Synthesis of Zinc Oxide nanorods

MISS. SUPAVEE CHAOVALIT

MISS. DUANGDAO ACHARYAKUL

MISS. AMORNRAT PENYOO

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Special Project Title	Synthesis of ZnO nanorods		
Students	Miss. Supavee	Chaovalit	ID. 50050553
	Miss. Duangdao	Acharyakul	ID. 50050571
	Miss. Amornrat	Penyoo	ID. 50050594
Degree	Bachelor of Science		
Department	Chemistry, Faculty of Science		
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Advisor	Asst. Prof. Dr. Pachernchaiyapat Chaiyasith		

ABSTRACT

In this research, ZnO nanorods have been prepared via solid state reaction method and two-step wet chemical bath deposition method. ZnO nanorods from solid state reaction method were prepared by using zinc acetate dihydrate and sodium hydroxide in mole ratio of 1:2. In two-step wet chemical method, the ZnO nanorods were growth on the glass substrates. The ZnO seed precursor was prepared by thermal decomposition of zinc acetate and subsequently ZnO nanorods were grown in aqueous solution of zinc acetate dihydrate and hexamethylenetetramine. The effect of number of coating in seeding step and time of growth on nanorods morphology were investigated systematically. The structure of ZnO nanorods were characterized by X-ray Diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM). The XRD patterns present that ZnO are hexagonal wurtzite structure with no impurity and the average particle size of ZnO nanoparticles is about 132 nm. The FESEM image of ZnO nanoparticles obtained from solid state reaction method shown needle-like morphology with diameters of 30-50 nm, lengths of about 300 nm and those obtained from wet chemical method shown hexagonal morphology. The diameter and the length of nanorods depend on number of coating in seeding step and time of growth.

Keyword : ZnO nanorod, Wet chemical, Solid state reaction.

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Miss Supavee Chaovalit

Miss Duangdao Acharyakul

Miss Amornrat Panyoo

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Chapter 1

Introduction

1.1 Motivation

In the last few years, nanotechnology has emerged as of the most widely use in many industries. "Nano" is used to qualify the science or technology, meaning "on the length scale which in S.I. units is closest to 1 nanometre (10^{-9} m), nanoparticle is defined as 100 nm or smaller. It includes entities that have at least one dimension in this size range and larger entities exhibiting features in this length scale, or those that can only be understood by reference to phenomena occurring on this length scale. This make nanotechnology have been played in the important role of many manufacturing such pharmaceutical, cosmetic, construction, medical and glass. Nanostructured zinc oxide (ZnO) is of interest in optonic, piezoelectric, sensor, biomedical and electro-chemical fields because of its interesting characteristic, such as a direct band gap of 3.37 eV, a large exciton binding energy of 60 meV at room temperature, transparent conductivity, non-centrosymmetric symmetry, bio-safety and bio-compatibility.

At present, ZnO nanorods can be prepared by vary methods such as hydrothermal method, vapor-liquid-solid (VLS) method, electrochemical deposition technique, patterned growth and vertical alignment method. However, these preparative methods are often limited in the practical application and complicated equipments due to suitably rigorous conditions such as high temperature, low pressures or accurate gas concentration and these methods also achieved by catalyst, scarce raw material or complex method. The wet chemical method exhibits several advantages like low cost, large scale production, low temperature process and no catalyst assistant. It can be performed on various substrates, which promotes its applications in versatile fields. Therefore it will be the most promising method to synthesis ZnO nanorods.

In this project ZnO nanoparticles and ZnO nanorods were prepared by using solid state reaction method and wet chemical bath deposition method respectively. The effect of number of coating in seeding step and growth period of ZnO nanorods on the glass surface by using wet chemical bath deposition method were studied.

1.2 Objectives

1. To study the preparation methods of ZnO nanorods.
2. To study the growth of ZnO nanorods on glass plates.
3. To study the properties of ZnO nanorods.

1.3 Scopes of study

1. To study the method for preparation of ZnO nanorods in lab scale by using Solid State reaction method and Wet chemical method under different conditions
2. To study the growth of ZnO nanorods for use on the glass substrate by two-step wet chemical bath deposition method.
3. To characterize the prepared ZnO nanorods by using X-ray Diffraction (XRD) and Field Emission Scanning Electron Microscope (FESEM)

1.4 Expected results

1. Obtain the ZnO nanoparticles from solid-state reaction method.
2. Get ZnO nanorods grown on the glass surface in well oriented manner.

Chapter 2

Theoretical Background and Literature Reviews

2.1 Nanotechnology [1]

Nanotechnology is the science of the small. It is the use and manipulation of matter at a tiny scale. At this size, atoms and molecules work differently, and provide a variety of surprising and interesting uses. Nanotechnology should not be viewed as a single technique that only affects specific areas. It is more of a 'catch-all' term for a science which is benefiting a whole array of areas, from the environment, to healthcare, to hundreds of commercial products .Some example of nanotechnology are given as follow

2.1.1 Nanomaterials

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, but also in 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 as nanoscale lubricants.

2.1.2 Complex materials [2]

Scientists and engineers often look to nature to solve complex problems or to develop technologies that have the capability of mimicking nature. For example, the gecko's ability to stick to surfaces and walk up walls with ease has led researchers to design materials that can mimic the microscopic elastic hairs that line this animal's feet (as shown in figure 2.1).

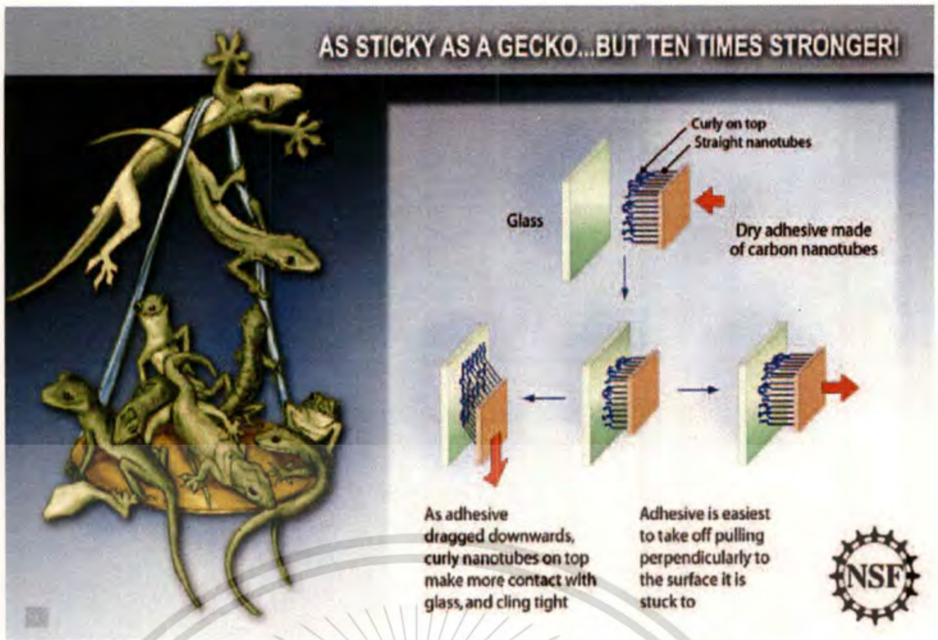


Fig. 2.1 Advanced nanotechnology is enabling scientists to develop sophisticated new materials that can be used in novel ways. For instance, researchers have created a gecko-inspired adhesive with ten times the stickiness of a gecko's foot, by combining vertically aligned nanotubes with curly spaghetti-like nanotubes.

Using carbon nanotubes, Liangti Qu and colleagues at the University of Dayton (Ohio) have created a material that has an adhesive force about 10 times stronger than that of a gecko's foot. These carbon nanotube materials have a much stronger adhesion force parallel to the surface they are on than that perpendicular to the surface. The result is a material that can be used to attach a heavy weight to a vertical surface, and yet be peeled off with ease. And just as a gecko is able to walk up vertical surfaces with ease, the material opens up the possibility of creating clothing that will enable humans to achieve the same feat.

2.1.3 Nanopowders [3]

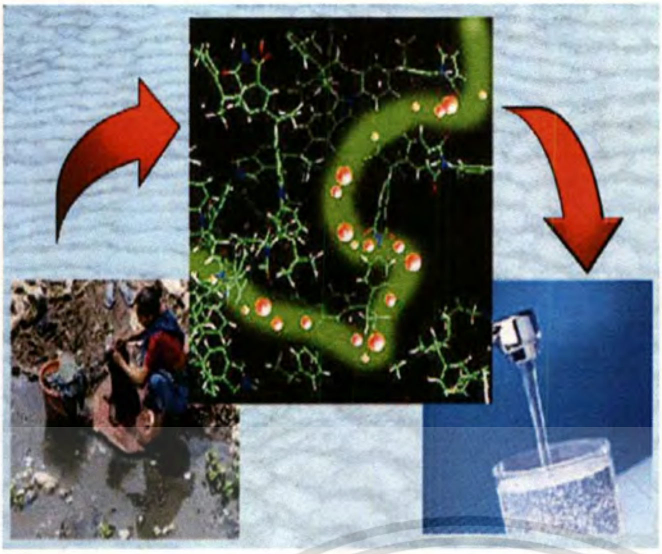
Nanopowders contain particles less than 100 nm in size — 1/10,000th the thickness of a human hair. The physical, chemical and biological properties of such small particles allow industry to incorporate enhanced functionalities into products. Some of the unique properties of interest to industry are enhanced transparency from particles being smaller than the wavelength of visible light, and high surface areas for enhanced performance in surface area-driven reactions such as catalysts and drug solubilisation.

These unique properties give rise to a range of new and improved materials with a breadth of applications. For example, nanotechnology allows plastics to retain transparency while also taking on characteristics such as resistance to abrasion, conductivity or UV protection found in ceramics or metals. New medical nanomaterials are being developed, such as synthetic bone and bone cement, as well as drugs with improved solubility to allow lower dosing, more efficient drug delivery and fewer adverse side effects.

The high surface areas of nanoparticles are being exploited by industry in catalysts that improve chemical reactions in applications such as cleaning up car exhausts and potentially to remove toxins from the environment. For example, petroleum and chemical processing companies are using nanostructured catalysts to remove pollutants — $30 billion industry in 1999 with the potential of $100 billion per year by 2015. Improved catalysts illustrate that improvements to existing technology can open up whole new markets — nanostructured catalysts look likely to be a critical component in finally making fuel cells a reality, which could transform our power generation and distribution industry.

2.1.4 Membranes [3]

Nanomembranes filtration devices that 'clean' polluted water, sifting out bacteria, viruses, heavy metals and organic material, are being explored by research teams in the US, Israel and Australia (at the UNESCO Centre for Membrane Science and Technology at the University of New South Wales and a consortium of CSIRO Divisions). 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. A parallel approach is being developed by nanotechnologists for the production of nanoarchitectures for cost-effective filtration systems in large-scale water purification(as can be seen in figure 2.2).



Clean, safe water passes through microstructured membranes.

Fig. 2.2 The cleaning process of safe water passes through microstructure membrances

2.1.5 Carbon nanotubes

The discovery that graphite can be rolled into a cylinder with a diameter of about one nanometre already has far-reaching consequences. These strong but light 'carbon nanotubes' are being developed for a raft of uses, such as sensors, fuel cells, computers and televisions. The applications of nanotubes are set to expand even further now that scientists have found that other materials besides carbon can form nanotubes. The historical development of the science and the business of nanotubes is illustrated in the following chart.

2.2 Zinc oxide[4]

Zinc oxide is an inorganic compound with the formula ZnO. It usually appears as a white powder (as shown in figure 2.3), nearly insoluble in water. The powder is widely used as an additive into numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g., car tires), lubricants, paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, first aid tapes, etc. ZnO is present in the Earth's crust as the mineral zincite; however, most ZnO used commercially is produced synthetically.

Fig. 2.3 ZnO powder

In materials science, ZnO is often called a II-VI semiconductor because zinc and oxygen belong to the 2nd and 6th groups of the periodic table, respectively. This semiconductor has several favorable properties: good transparency, high electron mobility, wide bandgap, strong room-temperature luminescence, etc. Those properties are already used in emerging applications for transparent electrodes in liquid crystal displays and in energy-saving or heat-protecting windows, and electronic applications of ZnO as thin-film transistors and light-emitting diodes are forthcoming as of 2009

2.2.1 History

It is hardly possible to trace the first usage of zinc oxide – various zinc compounds were widely used by early humans, in various processed and unprocessed forms, as a paint or medicinal ointment, but their exact composition is uncertain. The use of pushpanjan, probably zinc oxide, as a salve for eyes and open wounds, is mentioned in the Indian medical text the Charaka Samhita, thought to date from 500 BC or before. Zinc oxide ointment is also mentioned by the Greek physician Dioscorides (1st century AD.) Avicenna mentions zinc oxide in The Canon of Medicine (1025 AD), which mentioned it as a preferred treatment for a variety of skin conditions, including skin cancer. Though it is no longer used for treating skin cancer, it is still widely used to treat a variety of other skin conditions, in products such as baby powder and creams against diaper rashes, calamine cream, anti-dandruff shampoos, and antiseptic ointments.

The Romans produced considerable quantities of brass (an alloy of zinc and copper) as early as 200 BC by a cementation process where copper was reacted with zinc oxide. The zinc oxide is thought to have been produced by heating zinc ore in a shaft furnace. This liberated metallic zinc as a vapor, which then ascended the flue and condensed as the oxide. This process was described by Dioscorides in the 1st century AD. Zinc oxide has also been recovered from zinc mines at Zawar in India, dating from the second half of the first millennium BC. This was presumably also made in the same way and used to produce brass.

From the 12th to the 16th century zinc and zinc oxide were recognized and produced in India using a primitive form of the direct synthesis process. From India, zinc manufacture moved to China in the 17th century. In 1743, the first European zinc smelter was established in Bristol, United Kingdom.

