

CHAPTER 1

INTRODUCTION

Inorganic nano- and microcrystals with unusual and novel forms have attracted much attention during the past years due to their importance in fundamental research and potential application in fabricating electronic, optoelectronic, and sensing devices. It is well known that the size and shape of inorganic materials have much influence on their widely varying physical properties [1]. The control of the morphology of inorganic materials with nano and microscales has rapidly developed into a promising field in materials chemistry [2] because the physical and chemical properties of nano- and microcrystals depend not only on their composition but also on their structure, phase, shape, size and size distribution [3].

During the last decade, nanostructured materials are implicated in exponential increase in several domains such as chemistry, electronics, high density magnetic recording media, sensors and biotechnology. This is, in part, due to their novel properties, that differ from both the isolated atoms and the bulk phase.

Nanocrystalline materials with new functionalities show great promise for use in industrial applications. For example, one – dimensional nanostructures (nanotubes, nanowires, nanorods, nanobelts, etc) represent an interesting and important class of materials with potential applications such as electronic devices as well as biomedical materials [4,5].

Recently, I-V-VI ternary chalcogenide semiconducting materials have gained much attention in the synthesis and characterization because of their usage in linear, nonlinear, optoelectronic, thermoelectric devices and optical recording media [6-8].

Among them, AgBiS₂ has promising applications as a novel semiconductor because of its unusual electronic and magnetic properties. AgBiS₂ exists as two phases, namely, low temperature phase β -AgBiS₂ with hexagonal structure and high temperature phase α -AgBiS₂ with cubic structure. Since shape, size, and dimensionality of the semiconductors are important parameters to control their properties. Developing a facile method to synthesize ternary chalcogenide materials with various morphologies is of interest and importance for their further applications. Traditionally, AgBiS₂ can be prepared through solid state reactions, solution techniques and flux techniques [9-11]. However, it still has some weakness that is unable to obtain the desired morphologies.

Nowadays, solvothermal method, the process taking in a liquid medium above room temperature and at a pressure greater than 1 atm in a closed system, is becoming one of the most important tools for advanced material processing, particularly owing to its advantages in the processing of nanostructural materials for a wide variety of technological applications such as electronics, optoelectronics, catalysis, magnetic data storages, biomedical, biophotonics, etc [12]. Solvothermal reaction has a lot of advantage and can be used to give high product purity and homogeneity, crystal symmetry, metastable compounds with unique properties, narrow particle size distributions and lower sintering temperature. A wide range of chemical compositions, single-step process, dense sintered powder, nano-particles with a narrow size distribution using simple equipment, lower energy requirements, short reaction times, lowest residence time, as well as for the growth of crystals with polymorphic modifications, the growth of crystals with low and ultra low solubility, and host of other applications. An autoclave for a solvothermal route is a thick-walled

stainless steel reactor is able to withstand high pressure at elevated temperature. Powder dissolving in the bottom part of the reactor was heated and crystalline forms in the upper part. Crystals can gradually be lower the temperature of the entire reactor vessel. There are several other reactors popularly used for material processing under hydrothermal conditions with special provision for microwave, electrochemical or sonochemical energies, flow reactors and so on, which greatly assist in kinetics for solvothermal reactions [13,14]. To the best of our knowledge, there are not many reports on the synthesis of AgBiS₂ with different morphologies. Among them are dendrites by microwave synthesis [15], nanorods and coral-shaped crystals by a polyol route [16,17], and flowers and hexapods by cyclic microwave-assisted synthesis [18]. For the present research, production of purified AgBiS₂ nanostructured flowers using the solvothermal process was studied and reported.

For the research, AgBiS₂ with different morphologies will be synthesized using conventional solvothermal method. A various experimental conditions will be used to synthesize AgBiS₂; for example, reaction temperature, prolonged time, solvents and surfactants. In addition, the possible formation mechanism of AgBiS₂ will be investigated.

