CHAPTER 1

INTRODUCTION

Zinc oxide (ZnO) has extensive commercial use during the past 100 years. It has useful optical, chemical and electrical properties, and is nontoxic, inexpensive and chemically stable [1]. ZnO, a semiconductor with a direct wide band gap of 3.37 eV at room temperature and large exciton binding energy of 60 meV, is one of the most promising materials for the fabrication of optoelectronic devices operating in the blue and ultraviolet (UV) regions and gas sensing applications [2]. It has a wide range of technological applications including transparent conducting electrodes of solar cells, flat panel displays, surface acoustic devices, chemical and biological sensors and UV lasers [3]. Controlled synthesis of semiconductor nanostructures in terms of size and shape has strong motivation to researchers because their properties can be controlled by shape and size. Novel applications can be investigated and are dependent of their structural properties [4].

As the morphology of nano-materials is one of the key factors that affect their properties. ZnO nano-structures with novel morphologies are therefore needed urgently [3]. To date, ZnO with different nanostructures, such as nanotetrapods, nanomultipods, shuttle-like, combs-like, nanosheets, nanotubes, nano-flowers, nanowires, nanorods, nanobelts or nanoribbons, nanoneedles and nanorings [2, 3, 5, 6], have been successfully synthesized. During the past few years, attention has been focused on the research field of one-dimensional (1D) nanostructure materials, such as nanowires and nanorods, because of their fundamental importance and the wide range of potential applications for nanodevices [6].

One-dimensional (1D) ZnO have been prepared by various method such as thermal evaporation, cyclic feeding chemical vapor deposition, chemical vapor deposition (CVD), metal–organic CVD, vapor–liquid–solid (VLS), metal organic chemical vapor deposition (MOCVD), arc discharge and laser ablation [5, 6, 7]. However, these methods involve special equipment, complex process controlling or high temperature as unfavorable for industrialization. As a result; it is conceived that the preparation of 1D ZnO nano/micro structures via wet chemical routes such as template-based method, hydrothermal process, solvothermal process, microwave-heating route, ultrasonic technique [4, 2, 8] can produce such structures, with better crystal quality preferably at lower growth temperature. It works out to be an easier and economical process as well [4].

For the present research, ZnO nanocrystals were synthesized using microwave and ultrasonic radiations. A number of reaction conditions for example solvents, surfactants, precursors, acidity and basicity were used to synthesize ZnO nanocrystal with difference morphologies. The effects of the reaction conditions on the final products were systematically investigated.

1.1 General aspects of zinc oxide and its applications [9]

1.1.1 Physical properties

1.1.1.1 Crystal structure of zinc oxide

Zinc oxide crystallizes in three forms: hexagonal wurtzite, cubic zincblende, and the rarely observed cubic rocksalt). The wurtzite structure is most stable and thus most common at ambient conditions. The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, zinc and oxygen are tetrahedral structure. The rocksalt NaCl-type structure is only observed at relatively high pressures - ~10 GPa.

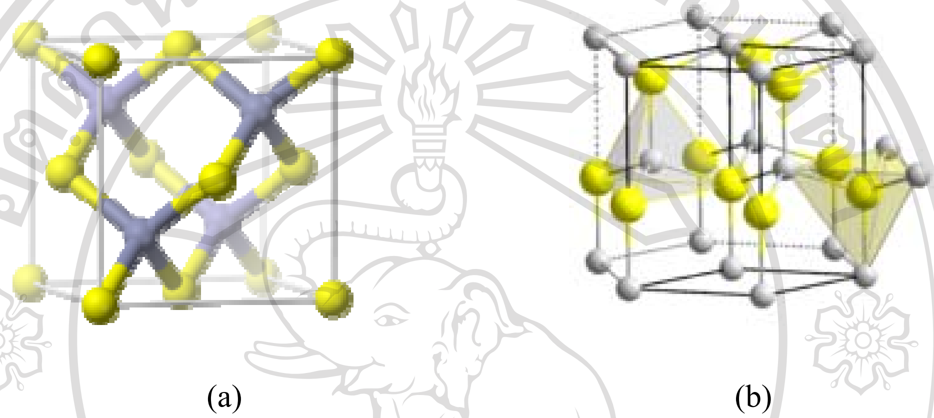

(a) (b)

Figure 1.1 Crystal structures of ZnO (a) zincblend structure (b) wurtzite structure

The sphalerite structure (Figure 1.1 (a)), which is known as the zinc-blend structure, is based on a ccp array of bulky anions (O^{2-}) but cations (Zn^{2+}) occupy one type of tetrahedral hole, one haft the tetrahedral holes present in a close-packed structure. Each ion is surrounded by neighbours and so the structure has (4,4)-coordination. In this notation, the first number in parenthesis is the coordination number of the cation, and the second number is the coordination number of the anion.

The wurtzite structure (Figure 1.1 (b)) differs from sphalerite structure in being derived from an expanded hcp anion array rather than a ccp array, but as in sphalerite the cations occupy one type of tetrahedral hole. This structure has (4,4)-coordination as same as sphalerite structure. The local symmetries of cations and anions are identical towards their nearest neighbours in wurtzite and sphalerite but differ at second - nearest neighbours.

1.1.1.2 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.

1.1.1.3 Electronic properties

ZnO has a relatively large direct band gap of ~3.3 eV at room temperature; therefore, pure ZnO is colorless and transparent. 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 from ~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 do 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 $cm^2/(V \cdot s)$ at ~80 Kelvin. Data on hole mobility are scarce with values in the range 5-30 $cm^2/(V \cdot s)$.