The main usage of zinc oxide (zinc white) was again paints and additive to ointments. Zinc white was accepted as a watercolor by 1834 but it did not mix well with oil. This problem was quickly solved by optimizing the synthesis of ZnO. In 1845, LeClaire in Paris was producing the oil paint on a large scale, and by 1850, zinc white was being manufactured throughout Europe. The success of zinc white paint was due to its advantages over the traditional white lead: zinc white is essentially permanent in sunlight, it is not blackened by sulfur-bearing air, it is non-toxic and more economical. Because zinc white is so "clean" it is very valuable for making tints with other colors; however, it makes a rather brittle dry film when unmixed with other colors. For example, during the late 1890s and early 1900s, some artists used zinc white as a ground for their oil paintings. All those paintings developed cracks over the years.

In the recent times, most zinc oxide was used in the rubber industry (see applications above). In the 1970s, the second largest application of ZnO was photocopying. High-quality ZnO produced by the "French process" was added into the photocopying paper as a filler. This application was however soon displaced.

2.2.2 The properties of ZnO

The physical and chemical properties of ZnO are given in Table 2.1

Table 2.1 The Physical and chemical property of ZnO

Zinc oxide	
Othernames Zinc white Calamine	
Identifiers	
CAS number	1314-13-2
PubChem	14806
EC number	215-222-5
RTECS number	ZH4810000
Properties	
Molecular formula	ZnO
Molar mass	81.408 g/mol
Appearance	White solid
Odor	Odorless
Density	5.606 g/cm^3
Melting point	1975 °C (decomposes)
Boiling point	2360 °C
Solubility in water	0.16 mg/100 mL (30 °C)
Band gap	3.3 eV (direct)
Refractive index (n_D)	2.0041
Thermochemistry	
Std enthalpy of formation $\Delta_f H^\circ_{298}$	-348.0 kJ/mol
Standard molar entropy S°_{298}	43.9 J·K^{-1}mol^{-1}
Hazards	

MSDS	ICSC 0208
EU Index	030-013-00-7
EU classification	Dangerous for the environment (**N**)
R-phrases	R50/53
S-phrases	S60, S61
NFPA 704	 1 2 0 ~~W~~
Flash point	1436 °C
Related compounds	
Other anions	Zinc sulfide Zinc selenide Zinc telluride
Other cations	Cadmium oxide Mercury(II) oxide

2.2.2.1 Chemical properties

ZnO occurs as white powder known as zinc white or as the mineral zincite. The mineral usually contains a certain amount of manganese and other elements and is of yellow to red color.[3] Crystalline zinc oxide is thermochromic, changing from white to yellow when heated and in air reverting to white on cooling. This color change is caused by a very small loss of oxygen at high temperatures to form the non-stoichiometric $Zn_{1+x}O$, where at 800 °C, $x = 0.00007$.

Zinc oxide is an amphoteric oxide. It is nearly insoluble in water and alcohol, but it is soluble in (degraded by) most acids, such as hydrochloric acid:

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O \text{ .... (Eq. 2.1)}$$

Bases also degrade the solid to give soluble zincates:

$$ZnO + 2NaOH + H_2O \longrightarrow Na_2(Zn(OH)_4) \text{ .... (Eq.2.2)}$$

ZnO reacts slowly with fatty acids in oils to produce the corresponding carboxylates, such as oleate or stearate. ZnO forms cement-like products when mixed with a strong aqueous solution of zinc chloride and these are best described as zinc hydroxy chlorides. This cement was used in dentistry.

ZnO also forms cement-like products when treated with phosphoric acid; related materials are used in dentistry. ZnO decomposes into zinc vapor and oxygen only at around 1975 °C, reflecting its considerable stability. Heating with carbon converts the oxide into the metal, which is more volatile than the oxide.

$$ZnO + C \longrightarrow Zn + CO \text{ ………….. (Eq.2.3)}$$

Zinc oxide can react violently with aluminium and magnesium powders, with chlorinated rubber and linseed oil on heating causing fire and explosion hazard. It reacts with hydrogen sulfide to give the sulfide: this reaction is used commercially in removing H_2S using ZnO powder (e.g., as deodorant).

$$ZnO + H_2S \longrightarrow ZnS + H_2O \text{ …….. (Eq 2.4)}$$

When ointments containing ZnO and water are melted and exposed to ultraviolet light, hydrogen peroxide is produced.

2.2.2.2 Crystal structure

Zinc oxide crystallizes in three forms: hexagonal wurtzite, cubic zincblende, and the rarely observed cubic rocksalt).

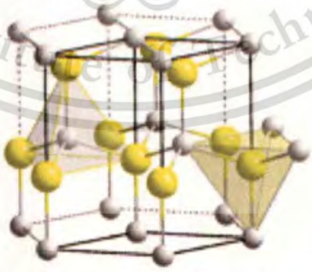


Fig. 2.4 A Wurtzite structure

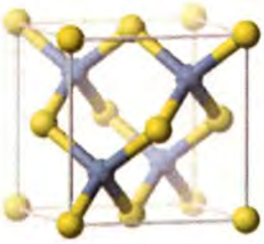


Fig. 2.5 A Zincblende unit cell

The wurtzite structure (Fig 2.4) is most stable at ambient conditions and thus most common. The zincblende (Fig 2.5) form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral. The rocksalt (NaCl-type) structure is only observed at relatively high pressures about 10 GPa.

Hexagonal and zincblende polymorphs have no inversion symmetry (reflection of a crystal relatively any given point does not transform it into itself). This and other lattice symmetry properties result in piezoelectricity of the hexagonal and zincblende ZnO, and in pyroelectricity of hexagonal ZnO. The hexagonal structure has a point group 6 mm (Hermann-Mauguin notation) or C_{6v} (Schoenflies notation), and the space group is $P6_3mc$ or C_{6v}^{4}. The lattice constants are a = 3.25 Å and c = 5.2 Å; their ratio c/a ~ 1.60 is close to the ideal value for hexagonal cell c/a = 1.633. As in most group II-VI materials, the bonding in ZnO is largely ionic, which explains its strong piezoelectricity. Due to the polar Zn-O bonds, zinc and oxygen planes bear electric charge (positive and negative, respectively). Therefore, to maintain electrical neutrality, those planes reconstruct at atomic level in most relative materials, but not in ZnO - its surfaces are atomically flat, stable and exhibit no reconstruction. This anomaly of ZnO is not fully explained yet.

2.2.2.3 Mechanical properties

ZnO is a relatively soft material with approximate hardness of 4.5 on the Mohs scale. Its elastic constants are smaller than those of relevant III-V semiconductors, such as GaN. The high heat capacity and heat conductivity, low thermal expansion and high melting temperature of ZnO are beneficial for ceramics. Among the tetrahedrally bonded semiconductors, it has been stated that ZnO has the highest piezoelectric tensor or at least one comparable to that of GaN and AlN.

This property makes it a technologically important material for many piezoelectrical applications, which require a large electromechanical coupling.

2.2.2.4 Electronic properties

ZnO has a relatively large direct band gap of ~3.3 eV at room temperature. Advantages associated with a large band gap include higher breakdown voltages, ability to sustain large electric fields, lower electronic noise, and high-temperature and high-power operation. The bandgap of ZnO can further be tuned to ~3–4 eV by its alloying with magnesium oxide or cadmium oxide.

Most ZnO has n-type character, even in the absence of intentional doping. Nonstoichiometry is typically the origin of n-type character, but the subject remains controversial. An alternative explanation has been proposed, based on theoretical calculations, that unintentional substitutional hydrogen impurities are responsible. Controllable n-type doping is easily achieved by substituting Zn with group-III elements such as Al, Ga, In or by substituting oxygen with group-VII elements chlorine or iodine.

Reliable p-type doping of ZnO remains difficult. This problem originates from low solubility of p-type dopants and their compensation by abundant n-type impurities. This problem is observed with GaN and ZnSe. Measurement of p-type in "intrinsically" n-type material is complicated by the inhomogeneity of samples.

Current limitations to p-doping does not limit electronic and optoelectronic applications of ZnO, which usually require junctions of n-type and p-type material. Known p-type dopants include group-I elements Li, Na, K; group-V elements N, P and As; as well as copper and silver. However, many of these form deep acceptors and do not produce significant p-type conduction at room temperature.

Electron mobility of ZnO strongly varies with temperature and has a maximum of ~2000 $\mathrm{cm^2/(V{\cdot}s)}$ at 80 K. Data on hole mobility are scarce with values in the range 5–30 $\mathrm{cm^2/(V{\cdot}s)}$.

2.3 Applications

The applications of zinc oxide powder are numerous, and the principal ones are summarized below. Most applications exploit the reactivity of the oxide as a precursor to other zinc compounds. For material science applications, zinc oxide has high refractive index, high thermal conductivity, binding, antibacterial and UV-protection properties. Consequently, it is added into various materials and products, including plastics, ceramics, glass, cement, rubber, lubricants, paints, ointments, adhesive, sealants, pigments, foods, batteries, ferrites, fire retardants, etc.

2.3.1 Rubber manufacture

About 50% of ZnO use is in the rubber industry. Zinc oxide along with stearic acid activates vulcanization, which otherwise may not occur at all. Zinc oxide and stearic acid are ingredients in the commercial manufacture of rubber goods. A mixture of these two compounds allows a quicker and more controllable rubber cure. ZnO is also an important additive to the rubber of car tires. Vulcanization catalysts are derived from zinc oxide, and it considerably improves the thermal conductivity, which is crucial to dissipate the heat produced by the deformation when the tire rolls. ZnO additive also protect rubber from fungi (see medical applications) and UV light.

2.3.2 Concrete industry

Zinc oxide is widely used for concrete manufacturing. Addition of ZnO improves the processing time and the resistance of concrete against water.

2.3.3 Medical

Zinc oxide as a mixture with about 0.5% iron(III) oxide (Fe_2O_3) is called calamine and is used in calamine lotion. There are also two minerals, zincite and hemimorphite, which have been historically called calamine. When mixed with eugenol, a chelate, zinc oxide eugenol is formed which has restorative and prosthodontic applications in dentistry.

Reflecting the basic properties of ZnO, fine particles of the oxide have deodorizing and antibacterialaction and for that reason are added into various materials including cotton fabric, rubber, food packaging, etc. Enhanced antibacterial action of fine particles compared to bulk material is not intrinsic to ZnO and is observed for other materials, such as silver.

Zinc oxide is widely used to treat a variety of other skin conditions, in products such as baby powder and barrier creams to treat diaper rashes, calamine cream, anti-dandruff shampoos, and antiseptic ointments. It is also a component in tape (called "zinc oxide tape") used by athletes as a bandage to prevent soft tissue damage during workouts.

When used as an ingredient in sunscreen, zinc oxide sits on the skin's surface i.e. is not absorbed into the skin, and blocks both UVA (320-400 nm) and UVB (280-320 nm) rays of ultraviolet light. Because zinc oxide (and the other most common physical sunscreen, titanium dioxide) are not absorbed into the skin, they are nonirritating and nonallergenic.

However, many sunscreens use nano zinc oxide (along with nano titanium dioxide) which does get absorbed into the skin. This could cause as of yet unknown health problems and requires further study. Zinc oxide can be used in ointments, creams, and lotions to protect against sunburn and other damage to the skin caused by ultraviolet light (see sunscreen). It is the broadest spectrum UVA and UVB reflector that is approved for use as a sunscreen by the FDA, and is completely photostable.

2.3.4 Cigarette filters

Zinc oxide is a constituent of cigarette filters for removal of selected components 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.

2.3.5 Food additive

Zinc oxide is added to many food products, e.g., breakfast cereals, as a source of zinc, a necessary nutrient. (Other cereals may contain zinc sulfate for the same purpose.) Some prepackaged foods also include trace amounts of ZnO even if it is not intended as a nutrient.

2.3.6 Pigment

Zinc white is used as a pigment in paints and is more opaque than lithopone, but less opaque than titanium dioxide. It is also used in coatings for paper. Chinese white is a special grade of zinc white used in artists' pigments. It is also a main ingredient of mineral makeup.

2.3.7 Coatings

Paints containing zinc oxide powder have long been utilized as anticorrosive coatings for various metals. They are especially effective for galvanised Iron. The latter is difficult to protect because its reactivity with organic coatings leads to brittleness and lack of adhesion. Zinc oxide paints however, retain their flexibility and adherence on such surfaces for many years.

ZnO highly n-type doped with Al, Ga or In is transparent and conductive (transparency ~90%, lowest resistivity ~10^{-4} Ωcm). ZnO:Al coatings are being used for energy-saving or heat-protecting windows. The coating lets the visible part of the spectrum in but either reflects the infrared (IR) radiation back into the room (energy saving) or does not let the IR radiation into theroom (heat protection), depending on which side of the window has the coating.

Various plastics, such as polyethylene naphthalate (PEN), can be protected by applying zinc oxide coating. The coating reduces the diffusion of oxygen with PEN. Zinc oxide layers can also be used on polycarbonate (PC) in outdoor applications. The coating protects PC form solar radiation and decreases the oxidation rate and photo-yellowing of PC.

2.3.8 Corrosion prevention in nuclear reactors

Main article: Depleted zinc oxide.Zinc oxide depleted in the zinc isotope with the atomic mass 64 is used in corrosion prevention in nuclear pressurized water reactors. The depletion is necessary, because ^{64}Zn is transformed into radioactive ^{65}Zn under irradiation by the reactor neutrons.

2.3.9 Electronics

ZnO has wide direct band gap (3.37 eV or 375 nm at room temperature). Therefore, its most common potential applications are in laser diodes and light emitting diodes (LEDs). Some optoelectronic applications of ZnO overlap with that of GaN, which has a similar bandgap (~3.4 eV at room temperature). Compared to GaN, ZnO has a larger exciton binding energy (~60 meV, 2.4 times of the room-temperature thermal energy), which results in bright room-temperature emission from ZnO. Other properties of ZnO favorable for electronic applications include its stability to high-energy radiation and to wet chemical etching. Radiation resistance makes ZnO a suitable candidate for space applications. ZnO is currently the most promising candidate in the field of random lasers to produce an electronically pumped UV laser source.

