CHAPTER II

LITERATURE REVIEWS

This chapter concerns with some literature reviews of representative reports involving nanoparticle synthesis in microemulsion. Several researchers used this method to synthesize nanoparticles with various size and shape. In general, micelles are expeted to act as a template to make uniformity of nanoparticles. Those previous investigations are the initiation of this work and can be summarized them as follow:

2.1 Synthesizing nanoparticles in microemulsion

Xu and Li (2003) synthesized ZnS nanocrystal in ternary water-in-oil (w/o) microemulsion systems stabilized by either nonionic or, in contrast, cationic surfactant. They used zinc sulfate and sodium sulfide as the reactant and CTAB and Triton X-100 as a surfactant. Products were analyzed by transmission electron microscopy (TEM) and identified by energy-dispersive X-ray spectroscopy (EDAX); electron diffraction (ED) was also performed for individual nanorods. With varying molar ratios of water to surfactant (w_o) in solution, hence changing droplet sizes of water pool of microemulsions consequently. They concluded that uniform ZnS nanorods could be prepared by using condition w_o=11 at room temperature, incubation time 24 hr, and using Triton X-100 as the surfactant. However, they could only prepare ZnS nanorods with aspect ratio of 70 but could not prepare other shape ZnS nanoparticles[1].

Qiu et. al. (1999) synthesized spherical Cu nanoparticles in sodium dodecyl sulfate (SDS) /isopentanol /cyclohexane/water microemulsions with sodium borohydride as a reducing agent. Nanoparticles formed in microemulsions were characterized by transmission electron microscopy(TEM), x-ray diffractometry (XRD), and small-angle X-ray scattering (SAXS). The size and polydisperity of particles were greatly affected by the mole ratio of water to surfactant (w) and the concentration of precursor salt. The ideal size and monodispersity of nanoparticles could be obtained at the smaller w value and lower concentration of Cu^{2+} solution[2].

Gao et. al. (2004) synthesized CuS nanoparticles with different morphologies by using microemulsion technique. CuS nanoparticles, nanorods, nanowires and tube-like structures were prepared while different quantities of surfactant were used. Transmission electron microscopy (TEM) was used to investigate the different morphology of the assynthesized products. X-ray powder diffraction (XRD) and electron diffraction (ED) were applied to characterize the properties of the products obtained. The mechanism of the nanocrystals with different shapes was discussed in this work[3] as shown in Figure 2.1.
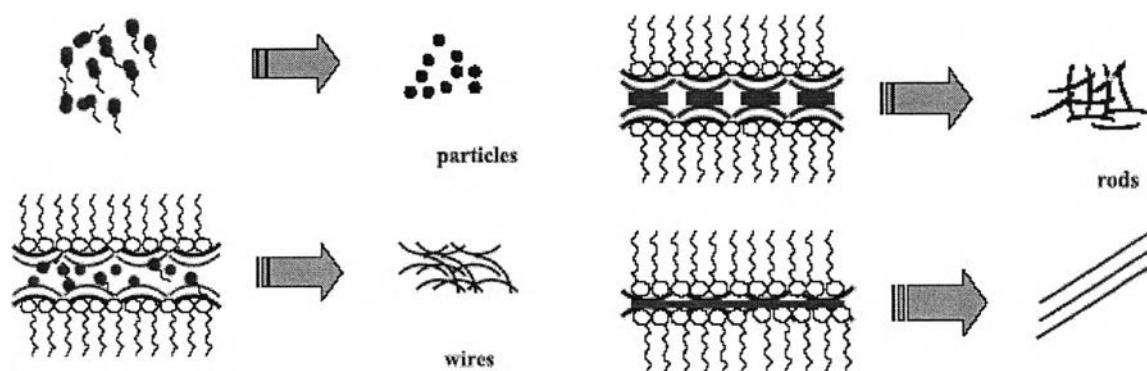
Figure 2.1 The possible formation process of different CuS nanostructures discussed in this work[3].

Xu et. al. (2002) have shown that silver iodide nanowires could synthesize in quaternary or ternary microemulsions. They used $AgNO_3$ and KI as a reactants. The reactant solution was added to a cyclohexane/Triton X-100/-pentanol system. AgI nanowires were visualized with a Hitachi Modle-800 tranmission electron microscope (TEM). With varying molar ratios of water to surfactant (w_0) in solution the size of AgI nanowires was partly tunable. In this paper at $w_0 = 11$, the length of AgI nanowires could reach ~ 8 μm and lead to an aspect ratio of 260[4].