Thus, a number of attempts have been made to develop the preparation of silver bismuth sulfide by applying soft solution method. This method has been widely used as one of the most effective approaches owing to availability of flexible adjustment of the experimental parameters of the synthetic system. The concepts of this method are to realize the low energy and low waste process for inorganic materials. Soft solution process means to fabricate shaped, sized and controlled advanced materials from aqueous solutions without excess heat, energy consumption,

expensive equipment and precursor, that is, one of the most economically and environmentally friendly preparation techniques for advanced materials. With this method, fabrication of various materials with the minimum amount of raw material resources by a single synthetic step at low energy can be realized [18].

1.1 Silver Bismuth Sulfide (AgBiS_2)

1.1.1 Physical properties

1.1.1.1 Crystal structure of AgBiS_2

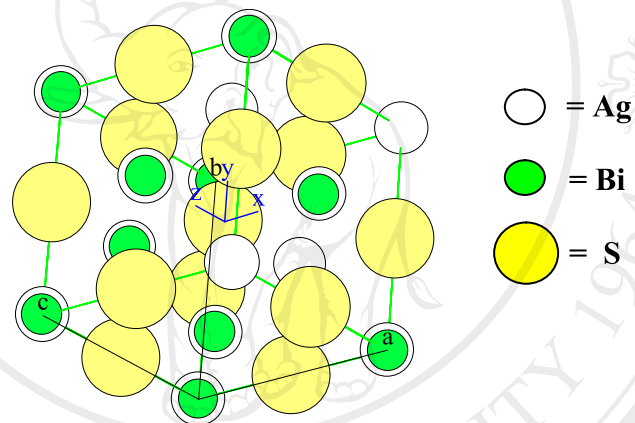


Figure 1.1 Crystal structures of AgBiS_2

1.1.2 Chemical properties

Silver Bismuth Sulfide is a Reddish-black. Empirical formula and Chemical formula is AgBiS_2 . Its chemical makeup is: Ag 28.31% Bi 54.85% S 16.83%.

1.1.3 Applications

AgBiS_2 compounds are important inorganic materials that have application potential in various fields. AgBiS_2 , one of the semiconducting ternary sulfides, has been very attractive, due to its linear and non-linear properties [15,16]. It has high potential to use as optoelectronic and thermoelectric devices, including optical recording media [15,16].

1.1.4 Literature Review

Shen *et al.* [17] have successfully prepared AgBiS₂ nanorods using refluxed method at 150 °C in polyol media. The XRD and ED showed pure cubic structure with lattice constant $a = 5.651 \text{ \AA}$. TEM images showed that the products consisted of uniform rod-like crystals with the length of 10 μm and 40 nm in diameters. In addition, they mentioned that this method was a more effective, convenient, less energy demand and time saving techniques. So, it was expected to prepare the other ternary chalcogenide materials.

Chen *et al.* [15] have synthesized AgBiS₂ dendrites in aqueous solution under microwave radiation for 30 min. The XRD pattern showed pure cubic phase which was consistent with SAED result. The morphologies of the products characterized using TEM showed dendritic structure. In addition, the formation mechanism was investigated.

Xie *et al.* [19] have prepared α -AgBiS₂ nanowhiskers by a solvothermal method at 160 °C. The results showed that the product was α -AgBiS₂ which was well crystallized as uniform nanowhiskers. The chain type structure of Bi-S compound under the circumstance of ethylenediamine was found crucial in the formation of α -AgBiS₂ nanowhiskers, explained by the possible mechanism.