The pointed tips of ZnO nanorods result in a strong enhancement of an electric field. Therefore, they can be used as field emitters.

Aluminium-doped ZnO layers are used as a transparent electrodes. The constituents Zn and Al are much cheaper and less poisonous compared to the generally used indium tin oxide (ITO). One application which has begun to be commercially available is the use of ZnO as the front contact for solar cells or of liquid crystal displays.

Transparent thin-film transistors (TTFT) can be produced with ZnO. As field-effect transistors, they even may not need a p–n junction, thus avoiding the p-type doping problem of ZnO. Some of the field-effect transistors even use ZnO nanorods as conducting channels.

2.3.10 Spintronics

ZnO has also been considered for spintronics applications: if doped with 1-10% of magnetic ions (Mn, Fe, Co, V, etc.), ZnO could become ferromagnetic, even at room temperature. Such room temperature ferromagnetism in ZnO:Mn has been observed, but it is not clear yet whether it originates from the matrix itself or from secondary oxide phases.

2.4 Preparation methods

2.4.1 Solid State Reaction [5]

A solid state reaction is a chemical reaction in which solvents are not used. 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, allows the reactants to chemically react without the presence of a solvent. 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.

The advantages of solid state reactions ripple throughout many industries. It is important to economics because the elimination of solvents means that products will cost less. 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.

2.4.2 Hydrothermal method [6]

Hydrothermal synthesis can be defined as a method of synthesis of single crystals which 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 vapour 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 Vapor Transport Synthesis [7]

Zn and oxygen or oxygen mixture vapor are transported and react with each other, forming ZnO nanostructures. There are several ways to generate Zn and oxygen vapor. Decomposition of ZnO is a direct and simple method, however, it is limited to very high temperatures (~1400°C). Another direct method is to heat up Zn powder under oxygen flow.This method facilitates relative low growth temperature (500~700°C), but the ratio between the Zn vapor pressure and oxygen pressure needs to be carefully controlled in order to obtain desired ZnO nanostructures. It has been observed that the change of this ratio contributes to a large variation on the morphology of nanostructures.The indirect methods to provide Zn vapor include metal-organic vapor phase epitaxy, in which organometallic Zn compound, diethyl-zinc for example, is used under appropriate oxygen or N_2O flow. Also in the widely used carbothermal method. ZnO powder is mixed with graphite powder as source material. At about 800-1100 °C, graphite reduces ZnO to form Zn and CO/CO_2 vapors. Zn and CO/CO_2 later react and result in ZnO nanocrystals. The advantages of this method lie in that the existence of graphite significantly lowers the decomposition temperature of ZnO. In the VS (Vapor Liquid) process, the nanostructures are produced by condensing directly from vapor phase. Although diverse nanostructures can be obtained, this method obviously provides less control on the geometry, alignment and precise location of ZnO nanostructures. Controlled growth of ZnO nanowires/nanorods/nanotubes has been achieved by catalyst assisted VLS (Vapor Liquid Solid) process . In this process, various nanoparticles or nanoclusters have been used as catalysts.

2.4.4 Patterned Growth and Vertical Alignment of ZnO Nano-Array [7]

The application prospect of ZnO nanostructures largely relies on the ability to control theirlocation, alignment and packing density. As mentioned above, they have been achieved by catalyst assisted VLS(Vapor Liquid Solid) synthesis process. To control the locations of ZnO nanowires, both lithographic and non-lithographic patterning techniques have been utilized. With photolithography technique,73 square and hexagonal catalytic gold dot array was generated on sapphire substrate, then small diameter ZnO nanowires were grown from the patterned catalysts via a typical VLS(Vapor Liquid Solid) process.

2.4.5 Wet chemical method [8]

Now various processes have been applied to synthesize ZnO nanostructure, such as electrochemical deposition technique, hydrothermal method, sputter deposition technique and vapor methods. But above methods require severe reaction conditions, such as high temperature or accurate gas concentration, flow rate or scarce raw materials or complex process, and so on. So it is important to find a simple and lowtemperature method for the synthesis of ZnO nanocrystals. Compared with above synthesis processes, wet chemical approach is relatively popular since it is easier, low-cost, large-scale production, low-temperature process, no catalyst assistant and environment protective. It can be performed on various substrates, which promotes its applications in versatile fields. Therefore, it will be the most promising method to synthesize ZnO nanorods. The morphology and characteristics of the wet chemical-derived 1D ZnO crystallites can be varied by changing the starting materials, the reactant concentrations, procedural details, and growth temperature and time.

2.4.6 Other Synthesis Methods [7]

These methods provide the possibility of forming ZnO nanostructures at low temperature. For example, in an electrodeposition method, AAM (anodic aluminum oxide membranes) with highly ordered nanopores was used as a template, zinc nanowires were fabricated into the nanopores via electrodeposition, forming zinc nanowires array, then the nanowire array was oxidized at 300 °C for 2 hours and ZnO nanowire array was obtained. In a sol-gel synthesis method, AAM (anodic aluminum oxide membranes) was also used as the template and immersed into a suspension containing zinc acetate for 1 minute, then heated in air at 120 °C for 6 hours. ZnO nanofibers were eventually obtained after removing the AAM (anodic aluminum oxide membranes) template.

2.5 Characterization [9]

2.5.1 X-Ray Diffraction (XRD)

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 Diffraction occurs as waves interact with a regular structure whose in powder and solid samples.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. For example, light can be diffracted by a grating having scribed lines spaced on the order of a few thousand angstroms, about the wavelength of light. It happens that X-rays have wavelengths on the order of a few angstroms, the same as typical inter-atomic distances in crystalline solids. That means X-rays can be diffracted 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. In 1912, W. L. Bragg recognized a predictable relationship among several factors as shown in figure 2.6

1. The distance between similar atomic planes in a mineral (the interatomic spacing) which we call the d-spacing and measure in angstroms.
2. The angle of diffraction which we call the theta angle and measure in degrees. For practical reasons the diffractometer measures an angle twice that of the theta angle. Not surprisingly, we call the measured angle '2-theta'.
3. The wavelength of the incident X-radiation, symbolized by the Greek letter lambda and, in our case, equal to 1.54 angstroms.

$$n\lambda - 2dsin\theta$$ ....(Eq.2.5)

Where

λ = wavelength of X-ray

d = interplaner spacing

θ = diffraction angle

n = 0, 1, 2, 3,...

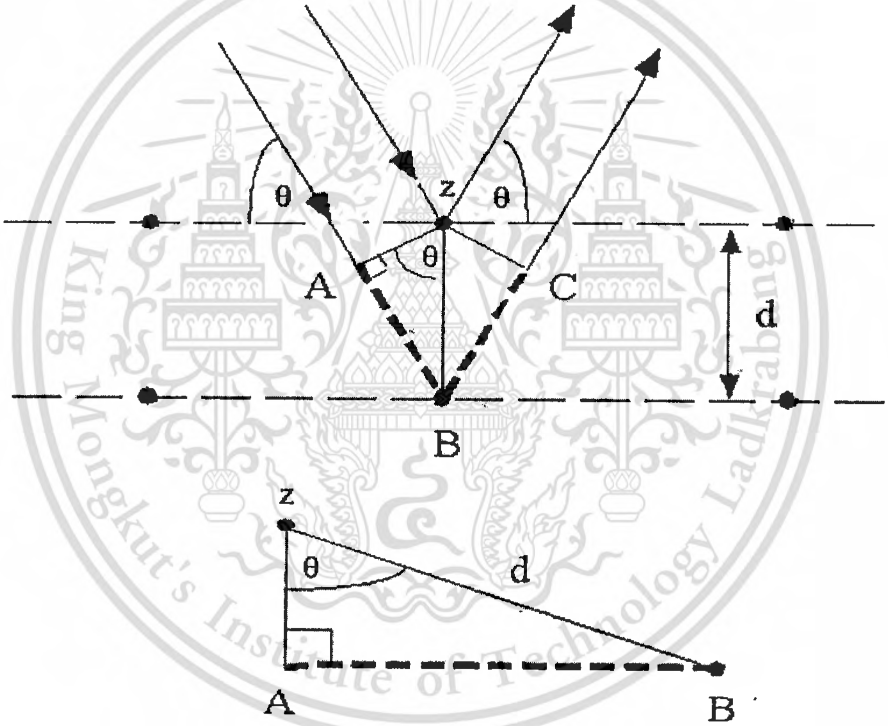


Fig. 2.6 Bragg's diffraction

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? with a PAN analytical system diffractometer (Model: DY-1656) using Cu K (=1.542A) with an accelerating voltage of 40 KV. Data were collected with a counting rate of 1?/min. The K doublets were well resolved. From XRD, the crystallite size can be found out by using the scherrer's formula ,

$$p = \frac{0.9\lambda}{\beta \cos\beta} \quad \text{................ (Eq.2.6)}$$

Where

p = crystalline size

λ = wavelength (1.54 A°)

β = Full maxima half width

θ = Diffraction angle

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_α and K_β. K_α consists, in part, of K_{α_1} and K_{α_2}. K_{α_1} has a slightly shorter wavelength and twice the intensity as K_{α_2}. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochromcters, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha_1}$and K_{α_2} are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuK_α radiation = 1.5418Å. These 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.

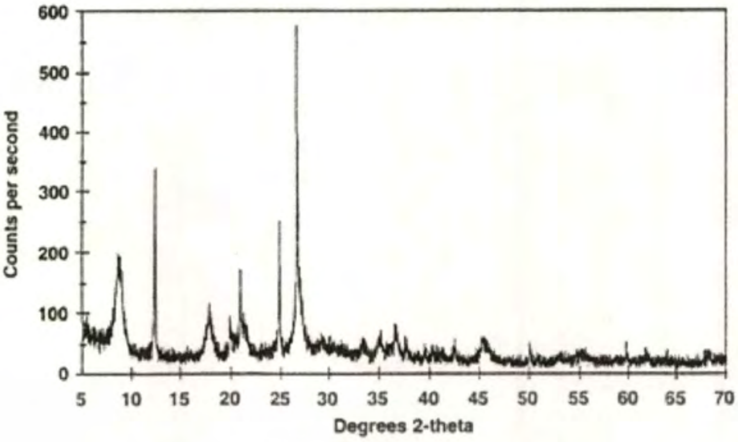


Fig. 2.7 XRD diffraction graph

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 2θ. The instrument used to maintain the angle and rotate the sample is termed a goniometer. For typical powder patterns, data is collected at 2θ from ~5° to 70°, angles that are preset in the X-ray scan.

Fig. 2.8 XRD diffraction machine

2.5.2 Scanning electron microscope (SEM)

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.

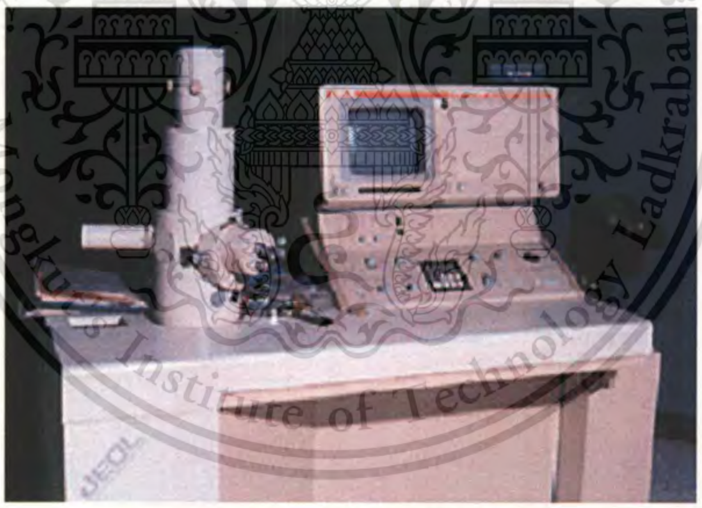


Fig. 2.9 SEM (JEOL-JSM 5800)

Fundamental Principles of Scanning Electron Microscopy (SEM) 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 (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.

2.6 Literature review

In 2005 , **XiangyangMa,HuiZhang,YujieJi,JinXu,DerenYang** [10] Sequential occurrence of ZnO nanopaticles ,nanorods, and nanotips during hydrothermal process in a dilute aqueous solution by consisting of 2 g. $Zn(AC)_2$ was dissolved in 110 ml de-ionized (DI) water and 10 ml 2M NaOH. X-ray diffraction (XRD) pattern indicates that the synthesized ZnO crystal is of hexagonal phase .By means of transmission electron Microscopy (TEM) and field emission scanning electron microscopy(FE-SEM),it has been revealed that the ZnO nano particles,nanorods and nanotips sequentially occur along with the hydrothermal process, during which the concentration of Zn source is ever decreasing. The Nanoparticles terminated with pyramids firstly generate at the early stage of hydrothermal process; subsequently, a number of seed-crystals Branch on the pyramids, further more,the homo-epitaxy based on which along the<0001> direction results in the formation of nanorods; finally,due to the extremely low concentration of Zn source,instead of the continual elongation of the nanorods, the nanotips dispersively occur on the top flat plane of nanorods as a result of selective epitaxy.

In 2005, Huihu Wang, Changsheng Xie_, Dawen Zeng [11] Controlled growth of ZnO by adding H2O. The wurtize ZnO particles were synthesized via $Zn(CH_3COO)_2$ hydrolyzing in methanol using chemical deposition method. The size and shape of ZnO particles were controlled well by adding H_2O. Without adding H_2O or with little volume ratio of adding H_2O/methanol, the ZnO nanoparticle film was synthesized. The characterization of the result by using SEM and XRD. For the result, on increasing volume ratio, the shape of ZnO particles varied from irregular particle, plate into regular cone with the size changing from nano-scale into micro-scale. Moreover, the height of the cone decreased as the volume of adding H_2O increased.