1.1.2 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, good thermal, 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.

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.

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.

Zinc Oxide nanorod sensor

Zinc oxide nanorod sensors are devices detecting changes in electrical current passing through zinc oxide nanowires due to adsorption of gas molecules. Selectivity to hydrogen gas was achieved by sputtering Pd clusters on the nanorod surface. The addition of Pd appears to be effective in the catalytic dissociation of hydrogen molecules into atomic hydrogen, increasing the sensitivity of the sensor device. The sensor detects hydrogen concentrations down to 10 parts per million at room temperature, whereas there is no response to oxygen.

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 Mn-containing precipitates.

Piezoelectricity

The piezoelectricity in textile fibers coated in ZnO have been shown capable of "self-powering nanosystems" with everyday mechanical stress generated by wind or body movements.

In 2008 the *Center for Nanostructure Characterization* at the Georgia Institute of Technology reported producing an electricity generating device (called flexible charge pump generator) delivering alternating current by stretching and releasing zinc oxide wires. This mini-generator creates an oscillating voltage up to 45 millivolts, converting close to seven percent of the applied mechanical energy into electricity. Researchers used wires with lengths of 0.2-0.3 mm and diameters of three to five micrometers, but the device could be scaled down to nanometer size.

Biosensor

ZnO has high biocompatibility and fast electron transfer kinetics. Such features advocate the use of this material as a biomimic membrane to immobilize and modify biomolecules.

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 flavour.

Rubber manufacture

About 50% of ZnO use is in rubber industry. Zinc oxide 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 tyres. 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 tyre rolls. ZnO additive also protect rubber from fungi (see medical applications) and UV light**.**

Concrete industry

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

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 called calamine historically.

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 antibacterial action 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 a component of barrier cream used in nappy rash or diaper rash. It is also a component in tape (called "zinc oxide tape") used by athletes as a bandage to prevent soft tissue damage during workouts.

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.

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. Because it reflects both UVA and UVB rays of ultraviolet light, zinc oxide can be used in ointments, creams, and lotions to protect against sunburn and other damage to the skin caused by ultraviolet light. It is the broadest spectrum UVA and UVB absorber that is approved for use as a sunscreen by the FDA, and is completely photo stable. It is also a main ingredient of mineral makeup.

Coatings

Paints containing zinc oxide powder have long been utilized as anticorrosive coatings for various metals. They are especially effective for galvanized 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 nitrogen 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 the room (heat protection), depending on which side of the window has the coating.

Various plastics, such as poly(ethylene-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.

1.2 Zinc Oxide processing route

1.2.1 Microwave irradiation method

Microwave irradiation is an electromagnetic wave containing normal electric and magnetic field components. The electric field applied a force on charged particles which start to migrate and vibrate. Due to the movement of charged particles, further polarization of polar particles precedes. The forces applied as the electric and magnetic components of microwave are the rapid change in direction, which created friction and collision of the molecules. Claimed effects of microwave irradiation include thermal and non-thermal. Microwave irradiation as a heating method has been used for a number of applications in chemistry. The synthesis is generally rapid, simple and efficient. It has been developed and is widely used in many areas such as the preparation of inorganic complexes and oxide, organic reactions, plasma chemistry, analytical chemistry and catalysts. The applications of microwave irradiation in the preparation of nanocrystalline materials have been reported in recent years. The irradiation has shown very rapid growth in its application to materials science and engineering due to its unique reaction effect, such as rapid volumetric heating and the consequent dramatic increase in the reaction rate. Comparing to the conventional methods, microwave synthesis has the advantages of short reaction time. The products have small particle size, narrow particle size distribution and high purity [10-15].

1.2.2 Ultrasonic irradiation method

Ultrasonic radiation or ultrasound is simply sound pitches above human hearing. It is well known that ultrasound can induce chemical modification on many materials. The chemical application of ultrasound called sonochemistry, has become an exciting new field of research during the past decade. It has proven to be a very useful tool in enhancing the reaction rate in a variety of reacting systems, by successful increasing the conversion, yield percent, change the reaction pathway and initiation the reaction in biological, chemical, and electrochemical systems. The study of sonochemistry concern with understanding the effect of sonic waves and wave properties on chemical systems. Recently, sonochemical method, chemical reaction of the starting materials in the presence of an applied high frequency ultrasonic waves, has been employed for several purposes, in various organic and inorganic subjects and fabrication of nanostructured materials including the synthesis of ZnO. The sonochemical method is a useful technique to obtain novel materials with interesting properties. It is based on acoustic cavitation resulting from the continuous formation, growth and implosive collapse of bubbles in a liquid. The effect of ultrasound in chemical reactions is not well understood. However, it is believed that when sonication acoustic cavitation phenomenon generates cavities in the liquid solution of the reactants. The cavitation process consists of the creation, growth and implosive collapse of bubbles vacuoles in the solution. According to the hot-spot theory, extreme temperatures (>5000 K) and high pressures (>1000 atm) occur within the bubbles during cavitation. Under such extreme conditions the solvent molecules undergo hemolytic bond breakage to generate radicals, H^+ and OH^- when H_2O is sonicated. The librated radicals may lead to various chemical and physical effects in reaction pathways and mechanisms. Moreover, the other benefit in using ultrasonic waves in reactions is believed to be providing high-intensive mixing especially in viscous medias. This would lead to an acceleration effect in chemical dynamics and rates of the reactions [16-20].