Pejova *et al.* [20] have developed a novel, convenient sonochemical approach for 3D arrays of close packed AgBiS₂ quantum dots (QDs) in thin film form. The proposed sonochemical deposition technique, combined with post deposition treatment, opens a wide range of possibilities for controllable synthesis of low dimensional nanostructured films of the investigated semiconductor and to design QD

size depending on the application point of view. The average QD radius of sonochemically synthesized colloidal crystals is 4.2 nm, and is two times smaller than the value for a QD solid obtained without ultrasonic irradiation of the reaction system. The optical band gap energy of the AgBiS₂ QDs (1.40 eV) is strongly blue shifted in comparison to macrocrystalline value (0.90 eV) and to the value of 1.10 eV for the nanostructured films synthesized by a conventional chemical route from the same reactor. Upon post deposition annealing treatment, the band gap energy of the films could be red-shifted to 1.00 eV. Thermal band gap energy of the films calculated on the basis of temperature dependence of the conductivity is 1.10 eV, whereas at conditions close to room temperature, the variable range hopping conduction mechanism (along with the thermionic emission) is predominant in the overall intercrystalline charge carrier transport through the 3D QD assemblies.

Photoconductivity of the nanostructured AgBiS₂ films is modulated by the intercrystalline barrier height decrease upon illumination.

Shen *et al.* [16] have synthesized coral-shaped nanocrystallites of AgBiS₂ at 195°C from single-source precursors by a rapid polyol process. X-ray powder diffraction (XRD), X-ray photoelectron spectra (XPS) and transmission electron microscope (TEM) were used to characterize the products, which reveal that the products are pure phase with coral-shaped nanostructures. They also discussed the formation mechanism of coral-shaped nanocrystallites.

Manolikas and Spyridelis [21] have studied phase transformations of the ternary compounds AgBiSe₂ and AgBiS₂ by means of electron microscopy and electron diffraction methods. In accordance with the results of other investigators, two phase transitions are observed upon heating above room temperature. The transition

from the high to the intermediate temperature phase is of the order to disorder type and is accompanied by the formation of a domain structure exhibiting orientation variants. A particular configuration of striations in each domain was attributed to ordering of APBs formed between orientation variants.

1.2 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 [23-28].

1.3 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 [29-33].

1.4 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 [34].



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 [35]. 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 [20]. According to this, the hydrothermal processing of advanced materials can be considered as environmentally benign.

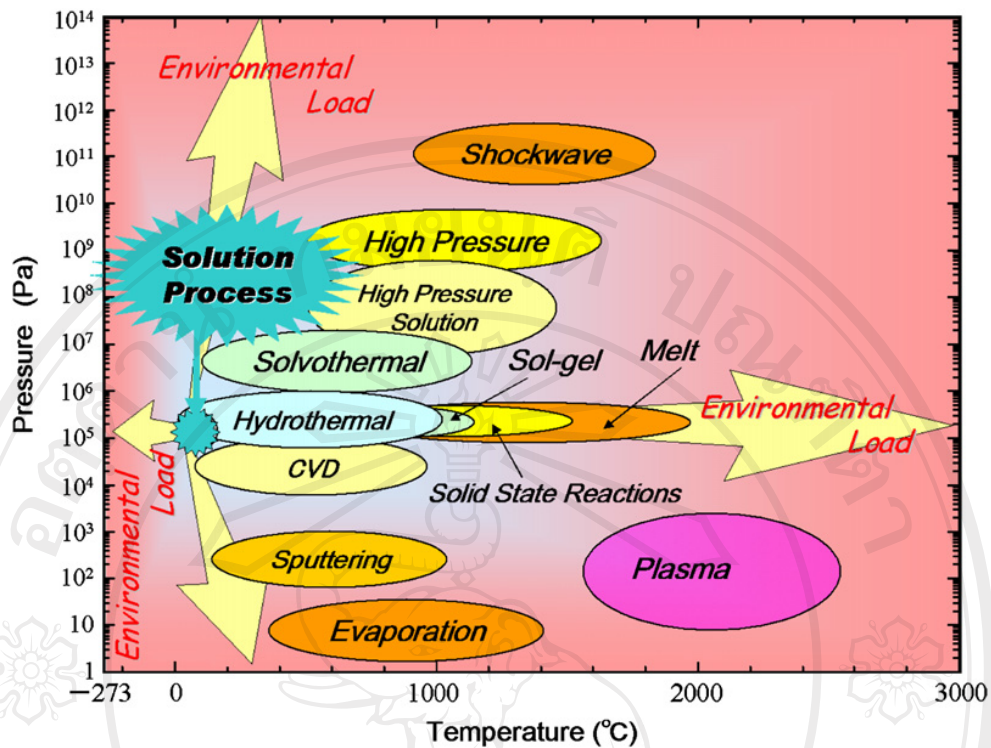


Figure 1.3 Pressure temperature map of materials processing techniques [35]