In 2007 , YuChen ,RunzhouYu ,QianShi ,JingliQin ,FengZheng [12] Hydrothermal synthesis of hexagonal ZnO clusters by using 1.48g (5mmol) $Zn(NO_3)_2$ $6H_2O$ was dissolved in 30 ml distilled water. Then 0.33 g. (2mmol) KI was added into the solution followed by dripping down 2 ml N_2H_4 H2O whilst stirring . The resulting transferred into a 50 ml Teflon-lined stainless steel autoclave and sealed tightly . Hydrothermal treatments were then carried out at 150 °C for 24 h. The autoclave was cooled down naturally and precipitates were collected , and washed with absolute ethyl alcohol for 3 times prior to dry in air at 75 °C. X-ray powder diffraction and scanning electron microscopy were used to Analyze the crystal structure and surface morphology. XRD pattern analysis showed that the ZnO clusters are single hexagonal phase of wurtzite structure .Also, SEM images revealed that the size of a single ZnO crystal is between 200-500 nm in (spacegroupP63mc) with no impurity of Zn and Zn(OH) Diameter and 25 min length. The influence of potassium iodide (KI) as a surfactant on the crystallinity of ZnO has been investigated.

In 2007, Hongxia Zhang, Jing Feng, Jun Wang, Minlin Zhang [13] Preparation of ZnO nanorods through wet chemical method in the present of polyethylene glycol (PEG, Mw=4000) by using zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and ammonium hydroxide ($NH_3 \cdot H_2O$) as the starting materials. Samples were characterized by XRD, EDS, TEM, SEM, ED and PL. XRD results prove the formation of ZnO with wurtzite structure. The ED and HRTEM reveal that single ZnO nanorod is single crystal and preferentially grows up along the [001] direction. The PL spectra showed that the ZnO nanorods have blue emission at 466 nm and green–yellow emission at 542 nm. The influence of reaction temperature, pH in system and evaporation of ammonia on the morphology has been investigated. A possible growth mechanism of ZnO with various morphologies is discussed.

In 2008, Parawee Tonto , Okorn Mekasuwandumrong , Suphot Phatanasri , Varong Pavarajarn , Piyasan Praserthdam [14] Preparation of ZnO nanorod by solvothermal reaction of zinc acetate in various alcohols. The solution of Zinc acetate ($Zn(CH_3CO_2)_2$) in a predetermined amount in the range of 10–25 g was suspended in 100 ml of alcohol in a glass vessel and the mixture was heated to desired temperature, in the range of 250–300°C, at a constant heating rate of 2.5 °C/min and held at that temperature for 2 h. The effects of reaction conditions on the product morphology as well as crystallization mechanism were investigated by using X-ray diffraction (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM) techniques. It was found that average diameter and length of the nanorods increased with an increase in reaction temperature or the initial concentration of zinc acetate.

In 2008 WEI Su-feng, JIANG Qing, LIAN Jian-she [15] The large-scale ZnO rods of submicrometer were prepared on the bare glass using a wet chemical method under different experimental parameters, such as the reactant concentration and the growth time. The microstructure of the ZnO rods was characterized by X-ray diffractometry(XRD) and field emission scanning electron microscopy (FESEM) with the energy dispersive X-ray spectroscopy(EDX), and the optical property was investigated by the room-temperature photoluminescence (PL) spectra. XRD and FESEM results show that the wurtzite structure and rod-like ZnO is obtained. The length (3-8 μm) and the diameter (400 nm^{-3}μm) vary with the experimental parameters. A strong UV emission at 384 nm and a weak visible yellow-green emission around 570 nm are observed in the PL spectrum. After annealing at 600 °C in air, the UV peak intensity increases obviously and the yellow-green peak intensity decreases greatly. The near-band-edge UV emission is attributed to the exciton recombination; the yellow-green emission can be associated with the defect recombination; and some defect complexes may be responsible for the latter emission.

In 2008 , J.T.Chen ,J.Wang ,R.F.Zhuo ,D.Yan ,J.J.Feng ,F.Zhang ,P.X.Yan [16] The effect of Aldoping on the morphology and optical property of ZnO nanostructure sprepared by hydrothermal process which the undoped and Al-doped ZnO nanostructures were fabricated on the ITO substrates pre-coated with ZnO seed layers. ZnO seed layer was loaded and the precursor solution containing zinc nitrate hexahydrate(3.5mmol), methenamine (3.5mmol) and distilled water (35ml). As the doping source, Aluminum chloridehexahydrate powders were added in the precursor solution. In the precursor solutions, Al doping concentrations (the atom ratio of Al to Zn) were chosen to 1at.%, 3at.% and 6at.% ,respectively. The ZnO pre-coated ITO. ZnO shows various morphologies. The morphology of ZnO changes froma ligned nanorods,tiltednanorods,nanotubes/nanorods to the nanosheets when the Al doping concentrations increase.The ZnO nanostructures were characterized by X-ray diffraction,field emission scanning electron microscopy,X-ray photoelectron spectroscopy,photoluminescence and Raman technology.The Aldoping concentrations play an important role on the morphology and optical properties of ZnO nanostructures.The possible growth mechanism of the ZnO nanostructures was discussed.

In 2009, Zhifeng Liu , Lei E, Jing Ya, Ying Xin [17] Growth of ZnO nanorods by aqueous solution method with electrodeposited ZnO seed layers.The ZnO seed layers were prepared by cathodic electrochemical deposition in zinc nitrate ($Zn(NO_3)_2.6H_2O$) aqueous solution. ZnO nanorod arrays on ZnO-coated seed layers were fabricated by aqueous solution method using zinc nitrate and hexamethylenetetramine at low temperature. The orientation and morphology of both the seed layer and successive nanorods were analyzed by using X-ray diffraction (XRD), SEM and TEM. The results show that the seed layer deposited at -700 mV has evenly distributed crystallites and (0 0 2) preferred orientation; the density of resultant nanorods is high and ZnO nanorods stand completely perpendicular onto substrates.

In 2009 , L.Z.Pei ,H.S.Zhao ,W.Tan ,H.Y.Yu ,Y.W.Chen ,C.G.Fan ,Qian-FengZhang [18] Hydrothermal oxidization preparation of ZnO nanorods on zinc substrate. The zinc substrate was put into distilled water cleaning for 10 min using supersonic to ensure the cleanliness of the surface. After the autoclave was sealed safely , it was heated to 350 °C, 5.8-6.5 MPa of pressure , 100 rpm of the rotating speed for the stirrer . The temperature and pressure were maintained for 24h. Finally , the substrate with bulk white deposit was obtained after the experiment. X-ray

Diffraction (XRD), scanning electron microscopy (SEM),energy dispersive X-ray spectrum(EDS), Transmission electron microscopy (TEM) and photo luminescence (PL) spectrum were used to Characterize the nanorods. The nanorods are single crystalline wurtzite structure with a length longer than10 micrometer.The effects of the hydro thermal temperature ,pressure and time on the morphology diameter and length of the ZnO nanorods have been also analyzed. It is considered that timekeeping. The temperature and pressure is the main factor that inuences the length of the ZnO nanorods. The PL Spectrum shows a strong blue light emission at 439 nm, which is considered to be caused by radiative recombination of photo-generated holes with singularly ionized oxygen vacancies. The growth process of the ZnO nanorods is proposed based on the solid liquid solid (SLS) mechanism.

In 2010, Chien-Te Hsieh, Shu-Ying Yang, Jia-Yi Lin [19] Electrochemical deposition and superhydrophobic behavior of ZnO nanorod arrays with different heights are grown on the ZnO seeded indium tin oxide substrate by cathodic electrochemical deposition from zinc nitrate at two temperatures of 60 °C and 80 °C. As-grown ZnO nanorods exhibit wurzite crystal structure and their heights can be well controlled by different deposition times. The fluorination coating tends to induce a superhydrophobicity of ZnO nanorods, i.e., the maximal value of contact angle: 166.9°. The super water repellency can be attributed to the fact that an air layer is confined in the nanorod arrays, and thus leads to water droplets sitting on the ZnO surfaces, referring as Cassie state. Interestingly, their water contact angles are found to vary with the heights of ZnO nanorods, ranged from 99.8 to 746 nm. The superhydrophobicity of ZnO surfaces can be well predicted by a proposed model that is capable of determining the wetted fraction of ZnO pillars. This satisfactory result would shed one light on how the variation of rod height would induce the superhydrophobic behavior of ZnO nanorod arrays.

In 2010, Shao-Hwa Hua, Yi-Chuan Chenb, Chyi-Ching Hwangb, Cheng-Hsiung Pengc, Dah-Chuan Gonga [20] Development of a wet chemical method for the synthesis of arrayed ZnO Nanorods using zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, $ZnAc_2$) and monoethanolamine ($NH_2CH_2CH_2OH$, MEA) as raw materials. The proposed method includes the predeposition of a thin ZnO seed layer using the sol–gel technique and the subsequent hydrothermal growth of ZnO nanorods at 130 °C for 2 or 4 h. The synthesis process was monitored using X-ray diffraction (XRD), Fourier transformation infrared (FTIR) spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The ZnO nanorods exhibited a diameter of 25–75 nm with an aspect ratio ranging from 10 to 50 after growing for 4 h. Each ZnO nanorod was confirmed to be a single crystal with a wurtzite structure and grow along the [0002] direction during the hydrothermal process. Photoluminescence (PL) measurements confirmed that the ZnO nanorods exhibited a near -UV emission at ~380nm together with a green emission that was centered at ~500 nm. We note that the PL properties may be affected by the hydrothermal time.

In2010, K. Prabakar , Heeje Kim [21] Growth control of ZnO nanorod density by sol–gel method which is ZnO nanorods were grown on seeded transparent conducting oxide substrates from 20 mM aqueous solutions of zinc nitrate and hexamethylenetetramine at different volume ratios and at 90 °C for 4°h. The crystallinity of the grown ZnO nanorods was investigated using X-ray diffraction pattern and SEM. The average diameters of the hexagonal ZnO nanorods were higher when equal volume ratios of the precursor solutions were used. The reduced zinc chemical potential inside the precursor solution split the single nanorod into many smaller nanorods with reduced density and average diameters.

In 2010 , Xianming Hou ,Lixia Wang ,Bo Yu ,Feng Zhou , Weimin Liu [22] Synthesis of branched ZnO nanorods on various substrates by a facile wet-chemistry route using a chemical bath deposition method at relatively low temperature.Substrates were immersed in a solution(50mL)composed of $Zn(NO_3)_2$ (0.005mol/L) and $C_6H_{12}N_4$ (0.01mol/L).The reaction system was then heated in a drying oven to 95 °C for5h.The zinc sheet was removed ,washed with deionized water and anhydrous alcohol ,and fully dried in air at room temperature. The structure ,morphology were characterized by X-ray diffraction(XRD) ,scanning electron microscopy(SEM) , UV-vis spectrometry and photoluminescence(PL) spectrometry. The XRD and SEM results show that branched ZnO nanorods formed on Zn substrates are not from epitaxial growth of Zinc sheet but spontaneous deposits of ZnO species from reaction solutions. The experimental results indicate insignicant effect of solution composition and supported substrates on morphologies and sizes of the products.

In 2010 , Shao-Hwa Hu ,Yi-Chuan Chen ,Chyi-Ching Hwang ,Cheng-Hsiung Peng ,Dah-Chuan Gong [23] Development of a wet chemical method for the synthesis of arrayed ZnO nanorods. Silica glass was used as the substrate material ,which was cleaned using a 5% H_2SO_4 aqueous solution ,then rinsed ultrasonically in acetone and deionized water,and finally dried in a vacuum oven. A two-step process was applied to prepare arrayed ZnO nanorods on glass substrates using zinc acetate dehydrate ($Zn(CH_3COO)_2$ $2H_2O$,$ZnAc_2$)and monoethanolamine ($NH_2CH_2CH_2OH$,MEA) as raw materials. The proposed method includes the pre-deposition of a thin ZnO seed layer using the sol gel technique and the subsequent hydrothermal growth of ZnO nanorods at 130 °C for 2 or 4 h. The synthesis process was characterized by X-ray diffraction (XRD) ,Fourier transformation infrared (FTIR) spectroscopy ,Atomic force microscopy(AFM) ,Scanning electron microscopy (SEM)and transmission electron microscopy(TEM).The ZnO nanorods exhibited a diameter of 25-75 nm with an aspect ratio ranging from 10 to 50 after growing for 4 h.Each ZnO nanorod was confirmed to be a single crystal with a wurtzite structure and grow along the [0002] direction during the hydrothermal process. Photoluminescence(PL) measurements confirmed that the ZnO nanorods exhibited a near UVemission at ~380 nm together with a green emission that was centered at ~500 nm.

In 2006, Zhitao Chen, Lian Gao [24] A facile route to ZnO nanorod arrays using wet chemical method. A glass substrate was coated with a droplet of 0.01 M zinc acetate dehydrate aqueous solution, rinsed with distilled water after 5 s, and then blow dry with a stream of nitrogen. The coating step is repeated five times to ensure the uniform coating uniformly on entire substrate. Then, the substrate coated with a film of zinc acetate crystallities is heated to 360 ^{0}C in air atmosphere for 30 min to yield layers of ZnO seeds on the substrate surface. Thermal decomposition deposition eas first used to grow a thin layer of ZnO nanocrystals on substrate serving as seeds for the subsequent growth of the nanorod arrays. X-ray diffraction analysis confirmed the high orientation of the ZnO nanorods. The effect of different substrate and the annealing temperature of the ZnO seeds on the morphology of the as-grown ZnO arrays were investigated. The diameter and the length of the nanorods can be controlled by contolled by the reaction times and reaction temperature.