Chen and Gao (2003) successfully synthesized NiS nanosheets, nanoneedles and nanotubes by using CTAB/n-pentanol/n-hexanol/water microemulsion under hydrothermal condition at 130 °C. X-ray diffraction, transmission electron microscopy (TEM) and field emission scanning electron microscopy were used to characterize the samples. The result showed that NiS nanosheets with small thickness (less than 5 nm)

and nanoneedles with hollow center and several microns in lengths, could be obtained by hydrothermally treating for 5 and 15 h, respectively. And from TEM images, revealed that the nanosheets firstly formed under the soft template action of the w/o micro-emulsion, and then resulting nanosheets rolled up into 1D nanoneedles or nanotubes[5].

Lv et. al. (2004) successfully synthesized ZnS nanowires, with diameters around 30 nm and lengths up to 2.5 µm, from solutions containing an anionic surfactant, sodium bis(2-ethylhexyl)sulfosuccinate (AOT). Powder X-ray diffraction (XRD) pattern, energy-dispersive X-ray spectroscopy (EDS) and selected-area electron diffraction (SAED) pattern indicated that the product was pure polycrystalline cubic-phase β-ZnS. The morphology and size of the as-synthesized product were determined by the transmission electron microscopy (TEM). The effects of some of the key reaction parameters (such as the ratio of surfactant to water, the reactant concentration and reaction temperature, etc.) had been explored in this work[7].

Lv et. al. (2004) studied about semiconductor ZnS nanotubes, with outer diameters in the range of 37-52 nm and lengths up to 3 micron synthesized in Triton x-100 O/W microemulsion. The reactant were zinc acetate $(Zn(AC)_2)$ as zinc source and CS_2 as the oil phase and sulfur source. In this reaction the molar ratio of water to surfactant would influence the formation of nanotubes remarkably. The as-synthesized nanotubes had been characterized by X-ray diffraction (XRD) and transmission electron microscope (TEM). The growth mechanism of ZnS nanotubes would be as the following:

When the concentration of the surfactant is ten times of the critical micelle concentration (CMC), the surfactant would form both hydrophobic and hydrophilic (O/W) rod-like micelle, in which the CS_2 could be enwrapped to form CS_2 cylinders. Due to the concentration difference between CS_2 oil phase (inside) and water phase (outside) of the rod-like micelle, the Zn^{2+} and NH_3 transfer to the micelle to react with CS_2 to produce ZnS. When the unreacted CS_2 cylindric cores were removed at a temperature above the boiling point of CS_2 (46-47 °C) and surfactant was removed by water and absolute ethanol, the ZnS tubular shell will be left as nanotubes[8].

Wu et. al. (2002) synthesized ZnS nanowires with diameters 40-80 nm and lengths up to tens of micron, which could bend and wind by the reaction of Zn^{2+} with S^{2-} in reverse micelle for the inducing template. The two reverse micelle solutions were mixed rapidly at room temperature. The final solution was aged about 24 h. The ZnS nanowire products were separated from the reverse micelle system by the procedure of demulsification, centrifugation, filtration, washing, and so on, which did not influence the nanostructure of ZnS nanowires. The probable formation mechanism of the ZnS nanowires is as follows:

1. The tube-linear micelle template formed through the chain link and fuse of the micelle under the drive force between Zn^{2+} and S^{2-} ions.

2. At the same time, the osmosis of Zn^{2+} and S^{2-} occurred, and the synthesis reaction proceeded: $Zn^{2+} + S^- === ZnS$.

3. ZnS nuclei formed and grew into nanoparticles.

4. The nanoparticles directionally aggregated and assembled under the inducement of the micelle template.

5. The nanoparticles further assembled, fused and crystallized.

6. The self-assembly nanowires formed and further crystallized into the single crystal structure in some areas or the whole of the nanowires[9].

Filankembo et. al. (2003) used copper nanocrystals produced by using $Cu(AOT)_2$—isooctane—water solution as a template to examine the effect of anion in the shape control. They varied the concentration of Cl- and Br- that affect in the copper nanocrystals shape. It was demonstrated that Cl- enabled the growth of nanorod with an aspect ratio varying with chloride concentration. Conversely, only a slight amount of bromide ion is needed to increase the nanorod with aspect ratio from 3 to 5. If used other ions, such as SO_4^{2-}, I^-, CO_3^{2-} and NO_3^-, the morphology of copper nanocrystals did not drastically changes[10].

Zhang et. al. (2004) synthesized CdS nanorods with uniform size by using micro-emulsion technique. Triton X-100 was used as a surfactant and employed n-hexanol as a cosurfactant. Thioacetamide was selected as the sulfide source. CdS nanorods with the aspect ratio of about 10 were found. The formation of nanorods depended on many factors. The reaction media was a key factor, nanorods could only form in diluted strong acid solution media such as hydrochloric acid and nitric acid. No rods were obtained in acetic media. When the concentration of the reactants was between 0.01-0.1 mol dm^{-3}, the size of the rods increased with the increase of concentration. But no rods could be formed when the concentration was higher than 0.2 mol dm^{-3}. Moreover, thicker and longer rods would be obtained at higher water content in the microemulsion system[11].