1.2.3 Hydrothermal/Solvothermal method

The hydrothermal/solvothermal method is one of the most promising solution techniques for advanced materials processing. The reaction can be carried out in water or in any other solvent. When water is used as a solvent, the process is called "hydrothermal process" and when non-aqueous / organic solvents such as methanol, ethanol, polyol, etc. are used, the process is termed "solvothermal process". In the usual hydrothermal process, the starting chemicals are dissolved in water. This solution is placed in a reactor (Figure 1.2) and the chemical reaction is carried out in closed systems under autogenous pressure and elevated temperature, which allow for greater solubility of solids for the reaction process, and the desired compounds can be synthesized at lower temperatures compared to the solid-state reaction method. This method has several advantages over the other conventional processes like energy saving, simplicity, cost effectiveness, better nucleation control, pollution free (since the reaction is carried out in a closed system), higher dispersion, higher rate of reaction, better shape control, and lower temperature of operation in the presence of an appropriate solvent, etc. The hydrothermal technique has a lot of other advantages like it accelerates interactions between solid and fluid species, phase pure and homogeneous materials can be achieved, reaction kinetics can be enhanced, the hydrothermal fluids offer higher diffusivity, lower viscosity, facilitate mass transport and higher dissolving power. Most important is that the chemical environment can be suitably tailored [21].

Figure 1.2 General purpose autoclave popularly used for hydrothermal synthesis

The hydrothermal processing of materials is a part of solution processing and it can be described as super heated aqueous solution processing. Figure 1.3 shows the pressure temperature map of various materials processing techniques [22]. When the production processing goes out of ambient temperature to higher or lower temperature and pressure condition to higher or lower pressure directions, particularly to vacuum, environmental loads would increase. In this regard, we cannot depend only on the high-technology industry for materials processing. On the other hand, solution processing is located in the p–T range characteristics of ambient conditions where all lives are living on the earth. Thus, solution processing should be the most environmentally friendly and should be used more as a low-energy process for producing even various artificial materials [23]. According to this, the hydrothermal processing of advanced materials can be considered as environmentally benign.

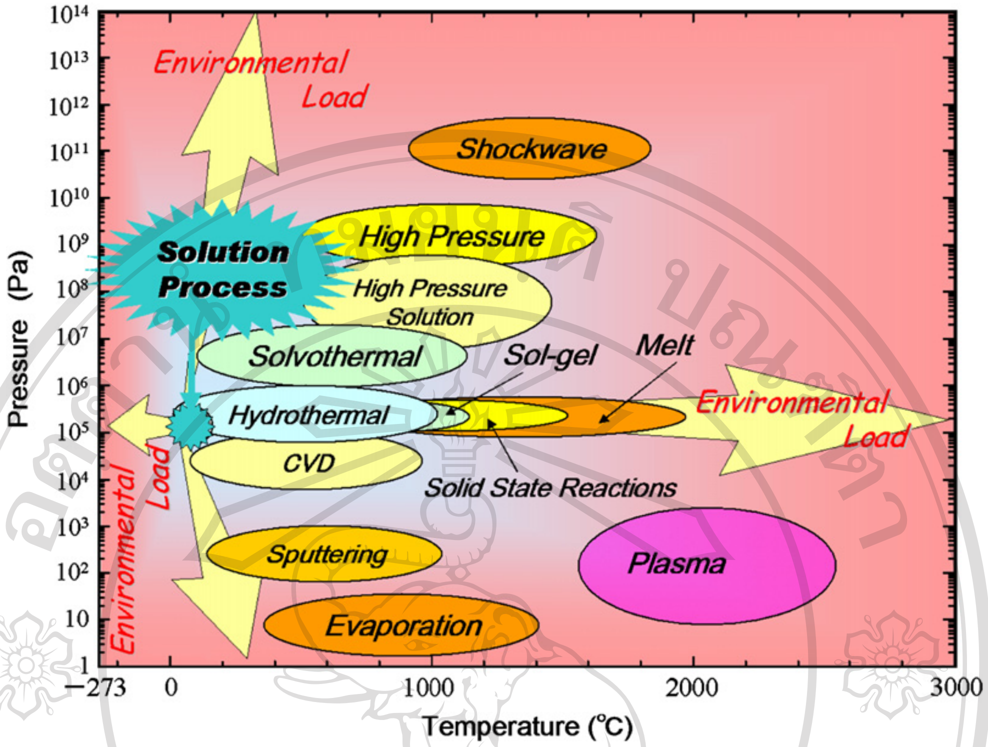


Figure 1.3 Pressure temperature map of materials processing techniques [22]