1.5 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) [37] and radiation track-etched polycarbonate (PC) membranes [38]. Other membranes have also been used, such as nanochannel array on glass [39], radiation tracketched mica [40], mesoporous materials [41], porous silicon obtained via electrochemical etching of silicon wafer [42], zeolites [43] and carbon nanotubes [62, 33]. Biotemplates have also been explored for the growth of nanowires [46] and nanotubes [47], such as Cu [48], Ni [48], Co [48], and Au [49] 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 [37, 50]. The pores can be arranged in a regular hexagonal array and densities as high as 1011 pores/cm² can be achieved [51]. Pore size ranging from 10 nm to 100 μm can be achieved [51,52]. PC membranes are made by bombarding a nonporous polycarbonate sheet, typically 6 to 20 μm in thickness, with nuclear fission fragments to create damage tracks, and then chemically etching these tracks into pores [38]. 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/cm². 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 densify 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.* [53] 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 $20\mu\text{m}$ [54]. ZnO nanowires were prepared by oxidizing metallic zinc nanowires

[55]. Hollow nanotubules of $\text{MoS}_2 \approx 30\mu\text{m}$ long and 50 nm in external diameter with wall thicknesses of 10 nm were prepared by filling a solution mixture of the molecular precursors, $(\text{NH}_4)_2\text{MoS}_4$ and $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13}$, 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 [56]. Certain polymers and proteins were also used to direct the growth of nanowires of metals or semiconductors. For example, *Braun* et al. [57] 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 [58].

1.6 Surfactant [59]

The term surfactant is a shortened form of "surface active agent". 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.

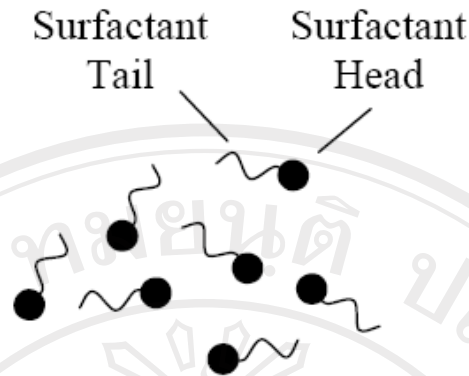


Figure 1.4 Schematic illustration of the micelle monomers

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 [60]