Yang et. al. (2005) Series of CdS nanoparticles with different morphologies and structure were self assembled in a simple reverse micelle solvent system containing cyclohexane, aqueous solution, *n*-pentanol and surfactant. CdS quasi-nanospheres (i.d. 200–500 nm), CdS nanoshuttles (i.d. 248 nm and length ~450 nm), CdS nanowires (i.d. ~46 nm and length 1.65–4.15 μm) and CdS nanotubes (inner i.d. 25 nm, outer i.d. 38 nm and length ~400 nm long) were produced by employing the surfactant of Tween-80, Peregals, C12E9 and Triton X-100, respectively. A mechanism involving the possible formation of nanomaterials based on surfactant microemulsion template was also proposed[12] as shown in Figure 2.2
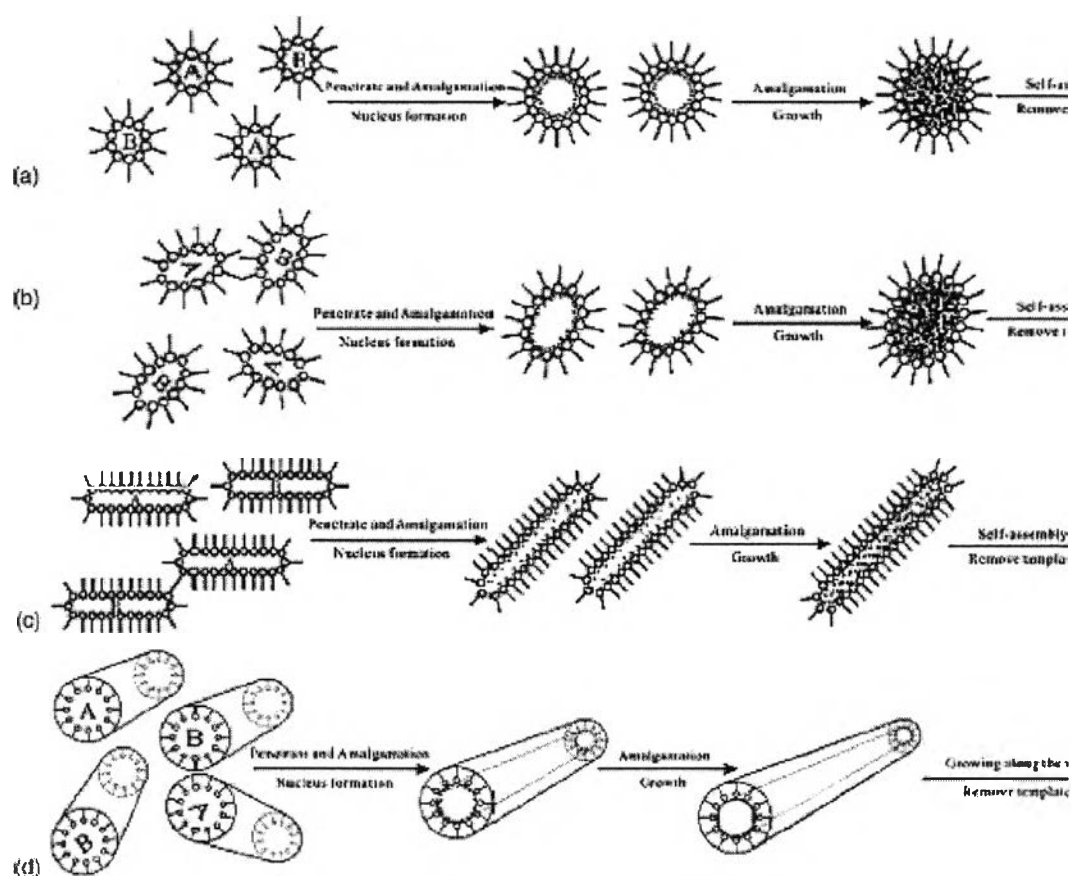

Figure 2.2 The possible mechanism of formation of a) nanospheres, b) nanoshuttles, c) nanowires, and d) nanotubes (A: S^{2-}, B: Cd^{2+})[12].

2.2 Synthesizing ZnS nanoparticles by using other liquid phase technique

Zhao et. al. (2003) synthesized ZnS nanorods by using solvothermal process with ethylenediamine as a bidentate ligand to form Zn^{2+} complexes and dodecylthiol providing an effective control over the crystal growth of ZnS nanorod. The diameter and length of ZnS nanorods obtained were 40 nm and 1.0 –1.5 μm, respectively. The microstructure and composition of the nanorods were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). The opticalproperties of ZnS nanorods were examined by photoluminescence (PL) spectrum. However, this method requires high temperature condition (about 170 °C) and only provides ZnS nanorods with aspect ratio of 40[13].

