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# Effects of cosurfactant on ZnS nanoparticle synthesis in microemulsion

Tawatchai Charinpanitkul<sup>a,\*</sup>, Amornsak Chanagul<sup>a,\*</sup>, Joydeep Dutta<sup>b</sup>,  
Uracha Rungsardthong<sup>c</sup>, Wiwut Tanthapanichakoon<sup>a,c</sup>

<sup>a</sup>Center of Excellence in Particle Technology, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

<sup>b</sup>Microelectronics and Microelectronics Laboratory, School of Advanced Technologies, Asian Institute of Technology, Pathumthani 12120, Thailand

<sup>c</sup>National Nanotechnology Center, National Science and Technology Development Agency, Pathumthani 12120, Thailand

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## Abstract

ZnS nanoparticles with different morphology; spherical, ellipsoidal particles' nanotubes and nanorods, could be successfully synthesized from quaternary W/O microemulsion system. The morphology of the final products could be clearly confirmed by the scanning electron microscopy (SEM) and the transmission electron microscopy (TEM). The effect of cosurfactant on size and morphology of the obtained products have been explored in this work. The key controlling parameters such as the molar ratio of water to surfactant ( $w_o$ ) and the reactant concentration, which affect the product characteristics, have also been investigated.

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**Keywords:** Microemulsion; Cosurfactant; Zinc sulfide; Nanoparticle

## 1. Introduction

At the moment nanostructural materials have become attractive because of their unique characteristics that can hardly be obtained from conventional bulk materials owing to their quantum size and surface effects. In particular, much attention has been paid to synthesis of group II–VI semiconductor materials due to their excellent prospective in catalysis, optical and magnetic functionality, and so on [1].

To date there are many methodologies available for synthesizing ZnS nanocrystals, such as laser ablation, electrochemical fabrication and solvothermal methods [2]. However, water-in-oil (w/o) microemulsions or reverse micelles technique is one of the most recognized methods due to its several advantages, for instance, soft chemistry, demanding no extreme pressure or temperature control, easy to handle, and requiring no special or expensive equipment. In general, microemulsion or ME is an isotropic,

thermodynamically stable dispersion of oil, water, surfactant and often cosurfactant, which is normally alcohol. Microemulsion can be characterized as oil-in-water (O/W), water-in-oil (W/O) or bicontinuous system. Oil-in-water is microemulsion containing an excess oil phase with surfactant molecules existing in the aqueous phase in form of normal micelles. On the other hand, water-in-oil (W/O) microemulsion is the coexistence of an excess water phase and the surfactant molecules which aggregate in the oil phase in the form of reverse micelle. It is well known that these micelles could perform as nano-scaled reactors [3]. Once two microemulsions of which one contains the precursor and the other contains the precipitating agent are uniformly mixed, the reaction will occur in controlled manner in the micelles which have the size in order of nanometers, resulting in formation of nanoparticles of controlled characteristics.

It is also known that addition of cosurfactant can reduce the surfactant concentration in microemulsion preparation. Normally, low molecular weight alcohols, such as *n*-butanol can be used for this purpose. Their short hydrophobic chain and terminal hydroxyl group is known to enhance the interaction with surfactant monolayers at the interface, which can influence the curvature of the interface and internal energy. The amphiphilic nature of cosurfactants

\* Corresponding author. Fax: +66 2 218 6480.

E-mail addresses: ctawat@chula.ac.th (T. Charinpanitkul), c\_amornsak@hotmail.com (A. Chanagul).

could also enable them to distribute between the aqueous and oil phase [4].