	Hydrophobic	Hydrophilic
<i>Anionic</i>		
Sodium dodecanoate	$\text{CH}_3(\text{CH}_2)_{10}$	COO^-Na^+
Sodium dodecyl (lauryl) sulphate	$\text{CH}_3(\text{CH}_2)_{11}$	$\text{OSO}_3^-\text{Na}^+$
Sodium dioctyl sulphosuccinate	$\text{CH}_3(\text{CH}_2)_7$	$\text{OOC.CHSO}_3^-\text{Na}^+$
	$\text{CH}_3(\text{CH}_2)_7$	OOC.CH_2
<i>Cationic</i>		
Hexadecyl trimethyl ammonium bromide (Cetrimide)	$\text{CH}_3(\text{CH}_2)_{15}$	$\text{N}^+(\text{CH}_3)_3\text{Br}^-$
Dodecyl pyridinium iodide	$\text{CH}_3(\text{CH}_2)_{11}$	$\text{N}^+\text{H} \text{I}^-$
<i>Non-ionic</i>		
Hexaoxyethylene mono-hexadecyl ether	$\text{CH}_3(\text{CH}_2)_{15}$	$(\text{OCH}_2\text{CH}_2)_6\text{OH}$
Polyoxyethylene sorbitan mono-oleate (polysorbate 80)	$\text{C}_{17}\text{H}_{33}$	$\text{COOCH}_2\text{CH}_2(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2$
		$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}$
		$\text{HO}(\text{OCH}_2\text{CH}_2)_n$
		$(\text{CH}_2\text{CH}_2\text{O})_n\text{OH}$
		$(\text{CH}_3\text{CH}_2\text{O})_n\text{OH}$
Sorbitan mono-oleate	$\text{C}_{17}\text{H}_{33}$	COOCH_2CH
		OH
		HO
		OH
<i>Ampholytic</i>		
N-dodecyl alanine	$\text{CH}_3(\text{CH}_2)_{11}$	$\text{NH}_2\text{CH}_2\text{CH}_2\text{COO}^-$
<i>Lecithin</i>		
	$\text{C}_{17}\text{H}_{35}$	COO.CH_2
	$\text{C}_{17}\text{H}_{35}$	COO.CH
		$\text{CH}_2\text{-O-P-O}^-(\text{CH}_2)_2\text{N}^+(\text{CH}_3)_3$

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 [61]. 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) [52].

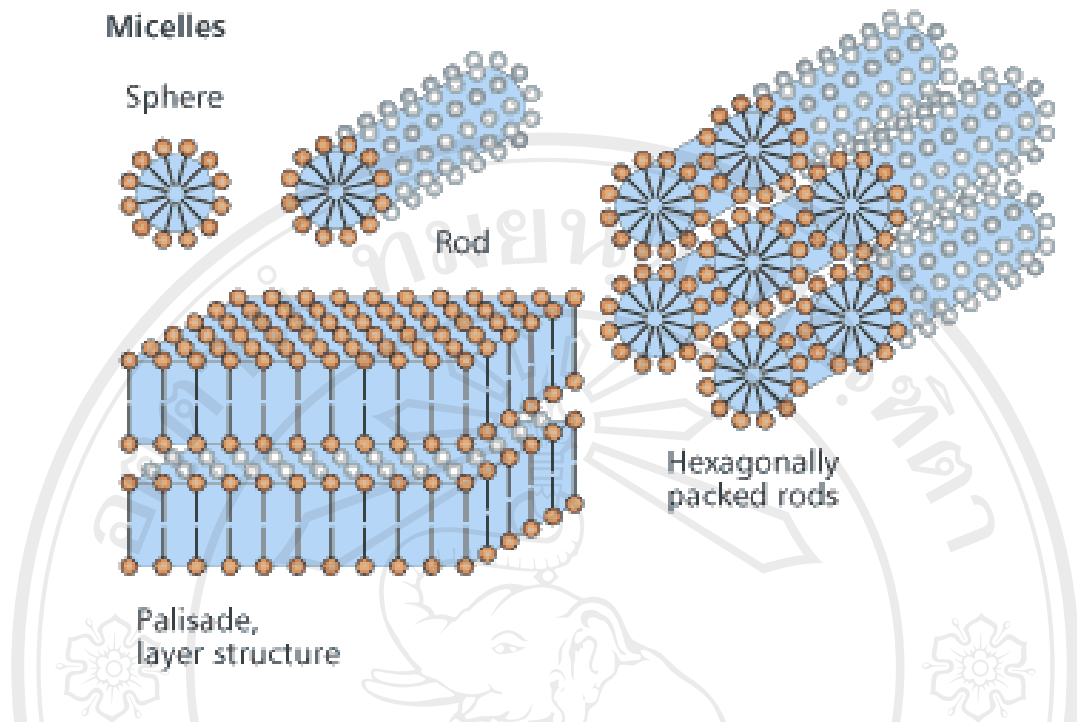


Figure 1.5 Schematic illustration of the commonly observed geometrical shapes of surfactant micelles in aqueous solution

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 [80].