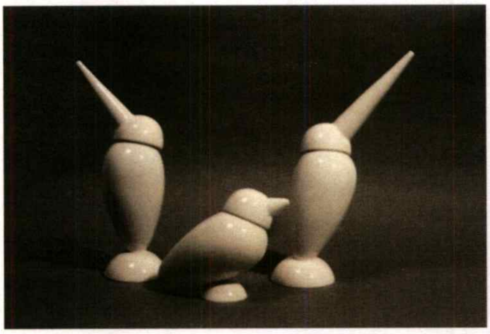


Figure 2.16: Ceramics

A widely used ZnO in ceramic industry are as white dyestuff. With the presence of ZnO, ceramic ware sintering temperature can lower to 400-600 °C, yet its surface is burned as polishing as a mirror.

ZnO imparts a unique combination of properties when used in glass. It is reduces the thermal expansion coefficient, imparts high brilliance and luster and high stability against deformation under stress. As a replacement flux for the more soluble constituents, it provides a viscosity curve of lower slope. The specific heat is decreased and the conductivity increased by the substitution of ZnO for BaO and PbO.

- **Cigarette filters**

ZnO as a constituent of cigarette filters is effective in removal of selected ingredients from tobacco smoke. A filter consisting of charcoal impregnated with zinc oxide and iron oxide removes significant amounts of HCN and H_2S from tobacco smoke without affecting its flavor.

- **Cosmetics industry**

Figure 2.17: Nano zinc oxide in sun protection

The optical and biochemical properties of ZnO and its derivatives impart special features to a variety of cosmetic preparations for care of the hair and skin. In powders and creams it protects the skin by absorbing the ultraviolet sunburn rays; UVA and UVB.

Simple salts of zinc provide astringent and skin-conditioning properties to creams, while more complex salts furnish fungistatic properties which contribute to the effectiveness of deodorants, soaps, and antidandruff preparations.

- **Ferrites**

ZnO continues as an essential ingredient in the "soft" type of ferromagnetic materials for television, radio, and tele-communication applications. In these fields ferrites based on magnetite, nickel oxide and zinc oxide are used as elements in many types of electronic devices.

Numerous electronic instruments for the consumer market utilize ferrites to impart specific functions. In portable and car radios, the antenna cores are ferrites designed to provide highly selective tuning. Television picture tubes constitute a major market for ferrites, particularly for use in flyback transformers and deflection yokes. In the communications area, ferrites are extensively used in the filter inductors of telephone circuits to permit precise inductance adjustment for the purpose of separating channels. Magnetic tape for recorders is improved by use of a magnetite precipitated in the presence of ZnO.

- **Fire retardants**

ZnO and its derivatives were used extensively in fire retardants for the military in World War II and those zinc compounds have since been the subject of extensive research and development for preparation of fire-retardant compositions for a variety of substances.

Solutions for fireproofing textiles contain zinc oxide, boric acid, and ammonia in various proportions. It deposits water-insoluble zinc borate on the fibers.

- **Lubricants**

Zinc dithiophosphates which are prepared by reacting zinc oxide with organic phosphates, are used in substantial quantities as additives to lubricating oils for automotive engines, to reduce oxidation corrosion and wear. ZnO has been found to contribute special properties in many types of lubricants, such as extreme-pressure lubricants, seizure-resistant lubricants, and greases. Improved adhesion is another feature which ZnO contributes.

ZnO imparts special properties to greases and other variety of lubricants. Such greases are useful in the lubrication of food–processing equipment.

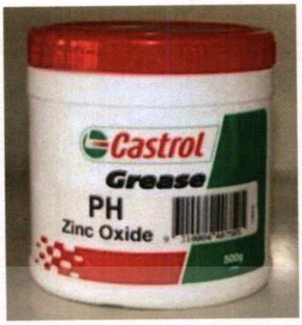


Figure 2.18: Castrol grease PH zinc oxide

- **Metal-protective coatings**

Zinc metal powder (zinc dust) and zinc compounds have long been utilized for their anticorrosive properties in metal-protective coatings, and today they are the basis of such important metal primers as zinc chromate primers.

Zinc dust-zinc oxide paints are especially useful as primers for new or weathered galvanized iron. Such surfaces are difficult to protect because their reactivity with organic coatings leads to brittleness and lack of adhesion. Zinc dust-zinc oxide paints however, retain their flexibility and adherence on such surfaces for many years. It is also provide excellent protection to steel structures under normal atmospheric conditions, as well as to steel surfaces in such under-water conditions as dam faces and the interior of fresh water tanks.

- **Paint industry**

Zinc oxide in organic coatings provides a broad spectrum of properties: optical, chemical, biochemical and physical. Over the past century of the paint industry, in its constant development of improved products, has utilized various aspects of those properties to high degree.

Manufacturers discovered that they could produce coatings of brushing consistency and good suspension properties by incorporation of ZnO into their pastes. Painters noted that they furnished better hiding power, whiteness, cleaner tints, tint retention, and durability as well as non-darkening in the presence of sulfur fumes.

- **Medical and pharmaceutical industry**

Zno is generally regarded as safe food additives under the condition of superb manufacturing process and feeding process. Daily-recommended intake for adult is 15 mg, and 25 mg for breast-feeding mother. ZnO features mild wound astringent, inflammation reduction/relief, and anti-microbial functions, also serve as a remedy for dermatitis and infection diseases, such as eczema, impetigo, ringworm, slack abscess, itch and psoriasis. The diameter of a nano ZnO measures approximately 10-20 nm. Most of them are fiber structure observed under microscope, with the features of fine grains, exceptional purity, and extraordinary whiteness.

Figure 2.19: Zinc oxide eugenol cement for dental use

- **Photocopying**

Some of the unique electronic properties of ZnO are distinctively utilized in the photocopying process. It is increased in photoconductivity and semiconductor properties by special heat and/or doping treatments (addition of foreign elements). Also, ZnO is greatly modified in optical properties to increase its absorption of light rays in the visible region, known as sensitization.

Commercial ZnO for photocopying is generally produced from metallic zinc, rather than ore, to obtain a product of higher purity.

- **Plastics industry**

Zinc compounds can provide a variety of properties in the plastics field. Heat resistance and mechanical strength are imparted to acrylic composites by ZnO. Addition of ZnO to epoxy resins cured with aliphatic polyamines imparts higher tensile strength and water resistance. ZnO imparts fire-resistant properties to nylon fibers and moldings. It is also useful in the preparation of nylon polymers and in increasing their resistance. The formation of polyesters in the presence of

ZnO imparts higher viscosity and other improvements. ZnO reacts with unsaturated polyesters to form higher viscosity and a thixotropic body. It also used to improve dye-ability of polyester fibers. The mixtures of ZnO stabilize polyethylene against aging and ultraviolet radiation. ZnO increases the transparency of poly(chlorofluoroethylene) molding resin. The addition of ZnO improves polyolefin's color, tensile strength, and vulcanization properties; thermal stabilization of PVC; Antistatic, fungistatic and emulsion stability of vinyl polymers.

- **Portland cement**

The beneficial effects of addition of ZnO to Portland cement have long been known as retardation of setting and hardening (to reduce the rate of heat evolution), improvement in whiteness and final strength.

- **Rubber industry**

The rubber industry, in its development over the past one hundred years, has utilized an increasing number of the many optical, physical and chemical properties of zinc oxide.

Figure 2.20: Tires

- **Activation and acceleration**

In the curing process for natural rubber and most types of synthetic rubbers, the chemical reactivity of Zinc Oxide is utilized to activate the organic accelerator.

The unreacted portion of the Zinc Oxide remains available as a basic reserve to neutralize the sulfur-bearing acidic decomposition products formed during vulcanization. Adequate levels of Zinc Oxide contribute markedly to chemical reinforcement, scorch control, and resistance to heat-aging and compression fatigue.

• Dielectric strength

In high-voltage wire and cable insulation, Zinc Oxide improves the resistance to corona effects by its dielectric strength, and at elevated operating temperatures it contributes to maintenance of the physical properties of the rubber compound by neutralization of Acidic decomposition product.

• Latex gelation

In the production of latex foam rubber products, ZnO is particularly effective in gelation of the foam with sufficient stability.

• Light Stabilization

Zinc Oxide is outstanding among white pigments and extenders for its absorption of ultraviolet rays. Thus, it serves as an effective stabilizer of white and tinted rubber compounds under prolonged exposure to the destructive rays of the sun.

• Pigmentation

Through its high brightness, refractive index, and optimum particle size, Zinc Oxide provides a high degree of whiteness and tinting strength for such rubber products as tire sidewalls, sheeting and surgical gloves.

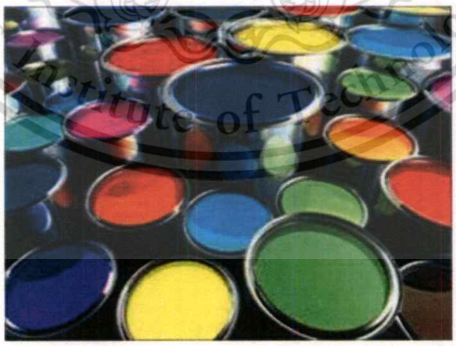


Figure 2.21: Pigments

• Thermoelements

ZnO plays an important role in semiconductor ceramic elements for operation at elevated temperatures or high voltages. Such thermoelements can be produced to cover a broad range of thermal and electrical properties.

Varistors are composed of semiconductor ZnO modified by other oxides. Developed for use as lightning arrestors and high-voltage surge arrestors in electric transmission lines, they are based on a unique electronic property of semiconductor ZnO, nonlinear resistance. ZnO varistors have high-temperature stability and resistance to humidity, electrical load, and current shocks.

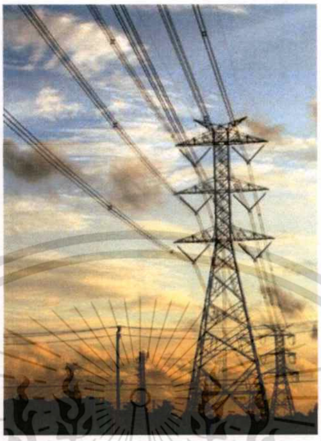


Figure 2.22: High voltage electricity post

2.4 Synthesis of zinc oxide [18]

Synthesis methods for nanoparticles are typically grouped into two categories: "top-down" and "bottom-up". The first involves division of a massive solid into smaller portions. This approach may involve milling or attrition, chemical methods, and volatilization of a solid followed by condensation of the volatilized components. The second, "bottom-up", method of nanoparticle fabrication involves condensation of atoms or molecular entities in a gas phase or in solution. The latter approach is far more popular in the synthesis of nanoparticles.

Dispersions of nanoparticles are intrinsically thermodynamically metastable, primarily due to their very high surface area, which represents a positive contribution to the free enthalpy of the system. If the activation energies are not sufficiently high, evolution of the nanoparticle dispersion occurs causing an increase in nanoparticle size as typified by an Ostwald ripening process. Thus, highly dispersed nanoparticles are only kinetically stabilized and cannot be prepared under conditions that exceed some threshold, meaning that so-called "soft-chemical" or "*chemie duce*" methods are preferred. In addition, the use of surface stabilization is employed in many nanomaterials to hinder sintering, recrystallization and aggregation.

2.4.1 Solid state reaction [19]

A solid state reaction, also called a dry media reaction or a solventless reaction, is a chemical reaction in the absence of solvent. In a normal reaction, the reacting agents, also called the reactants, are placed in a solvent before the reaction can take place. These reactants react to form a new substance. After the reaction is completed, scientists are able to remove the new product from the solvent. A solid-state reaction, however, can perform without the presence of a solvent and reactants are able to chemically react.

There are many positives of *solid state reaction* which has been flowing through most of the industries worldwide [20]. It is important to economics because the elimination of solvents means that products will costless. This, in turn, will make those products cheaper to buy. With normal reactions, scientists need to remove the residual solvent from the resulting product after a reaction has finished. Producing materials from a solid state reaction will mean that scientists are able to bypass the purification process. Eliminating the solvent from the reaction means that a solid state reaction produces more product than a normal reaction can. It also is more environmentally friendly. Since there is no solvent, there is no waste to eliminate at the end of the reaction.

An example of a solid state reaction revolutionizing other industries is the development of a recyclable catalyst. This catalyst is able to be completely removed and reused at the end of the reaction. The catalyst is first dissolved in the reactants. Once the reactants are introduced to one another, the catalyst slowly precipitates into a sticky solid. The reactants are able to fully react with each other, and the catalyst separates itself from the resulting products and is able to be separated and recycled.

There are several conditions under which a solid state reaction can take place. Oven techniques use high temperatures to encourage reactions without solvents. In a melt technique, the reactants are melted together. The melted reactants interact in the liquid state and become a paste which then hardens into a solid. Some reactants are highly reactive in the presence of a gas. Therefore, scientists expose the substance to a stream of reactive gas. This process is called a gas reaction.

Though there are many benefits to developing solid state reactions, there are also many drawbacks. The high friction of solid reactants would not result in a good mixing homogeneous system. The one useful technique is "liquid-assisted" solid state reaction. A small amount of liquid is added to help mixing solid reactants. The liquid-assisted have ability to control product morphology and crystallinity. However, they must not have hydrate site which may react with the reactants such as alcohol and ketone.