The most challenging problem for this synthesizing method is how to precisely control morphology and size of nanoparticles. The uniformity of morphology and size of the synthesized product is expected for being effective utilization in various specific applications, such as optical sensitizers, photocatalysts, light converting electrodes and inorganic light emitting diodes (ILEDs). Xu and Li reported that they could synthesize ZnS nanoparticles and nanorods in ternary water-in-oil microemulsion by varying some parameters such as the molar ratio of water to surfactant ( $w_o$ ) and temperature. Uniform nanorods could be obtained at  $w_o$  of 11 and reactant concentration of  $0.1 \text{ mol/dm}^3$  after aging for 2 days [1]. Similarly, Xu et al. could obtain AgI nanowires of uniform diameter from a system of Triton X-100 microemulsion with *n*-pentanol as a cosurfactant at  $w_o$  of 11 [5]. Lv et al. studied ZnS nanowires synthesis by sodium bis(2-ethylhexyl)sulfosuccinate (AOT) micelle-template inducing reaction and found that the morphology and size of ZnS nanoparticles would also be affected by reactant concentration and  $w_o$  [6]. Moreover, Lv et al. also reported that ZnS nanotubes could be obtained from O/W microemulsion by using  $\text{CS}_2$  as an oil phase and Triton X-100 as a surfactant [7]. In this paper, we have mainly focused on investigating the dependence of morphology of ZnS nanoparticles on cosurfactant types. Meanwhile, other variables, which are  $w_o$  and reactant concentration, have also been investigated.

## 2. Experiment

All of the solvents, which are cyclohexane and Triton X-100, and reactants ( $\text{Zn}^{2+}$  and  $\text{S}^{2-}$ ) used in this experiment are analytical grade and used without any further purification. First, the solution of Triton X-100, cyclohexane and cosurfactant were prepared and mixed in two accurate beakers. Then aqueous solutions of  $\text{ZnSO}_4$  or  $\text{Na}_2\text{S}$  are added into each microemulsion solution in separate beaker and vigorously agitated by a magnetic stirrer. After mechanical agitation for about 15 min, two separate microemulsion solutions were mixed together. The resulting mixture was then incubated for 2 days at room temperature. Samples were taken to analyze by SEM (JEOL JSM 5410LV), Energy Dispersive X-ray Spectroscopy (EDS) and TEM (JEOL JEM-1230).

## 3. Results and discussion

### 3.1. Effect of cosurfactant

In order to investigate the effects of cosurfactants, *n*-hexanol, *n*-pentanol, and *n*-butanol were selected and individually added into the microemulsion system with

concentration ratio of  $C_{\text{Triton X-100}}/C_{\text{cosurfactant}}=1$  while  $w_o$  were varied within the range of 5.5–20.0. The reactant concentration was tentatively kept constant at  $0.1 \text{ mol/dm}^3$ . All syntheses were conducted at room temperature.

Without cosurfactant, the microemulsion with  $w_o$  of 5.5 and reactant concentration of  $0.1 \text{ mol/dm}^3$  could provide ZnS nanoparticles with the morphology of long and short rods as well as ellipsoid as shown in Fig. 1. These ZnS nanorods have an aspect ratio of approximately 80 (200–750 nm in diameter and up to  $30 \mu\text{m}$  in length). Meanwhile ellipsoidal ZnS nanoparticles have breadth in the range of about 90–200 nm. With an increase in  $w_o$  up to 11, more agglomeration of ZnS particles and only few nanorods were observed. In order to identify the constituent of these synthesized products, typical EDS analysis was conducted to demonstrate that these products are ZnS nanocrystals (Fig. 2). The X-ray fluorescence peaks at 1.0 and 2.3 keV exhibit the combination of Zn and S. Meanwhile, the smaller peaks at 8.6 and 9.6 keV correspond to the transition of Zn  $K\alpha$  and  $K\beta$ , respectively.

By employing *n*-hexanol as cosurfactant at relatively low  $w_o$ , Fig. 3(a) and (b) show that the synthesized