1.2.4 Template-based method

Hard template

The template approach to preparing free-standing, non-oriented and oriented nanowires and nanorods has been investigated extensively. The most commonly used and commercially available templates are anodized alumina membrane (AAM) [24] and radiation track-etched polycarbonate (PC) membranes [25]. Other membranes have also been used, such as nanochannel array on glass [26], radiation tracketched mica [27], mesoporous materials [28], porous silicon obtained via electrochemical etching of silicon wafer [29], zeolites [30] and carbon nanotubes [31, 32]. Biotemplates have also been explored for the growth of nanowires [33] and nanotubes [34], such as Cu [35], Ni [35], Co [35], and Au [36] nanowires. Commonly used alumina membranes with uniform and parallel pores are produced by the anodic oxidation of aluminium sheet in solutions of sulfuric, oxalic, or phosphoric acids [24, 37]. The pores can be arranged in a regular hexagonal array and densities as high as 1011 pores/cm^2 can be achieved [38]. Pore size ranging from10nmto 100 μm can be achieved [38, 39]. PC membranes are made by bombarding a nonporous polycarbonate sheet, typically 6 to 20μm in thickness, with nuclear fission fragments to create damage tracks, and then chemically etching these tracks into pores [25]. In these radiation track-etched membranes, the pores are of uniform size (as small as 10 nm), but they are randomly distributed. Pore densities can be as high as 109 pores/ cm^2. In addition to the desired pore or channel size, morphology, size distribution and density of pores, template materials must meet certain requirements. First, the template materials must be compatible with the processing conditions. For example, an electrical insulator is required when a template is used in electrochemical deposition. Except in the case of template-directed synthesis, the template materials should be chemically and thermally inert during synthesis and the following processing steps. Secondly, the material or solution being deposited must wet the internal pore walls. Thirdly, for the synthesis of nanorods or nanowires, the deposition should start from the bottom or from one end of the template channel and proceed from one side to the other. However, for the growth of nanotubules, deposition should start from the pore wall and proceed inwardly. Inward growth may result in pore blockage, so this should be avoided during the growth of “solid” nanorods or nanowires. Kinetically, the correct amount of surface relaxation permits maximal packing density, so a diffusion-limited process is preferred. Other considerations include the ease of release of the nanowires or nanorods from the templates and the ease of handling during the experiments. AAM and PC membranes are most commonly used for the synthesis of nanorod or nanowire arrays. Both templates are very convenient for the growth of nanorods by various growth mechanisms, but each type of template also has its disadvantages. The advantages of using PC as the template are its easy handling and easy removal by means of pyrolysis at elevated temperatures, but the flexibility of PC is more prone to distortion during the heating process, and removal of the template occurs before complete densification of the nanorods. These factors result in broken and deformed nanorods. The advantage of using AAM as the template is its rigidity and resistance to high temperatures, which allows the nanorods to density completely before removal. This results in fairly free-standing and unidirectionally-aligned nanorod arrays with a larger surface area than for PC. The problem with AAM is the complete removal of the template after nanorod growth, which is yet to be achieved when using wet chemical etching.

Soft template

Nanorods or nanowires can also be synthesized using consumable templates, although the resultant nanowires and nanorods are generally not ordered to form aligned arrays. Nanowires of compounds can be prepared using a template-directed reaction. First nanowires or nanorods of one constituent element are prepared, and then these are reacted with chemicals containing the other element desired in order to form the final product. *Gates* et al. [40] converted single crystalline trigonal selenium nanowires into single crystalline nanowires of Ag_2Se by reacting Se nanowires with aqueous $AgNO_3$ solutions at room temperature. Nanorods can also be synthesized by reacting volatile metal halides or oxide species with carbon nanotubes to form solid carbide nanorods with diameters of between 2 and 30 nm and lengths of up to 20μm [41]. ZnO nanowires were prepared by oxidizing metallic zinc nanowires [42]. Hollow nanotubules of MoS_2 ≈ 30μm long and 50 nm in external diameter with wall thicknesses of 10 nm were prepared by filling a solution mixture of the molecular precursors, $(NH_4)_2MoS_4$ and $(NH_4)_2Mo_3S_{13}$, into the pores of alumina membrane templates. Then the template filled with the molecular precursors was heated to an elevated temperature and the molecular precursors were thermally decomposed into MoS_2 [43]. Certain polymers and proteins were also used to direct the growth of nanowires of metals or semiconductors. For example, *Braun* et al. [44] reported a two-step procedure using DNA as a template for the vectorial growth of a silver nanorods 12 μm in length and 100 nm in diameter. CdS nanowires were prepared by polymer-controlled growth [45]. For the synthesis of CdS nanowires, cadmium ions were well distributed in a polyacrylamide matrix. The Cd^{2+}-containing polymer was treated with thiourea (NH_2CSNH_2) solvothermally in ethylenediamine at 170 °C, resulting in degradation of polyacrylamide. Single crystal CdS nanowires 40 nm in diameter and up to 100μm in length were obtained with preferential [001] orientations.

1.3 Surfactant [46]

The term surfactant is a shortened form of "**surf**ace **act**ive **a**ge**nt**". Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic tail portion groups usually a long-chain hydrocarbon and hydrophilic polar head groups, which is often ionic (see Figure 1.4). Therefore, they are soluble in both organic solvents and water. Surfactants have the properties to reduce the surface tension of water by adsorbing at the liquid-gas interface. They are able to reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface as well.

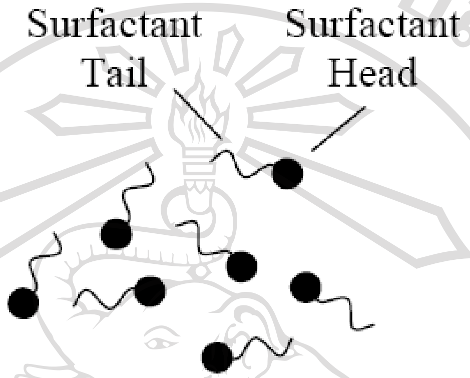


Figure 1.4 Schematic illustration of the micelle monomers

A surfactant can be classified by the presence of formally charged groups in its head. A nonionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic. Some commonly encountered surfactants of each type include:

1) Ionic surfactant

1.1) Anionic (based on sulfate, sulfonate or carboxylate anions)

- Sodium dodecyl sulfate (SDS), ammonium lauryl sulfate, and other alkyl sulfate salts
- Sodium laureth sulfate, also known as sodium lauryl ether sulfate (SLES)