2.4.2 Hydrothermal synthesis [21]

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures, also termed "hydrothermal method". The term "hydrothermal" is of geologic origin. Geochemists and mineralogists have studied hydrothermal phase equilibria since the beginning of the twentieth century. George W. Morey at the Carnegie Institution and later, Percy W. Bridgman at Harvard University did much of the work to lay the foundations necessary to containment of reactive media in the temperature and pressure range where most of the hydrothermal work is conducted.

Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water. A gradient of temperature is maintained at the opposite ends of the growth chamber so that the hotter end dissolves the nutrient and the cooler end causes seeds to take additional growth.

Possible advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapor pressure near their melting points can also be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good quality crystals while maintaining good control over their composition. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows.

2.4.3 Sol-gel technique [22]

The sol-gel process is a wet chemical technique widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically metal oxides) starting from a colloidal solution (*sol*) that acts as the precursor for an integrated network (or *gel*) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal salts (such as chlorides, nitrates and acetates), which undergo various forms of hydrolysis and polycondensation reactions.

In this chemical procedure, the 'sol' (or solution) gradually evolves towards the formation of a gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks. In the case of the colloid, the volume fraction of particles (or particle density) may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation.

Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes imposed upon the structural template during this phase of processing.

Afterwards, a thermal treatment, or firing process, is often necessary in order to favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the distinct advantages of using this methodology as opposed to the more traditional processing techniques is that densification is often achieved at a much lower temperature.

The precursor sol can be either deposited on a substrate to form a film (e.g., by dip-coating or spin-coating), cast into a suitable container with the desired shape (e.g., to obtain monolithic ceramics, glasses, fibers, membranes, aerogels), or used to synthesize powders (e.g., microspheres, nanospheres). The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product. It can be used in ceramics processing and manufacturing as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, biosensors, medicine (e.g., controlled drug release), reactive material and separation (e.g., chromatography) technology.

2.4.4 Precipitation process [23]

The precipitation of solids from a metal ion containing solution is one of the most frequently employed production processes for nanomaterials. Metal oxides as well as non-oxides or metallic nanoparticles can be produced by this approach. The process is based on reactions of salts in solvents. A precipitating agent is added to yield the desired particle precipitation, and the precipitate is filtered out and thermally post-treated. In precipitation processes, particle size and size distribution, crystallinity and morphology (shape) are determined by reaction kinetics (reaction speed). The influencing factors include, beyond the concentration of the source material, the temperature, pH value of the solution, the sequence in which the source materials are added, and mixing processes.

A good size control can be achieved by using self-assembled membranes, which in turn serve as nanoreactors for particle production. Such nanoreactors include microemulsions, bubbles, micelles and liposomes. They are composed of a polar group and a non-polar hydrocarbon chain. Micro-emulsions, for example, consist of two liquids that cannot be mixed with one another in the concentrations used, usually water and oil along with at least one tenside (substance that reduces the surface tension of liquids). In certain solvents this gives rise to small reactors in which nucleation and controlled particle growth take place. Particle size is determined by the size of the nanoreactors and, at the same time, particle agglomeration is prevented. Microemulsion processes are often used to produce nanoparticles for pharmaceutical and cosmetics applications.

An additional process that is based on selforganized growth with templates and coatings is hydrothermal synthesis. Zeolites (microporous aluminum-silicon compounds) are produced from aqueous superheated solutions in autoclaves (airtight pressure chambers). The partial vaporization of the solvent creates pressure in the autoclaves (several bars), triggering chemical reactions that differ from those under standard conditions, for example by altering the solubility. Nanoparticle formation and cavity shape can be controlled by adding templates. Templates are particles with bonds that enable the formation of certain forms and sizes.

2.4.5 Gas phase process or Aerosol Process [24]

Nanoparticles are created from the gas phase by producing a vapor of the product material using chemical or physical means. The production of the initial nanoparticles, which can be in a liquid or solid state, takes place via homogeneous nucleation. Depending on the process, further particle growth involves condensation, chemical reaction on the particle surface and coagulation processes, as well as coalescence processes [23].

Aerosol processes are used routinely for the commercial production of ultrafine particles ($d_p < 100$ nm) and materials fabricated from them, and for pilot and laboratory scale production as well. The most important process conditions are usually the aerosol volume concentration (volume of particles per unit volume of gas) and the time/temperature history of the system. Powdered material produced commercially by aerosol reactors is usually in the form of large agglomerates of particles held together by bonds of varying strength. These combine to form *aggregates* held together by necks resulting from sintering.*Agglomerates* are undispersed clusters of aggregates held together by weak (van der Waals) forces or binders.

Product properties of interest include primary particle size (and/or size distribution) and substructure (grain boundary, pore size and defect concentrations, and crystalline state). Also of great interest are the properties of the aggregates, including fractal dimension and particle bond energies. Methods have been developed for relating particle size to process conditions and material properties.

Fine particle formation by aerosol processes almost always takes place by gas-to-particle conversion. Condensable molecules produced by physical or chemical processes self-nucleate to form particles. The nuclei may be as small as a single molecule for refractory materials, but subsequent collision and coalescence leads to the formation of larger particles. Many lab-scale studies have been made to demonstrate novel methods for particle synthesis or to elucidate the mechanisms of particle formation.

2.4.6 Spray pyrolysis

Spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated surface, where the constituents react to form a chemical compound. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition. The process is particularly useful for the deposition of oxides [25].

Most spray pyrolysis is done from aqueous solutions. This is conducive to a low-cost process, and spraying flammable liquids on a heated surface can be exciting, if not dangerous. However, some investigators have developed processes using nonaqueous solutions.

2.4.7 Other methods

Several chemical methods for the synthesis of zinc oxide and mixed metal oxides have been reported; for example, precipitation from alcohols and amines. In most of these studies, the control of particle morphology and the rate of particle growth have been considered in order to avoid the formation of large particles.

2.5 Characterization technique

2.5.1 X-ray Diffraction (XRD)

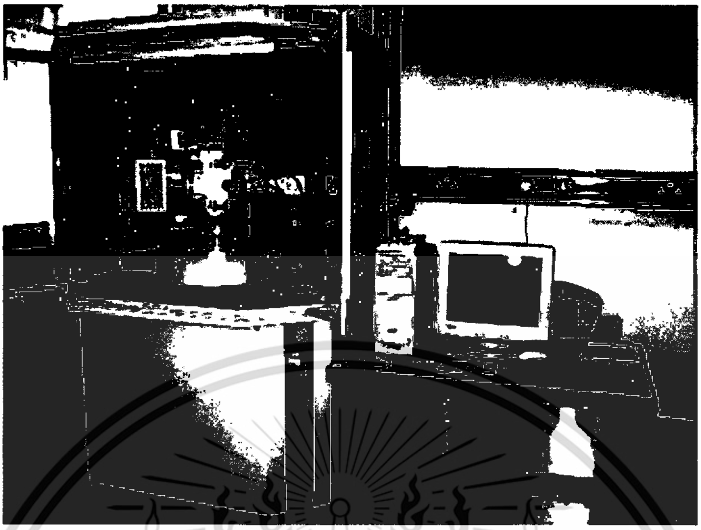


Figure 2.23: X-ray diffractometer

X-ray diffraction is a versatile, non-destructive analytical method for identification and quantitative determination of various crystalline forms, known as 'phases' of compound present in powder and solid samples. Diffraction occurs as waves interact with a regular structure whose repeat distance is about the same as the wavelength. The phenomenon is common in the natural world, and occurs across a broad range of scales. X-rays can diffract from minerals which, by definition, are crystalline and have regularly repeating atomic structures. When certain geometric requirements are met, X-rays scattered from a crystalline solid can constructively interfere, producing a diffracted beam [26].

X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2. The instrument used to maintain the angle and rotate the

The spacing between reflecting planes is *d* and the glancing angle of the incident x-ray beam is θ, the path difference for waves reflected by successive planes is $2d\sin\theta$. Hence the condition for diffraction (the Bragg condition) is;

$$n\lambda = 2d\sin\theta$$

where n = 0, 1, 2, 3, …
λ = X-ray wavelength
d = d-spacing
θ = diffraction angle

The distances between similar atomic planes in mineral (the interatomic spacing) is called the d-spacing. The diffraction angle which called the theta angle is measured in degrees. For practical reasons the diffractometer measures an angle twice of that the theta angle. Not surprisingly, we call the measured angle '2-theta'.

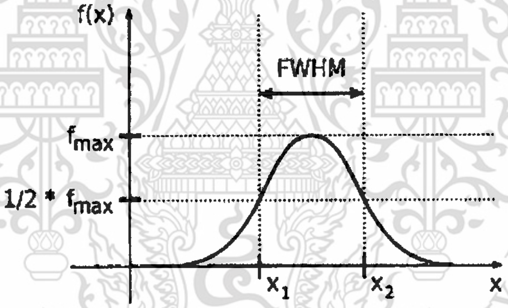


Figure 2.26: Scheme of Scherrer's equation

Here XRD was done by the X-ray diffraction of the as milled powder samples were performed using the diffractometer. X-Ray diffraction patterns were recorded from 20° to 90° using Cu-K_α (λ = 1.5406 A°) with an accelerating voltage of 40 KV. Data were collected with a counting rate of 1 °/min. The K_α doublets were well resolved. From XRD, the crystallite size can be found out by using the scherrer's formula [26];

$$Particle\ size = \frac{K\lambda}{\beta\cos\theta}$$

where K = crystallite shape factor
λ = wavelength of x-rays
β = FWHM (full width at half maximum)
θ = diffraction angle

2.5.2 Scanning electron microscopy (SEM) [29]

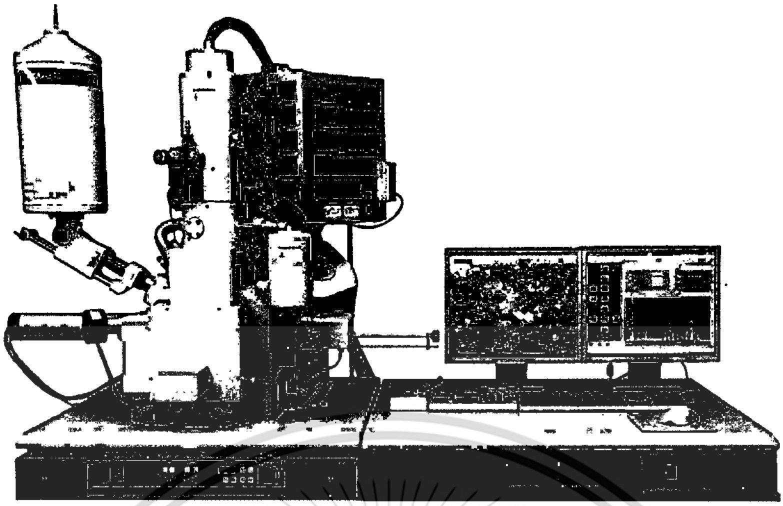


Figure 2.27: Scanning electron microscope

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD). The design and function of the SEM is very similar to the EPMA and considerable overlap in capabilities exists between the two instruments.

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons sample is termed a *goniometer*. For typical powder patterns, data is collected at 2θ from about 5° to 70° which are preset in the X-ray scan [27].

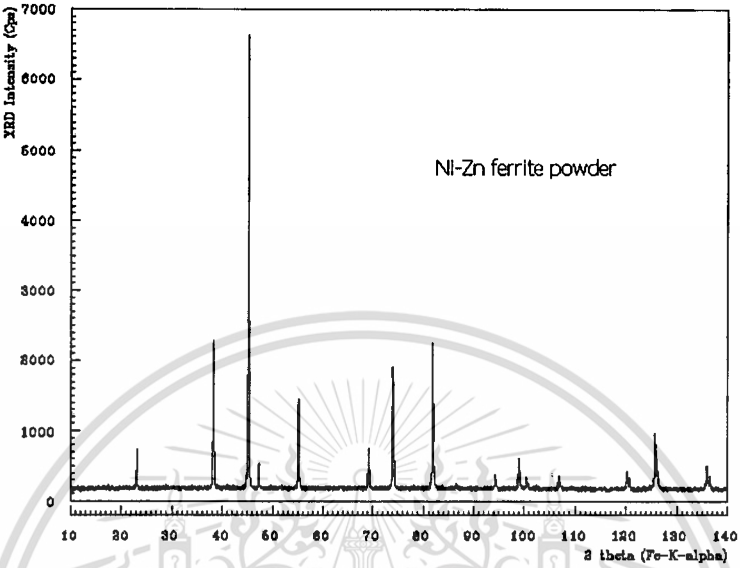


Figure 2.24: XRD pattern of Ni-Zn ferrite powder

One method of interpreting x-ray diffraction is the Bragg formulation. The x-ray waves are considered as being reflected by sheets of atoms in the crystal. When a beam of monochromatic (uniform wavelength) x-rays strikes a crystal, the wavelets scattered by the atoms in each sheet combine to form a reflected wave. If the path difference for waves reflected by successive sheets is a whole number of wavelengths, the wave trains will combine to produce a strong reflected beam [28].