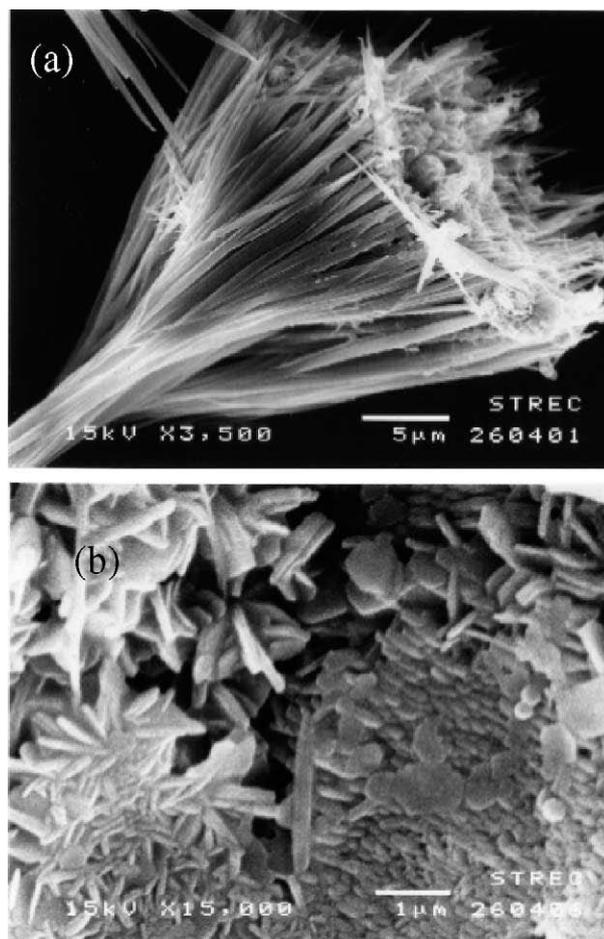


Fig. 1. SEM images of ZnS nanoparticles synthesized in ternary W/O microemulsion with  $w_o=5.5$  and reactant concentration of  $0.1 \text{ mol/dm}^3$ . No cosurfactant is added.

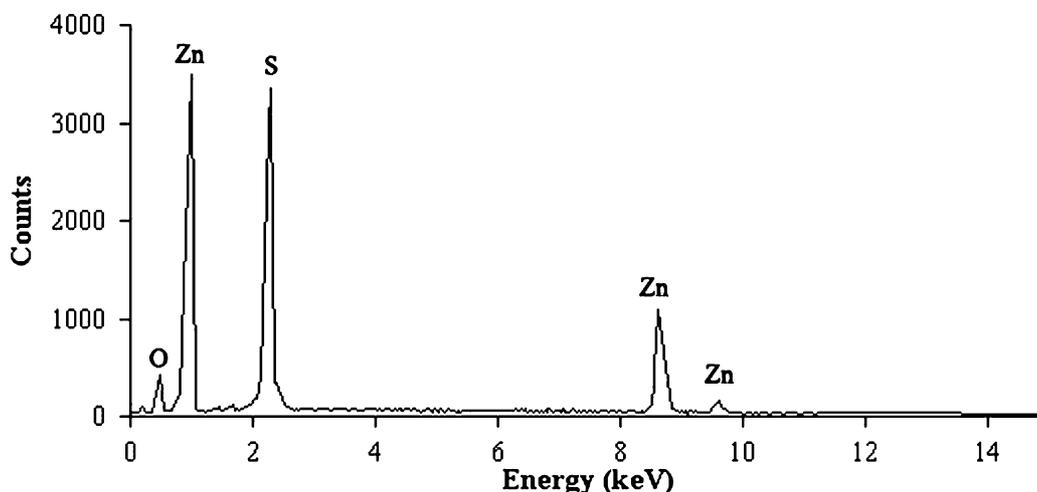


Fig. 2. The EDS of typical ZnS nanoparticle samples obtained from w/o microemulsion.

products were quantum dots with diameters less than 5 nm. These quantum dot particles could agglomerate to form secondary particles with larger diameters of between 40–100 nm, which however are much smaller than those obtained from heat treatment method [8]. Typically ZnS can be used as light emitting phosphor once it is doped with elements such as terbium (Tb) or samarium (Sm). The smaller the size of quantum dots the higher the light emission efficiency they could provide. Therefore it is reasonable to expect that the synthesized products in this work could potentially be used in electroluminescent applications upon doping.

However, it is noteworthy that at  $w_o$  of 15 ZnS nanotubes with diameters of 20–40 nm and length of up to 2  $\mu\text{m}$  could be successfully synthesized (Fig. 3(c)). It could be confirmed from repeatability test that such hollow

nanotubes of ZnS exhibit a very narrow distribution with respect to their diameters.