- Alkyl benzene sulfonate
- Soaps, or fatty acid salts

1.2) Cationic (based on quaternary ammonium cations)

- Cetyl trimethylammonium bromide (CTAB) a.k.a. hexadecyl trimethyl ammonium bromide, and other alkyltrimethylammonium salts
- Cetylpyridinium chloride (CPC)
- Polyethoxylated tallow amine (POEA)
- Benzalkonium chloride (BAC)
- Benzethonium chloride (BZT)

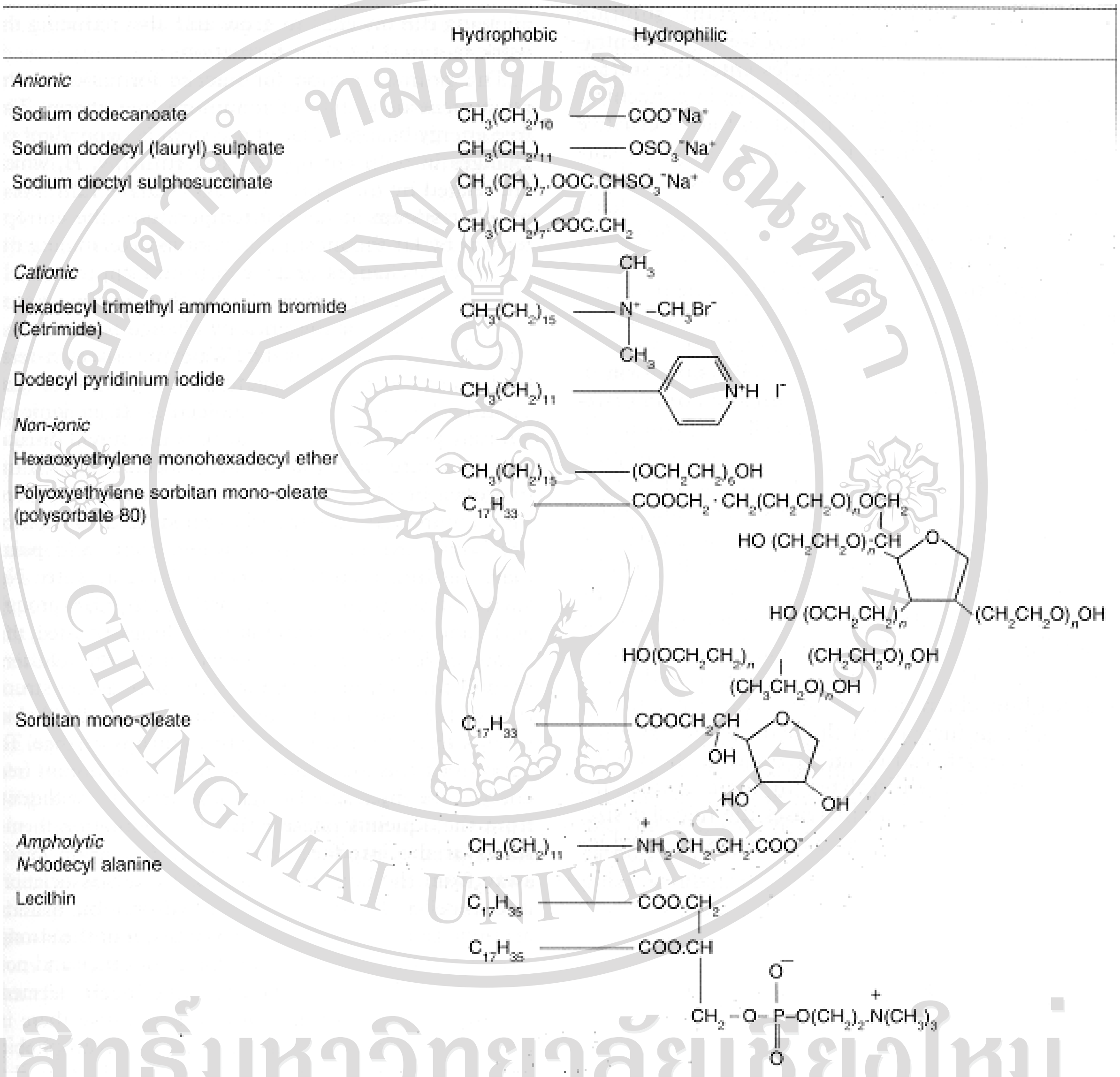
1.3) Zwitterionic (amphoteric) surfactant

- Dodecyl betaine
- Dodecyl dimethylamine oxide
- Cocamidopropyl betaine
- Coco ampho glycinate

1.4) Nonionic surfactant

- Alkyl poly(ethylene oxide)
- Alkyl polyglucosides, including: Octyl glucoside, Fatty alcohols, Cetyl alcohol and Oleyl alcohol

Table 1.1 Surfactant classification [47]