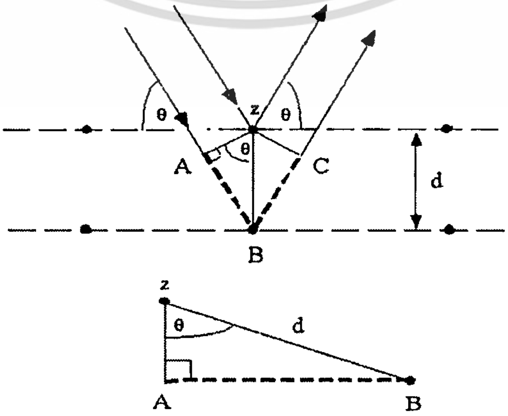


Figure 2.25: Scheme of Bragg's equation

(characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence-CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete ortitals (shells) of atoms in the sample..As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

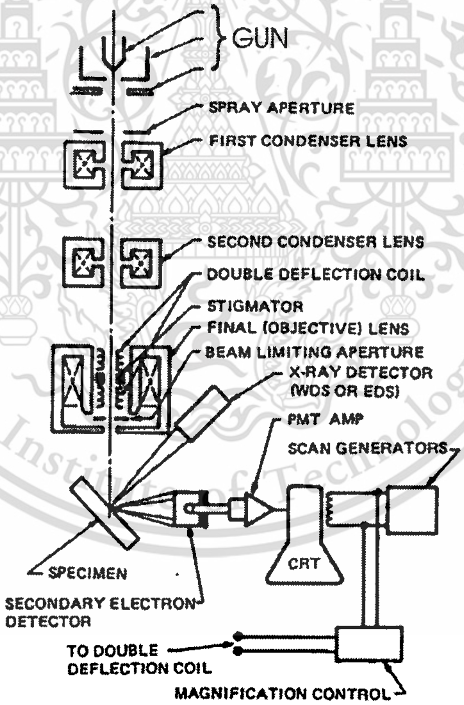


Figure 2.28: Scheme drawing of the electron and x-ray optics of a combined SEM-EPMA

SEMs always have at least one detector (usually a secondary electron detector), and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on which detectors it accommodates.

2.6 Literature review

In 2005, V. Prasad, C. D'Souza, D. Yadav, A.J. Shaikh, and N. Vigneshwaran [30] had been synthesized a well-crystallized ZnO nanorods by solid state reaction at room temperature. The anionic detergent sodium lauryl sulfate (SLS) as stabilizing agent was added to zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$). After the mixture was allowed to stand for 2 h, sodium hydroxide (NaOH) pellets were added into the mixture and ground for 30 min. The product was washed in ultrasonic bath with deionized water and alcohol to remove by-product and excess SLS. After washing, the product mixture was centrifuged at 10,000 rpm and the settled ZnO was dried at 80 °C for 2 h. The X-ray diffraction (XRD) analysis revealed the single crystals, hexagonal wurtzite structure of ZnO nanorods. The average thickness of ZnO nanorods characterized by transmission electron microscope (TEM) and XRD was estimated to be 21 nm while the length was around 48 nm. Fourier transform infrared (FT-IR) analysis confirmed the binding of SLS with ZnO nanorods which found to be 1:10 SLS:ZnO mass ratio, based on thermogravimetric analysis (TGA).

In 2006, Xianming Hou, Feng Zhou, and Weimin Liu [31] had been synthesized ZnO nanorods via solid state reaction at relatively low temperature. Anhydrous zinc sulfate ($ZnSO_4$) and sodium hydroxide as starting material were ground together for 20 min under the irradiation of a 250WIR lamp. The product was washed and dried at 60 °C in vacuum for 10 h. The diffraction peaks of XRD are welled indexed to higt crystallinity hexagol ZnO with no impurities detected. The difference of the growth rates in the different crystalline facets have also been observed in the solution-phase synthesis. The influence of Zn^{2+}/OH^{-} ratio on the size and morphology of the as-prepared ZnO showed that when Zn^{2+}/OH^{-} ratio was 1:4, a good rod-like morphology with the diameter of 30 - 50 nm and length of ca. 600 nm can be obtained.

In 2008, Y. Caoa, P. Hu,W. Pan, Y. Huang, and D. Jia [32] had been synthesized ZnO nanoparticles-0, and ZnO nanorods-1 and -2 by solid state reaction at room temperature. For the first reaction, solid zinc chloride ($ZnCl_2$) and sodium hydroxide (NaOH) with a molar ratio of 1:2 were ground for 5 min. Then the mixture was washed with distilled water to remove sodium chloride (NaCl). The product ZnO nanoparticles-0 was dried in air. And for the second reaction, solid $ZnCl_2$ was first ground and blended with polyethylene glecol-600 (PEG-600). After that NaOH powder was added at a 1:2 molar ratio with $ZnCl_2$. The mixture was then ground for 30 min and washed with distilled water and alcohol to remove NaCl and PEG-600. The product ZnO nanorods-1 was dried in air. For the third reaction, $ZnCl_2$ and $Na_2WO_4 \cdot 2H_2O$ at a molar ratio of 1:2 were mixed and ground for 30 min. Next added PEG-600 into the mixture and allowed to deposit for 10 min, and NaOH powder was add a molar ratio of 1:2 with $ZnCl_2$. The mixture was then ground for 30 min and wash with distilled water and alcohol to remove NaCl, Na_2WO_4, and PEG-600. The product ZnO nanorods-2 was dried in the air. The XRD, TEM, SEM were used to characterize the ZnO nanoparticles and nanorods product.

In 2008, Tarek Alammar and Anja-Verena Mudring [33] had been synthesized ZnO nanorods ultrasound-assisted method. Zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was ground in agate mortar in the neat room temperature, followed by the addition of sodium hydroxide (NaOH) and ionic-liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide or $[C_4mim][Tf_2N]$. The reaction mixture was then sealed air-tight in a glass tube and irradiated with ultrasound at room temperature for 12 h. The product was separated by centrifugation, washed with ethanol and demineralized water and finally dried at 90 °C for 2 h under vacuum. The XRD pattern proves that the obtained product is a single phase ZnO with the hexagonal Wurzite structure. The TEM images also show that the sample is composed of crystalline nanorods with about 20 nm in diameters and 50 - 100 nm in length.

In 2009, Y. Caoa,W. Pana, Y. Zonga, and D. Jia [34] had been synthesized ZnO nanorods by low heating solid state reaction. Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), sodium dodecyl sulfate (SDS), and sodium hydroxide (NaOH) were mixed (molar ratio 1:1:2.5) and ground together for 50 min at room temperature. The mixture was washed with distilled water in an ultrasonic bath and then dried in air at 60 °C for 2 h. From XRD pattern was indicated the hexagonal wurtzite of ZnO. SEM and TEM image was shown uniform nanorods' structure with a diameter of 60–80 nm and a length up to 900 nm.

In 2011, Kangfeng Li, Hao Luo, and Taokai Ying [35] had been synthesized ZnO nanoparticles by solid state reaction in an ionic liquid (1-butyl-3-methylimidazo-lium chloride, [BMIM]Cl) at room temperature. The starting materials zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was ground for 5 min, then [BMIM]Cl and sodium hydroxide (NaOH) flake were added and the mixture was ground together for 30 min to obtain a white batter. The product was then washed with distilled water and alcohol, and dried in vacuum at 60 °C for 6 h to yield 78-83% ZnO nanoparticles. The results from the XRD, SEM, and TEM images of ZnO nanoparticles had shown the hexagonal wurtzite structure of a homo-sized particle with 15-20 nm spherical morphology.

Chapter 3

Experimental

3.1 Chemicals

- Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$)
- Sodium hydroxide pellets (NaOH), analytical grade
- Acetone ($(CH_3)_2CO$)
- Glycerol ($C_3H_5(OH)_3$), commercial grade
- Methanol (CH_3OH)
- Distilled water

3.2 Apparatus

- Glassware
- Digital balance
- Hot plate with magnetic stirrer
- pH paper
- Mortar and pestle
- Oven
- Ultrasonic bath
- Analytical instruments
  - X-ray Diffractometer (XRD)
  - Scanning Electron Microscope (SEM)

3.3 Experimental

3.3.1 Synthesis of zinc oxide nanoparticles by liquid assisted solid state reaction

The solid state reaction of zinc acetate dihydrate with sodium hydroxide produces zinc oxide. The mixture of water with acetone, glycerol, and methanol at different concentrations (%wt/wt); 10%, 20%, 30%, 40%, 100%; were used as assisted liquid. The synthesis procedure of zinc oxide nanoparticles is done in following steps;

1. Zinc acetate dihydrate 54.85 g and excess of sodium hydroxide 30 g (mole ratio 1:3) are ground in mortar.
2. During grinding, slowly add 30 ml of 10% acetone as liquid-assisted to the mixture.
3. Continue grinding for 20 minutes.
4. Wash the mixture with distilled water in ultrasonic bath until its pH value of 7.
5. Dry the product in the oven at 80 °C for 24 hours.
6. Repeat the steps 1 to 5 by using another liquid-assisted.
7. The synthesized zinc oxide nanoparticles are characterized by using XRD and SEM.

The reaction process can be described as followed;

$$\mathrm{Zn(CH_3COO)_2 \cdot 2H_2O + 2NaOH \xrightarrow{liquid-assisted} ZnO + 2CH_3COONa}$$

Flow diagram

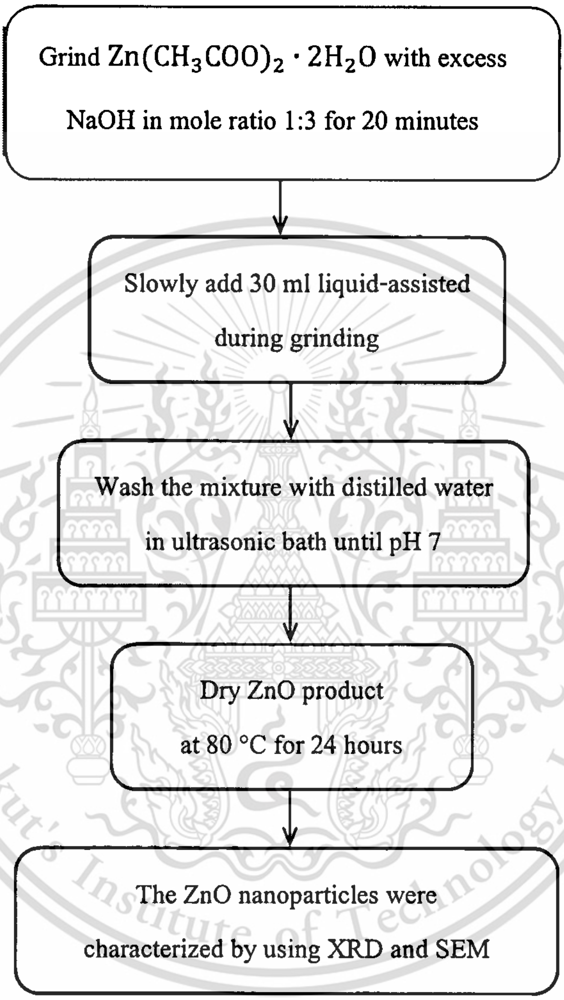


Figure 3.2: Synthesis of ZnO nanoparticles flow diagram

Chapter 4

Results and Discussion

4.1 Synthesis of zinc oxide nanoparticles by liquid assisted solid state reaction

Synthesized ZnO nanoparticles prepared from 3.3.1 were characterized by XRD and SEM as shown in Figure 4.1, 4.2, 4.3 and 4.4. The percent yield of synthesized ZnO nanoparticles is also shown in Table 4.4.