It should be noted that there were some significant changes in the morphology of the synthesized ZnS nanoparticles when *n*-pentanol or *n*-butanol was employed as cosurfactant. At  $w_o=7$ , comparison of Figs. 3(a) and 4(a) reveals that predominant morphology of the synthesized ZnS are quantum dots and their agglomeration of which diameters are smaller than 100 nm. However, when increasing  $w_o$  value to 11 and 15 *n*-pentanol could result in ZnS nanorods with some agglomerations as shown in Fig. 4(b) and (c). Interestingly, Fig. 5(a) and (b) show that with  $w_o$  of 11 and 15 ZnS nanotubes with some quantum dot depositing on their surface could again be successfully grown when *n*-butanol was employed as cosurfactant.

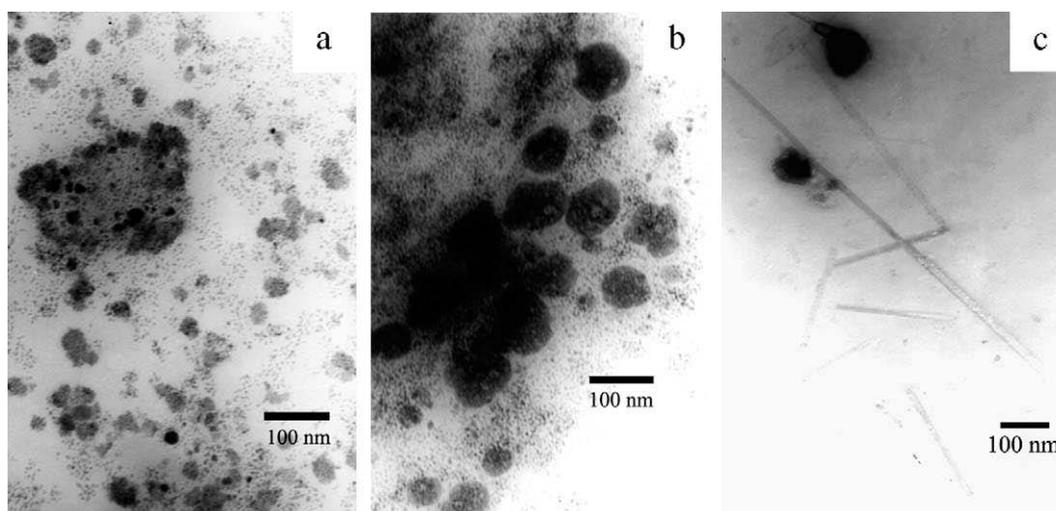


Fig. 3. TEM images of ZnS nanoparticles synthesized in microemulsions with *n*-hexanol as a cosurfactant at: (a)  $w_o=7$ , (b)  $w_o=11$ , and (c)  $w_o=15$ .