2.3 Phase behavior of microemulsion that relate in this thesis

Gu and Schelly (1997) have shown that nonionic surfactant Triton X-100 (TX-100) could be separated by column chromatography into its poly(oxyethylene tert-octylphenyl ether) (OPE_n) components. The phase behavior in the neighborhood of the L_2 phase (a clear, optically isotropic solution) was investigated for ternary (cyclohexane/H_2O) and quaternary (cyclohexane/H_2O/n-hexanol) systems of TX-100 and OPE_n (n = 5, 7 and 9). The extent of the L_2 domain and the maximum amount of water $w_{o,max}$ that could be solubilized by isotropic solutions strongly depended on the concentration and the length (n) of the polar chain of the surfactant, temperature, and the amount of n-hexanol present. Depending on these variables, with increasing w_o (molar ratio of water to surfactant) some of the following phase transitions occured: $L_2 \longrightarrow$ LC $\longrightarrow$ L $\longrightarrow$ liquid/gel.

Except for the liquid crystalline LC phase, all phases involved were optically isotropic, and the liquid L phase was most likely bicontinuous[14].

Table 2.1 Phase Behavior of the TX-100 Ternary System, C_{TX-100}=0.60 m[a]

composition (% by weight)				temperature (°C)					
H_2O	TX-100	oil	w_n	20	25	30	35	40	45
0.00	27.12	72.88	0	−	−	−	−	−	−
0.78	26.91	72.31	1	x	x	−	−	−	−
1.93	26.60	71.47	2.5	x	x	−	−	−	−
3.05	26.29	70.65	4	x	x	−	−	−	−
3.79	26.10	70.11	5	x	x	−	−	−	−
4.51	25.90	69.59	6	x	x	−	−	−	−
5.23	25.71	69.07	7	x	x	x	−	−	−
5.93	25.52	68.56	8	x	x	x	x	x	x

[a] x → L_2 + aqueous phase.

Table 2.2 Phase Behavior of the TX-100 Quarternary System, C_{TX-100}=0.60 m,

C_{hex}/C_{TX-100}

composition (% by weight)					temperature (°C)			
H_2O	TX-100	hex	oil	w_n	20	25	30	35
0.00	25.96	4.28	69.76	0	−	−	−	−
0.75	25.77	4.24	69.24	1	−	−	−	−
1.49	25.58	4.21	68.72	2	−	−	−	−
2.21	25.39	4.18	68.22	3	−	−	−	−
2.93	25.20	4.15	67.72	4	−	−	−	−
3.63	25.02	4.12	67.23	5	−	−	−	−
5.69	24.49	4.03	65.79	8	−	−	−	−
7.01	24.14	3.98	64.87	10	−	−	−	−
8.30	23.81	3.92	63.97	12	−	−	−	−
10.16	23.33	3.84	62.67	15	≡	≡	≡	−
10.77	23.17	3.81	62.25	16	≡	≡	≡	≡
11.36	23.01	3.79	61.83	17	≡	≡	≡	≡
11.95	22.86	3.77	61.42	18	≡	≡	≡	≡
12.53	22.71	3.74	61.02	19	≡	≡	≡	≡
13.10	22.56	3.72	60.62	20	≡	≡	≡	≡
14.23	22.27	3.67	59.83	22	≡	≡	≡	≡
15.86	21.85	3.60	58.70	25	≡	≡	≡	≡
18.45	21.17	3.49	56.89	30	−[a]	≡	≡	≡
20.88	20.54	3.38	55.19	35	x[b]	−[a]	−[a]	≡
23.17	19.95	3.29	53.60	40	liq/gel	x[b]	x[b]	x[b]
25.33	19.39	3.19	52.09	45	liq/gel	liq/gel	liq/gel	liq/gel

[a] Probably a bicontinuous L phase. [b] x → ? + ??.

− : A clear, optically isotropic solution

≡ : Liquid crystalline phase

x : A turbid solution

Lang and Zana studied the effect of the cosurfactant chain length on some properties of quaternary W/O microemulsions, such as water solubility, droplet size, electrical conductivity, and rate of exchange of material between droplets. They used dodecyl, tetradecyl, and hexadecyltrimethylammonium (DTAB, TTAB, and HTAB) as surfactants and n-propanol, n-butanol, n-pentanol, n-hexanol, n-heptanol, and n-undecanol as cosurfactants. The experimental results showed an increase of droplet size and electrical conductivity upon decreasing the chain length of alcohols while all other parameters remaining unchanged[15].