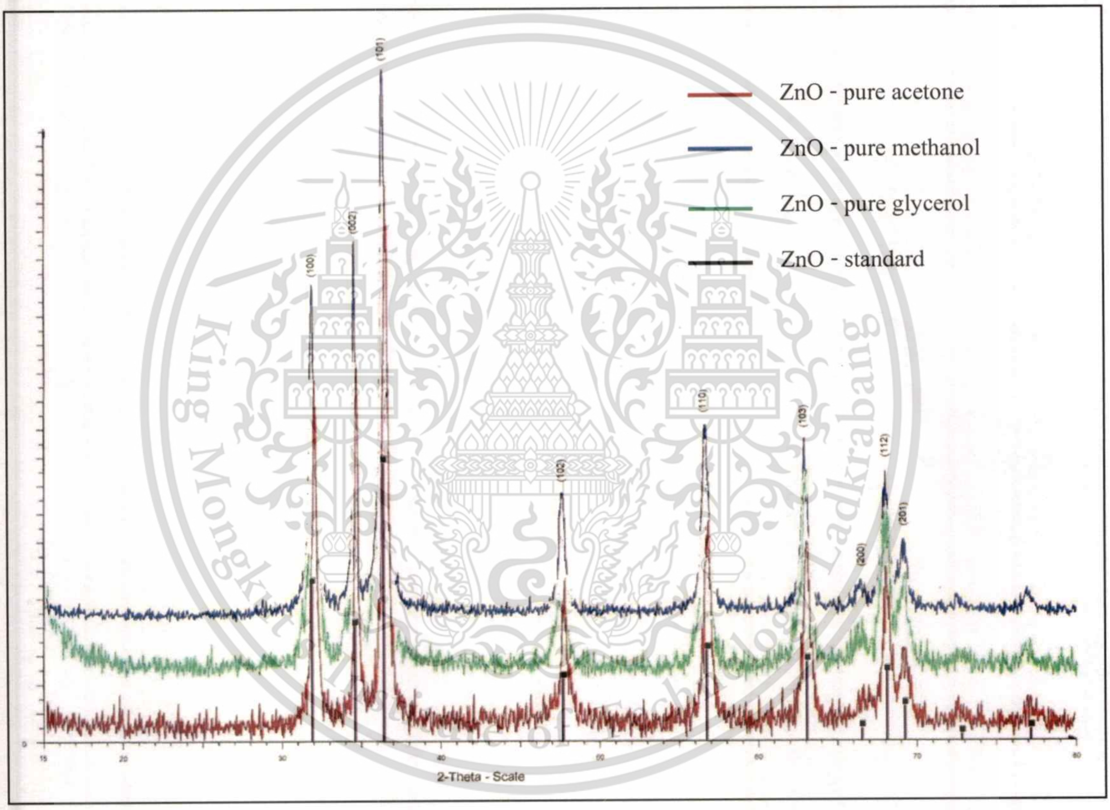


Figure 4.1: XRD pattern of ZnO via liquid assisted solid state reaction

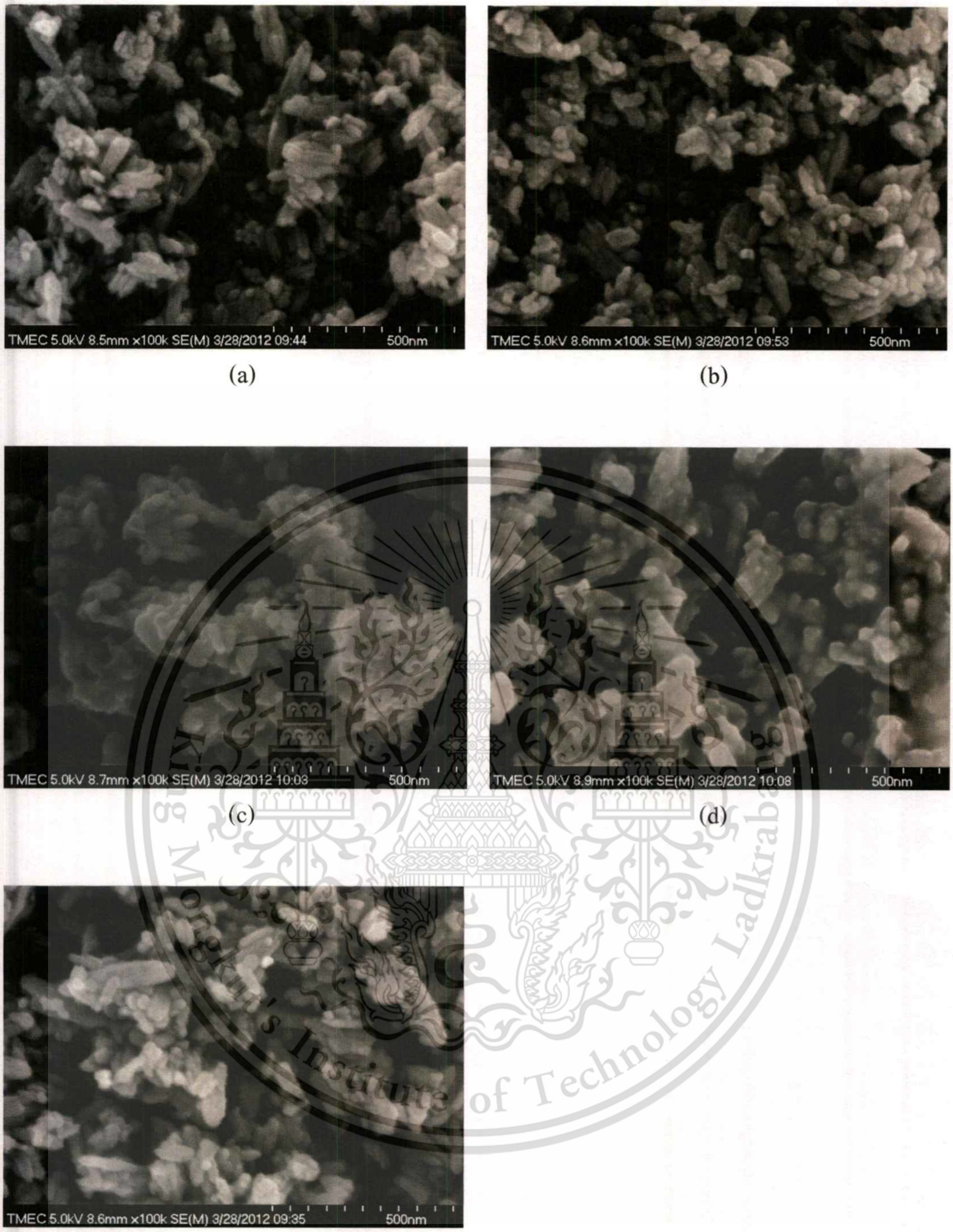
Figure 4.1 shows the XRD patterns of synthesized ZnO by various liquid assisted solid state reactions. The diffraction patterns of ZnO samples have the same peak positions when compared to the standard ZnO (JCPDS No.79-0205). All diffraction peaks are indicated to the hexagonal wurtzite structure of ZnO. Synthesized ZnO has high purity and good crystallinity, since all peaks are sharp and in good agreement with standard ZnO. The broad peaks also indicate that synthesized ZnO nanoparticles are in nano range which is corresponding to SEM images as shown in Figure 4.2, 4.3, and 4.4 and also the calculated values as shown in Table 4.1, 4.2, and 4.3. (The other XRD patterns are shown in Appendix B.2)

The crystallite size of synthesized ZnO nanoparticles was calculated by the Debye–Scherrer equation;

$$particle\ size = \frac{K\lambda}{\beta cos\theta}$$

where K is a crystallite shape factor (K=0.89), λ is X-rays wavelength (λ=0.15406 nm), β is the full width in radians at half-maximum (FWHM) of diffraction peaks, and θ is the Bragg angle of the X-ray pattern. The calculated values of crystallite size of ZnO nanoparticles synthesized by various liquid assistedare shown in Table 4.1, 4.2, and 4.3.

The SEM images of ZnO nanoparticles synthesized by various liquid assisted at different concentrations via solid state reactions are shown in Figure 4.2, 4.3, and 4.4. It can be seen that all ZnO nanoparticles synthesized from various assisted liquid have rod-like morphology. The crystalline ZnO nanorods are about 20-35 nm in width and 70 – 100 nm in length.



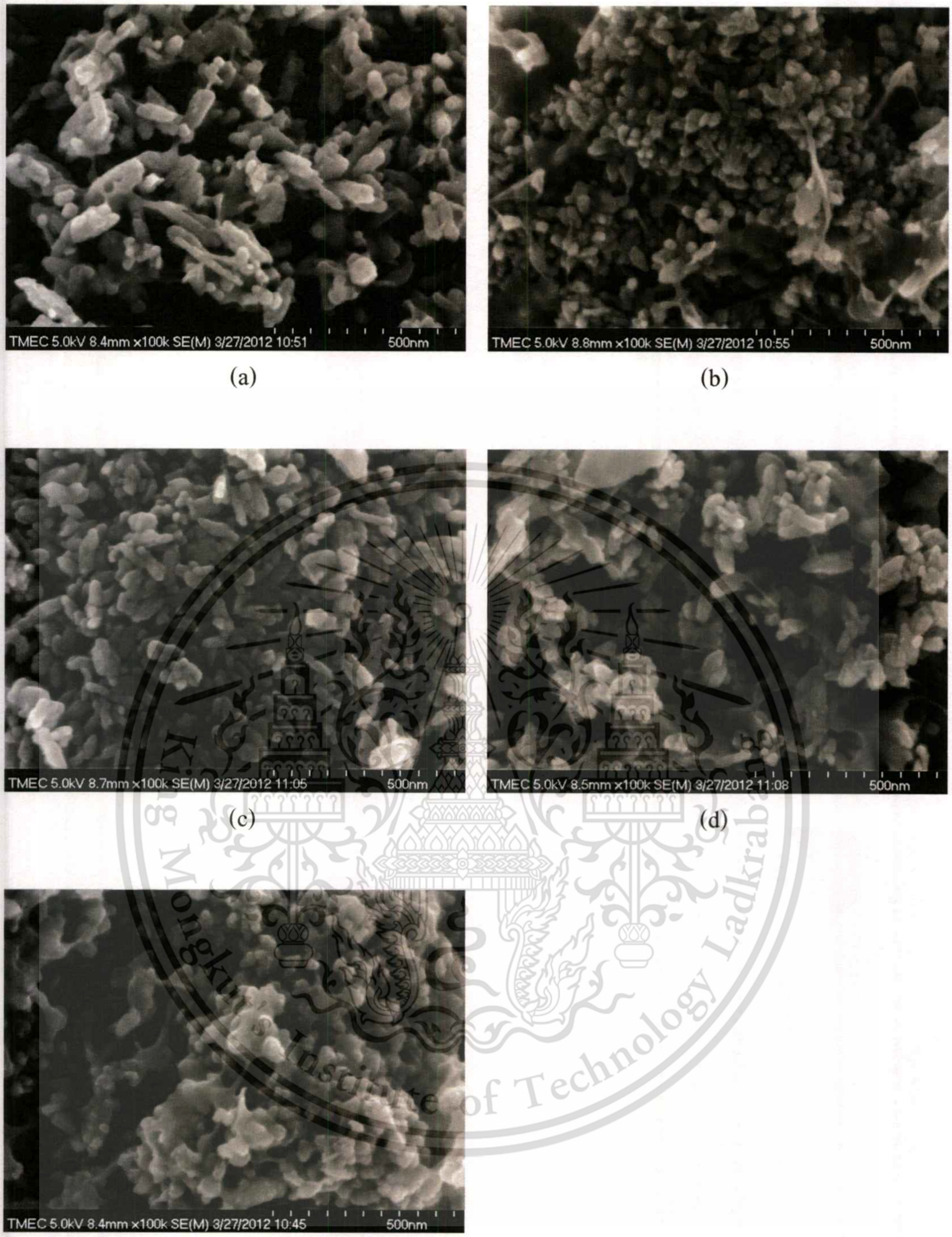
(a) (b)

(c) (d)

(e)

Figure 4.2: SEM images of ZnO nanorods via acetone as liquid-assisted;

(a) 10% (b) 20% (c) 30% (d) 40% (e) 100%



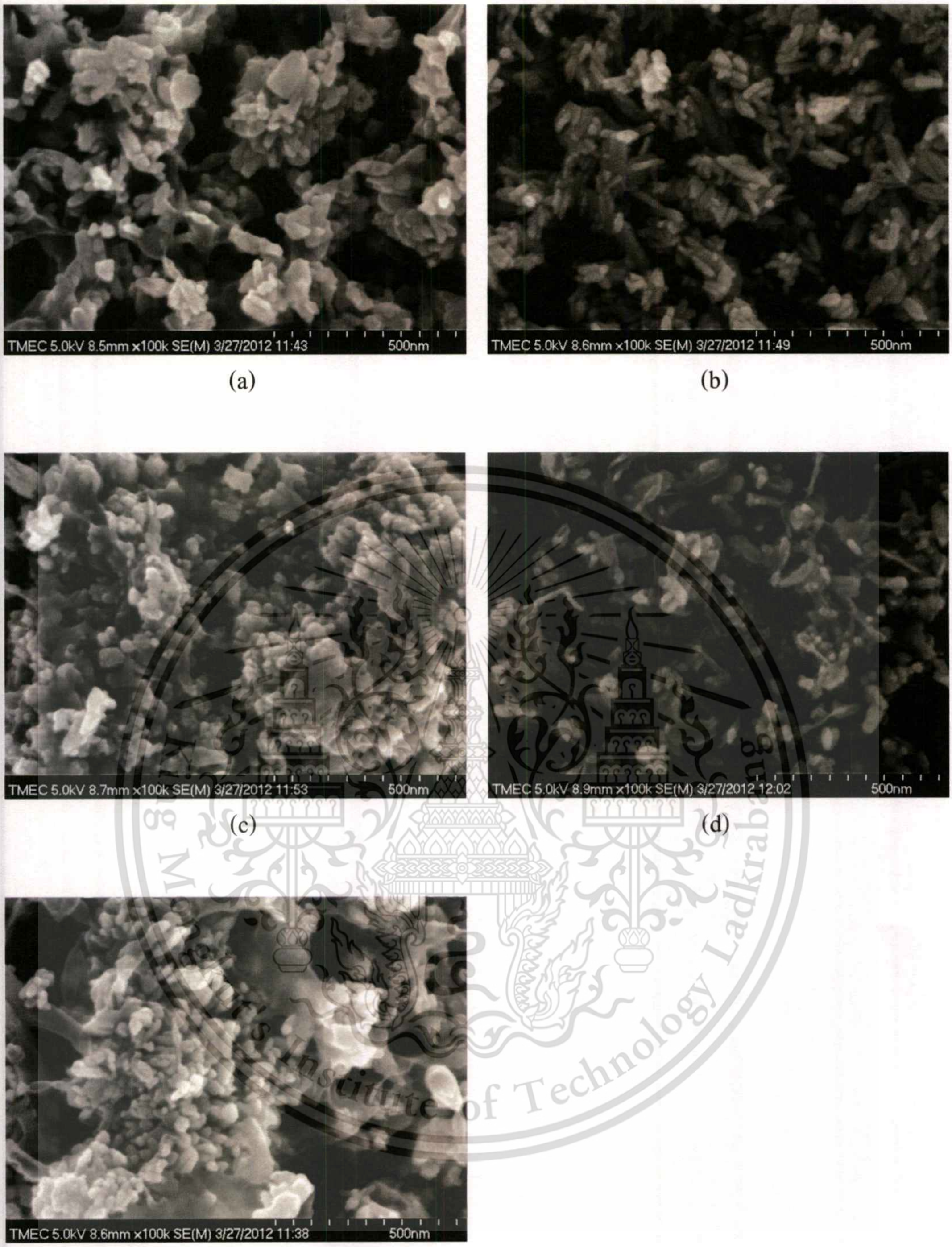
(a) (b)

(c) (d)

(e)

Figure 4.3: SEM images of ZnO nanorods via glycerol as liquid-assisted;

(a) 10% (b) 20% (c) 30% (d) 40% (e) 100%



(a) (b)

(c) (d)

(e)

Figure 4.4: SEM images of ZnO nanorods via methanol as liquid-assisted; (a) 10% (b) 20% (c) 30% (d) 40% (e) 100%

The mean width and length of ZnO nanorods obtained from SEM images and the crystallite size calculated from XRD data (via Debye Scherrer equation) are shown in Table 4.1, 4.2, and 4.3.