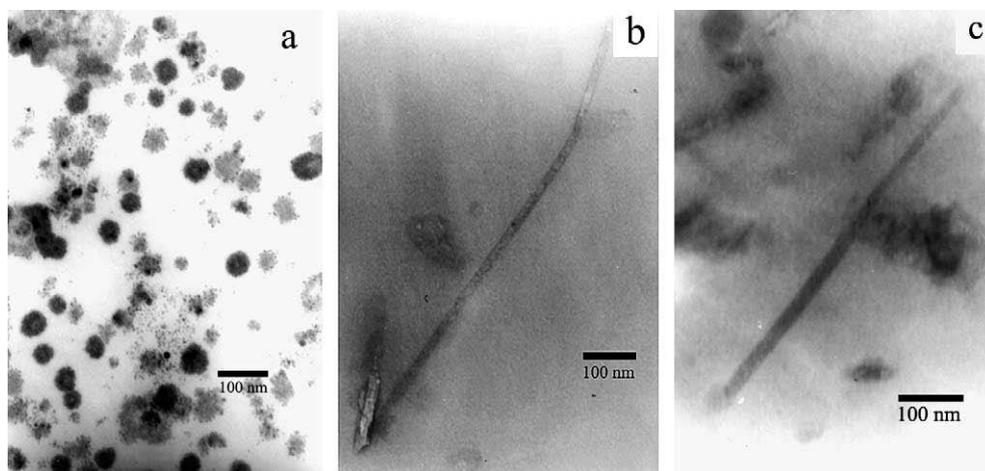


Fig. 4. TEM images of ZnS nanoparticles synthesized in microemulsion with *n*-pentanol as a cosurfactant at: (a)  $w_o=7$ , (b)  $w_o=11$ , and (c)  $w_o=15$ .

### 3.2. Effect of reactant concentration

The effect of absolute reactant concentration  $[\text{Zn}^{2+}]$  and  $[\text{S}^{2-}]$  on the morphology of ZnS nanoparticles synthesized in microemulsion systems was investigated by varying both  $[\text{Zn}^{2+}]$  and  $[\text{S}^{2-}]$  in the range of 0.10–0.05 mol/dm<sup>3</sup>. With a decrease in the reactant concentration to 0.05 mol/dm<sup>3</sup>, the synthesized ZnS nanoparticles mainly showed ellipsoidal morphology. With  $w_o$  of either 11 or 20, the morphology of the ZnS nanoparticles synthesized in the microemulsion using *n*-hexanol as cosurfactant exhibited insignificant difference. As could be observed in Fig. 6(a) and (b), the agglomeration of ZnS nanoparticles, which formed larger aggregates with diameter up to 200 nm, were found all over the TEM grid but no nanorods or nanotubes were observed.

In addition, by employing *n*-pentanol as cosurfactant, the effect of reactant concentration on the morphology of the synthesized ZnS nanoparticles with various  $w_o$  became insignificant. With the reactant concentration of 0.05 mol/dm<sup>3</sup>, at  $w_o=11$  or 15 few ZnS nanorods with diameter of between 60 and 120 nm were found to co-exist with a widely spreading ZnS quantum dots as shown in Fig. 7(a) or (b). From Fig. 7(c) with a further increase in  $w_o$  to 20, long nanorods no longer existed but some ellipsoidal ZnS nanoparticles and ZnS quantum dots were found to disperse thoroughly within samples. The approximated diameter of these ellipsoidal nanoparticles were about 70–120 nm with the breadth of about 400 nm.

Finally, when *n*-butanol was used as cosurfactant, a similar trend was still observed. With lower concentration

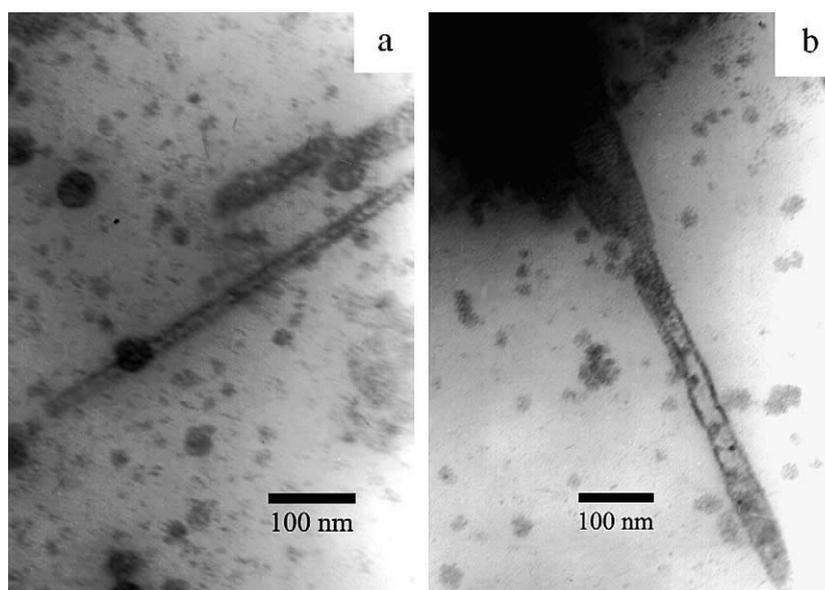


Fig. 5. TEM images of ZnS nanoparticles prepared in microemulsion with *n*-butanol as a cosurfactant: (a)  $w_o=11$ , and (b)  $w_o=15$ .