Chapter 3

Experimental Details

3.1 Apparatus and Instrument.

1. X-ray diffractometer, XRD (D8 Advance model, Burker AXS GmbH Company Limited.)
2. Field Emission Scanning electron microscope, FESEM (Hitachi 4700 FE-SEM)
3. Oven
4. Mortar and pestle
5. Hotplate with stirrer
6. pH paper
7. Balance
8. Thermometer
9. Glass apparatus
10. Hair dryer
11. Water bath
12. Glass slices

3.2 Chemicals

1. Zinc oxide (ZnO), Premium grade, Nano materials Technology Company Limited.
2. Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$)
3. Glacial Acetic acid (CH_3COOH), Commercial grade, Lab System Company Limited.
4. Sodium hydroxide (NaOH), Analytical grade, Italma Company Limited.
5. Glycerol ($C_3H_5(OH)_3$), Comercial grade, Lab System Company Limited.
6. Acetone (CH_3COCH_3), Comercial grade, Lab System Company Limited.
7. Buthanol, Comercial grade, Apex Company Limited.
8. Ethanol, Comercial grade, The Liquor Distillery Organization.
9. Hexamethylenetetramine ($C_6H_{12}N_4$), Comercial grade, Lab System Company Limited.

10. Sulfuric acid (H_2SO_4), Comercial grade, Lab System Company Limited.

3.3 Preparation of ZnO nanoparticles by using solid state reaction method

1. Mix Zinc acetate dihydrate 18.3 g. with sodium hydroxide 8 g. (mole ratio 1 : 2) and grinding in mortar about 20 minute until fine homogeneous solid is obtained.
2. Wash the mixture with DI water until pH value of 7 (for eliminate some soluble substances.)
3. Dry the obtained product by using hot plate.
4. Repeat step 3 by using in another mole ratio; 1 : 1, 1 : 1.5 respectively.

3.4 Growth of ZnO nanorods on glass substrate by using two-step wet chemical bath deposition method.

3.4.1 Cleaning

1) Silica glass is used as the substrate material, which is washed by detergent.

2) Glass substrates are cleaned by using 5% H_2SO_4 aqueous.

3) Rinse throughly with distilled water.

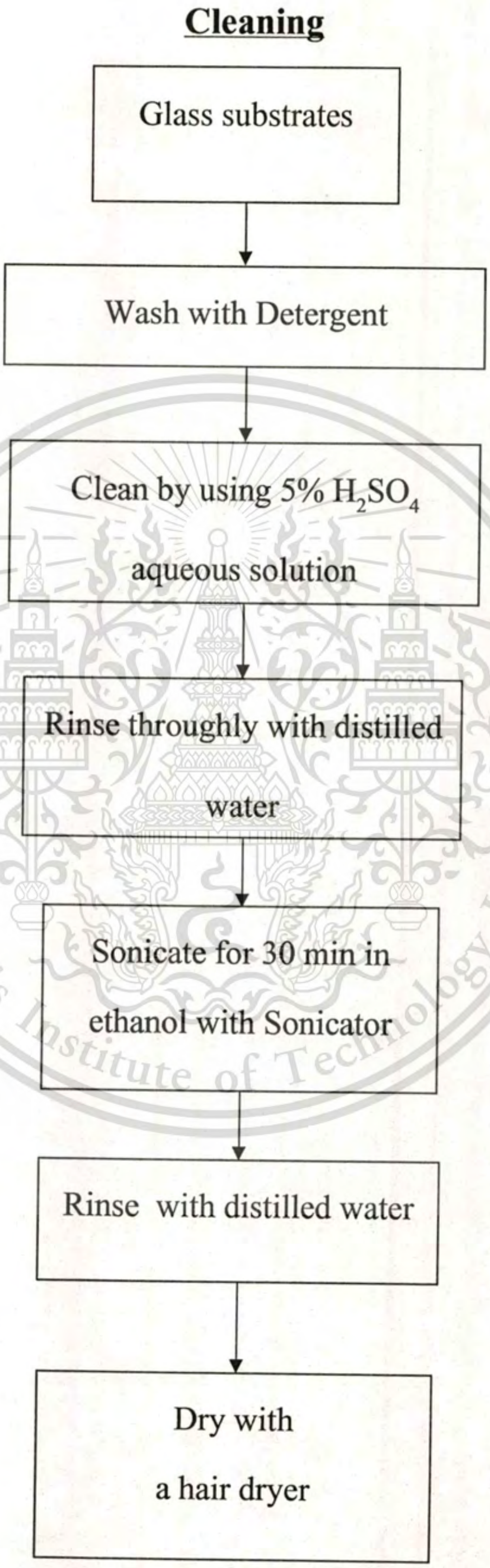
4) The Glass substrate are sonicated for 30 mins. in ethanol with sonicator .

5) Rinse with distilled water.

6) Dry with a hair dryer.

Step1-6 are shown in diagram 3.1

Diagram 3.1 : Diagram of Cleaning method



3.4.2 Seed preparation method of ZnO nanorods on glass substrates.

1) A glass substrate is immersed into 0.1 M $Zn(CH_3COO)_2\ 2H_2O$ aqueous solution for 5 s.

2) Dry with hair dryer.

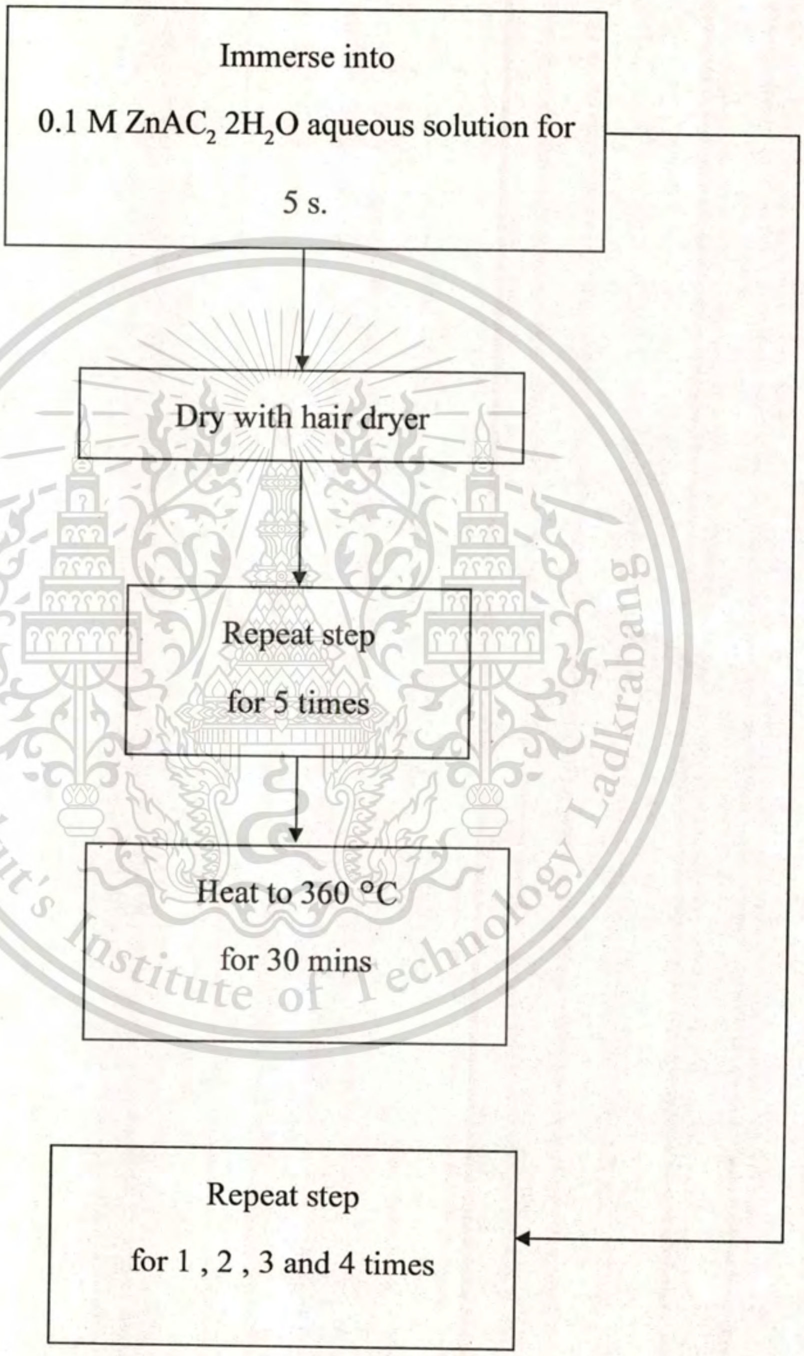
3) The step 1 and 2 are repeated five times to ensure the uniformly on entire substrate.

4) Then the glass substrates which coated with a film of Zinc acetate were heated to 360°C for 30 mins.
5) To study the effect of the coating times in the seeding step. The immersing times in step 3 were changes to 1, 2, 3 and 4 respectively.

Step1-5 are shown in diagram 3.2

Diagram 3.2 : Diagram of preparation of ZnO nanorods seed

Preparation of ZnO nanorods seed.

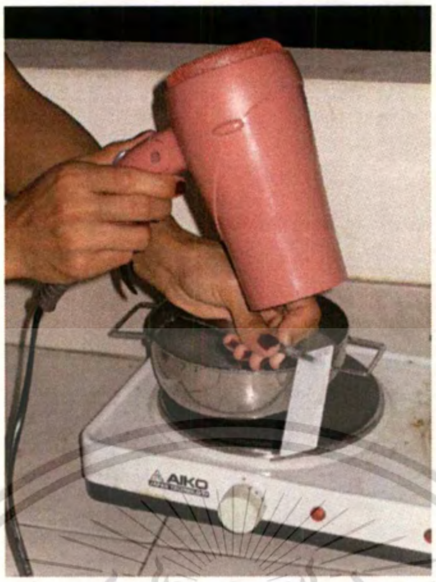


3.4.3 Growth of ZnO nanorods on glasses.

1) A glass substrates is immersed in 300 ml solution composed of 150 ml of 0.005 M $Zn(CH_3COO)_2.2H_2O$ and 150 ml of 0.1 M $C_6H_{12}N_4$ and heated to 95°C for 5 h by using the hot plate.

2) The glass substrates is removed and washed with distilled water.

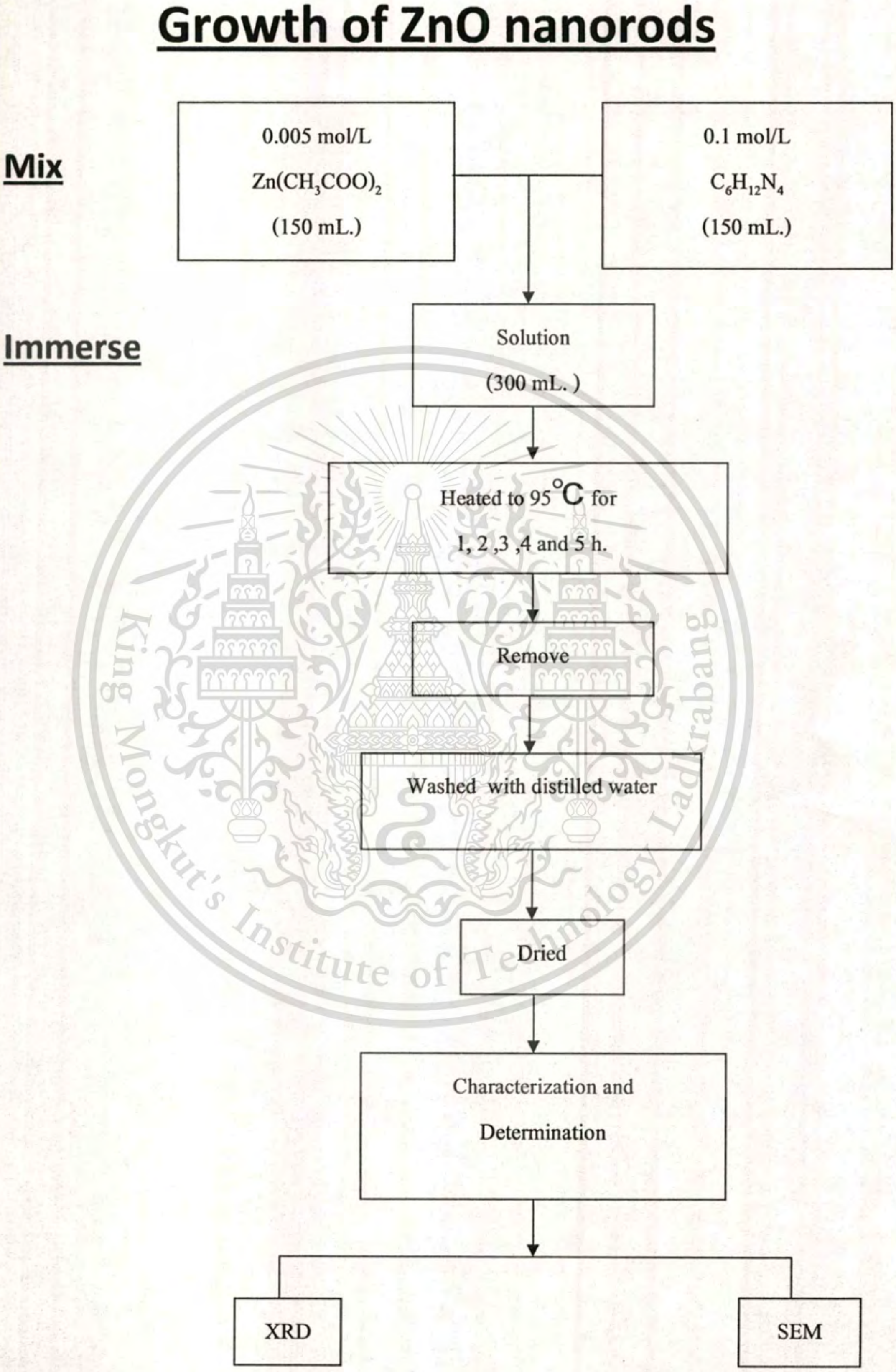
3) Dry with hair dryer.



4) The step 1-3 are repeated by changing the period of growth step to 1, 2, 3 and 4 h. respectively.