Table 4.1: Crystallite size of ZnO nanoparticles via acetone as liquid-assisted

Concentration of acetone	Crystallite size of ZnO (nm)		
	XRD	SEM	
		Width	Length
10%	24.81	29.76	90.24
20%	23.51	27.14	86.38
30%	18.56	29.17	94.05
40%	21.33	28.57	92.86
100%	25.81	32.81	102.67

Table 4.2: Crystallite size of ZnO nanoparticles via glycerol as liquid-assisted

Concentration of glycerol	Crystallite size of ZnO (nm)		
	XRD	SEM	
		Width	Length
10%	22.40	35.33	113.09
20%	21.26	25.23	69.05
30%	21.84	27.86	90.00
40%	17.28	28.57	92.52
100%	22.19	37.29	96.05

Table 4.3: Crystallite size of ZnO nanoparticles via methanol as liquid-assisted

Concentration of methanol	Crystallite size of ZnO (nm)		
	XRD	SEM	
		Width	Length
10%	21.65	23.33	78.95
20%	20.91	25.00	80.38
30%	25.05	25.38	81.76
40%	20.63	25.00	83.09
100%	23.93	30.29	99.00

We assume that the crystallite size of synthesized ZnO nanoparticles, calculated from Debye Scherrer equation, have spherical morphology. Therefore, the crystallite size of ZnO nanorods from SEM images is inconsistent with the result from XRD data.

There are several ways to synthesis nanoparticles such as sol-gel, hydrothermal, and spray pyrolysis. However, sol-gel method is hard to recover nanoparticles product. Hydrothermal process uses high temperature and pressure. Spray pyrolysis also consumes large amount of energy. Therefore, solid state reaction is a conventional method to produce nanoparticles with high percent yield as shown in Table 4.4.

Table 4.4: Percent yield of ZnO nanorods via acetone, glycerol, and methanol as liquid-assisted

Concentration of liquid-assisted	Percent yield (%)		
	Acetone	Glycerol	Methanol
10%	98.22	96.87	94.75
20%	97.56	96.22	96.60
30%	96.10	98.33	97.81
40%	98.99	96.15	95.42
100%	97.31	95.38	99.49

Chapter 5

Conclusion and Suggestion

5.1 Conclusion

Liquid assisted solid state reaction is an alternative way to synthesize ZnO nanoparticles. The good liquid-assisted should be inert and not react with the starting materials. The advantage of liquid-assisted is to reduce friction between particles and help mixing solid materials. Although, each assisted liquid has a different characteristic. Acetone has high volatility so it is easy to recover the product but it is unfriendly to environment. Glycerol and methanol are better in help mixing solid materials. However, a viscous liquid like glycerol is difficult to wash off and methanol is also harmful when it is inhaled.

From our study, we can conclude that;

1. ZnO nanorods were synthesized by using acetone, glycerol, and methanol as liquid-assisted at different concentrations via solid state reaction at room temperature.
2. The different assisted liquid in various concentrations have insignificantly affect on both size and morphology of ZnO nanorods.

5.2 Suggestion

For further study, ZnO nanorods synthesized from solid state reaction could be done in more various conditions such as changing the ratio and type of base reactants. Researching more detailed in the mixing between two or more types of base reactants would also be new. The liquid assisted solid state reaction is a new method that is simple and produces high product yields. Furthermore, studies of other liquid-assisted would be more useful for predicting and controlling morphology and particle size of nanoparticles.

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Appendix

Appendix A

Physicals Properties

A.1 Zinc oxide

Table A.1: Physical properties of zinc oxide

Chemical formula	ZnO
Molecular weight	81.4 g/mol
Density	5.606 g/cm^3
Appearance	White solid powder
Odor	Odorless
Taste	Bitter
Solubility	- insoluble in water - soluble in dilute acetic acid, ammonia, and ammonium carbonate

A.2 Acetic acid

Table A.2: Physical properties of acetic acid

Chemical formula	CH_3COOH
Molecular weight	60 g/mol
Density	1.049 g/cm^3
Appearance	Colorless liquid
Odor	Pungent, vinegar-like
Taste	Vinegar, sour (strong)
Solubility	- soluble in water, diethyl ether, and acetone

A.3 Zinc acetate dihydrate

Table A.3: Physical properties of zinc acetate dihydrate

Chemical formula	$Zn(CH_3COO)_2 \cdot 2H_2O$
Molecular weight	219.4 g/mol
Density	1.735 g/cm^3
Appearance	White solid (slightly efflorescence)
Odor	Vinegar-like (slight)
Taste	Astringent
Solubility	Soluble in water and Alcohol

A.4 Sodium hydroxide

Table A.4: Physical properties of sodium hydroxide

Chemical formula	NaOH
Molecular weight	40 g/mol
Density	2.13 g/cm^3
Appearance	White solid, opaque Crystals
Odor	Odorless
Solubility	Soluble in water, ethanol and methanol

A.5 Acetone

Table A.5: Physical properties of acetone

Chemical formula	$CH_3C(=O)CH_3$
Molecular weight	58 g/mol
Density	0.786 g/cm^3
Appearance	Colorless liquid
Odor	Pungent
Volatility	100%
Solubility	Completely soluble in Water

A.6 Glycerol

Table A.6: Physical properties of glycerol

Chemical formula	$C_3H_5(OH)_3$
Molecular weight	92 g/mol
Density	1.261 g/cm^3
Appearance	Clear viscous liquid
Odor	Mild
Taste	Sweet
Solubility	- miscible in water - partially soluble in acetone - Insoluble in carbon tetrachloride, benzene, chloroform, petroleum ethers, and oils

A.7 Methanol

Table A.7: Physical properties of methanol

Chemical formula	CH_3OH
Molecular weight	32 g/mol
Density	0.791 g/cm^3
Appearance	Colorless liquid
Odor	Alcohol-like
Solubility	Soluble in water

Appendix B

Experimental Data

B.1 Data Recorded

B.1.1 Synthesis of zinc oxide nanoparticles by liquid assisted solid state reaction

Table B.1: Weight of ZnO nanorods via acetone as liquid-assisted

Acetone concentration	Weight (g)		
	$Zn(CH_3COO)_2 \cdot 2H_2O$	Predicted ZnO	Actual ZnO
10%	54.8457	20.3484	19.9868
20%	54.9401	20.3834	19.8868
30%	54.8563	20.3523	19.5591
40%	54.8879	20.3641	20.3624
100%	54.9015	20.3691	19.8212

Table B.2: Weight of ZnO nanorods via glycerol as liquid-assisted

Glycerol concentration	Weight (g)		
	$Zn(CH_3COO)_2 \cdot 2H_2O$	Predicted ZnO	Actual ZnO
10%	54.8569	20.3526	19.7153
20%	54.8443	20.3479	19.5792
30%	54.8498	20.3499	20.0105
40%	54.8544	20.3516	19.5690
100%	54.8439	20.3477	19.4070

Table B.3: Weight of ZnO nanorods via methanol as liquid-assisted

Methanol concentration	Weight (g)		
	$Zn(CH_3COO)_2 \cdot 2H_2O$	Predicted ZnO	Actual ZnO
10%	54.8418	20.3470	19.2787
20%	54.8535	20.3513	19.6599
30%	54.8394	20.3461	19.9011
40%	54.8399	20.3463	19.4154
100%	54.8587	20.3532	20.2503

B.2 XRD Data

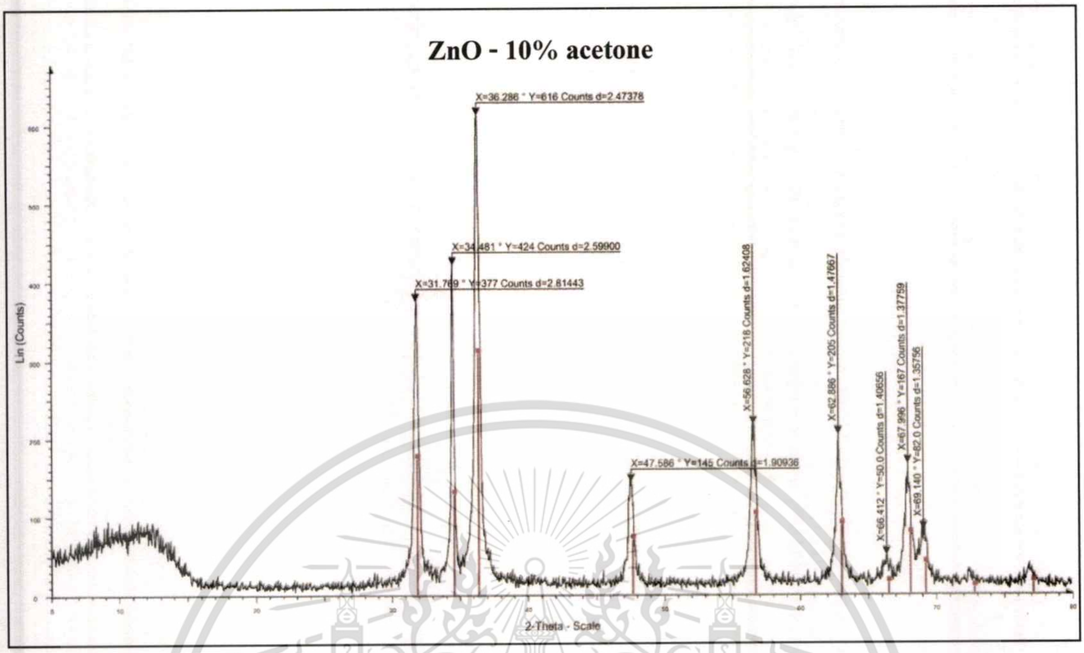


Figure B.1: XRD pattern of ZnO nanoparticles via 10% acetone as liquid-assisted

∿ 10% acetone– File: XD55_0089_07_10% acetone.RAW – Type: 2Th locked – Start: 5.000° – End: 80.000° – Step: 0.040° – Step time: 1. S – Temp.: 25 °C (Room) – Time Started: 0 s – 2-Theta: 5.000° – Theta: 2.500° – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – l/lc PDF 5.7 –

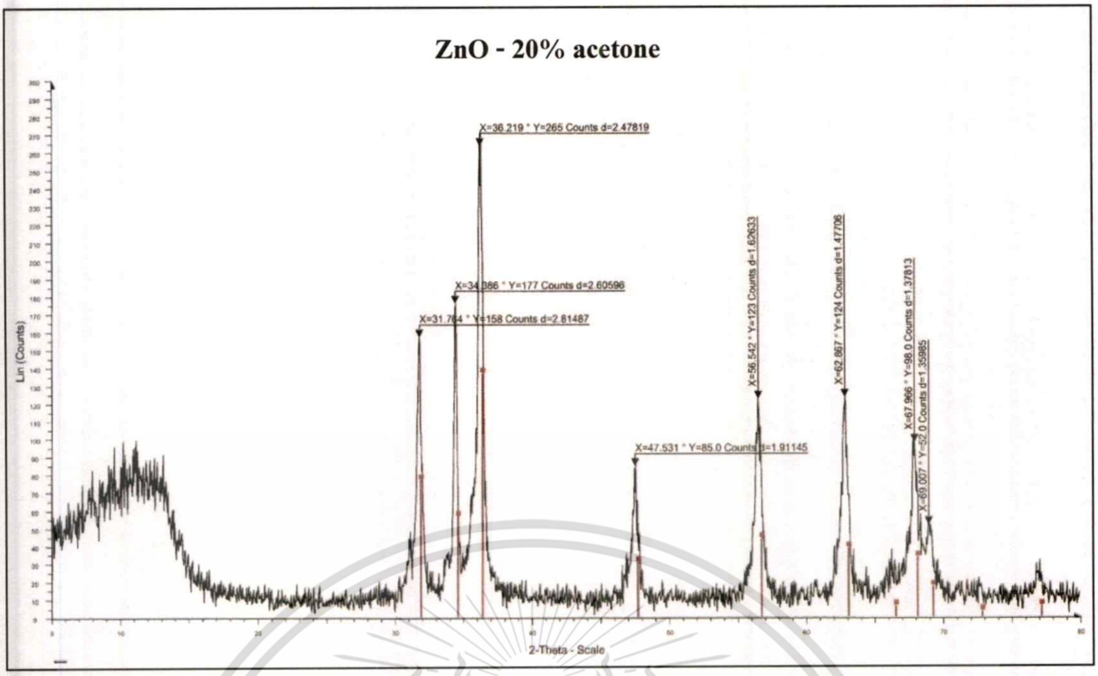


Figure B.2: XRD pattern of ZnO nanoparticles via 20% acetone as liquid assisted

〽 20% acetone – File: XD55_0089_08_20% acetone.RAW – Type: 2Th locked – Start: 5.000^{o} – End: 80.000^{o} – Step: 0.040^{o} – Step time: 1. S – Temp.: 25 ^{o}C (Room) – Time Started: 0 s – 2-Theta: 5.000^{o} – Theta: 2.500^{o} – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – I/Ic PDF 5.7 –