	Hydrophobic	Hydrophilic
Anionic		
Sodium dodecanoate	$CH_3(CH_2)_{10}$	COO^-Na^+
Sodium dodecyl (lauryl) sulphate	$CH_3(CH_2)_{11}$	$OSO_3^-Na^+$
Sodium dioctyl sulphosuccinate	$CH_3(CH_2)_7.OOC.CHSO_3^-Na^+$ $CH_3(CH_2)_7.OOC.CH_2$	
Cationic		
Hexadecyl trimethyl ammonium bromide (Cetrimide)	$CH_3(CH_2)_{15}$	$N^+(CH_3)_2-CH_3Br^-$
Dodecyl pyridinium iodide	$CH_3(CH_2)_{11}$	N^+H I^-
Non-ionic		
Hexaoxyethylene monohexadecyl ether	$CH_3(CH_2)_{15}$	$(OCH_2CH_2)_6OH$
Polyoxyethylene sorbitan mono-oleate (polysorbate 80)	$C_{17}H_{33}$	$COOCH_2 \cdot CH_2(CH_2CH_2O)_nOCH_2$ $HO(CH_2CH_2O)_nCH$ $HO(OCH_2CH_2)_n$ $(CH_2CH_2O)_nOH$ $HO(OCH_2CH_2)_n$ $(CH_2CH_2O)_nOH$ $(CH_3CH_2O)_nOH$
Sorbitan mono-oleate	$C_{17}H_{33}$	$COOCH_2CH$ OH HO OH
Ampholytic		
N-dodecyl alanine	$CH_3(CH_2)_{11}$	$\overset{+}{N}H_2.CH_2.CH_2.COO^-$
Lecithin	$C_{17}H_{35}$ $C_{17}H_{35}$	$COO.CH_2$ $COO.CH$ $CH_2-O-P(=O)(O^-)-O(CH_2)_2.\overset{+}{N}(CH_3)_3$

Many surfactants can also assemble in the bulk solution into aggregates. Some of these aggregates are known as micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration (CMC). When micelles form in water, their tails form a core that is like an oil droplet. Their (ionic/ polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle of which the heads are in the core and the tails maintain favorable contact with oil. Micelles are labile entities formed by the noncovalent aggregation of individual surfactant monomers and can be spherical, cylindrical, or planar (discs or bilayers). Micelle shape and size can be controlled by changing the surfactant chemical structure as well as by varying solution conditions, including temperature, overall surfactant concentration, surfactant composition (in the case of mixed surfactant systems), ionic strength, and pH. In particular, depending on the surfactant type and on the solution conditions, spherical micelles can grow one-dimensionally into cylindrical micelles or two dimensionally into bilayers or discoidal micelles.

Different concentrations of surfactants can form micelles with different morphologies, which result in the modification of crystal growth. When the concentration of surfactant is larger than that of the CMC, micelles will be formed in the aqueous solutions. At a lower concentration of surfactant, spherical micelles are formed. However, at higher concentration of surfactant, sandwich micelles are formed [48]. Micelle growth is controlled primarily by the surfactant heads, since both one-dimensional and two-dimensional growth require bringing the surfactant heads closer to each other in order to reduce the available area per surfactant molecule at the micelle surface, and hence the curvature of the micelle surface (see Figure 1.5) [49].

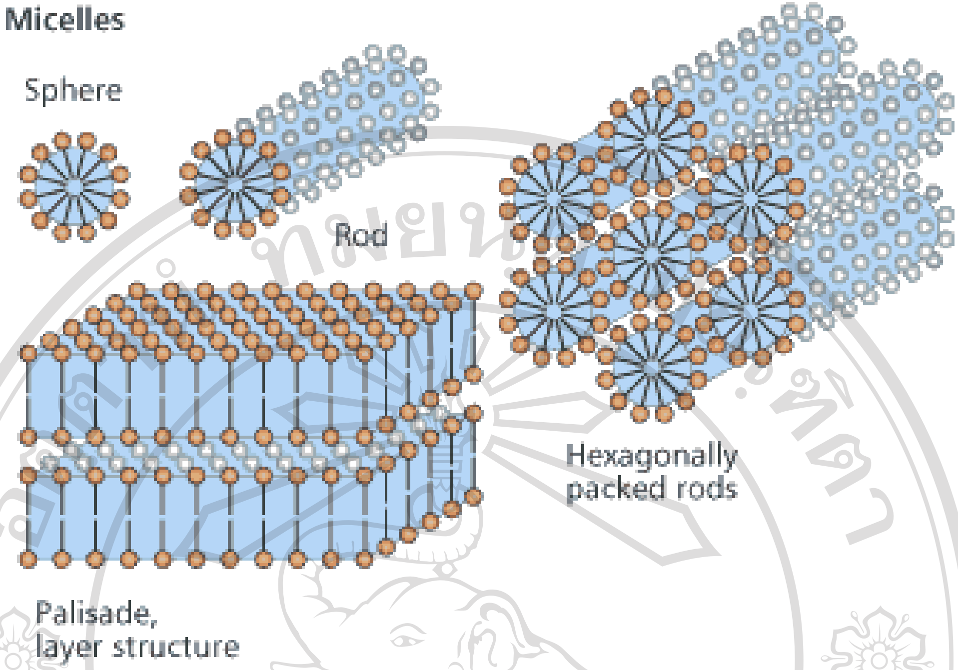


Figure 1.5 Schematic illustration of the commonly observed geometrical shapes of surfactant micelles in aqueous solution

When micelles form in aqueous solution above the CMC, the surfactant monomers aggregate (self-assemble) with the tails inside the micelle shielded from water and the heads at the micelle surface in contact with water [49].

1.4 Literature Review

Ghoshal *et al.* [1] have synthesized perfectly single crystal hexagonal cones and columns of ZnO via solvothermal method. Zinc nitrate hexahydrate [$Zn(NO_3)_2$,6H2O] and soldium hydroxide were selected as starting materials with water, ethanol or ethanol-water mixture as solvents. The pH was adjusted using NaOH or HCl. It was found that pH and solvent were the major variables to control the size and morphology of ZnO crystals. In addition, the highest emission intensity of PL spectra of the ZnO nanocrystals was obtained when the sample was prepared with the highest pH value in water.