Step1-4 are shown in diagram 3.3

Diagram 3.3 Diagram Growth of ZnO nanorods



Chapter 4

Results and Discussion

4.1 Solid state reaction method

ZnO nanoparticles have been prepared via a solid-state reaction between $Zn(CH_3COO)_2$ and NaOH (ratio 1:2) at room temperature. The ZnO nanoparticle were characterized by X-ray Diffraction (XRD) and Field Emission Scanning Electron Microscope(FESEM). The overall reaction for the synthesis of ZnO nanorods from Zinc acetate can be written as :

$$Zn(CH_3COO)_2 + 2NaOH \longrightarrow ZnO + 2CH_3COONa + H_2O \quad \text{............. (Eq. 4.1)}$$

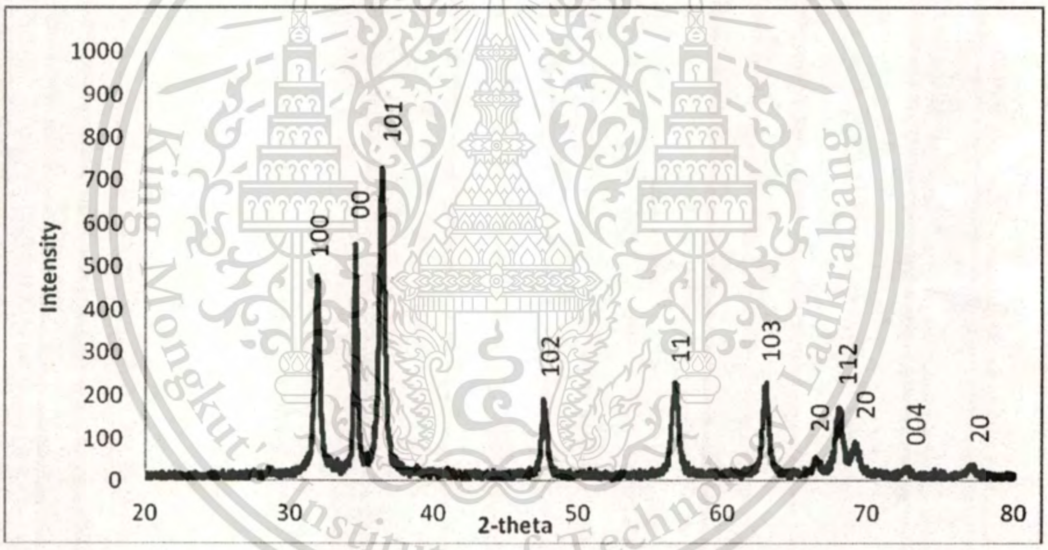


Fig. 4.1 XRD pattern of ZnO nanoparticles via solid state reaction.

Fig 4.1 shows that the XRD pattern of ZnO nanoparticles. All the diffraction peak are well indexes to hexagonal wurtzite structure and no characteristic peaks are observed for other impurities. The crystalline size (d) of the nanoparticles was calculated by the Debye –Scherrer formula. The average particle size of ZnO nanoparticles is about 132 nm.

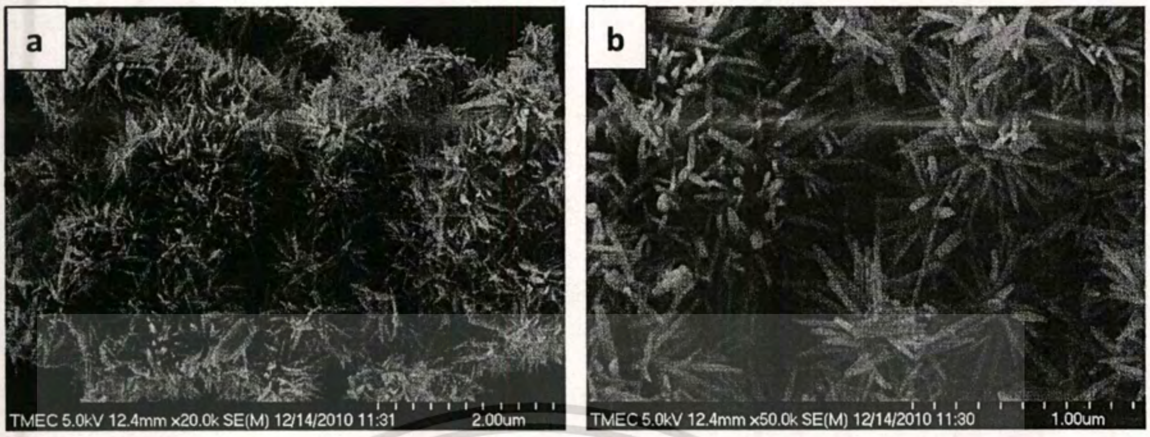


Fig. 4.2 SEM image of ZnO nanoparticles: (a) 2000x magnification and (b) 5000x magnification

The FESEM image of solid state reaction method shown needle-like morphology in fig 4.2 ZnO nanoparticles with diameters of 30-50 nm have been synthesized conveniently with this method. The lengths of the ZnO nanoparticles are about 300 nm which is quite difference with the result calculated from Debye –Scherrer formula.

4.2 Two-step wet chemical bath deposition method

4.2.1 The effect of number of coating in seeding step on the glass substrate and characteristic of ZnO nanorods.

The growth of ZnO nanorods from aqueous solution involves two steps which are seeding and growth. In seeding step, the glass substrate was immersed into 0.1 M $Zn(CH_3COO)_2.2H_2O$ aqueous solution by varying in number of coating and fixed the period of growth at 3 h. The seed decomposition of $Zn(CH_3COO)_2.2H_2O$, when the glass substrate was immersed with 1 times, the coating area has a empty space therefore the ZnO nanorods is parallel to the substrate and can grow in any direction. When the number of immersing is increased, the coating area has high intensity of seed. It means that the ZnO nanorods were forced to grow in the c-axis direction. The results indicate that in the growth step, 0.005 M $Zn(CH_3COO)_2.2H_2O$ and 0.1 M $C_6H_{12}N_4$ was used as a growth solution by varying the period of growth and fixed number of coating 3 times.

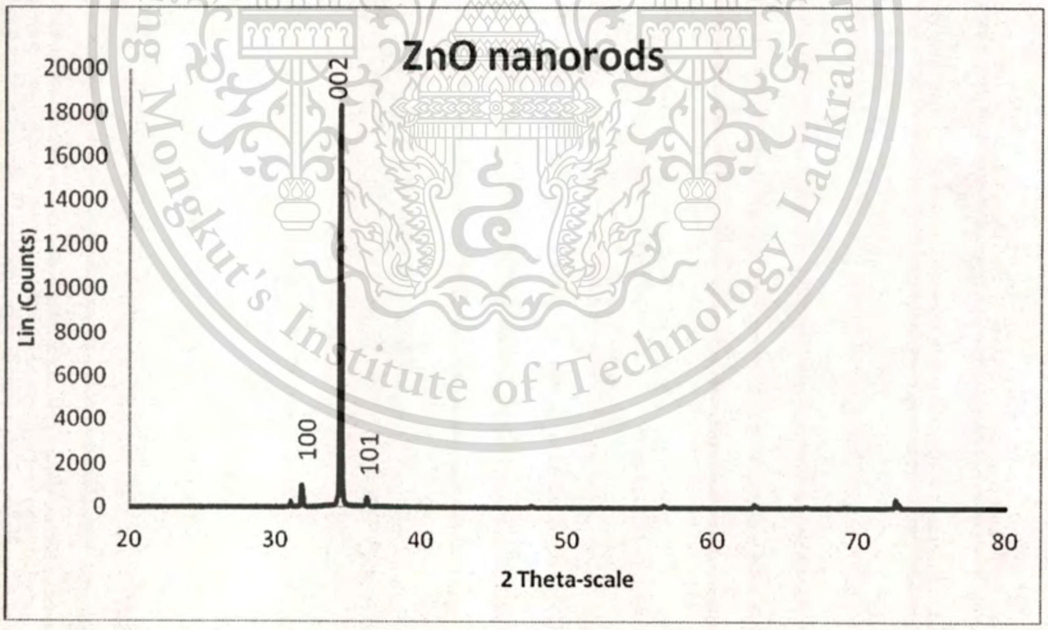


Fig. 4.3 XRD pattern of ZnO nanorods via Two-step wet chemical bath deposition method

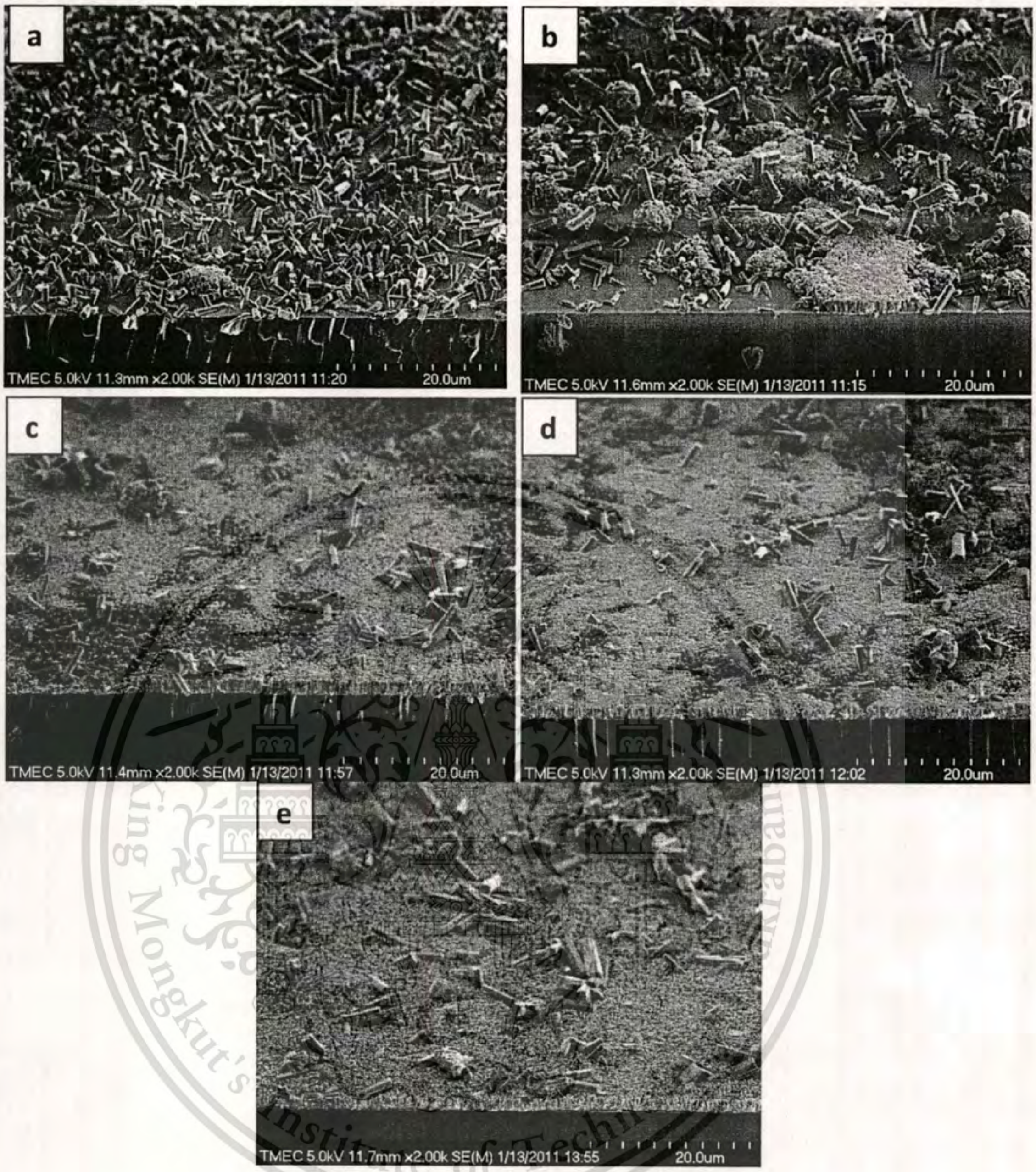


Fig. 4.4 Top view SEM images of ZnO nanorods on glass substrate obtained at 3 h with different number of coating in seeding step: (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5 times at 2000x magnification.