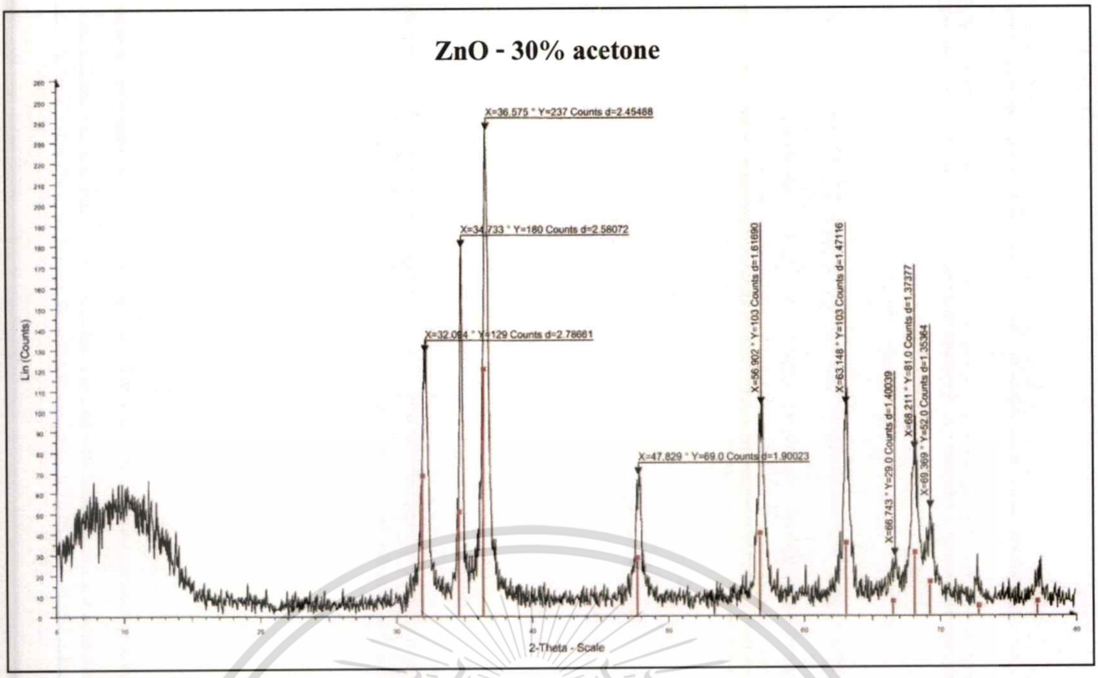


Figure B.3: XRD pattern of ZnO nanoparticles via 30% acetone as liquid-assisted

〰 30% acetone – File: XD55_0089_09_30% acetone.RAW – Type: 2Th locked – Start: 5.000^{o} – End: 80.000^{o} – Step: 0.040^{o} – Step time: 1. S – Temp.: 25 ^{o}C (Room) – Time Started: 0 s – 2-Theta: 5.000^{o} – Theta: 2.500^{o} – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – l/lc PDF 5.7 –

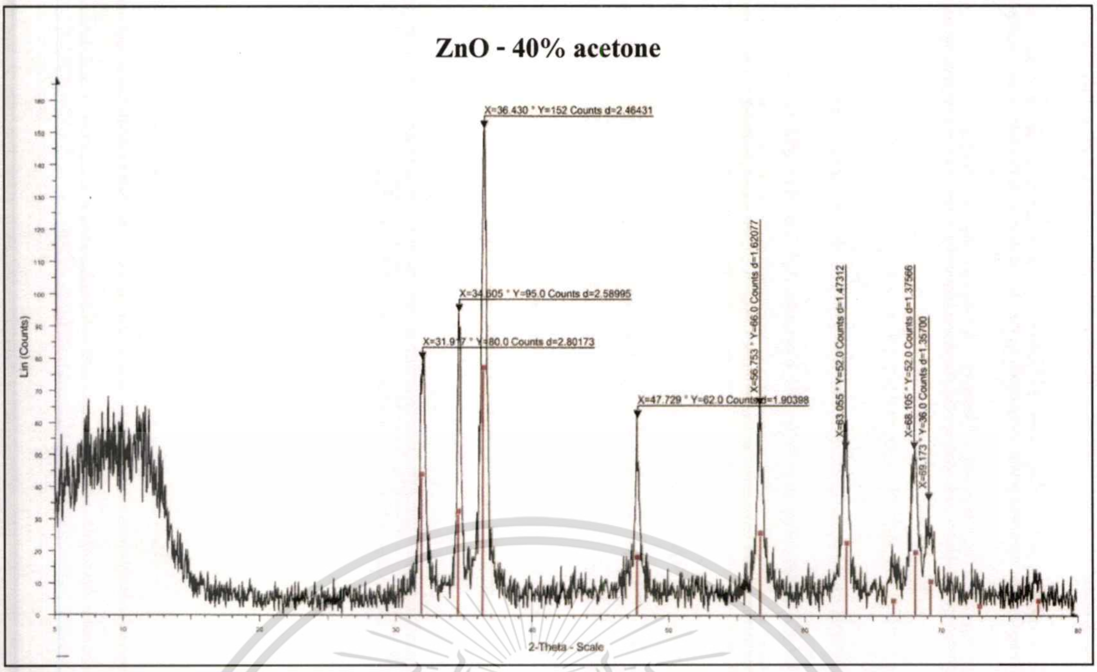


Figure B.4: XRD pattern of ZnO nanoparticles via 40% acetone as liquid-assisted

40% acetone – File: XD55_0089_10_40% acetone.RAW – Type: 2Th locked – Start: 5.000° – End: 80.000° – Step: 0.040° – Step time: 1. S – Temp.: 25 °C (Room) – Time Started: 0 s – 2-Theta: 5.000° – Theta: 2.500° – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – I/Ic PDF 5.7 –

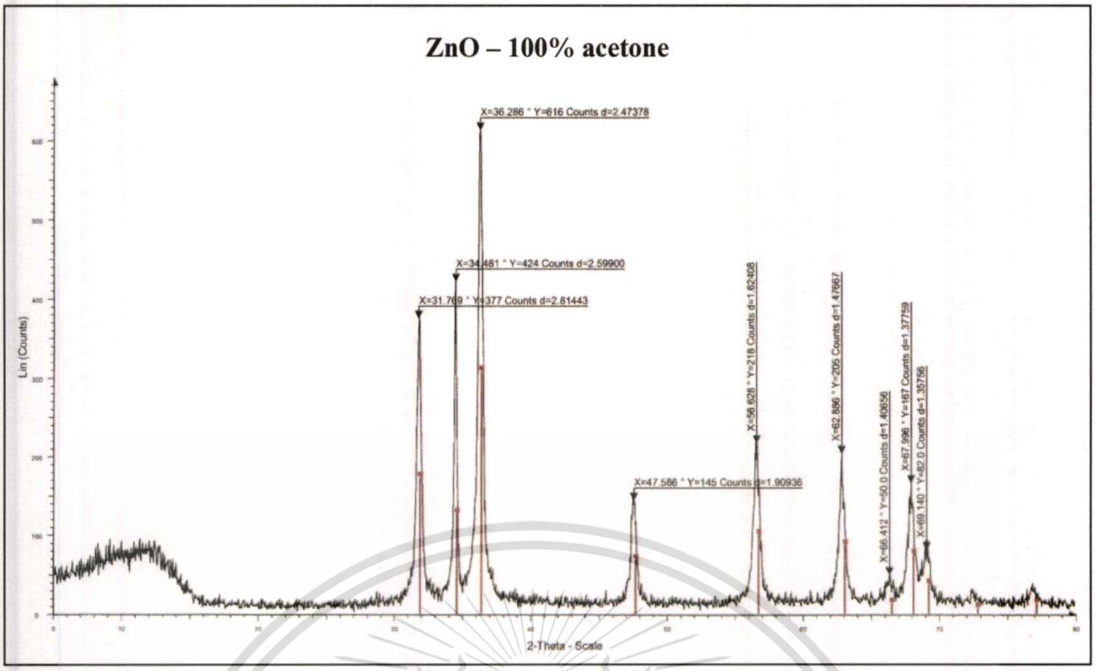


Figure B.5: XRD pattern of ZnO nanoparticles via pure acetone as liquid-assisted

100% acetone – File: XD55_0089_06_100% acetone.RAW – Type: 2Th locked – Start: 5.000° – End: 80.000° – Step: 0.040° – Step time: 1. S – Temp.: 25 °C (Room) – Time Started: 0 s – 2-Theta: 5.000° – Theta: 2.500° – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – l/lc PDF 5.7 –

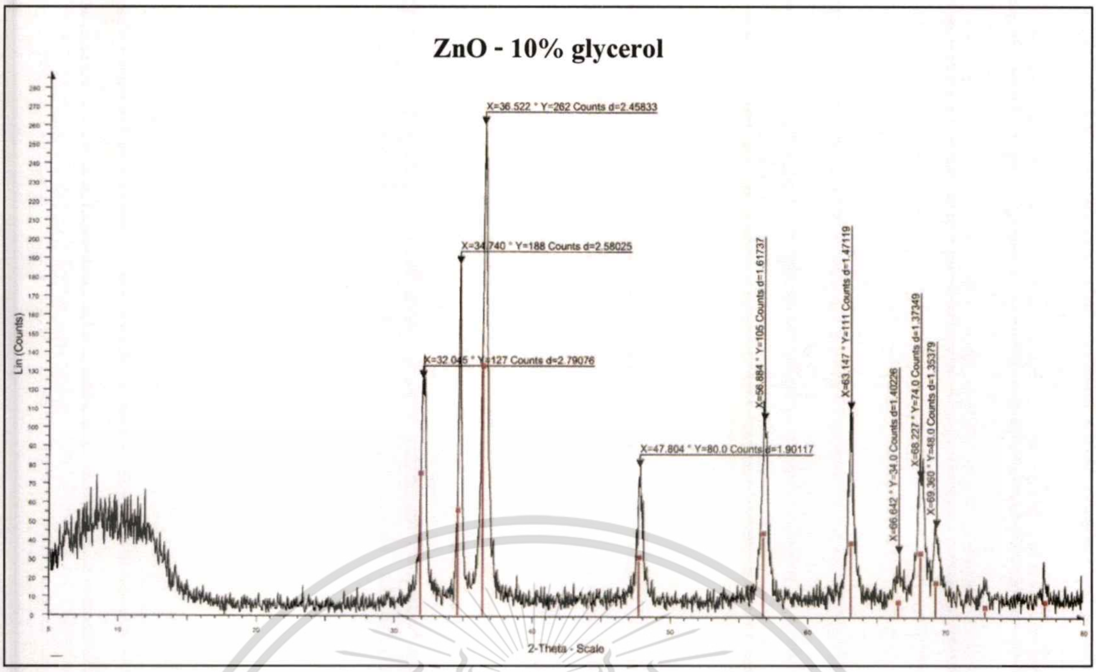


Figure B.6: XRD pattern of ZnO nanoparticles via 10% glycerol as liquid-assisted

10% glycerol – File: XD55_0089_02_10% glycerol.RAW – Type: 2Th locked – Start: 5.000° – End: 80.000° – Step: 0.040° – Step time: 1. S – Temp.: 25 °C (Room) – Time Started: 0 s – 2-Theta: 5.000° – Theta: 2.500° – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – I/Ic PDF 5.7 –