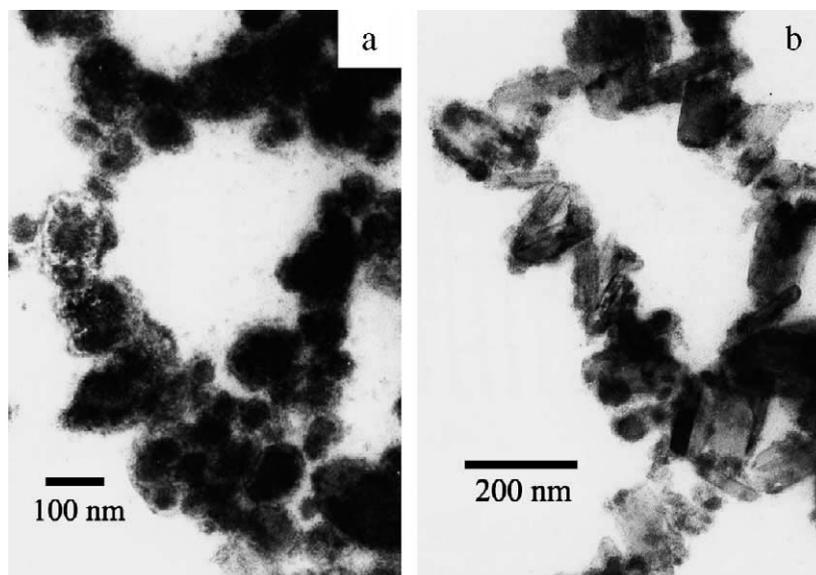


Fig. 6. TEM images of ZnS nanoparticles prepared in microemulsion with *n*-hexanol as a cosurfactant and reactant concentration = 0.05 mol/dm<sup>3</sup>: (a)  $w_o = 11$ , and (b)  $w_o = 20$ .

of the reactant, no ZnS nanotubes could be synthesized regardless of the increasing  $w_o$ . However, it is noteworthy that the elongated ellipsoidal morphology of ZnS nanoparticles could be obtained at  $w_o = 7$  as shown in Fig. 8(a). With a further increase in  $w_o$  to 15 and 20, those ZnS nanoparticles with high aspect ratio disappeared. Fig. 8(b) and (c) show that only ZnS quantum dots and their agglomeration were randomly dispersed in the samples. The agglomerated nanoparticles have the approximated size of 20–100 nm. Also, it should be noted that further increasing  $w_o$  led to a decrease in the population density of the ZnS quantum dots and an increase in the number of agglomerated particles. This implies that the higher polarity

of an increased water amount might enhance the agglomerating process of synthesized ZnS nanoparticles.

#### 4. Conclusions

ZnS nanoparticles with distinguishable morphology could be synthesized in quaternary W/O microemulsion systems using various types of cosurfactant. According to the above mentioned experimental results, it could be clearly shown that the size and the morphology of the ZnS nanoparticles are dependent upon the types of cosurfactant and the reactant concentration as well as the molar ratio of