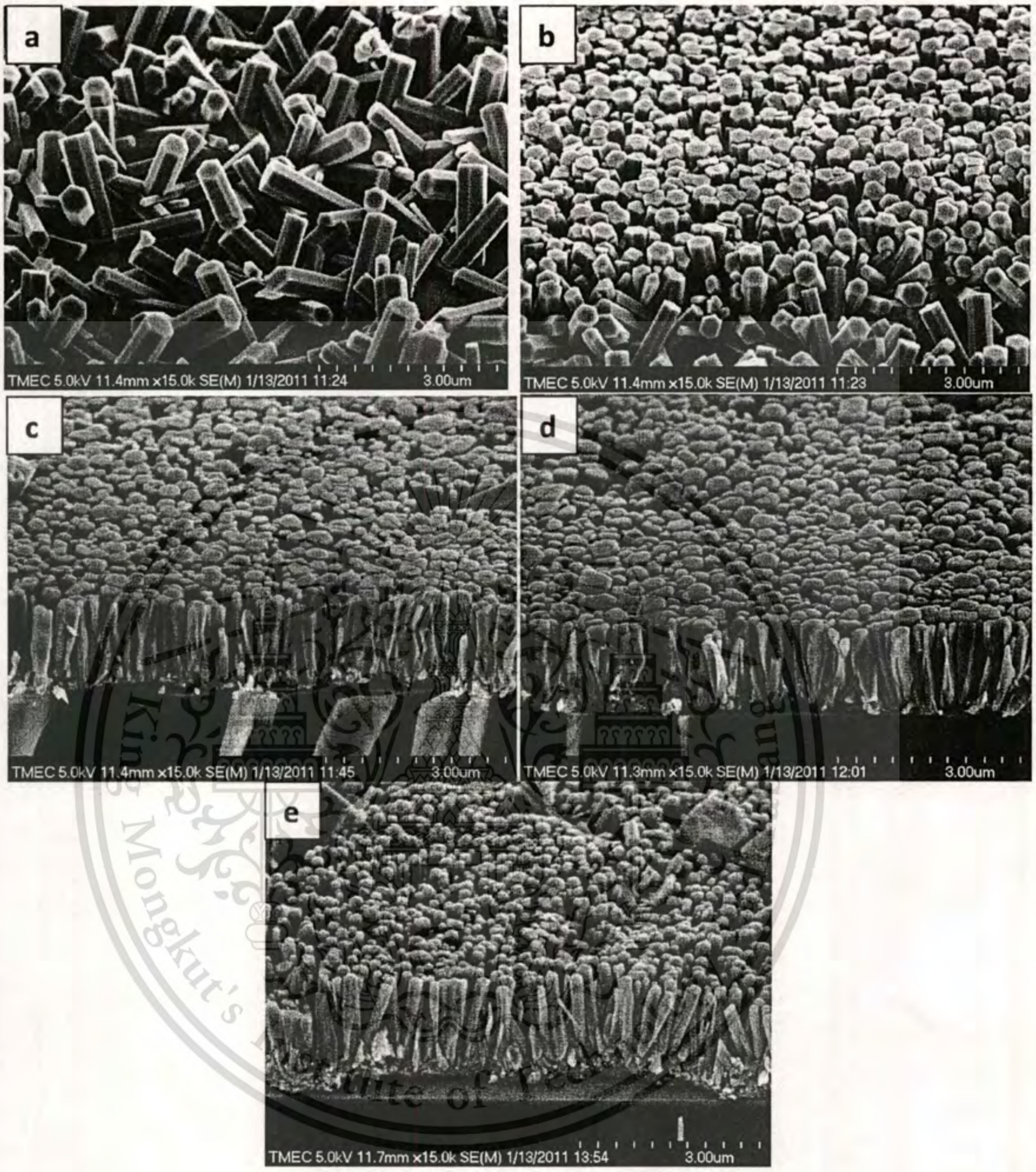


Fig. 4.5 Top view SEM images of ZnO nanorods on glass substrate obtained at 3 h. with different number of coating in seeding step: (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5 times at 1500x magnification.

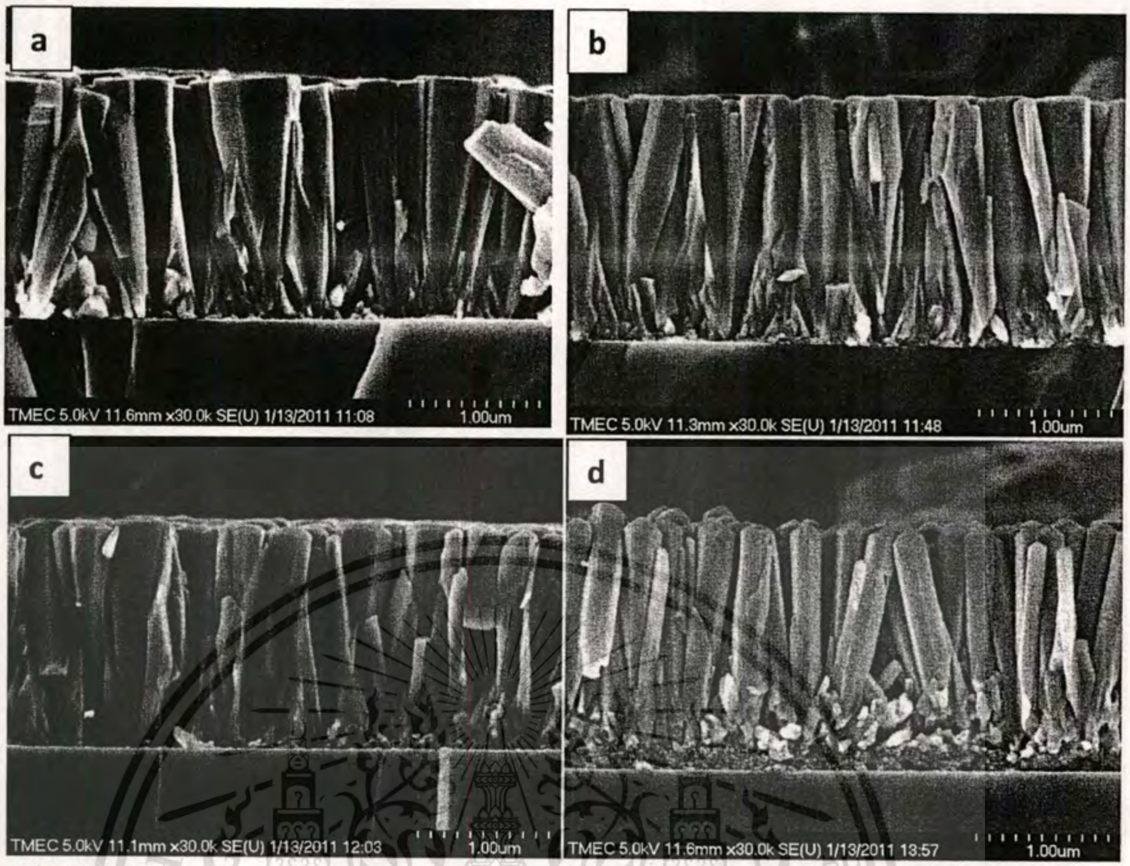


Fig. 4.6 cross-sectional SEM images of ZnO nanorods on glass substrate obtained at 3 h. with different number of coating in seeding step: (a) 2, (b) 3, (c) 4 and (d) 5 times at 3000x magnification.

The morphologies of ZnO nanorods grown on the glass substrate with different number of coating zinc acetate dihydrate solution in seeding step, were varied from 1-5 times at a fixed growth period of 3 h and shown in Fig 4.4, 4.5 and 4.6 .The inserts of Fig 4.5 (a) and (b) are on their top view images. It is clearly seen that hexagonal ZnO rods are obtained. They always grow along the c axis that it is lowest energy in hexagonal structure. As shown in Fig 4.4 at lower number of coating in seeding step, the ZnO rods are parallel to the substrate. Several rods are perpendicular to the substrate appearing gradually and increasing the number of coating. When the number of coating reaches 3 times, the rods are perpendicular to the substrate as shown in Fig 4.3, the XRD patterns of ZnO rods on glass substrate. All diffraction peaks can be indexed to hexagonal wurtzite ZnO, and no diffraction peaks of any other impurities are detected. The most of the ZnO rods along c-axis growth lay parallelly on the substrate. The (100) and (101) peak are weak, which means that most of the ZnO rods growth lay parallelly on the substrate and the (002) preferred-orientation growth is eventually observed. It is implies that most of the ZnO rods grow with c-axis vertical to the glass substrate.

Table 4.1 Geometrical parameters of as-grown ZnO rods by fixing growth period and number of coating in seeding step was varied.

Growth period (h)	Number of coating in dipping step (times)	Average diameter (nm)	Average length (µm)	Ratio of length to diameter
3	1	600	-	-
3	2	400	1.87	3.11
3	3	300	1.93	6.43
3	4	200	1.76	8.8
3	5	150	1.98	13.2

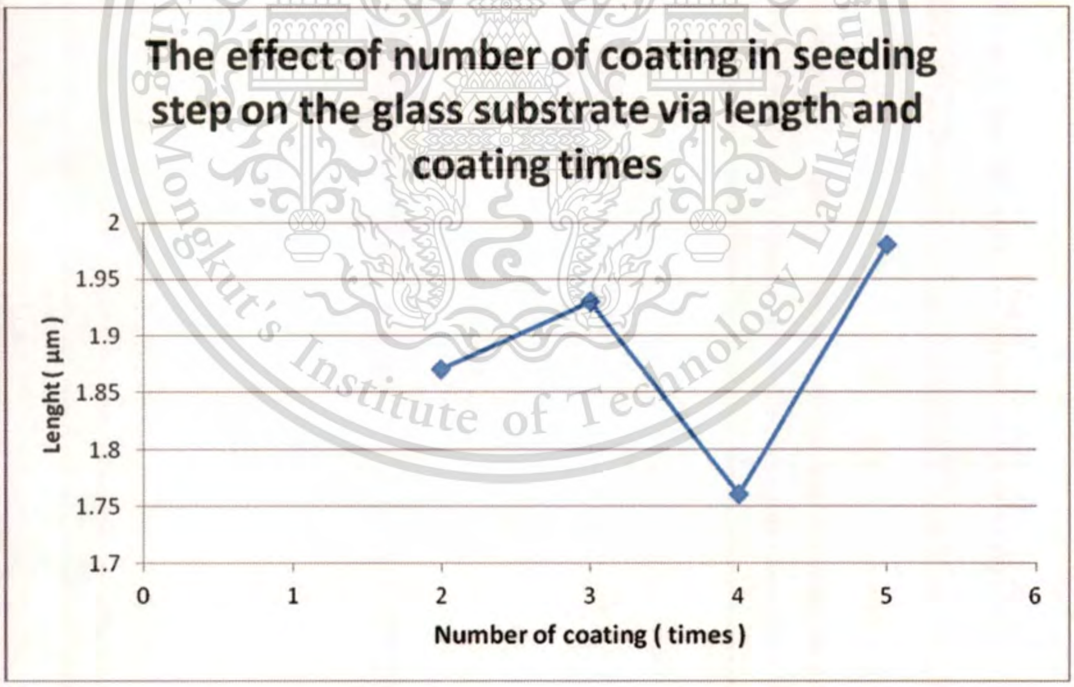


Fig. 4.7 The graph shown the effect of number of coating in seeding step on the glass substrate via length and coating times.

4.2.2 The effect of growth time on the glass substrate

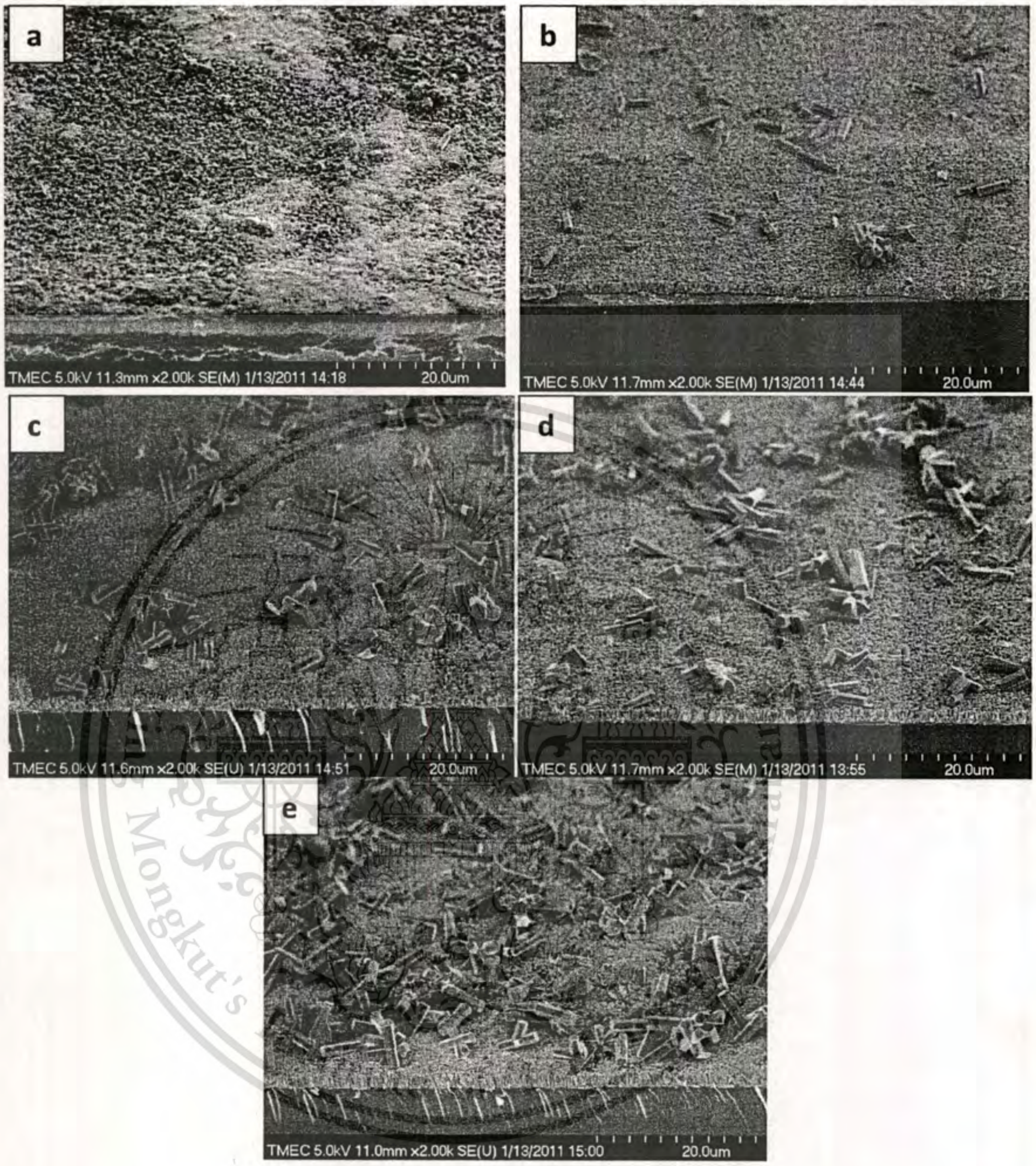


Fig. 4.8 Top view SEM images of ZnO nanorods on glass substrate obtained number of coating 3 times with different growth period: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h and (e) 5 h at 2000x magnification.