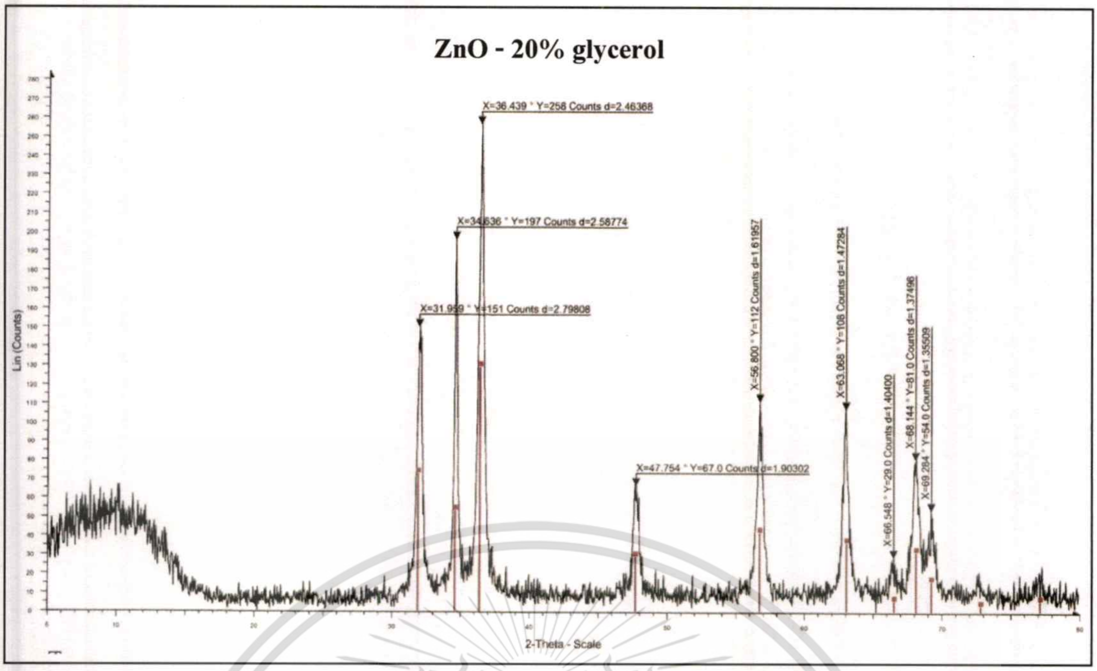


Figure B.7: XRD pattern of ZnO nanoparticles via 20% glycerol as liquid-assisted

20% glycerol – File: XD55_0089_03_20% glycerol.RAW – Type: 2Th locked – Start: 5.000° – End: 80.000° – Step: 0.040° – Step time: 1. S – Temp.: 25 °C (Room) – Time Started: 0 s – 2-Theta: 5.000° – Theta: 2.500° – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – I/Ic PDF 5.7 –

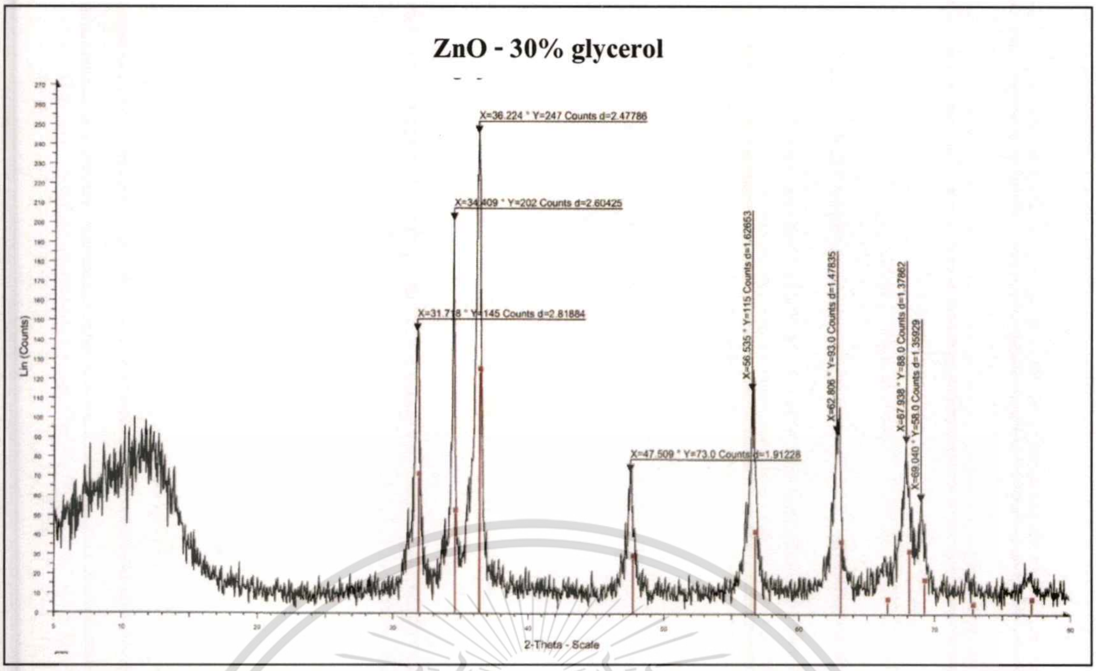


Figure B.8: XRD pattern of ZnO nanoparticles via 30% glycerol as liquid-assisted

〰 30% glycerol – File: XD55_0089_04_30% glycerol.RAW – Type: 2Th locked – Start: 5.000° – End: 80.000° – Step: 0.040° – Step time: 1. S – Temp.: 25 °C (Room) – Time Started: 0 s – 2-Theta: 5.000° – Theta: 2.500° – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – I/Ic PDF 5.7 –

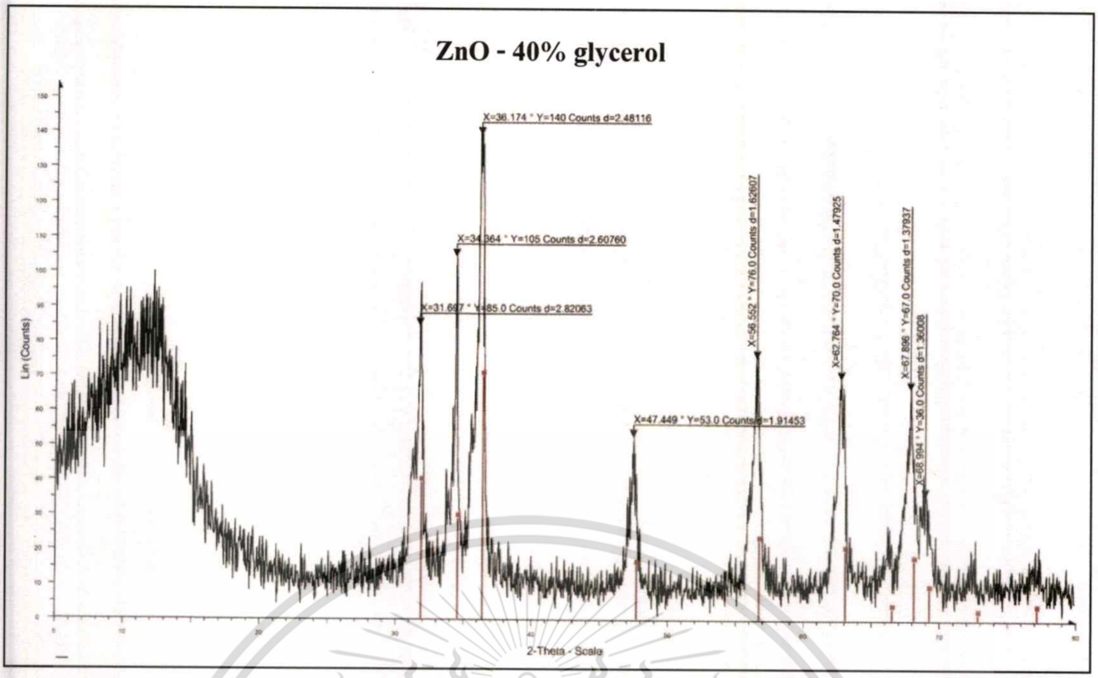


Figure B.9: XRD pattern of ZnO nanoparticles via 40% glycerol as liquid-assisted

40% glycerol – File: XD55_0089_05_40% glycerol.RAW – Type: 2Th locked – Start: 5.000° – End: 80.000° – Step: 0.040° – Step time: 1. S – Temp.: 25 °C (Room) – Time Started: 0 s – 2-Theta: 5.000° – Theta: 2.500° – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – I/Ic PDF 5.7 –

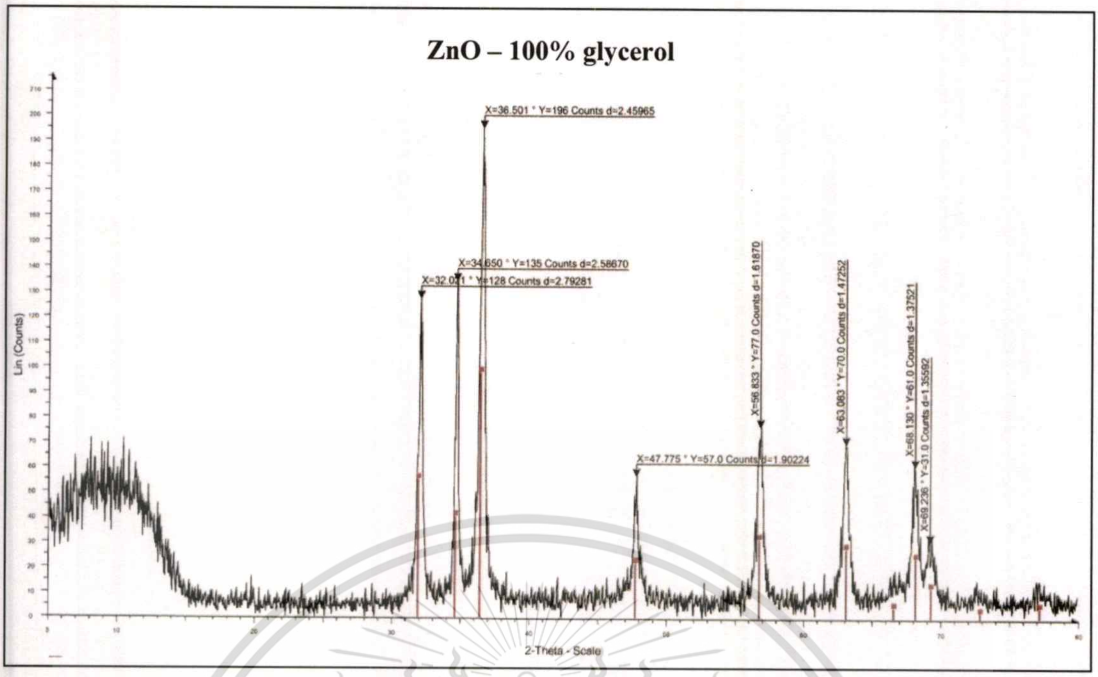


Figure B.10: XRD pattern of ZnO nanoparticles via pure glycerol as liquid-assisted

100% glycerol – File: XD55_0089_01_100% glycerol.RAW – Type: 2Th locked – Start: 5.000° – End: 80.000° – Step: 0.040° – Step time: 1. S – Temp.: 25 °C (Room) – Time Started: 0 s – 2-Theta: 5.000° – Theta: 2.500° – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – I/Ic PDF 5.7 –