Wang *et al.* [2] have synthesized multipod, flower-like and shuttle-like ZnO nano-/microstructures via microwave-heating in new solvent system (Room-Temperature Ionic Liquid, RTIL). They found that both the RTIL and microwave heating have important role on the final morphologies of the products. They suggested that it is environmentally benign green method, which is an effective route to synthesize the micro- and nano- materials. It has a number of advantages for example fast reaction time, seedless and template-free routes.

Wahab *et al.* [5] have prepared perfect ZnO nano-flowers by solution process using zinc acetate dihydrate and NaOH as a source materials at 90 °C for 30 min. They found that this method were simple, cost effective, and convenient route to obtain larger quantity of nanostructured zinc oxide. Due to the results of UV–vis, Raman scattering and room-temperature photoluminescence (PL), they found that the flower-shaped ZnO nanostructures have good optical properties with very less structural defects.

Wu *et al.* [50] have prepared ZnO with flower-like structure using thermal treatment of zinc acetate dihydrate precursor in aqueous solvent, and using ammonia as the structure directing agent. They have studied the growth mechanism of ZnO nanoflower structure by using various techniques such as XRD, TEM and TGA. The optical properties of the obtained products were studied by using PL spectrometer. They found that the absorbed acetate ions have less influence on photoluminescence of obtained products using this synthesis process.

Yadav *et al.* [51] have synthesized ZnO nanoparticles by ultrasonic irradiation of an aqueous-alcoholic/aqueous-alcoholic-ethylenediamine (EDA) solutions of zinc nitrate and sodium hydroxide. The effect of chelating agent on the growth of ZnO nanoparticles was studied. They found that the crystallinity of ZnO nanoparticles synthesized in ethylenediamine is better than that of ZnO synthesized without EDA. In addition, the ultrasonic irradiation time and the solvents influenced to either the growth mechanism or optical properties of ZnO nanoparticles.

Xiao *et al.* [52] have successfully synthesized ZnO nanosheets by a sonochemical method. The starting zinc compounds were used in the process. They were zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), zinc acetate dihydrate ($Zn(C_2H_4O_2)_2.2H_2O$), zinc sulfate heptahydrate ($Zn(SO_4)_2.7H_2O$), zinc chloride ($ZnCl_2$), together with sodium hydroxide (NaOH). For the present research, ZnO powder exhibited rod-like, sheet-like, sheet-like and ellipsoidal shapes using $Zn(NO_3)$, $ZnCl_2$, $ZnSO_4$ and $Zn(C_2H_4O_2)_2$ as zinc resources, respectively.

Hou *et al.* [53] have synthesized ZnO nanostructures. Zinc acetate ($Zn(CH_3COO)_2.2H_2O$) and sodium hydroxide (NaOH) were used as starting materials in a solution of PEG (200, 400, 600, and 1000) as the template at room temperature. The XRD result showed that the obtained products were hexagonal wurtzite structure and high crystallinity. They also found that the intensity of the (002) diffraction peak is much stronger than that of bulk ZnO. It can ascribe to the preferential growth along [0001] direction of wurtzite structure. In addition, they have investigated the effect of both amount and molecular weight of PEG on morphologies and sizes of the products. They found that rod-like and needle-like structure were obtained when 5 ml PEG400 was used. But for 15 or 20 ml PEG, flower-like ZnO nanostructure was produced.

When PEG400 was substituted with PEG200 or PEG1000, the products were mainly composed of nanoneedles and flower-like nanostructure, respectively. This method is simple and mild synthetic, but it still has a weakness of using the long incubation time.

Dileo *et al.* [54] have investigated the effect of three multidentate ligands, diethylenetriaminepentaacetate (DTPA), ethylenediaminetetraacetate (EDTA) and tetraethylenepentamine (tetren) on the physical properties of zinc oxide (ZnO). Aqueous solutions containing zinc-ligand complexes and KOH were hydrothermally reacted, and the products were examined. They found that the crystals with needles and plates were obtained when EDTA and DTPA were used as complexing agent, respectively. At high pH, the needle structure was observed for all samples. ZnO with largest crystals was produced only in EDTA, comparing to that produced in DTPA. They also found the empirical correlation between crystal size, ligands polarity and relative complex strain of each ligands.

Zhang *et al.* [55] The different morphologies of nanorods have been obtained via a simple 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. They also found that single ZnO nanorod is single crystal and preferentially grows up along the [001] direction. The morphologies of ZnO whisker are influenced by reaction temperature, pH in system and evaporation of ammonia. Nanorods with six arms, single nanorods and nanorods with eight arms can be obtained when temperature is at 60 °C, 70 °C and 80 °C. The length of bundled nanorods can be controlled by pH in system and time of ammonia retained in solution. Nanorods as synthesized exhibit blue emission at 466 nm and green–yellow at 542 nm for a large quantity of oxygen vacancies, zinc vacancies and zinc interstitial defects.

Xingfu *et al.* [56] Growth and assembly of ZnO nanosheets into hollow microsphere are performed using PEG 200 as directing agent. FESEM images show that the average width of these assemblied ZnO nanosheets is around 250 nm, the length is about 500–800 nm and the thickness is about 25 nm, the diameter of ZnO-assembled microsphere is about 2–4 µm. Study shows that microsphere of ZnO nanosheets have a centre cavity, these microsphere assemblied ZnO nanosheets have a wide visible yellow emission at 567 cm^{-1}, confocal laser microscopy of an individual ZnO nanosheets assemblied microsphere also show the intense yellow light emission. The oriented attachment of 5 nm ZnO nanoparticle building blocks eventually form the ZnO nanosheets.