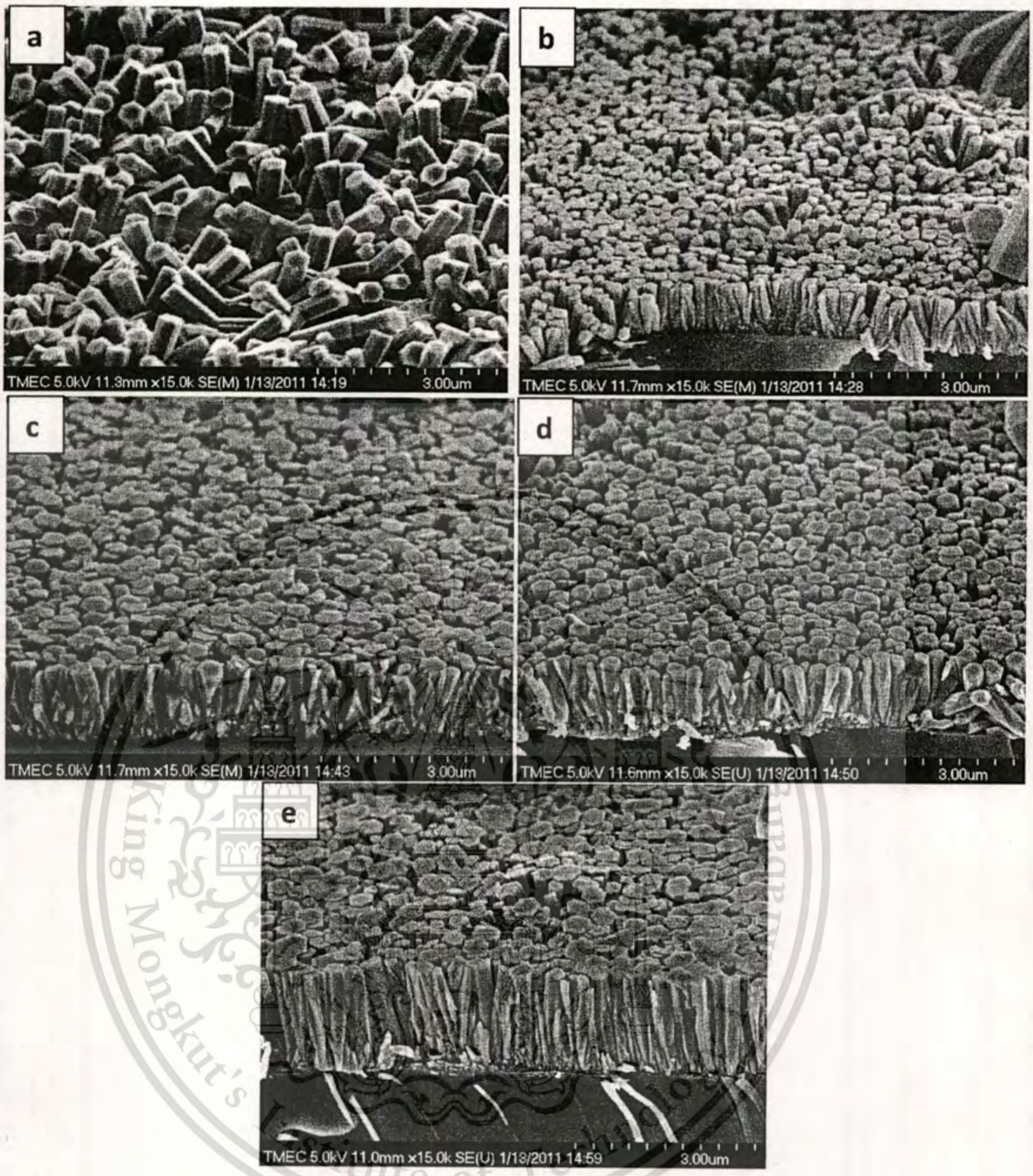


Fig. 4.9 Top view SEM images of ZnO nanorods on glass substrate obtained number of coating 3 times with different growth period: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h and (e) 5 h at 1500x magnification.

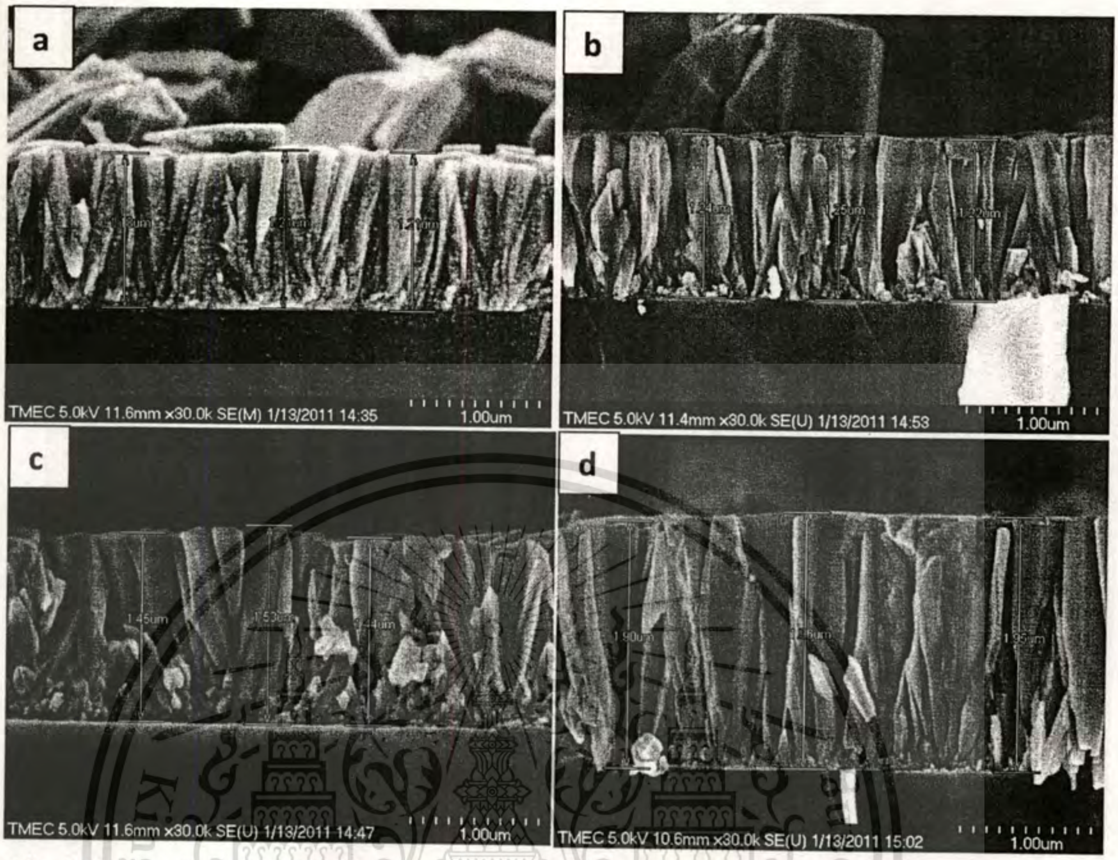


Fig. 4.10 cross-sectional SEM images of ZnO nanorods on glass substrate obtained number of coating 3 times with different growth period: (a) 2 h, (b) 3 h, (c) 4 h and (d) 5 h at 3000x magnification.

A set of samples were grown on glass substrate under the condition of immersed 3 times by changing a period of growth time 1 to 5 h. The 3 times- immersed condition was selected in growth method due to the reason from the effect of number of coating in seeding step above. The SEM images of this set of samples were shown in Fig 4.8, Fig 4.9 and Fig 4.10 . The average length of ZnO nanorods significantly increased with the growth time for 2 h, 3 h, 4 h and 5 h., the average length was about 1.20, 1.24, 1.48 and 1.96 um, respectively. The average diameter of sample decrease with the increasing period of growth, while the average length increase. Therefore, the diameter and the length of ZnO nanorods on glass substrate can be controlled through changing period of growth when number of coating in the seeding step are fixed. Table 4.1 summarizes the geometrical parameters of as-grown ZnO nanorods under different experimental conditions.

Table 4.2 Geometrical parameters of as-grown ZnO rods by fixing number of coating and growth period was varied.

Growth period (h)	Number of coating in dipping step (times)	Average diameter (nm)	Average length (µm)	Ratio of length to diameter
1	3	550	-	-
2	3	400	1.20	3
3	3	330	1.24	3.76
4	3	300	1.48	4.93
5	3	200	1.96	9.8

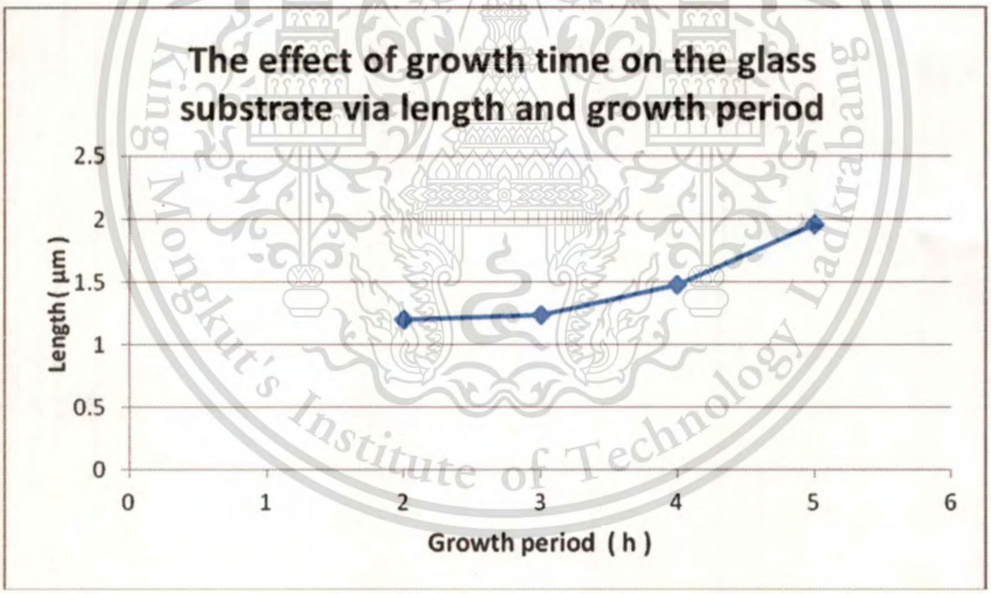


Fig. 4.11 The graph shown the effect of growth time on the glass substrate via length and growth period.

Chapter 5

Conclusion and Recommendations

5.1 Conclusion

In summary, ZnO nanoparticles have been synthesized using a solid state reaction technique at room temperature. SEM observation revealed that the nanoparticles are mainly uniformly with diameters of 30-50 nm and lengths of about 300 nm. The technique is a convenient, inexpensive and effective method of preparation for ZnO nanoparticles. The XRD pattern of ZnO nanoparticles indexes to hexagonal wurtzite structure, no other impurities and the average particle size of ZnO nanoparticles is about 132 nm.

ZnO nanorods arrays were successfully synthesized on the Si substrate by the wet chemical bath deposition (CBD) method. The effect of number of coating in seeding step on the glass substrate and characteristic of ZnO nanorods and The effect of growth time on the glass substrate were investigated systematically. The XRD and SEM indexed to hexagonal wurtzite structure with no impurities. The most of the ZnO rods grows along c-axis on the glass substrates. The ZnO nanorods varies from parallel at lower number of coating to perpendicular to the substrate when the number of coating increases and the vertical rods become a compact array ensemble as growth period increases to 3 h. the ratio of the length to diameter increases with increasing the growth period.

5.2 Recommendations

For Further more study

1. The effect of helping liquid on the morphology of ZnO nanoparticles prepared by using solid state reaction will be investigated.
2. The effect of concentration of seeding solution and immersing times on the growth of nanorods on the glass substrates will be studied.
3. The effect of orientation of the glass substrates on the direction of growthing of nanorods will be studied.

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Appendix

Appendix

Calculation

1. Calculation of Percent Yield

$$\text{Percentage Yield} = \frac{\text{mass of Actual yield}}{\text{mass of Theoretical}} \times 100$$

Theoretical Yield

$$\text{Mass} = \text{No. of moles} \times \text{molar mass}$$

$$= (1\text{ moles}) \times (81.408\text{ g/mole})$$

$$= 81.408\text{ g}$$

$$\text{Percentage Yield} = \frac{48.34}{81.408} \times 100$$

$$= 59.38\ \%$$

2. Calculate concentration of growth solution

$Zn(CH_3COO)_2$ 0.1 mol/L

$$\frac{g}{MW} = \frac{CV}{1000}$$

$$\frac{g}{183} = \frac{0.1(150)}{1000}$$

$$g = 2.745$$

$C_6H_{12}N_4$ 0.1 mol/L

$$\frac{g}{MW} = \frac{CV}{1000}$$

$$\frac{g}{140} = \frac{0.1(150)}{1000}$$

$$g = 2.1$$

3. Calculate concentration of cleaning solution

H_2SO_4 5 mol/L

$$C_1V_1 = C_2V_2$$

$$96\ V_1 = 5(100)$$

$$V_1 = 5.21$$

4. Calculation concentration of seed solution

$Zn(CH_3COO)_2$ 0.1 mol/L

$$\frac{g}{MW} = \frac{CV}{1000}$$

$$\frac{g}{140} = \frac{0.1(100)}{1000}$$

$$g = 1.83$$

5. 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 :

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

K = constant dependent on crystallite shape, K = 0.9 for unknown shape

λ = wavelength of x-rays of Cu k_α, λ = 0.1542 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 of x-rays

Example : calculation of particle size of sample

Where; $\lambda = 1.5406$

$K = 0.9$

Find; $\theta = 18.2^\circ$ (from the figure 4.1)

$= (18.2 \times \pi) \div 180 \quad ; \pi = 22/7$

$= 0.3175$

$\cos\theta = 0.9998$

From figure 4.1 XRD pattern of ZnO nanoparticles via solid state reaction

2θ high(°) = 36.8

2θ low(°) = 36.2

FWHM(°) = 36.8-36.2 = 0.6

FWHM = $(0.6 \times \pi) \div 180 \; ; \pi = 22/7$

$= 0.0105$

$$\text{The particle size} = \frac{(0.9)(1.5406)}{(0.0105)(0.9999)}$$

$= 132.054$