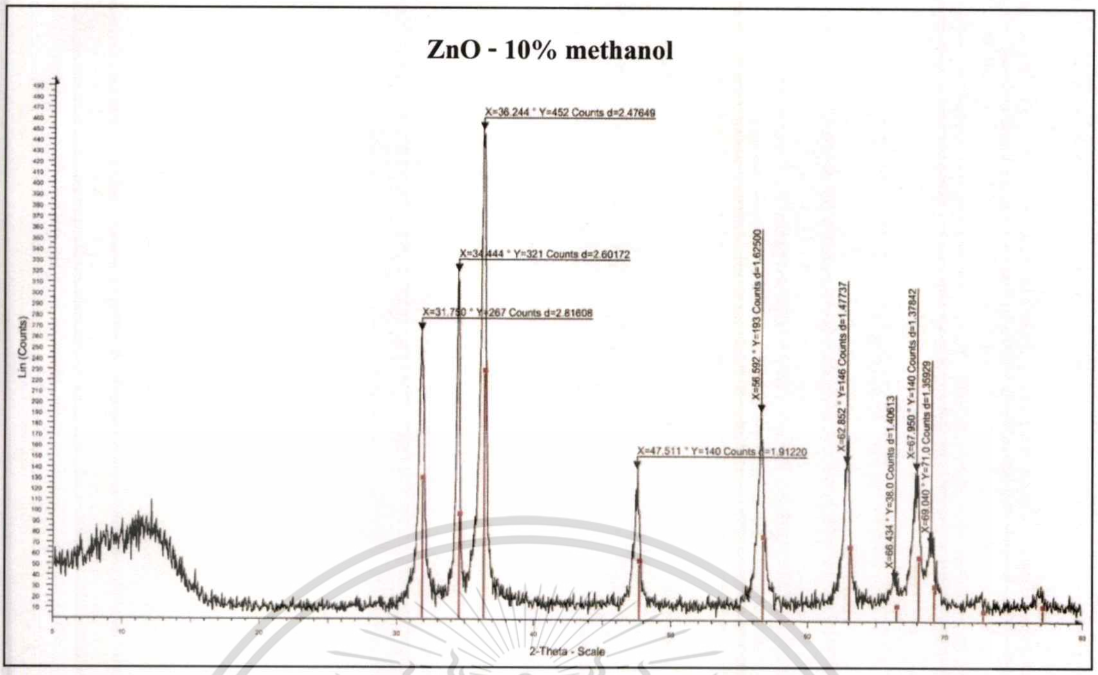
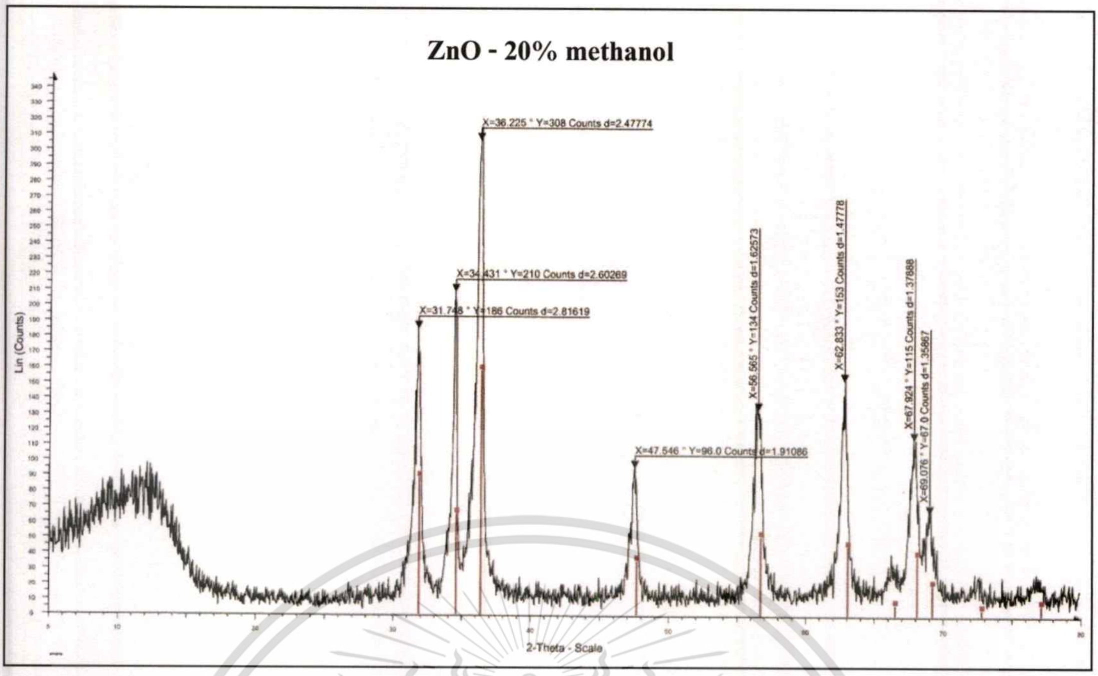


Figure B.11: XRD pattern of ZnO nanoparticles via 10% methanol as liquid-assisted

📈 10% methanol – File: XD55_0089_12_10% methanol.RAW – Type: 2Th locked – Start: 5.000^{o} – End: 80.000^{o} – Step: 0.040^{o} – Step time: 1. S – Temp.: 25 ^{o}C (Room) – Time Started: 0 s – 2-Theta: 5.000^{o} – Theta: 2.500^{o} – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – I/Ic PDF 5.7 –



ZnO - 20% methanol

Figure B.12: XRD pattern of ZnO nanoparticles via 20% methanol as liquid-assisted

📈 20% methanol – File: XD55_0089_13_20% methanol.RAW – Type: 2Th locked – Start: 5.000° – End: 80.000° – Step: 0.040° – Step time: 1. S – Temp.: 25 °C (Room) – Time Started: 0 s – 2-Theta: 5.000° – Theta: 2.500° – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – I/Ic PDF 5.7 –

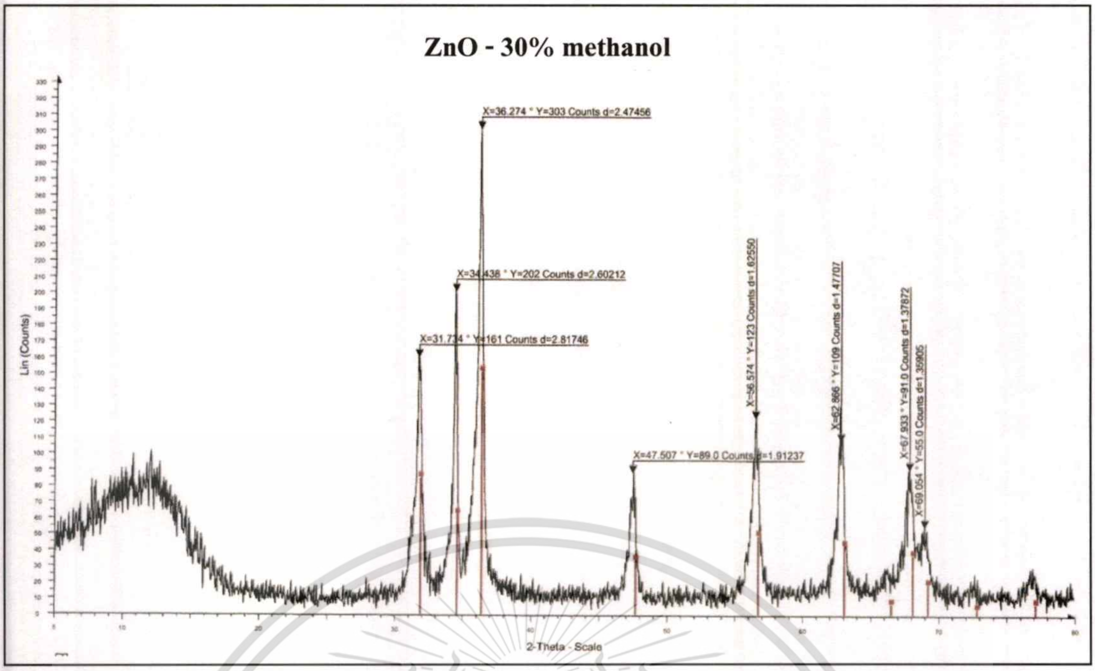


Figure B.13: XRD pattern of ZnO nanoparticles via 30% methanol as liquid-assisted

📈 30% methanol – File: XD55_0089_14_30% methanol.RAW – Type: 2Th locked – Start: 5.000° – End: 80.000° – Step: 0.040° – Step time: 1. S – Temp.: 25 °C (Room) – Time Started: 0 s – 2-Theta: 5.000° – Theta: 2.500° – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – l/lc PDF 5.7 –

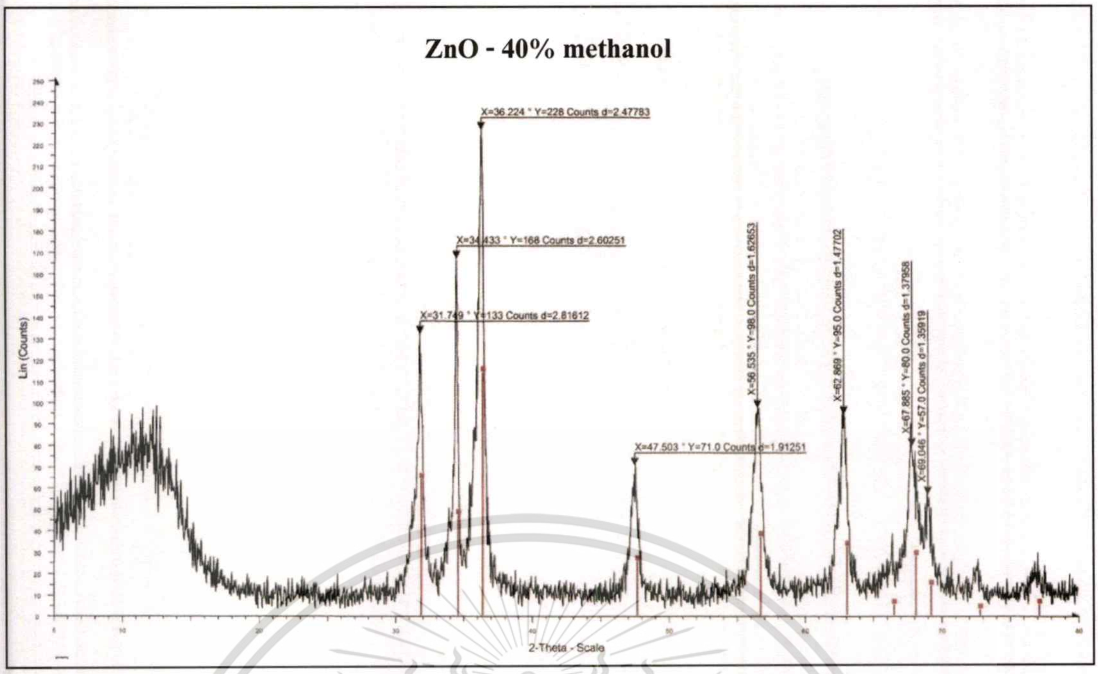


Figure B.14: XRD pattern of ZnO nanoparticles via 40% methanol as liquid-assisted

40% methanol – File: XD55_0089_15_40% methanol.RAW – Type: 2Th locked – Start: 5.000° – End: 80.000° – Step: 0.040° – Step time: 1. S – Temp.: 25 °C (Room) – Time Started: 0 s – 2-Theta: 5.000° – Theta: 2.500° – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – I/Ic PDF 5.7 –

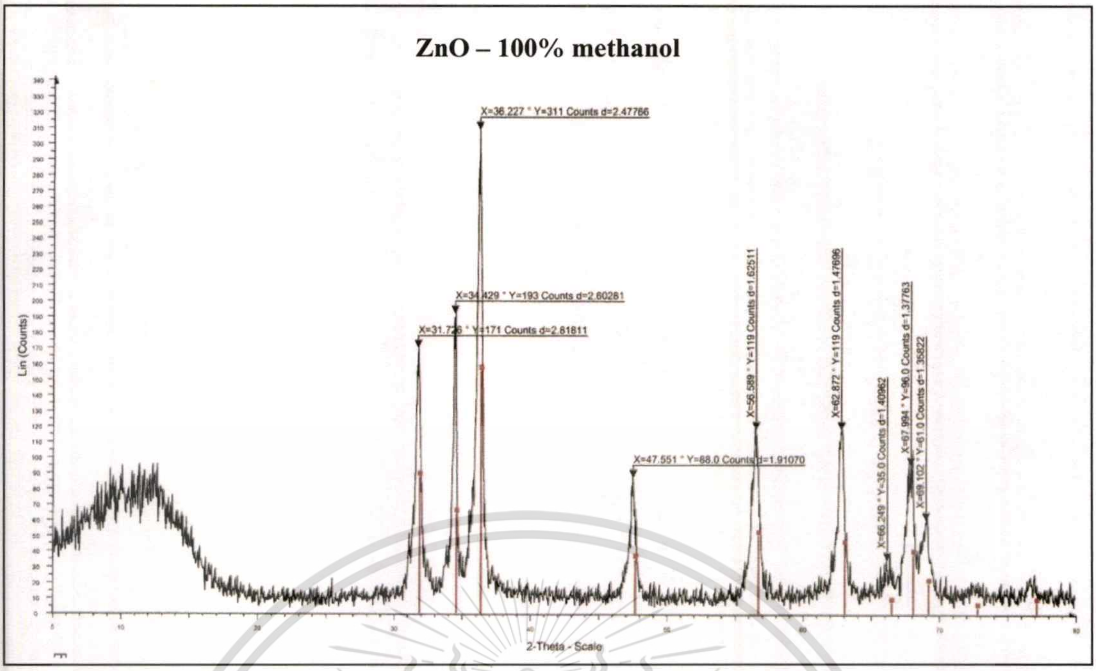


Figure B.15: XRD pattern of ZnO nanoparticles via pure methanol as liquid-assisted

100% methanol – File: XD55_0089_11_100% methanol.RAW – Type: 2Th locked – Start: 5.000° – End: 80.000° – Step: 0.040° – Step time: 1. S – Temp.: 25 °C (Room) – Time Started: 0 s – 2-Theta: 5.000° – Theta: 2.500° – Operation: Import

🟥 79-0205 (C) – Zinc Oxide – ZnO – Y: 50.00 % - d x by: 1 – WL: 1.5406 – Hexagonal - a 3.24170 – b 3.24170 – c 5.18760 – alpha 90.000 – gamma 120.000- Primitive – P63mc (186) – 2 47.2110 – I/Ic PDF 5.7 –

Appendix C

Calculation

C.1 Calculation of percent yield.

$$\text{Percent yield} = \frac{\text{weight of actual yield}}{\text{weight of predicted yield}} \times 100$$

Example: from the experiment data B.1 example.

$$\text{Percent yield of 10\% Acetone} = \frac{19.9868}{20.3485} \times 100$$

The result of percent yield of other samples are shown in chapter 4, Table 4.4

C.2 Calculation of Particle Size

The crystallite size was calculated from the half-height width of the diffraction peak of XRD pattern using the Debye – Scherrer equation.

From Scherrer equation:

$$Particle\ size = \frac{K\lambda}{\beta cos\theta}$$

K = crystallite shape factor, K = 0.89

λ = wavelength of x-rays (Cu-Kα), λ = 0.15406 nm

β = FWHM (full width at half maximum of the reflection peak that has the same maximum intensity in the diffraction pattern)

θ = diffraction angle