Zhao *et al.* [57] ZnO nanorods on ZnO-coated seed surfaces were fabricated by a solution chemical method using supersaturated $Zn(NO_3)_2$/NaOH solution. The seed surfaces were coated on glass substrates by sol–gel processing and PEG addition. The average diameter and length of the ZnO nanorods increase to different degree with increasing precursor concentration. The dependence of rod growth on temperature shows that the maximum rod growth rate at any given concentration of Zn^{2+} occurs at a specific temperature, and the optimal temperature increases with Zn^{2+} ion concentration. Densely thick nanorods oriented perpendicularly to the substrate can be obtained by controlling the seed surface with PEG assistance.

Wang *et al.* [58] Synthesis of flower-shaped ZnO nanostructures composed of ZnO nanosticks was achieved by the solution process using zinc acetate dihydrate, sodium hydroxide and polyethylene glycol-20000 (PEG-20000) at 180 °C for 4 h. The diameter of individual nanosticks was about 100 nm. Detailed structure characterizations demonstrate that the synthesized products are wurtzite hexagonal phase, grown along the [001] direction. The infrared (IR) spectrum shows the standard peak of zinc oxide at 571 cm^{-1}. Raman scattering exhibits a sharp and strong E2 mode at 441 cm^{-1} which further confirms the good crystal and wurtzite hexagonal phase of the grown nanostructures. We believe that the present method is simple, low-cost, and is expected to allow the large-scale production of other oxides with controllable morphologies.

Mazloumi *et al.* [59] have synthesized cauliflower-like ZnO nanostructures with average crystallite size of about 55 nm which have surface one dimensional (1D) nanoarrays with 10 nm diameter through a simple sonochemical route. The various techniques such as X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and room temperature photoluminescence (PL) were used to investigate the morphological and structural properties of the obtained nanostructures. We found that ultrasonic irradiation resulted in the formation of prickly nanoarrays on the surface of the ZnO particles. Photoluminescence characterization exhibited a UV irradiation at around 385 nm and an intense green peak in the visible band. In addition, the post-treatment of the particles for about 2 h increased the density of surface defects resulted in an increase in the green emission intensity.

Liu *et al.* [60] have successfully synthesized single-crystal ZnO nanotubes and tubular whiskers by employing $Zn(NO_3)_2.6H_2O$, $NH_3.H_2O$ as the starting materials in the solution containing polyethylene glycol (PEG, MW = 2000) at ambient pressure and low temperature (70 ^oC). Characterizations were carried out by X-ray powder diffraction (XRD), X-ray energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), transmission electron microscopy (TEM, HRTEM) and photoluminescence (PL) measurement. The results show that the as-prepared ZnO were tubular textures, which had average cross-sectional dimensions of 200–300 nm, lengths of 2–3.5 mm, and wall thickness of 80 nm. The products exhibited strong UV excitonic emission at 385 nm with a negligible defect emission, which indicating of high crystal quality the products. In addition, these novel tubular structures may well be used in nano-optoelectronics (UV light source), catalysis and waveguides, etc.

Kandjani *et al.* [61] have studied the effect of sonication output power and temperature on the properties of ZnO products synthesized using ultrasonic radiation method. The morphologies and structure of the products were characterized by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). The morphology of the products was determined to be a mixture of nanorods as well as nanoparticles depending to sonication output power and temperature. Increasing the reaction temperature and sonication output power lead to ZnO nanoparticles with spherical morphology as the principle morphology of the particles. Meanwhile, higher reaction temperature and higher sonication output power was detected to be effective in particle and aggregate average size reduction and narrowness of size distribution.

Phuruangrat *et al.* [62] have synthesized spear-shaped nanorods in flower-like clusters from a 15:1 molar ratio of $Zn(CH_3COO)_2.2H_2O$ to KOH using 180W microwave radiation for 20 min. The product phase detected using X-ray diffraction (XRD) and selected area electron diffraction (SAED) showed pure ZnO hexagonal structure. By using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), the morphology was flower-like structures composed of hexagonal ZnO spear-shaped nanorods with diameters and lengths of 50 nm and 2- 4 μm, respectively. High resolution TEM (HRTEM) showed that growth of the spear-shaped nanorods was in the [001] direction, which was normal to the (002) planes composing a lattice fringe of the nanorods. Raman spectrometry revealed the presence of four vibration peaks at 337.85, 381.13, 437.54 and 583.30 cm^{-1}.

Phuruangrat *et al.* [63] have synthesized nano-structured ZnO with different morphologies using a sonochemical method. XRD, SAED and Raman analyses revealed the presence of wurtzite ZnO, with the strongest vibration intensity at 435 cm^{-1}. The formation of 72 ± 17 nm nano-particles, and nano-plates and spear-shaped particles in flower-like clusters, characterized using SEM and TEM, was strongly influenced by basicity conditions. A spear, characterized using HRTEM, grew in the [001] direction normal to its (002) plane.

Hu *et al.* [64] have developed two novel routes to the fabrication of linked ZnO rods with various morphologies such as bipods, tripods, tetrapods and multipods by ultrasonic irradiation and microwave heating. Both methods do not need any templates, seeds or surfactants, and are suitable for large-scale production in terms of speediness, low cost, simplicity and energy-efficiency. The yields of ZnO powders were higher than 90%. These ZnO structures may find new applications in electronic and optoelectronic devices. Furthermore, these methods may be extended to synthesize 1D structures of other metal oxides.