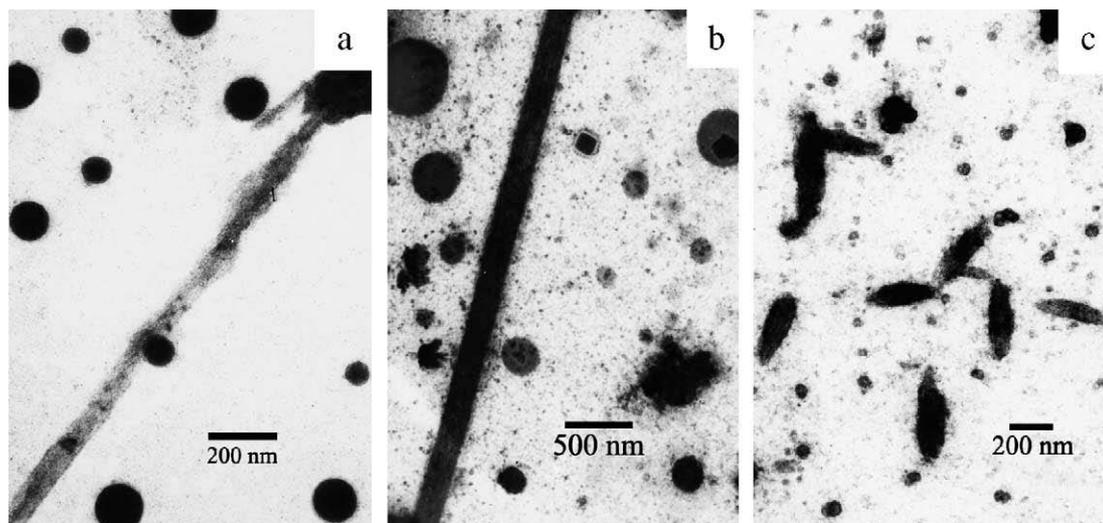


Fig. 7. TEM images of ZnS nanoparticles synthesized in microemulsion with *n*-pentanol as a cosurfactant and reactant concentration = 0.05 mol/dm<sup>3</sup>: (a)  $w_o = 11$ , (b)  $w_o = 15$ , and (c, d)  $w_o = 20$ .

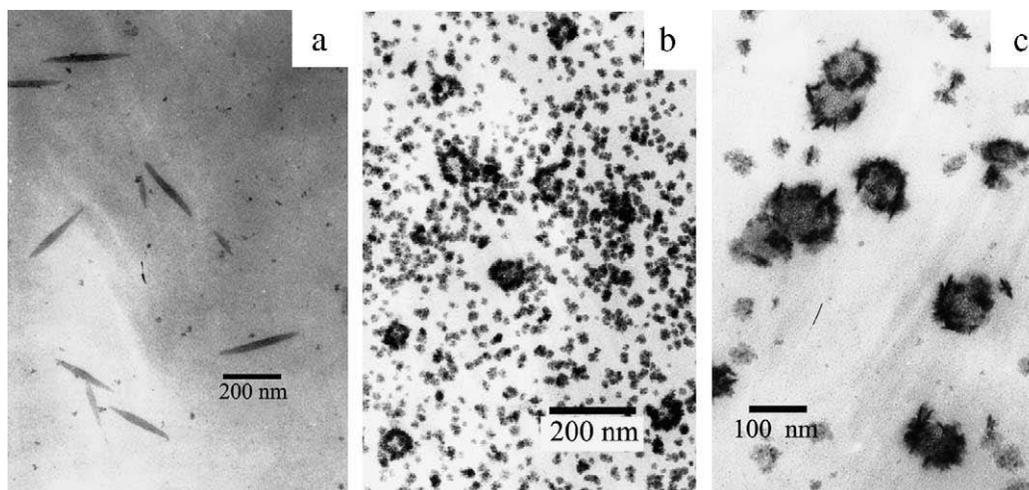


Fig. 8. TEM images of ZnS nanoparticles synthesized in microemulsion with *n*-butanol as a cosurfactant and reactant concentration = 0.05 mol/dm<sup>3</sup>: (a)  $w_o=7$ , (b)  $w_o=15$ , and (c)  $w_o=20$ .

water to surfactant ( $w_o$ ). Cosurfactants with larger molecular size such as *n*-hexanol could provide higher possibility to synthesize ZnS nanoparticles with higher aspect ratio, like nanorod or nanotube. With relatively high reactant concentration, some certain amount of ZnS nanorod and nanotubes could be successfully synthesized. With *n*-hexanol at  $w_o=15$ , and reactant concentration of 0.1 mol/dm<sup>3</sup>, ZnS nanoparticles with the morphology of hollow tubes could be repeatedly synthesized. However, with lower reactant concentration, spherical ZnS quantum dots or ellipsoidal nanoparticles were predominantly obtained regardless of cosurfactant types or  $w_o$ .

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