Preparation of nanosized ZnS particles in water/oil emulsions by microwave heating

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The preparation of ultrafine particles (particles of sizes in the nanometre range) is one of the most important challenges of the new technologies [1]. A variety of methods has been proposed for obtaining ultrafine particles, which include precipitation in aqueous and organic media, thermal decomposition, hydrothermal synthesis and cryochemical processing. Recently, compartmentalized liquids such as micro-emulsion [2], vesicle [3] and liquid crystals [4] have been used successfully to prepare ultrafine particles. These compartmentalized liquids offer the advantage of reducing the reaction vessel to the size of the particles. In water/oil (w/o) micro-emulsions, for example, the aqueous phase is dispersed as nano-sized droplets surrounded by oil (continuous phase). Nanoparticles of metals, metal borides, sulphides and oxides [5] have been synthesized in a simple and convenient manner by using w/o micro-emulsions as reaction media. However, low yield and high cost due to the use of a large amount of surfactant to prepare the micro-emulsion have hindered the industrial application of the micro-emulsion method. On the other hand, conventional emulsion precipitation offers an alternative method for preparing particles with spherical morphologies and submicrometre size by using a relatively small amount of surfactant as emulsifier [6, 7]. In the work reported here, a new method of preparing nanosized ZnS particles in conventional w/o emulsions by using microwave heating was developed.

To prepare a stable emulsion as reaction medium, toluene was used as oil phase, and an aqueous solution containing $Zn(Ac)_2$ and thioacetamide (TAA) in equal molar ratio was used as the water phase. A mixture of Span 80 and Tween 80 with a molar ratio of about 5:1 was chosen as the emulsifier. A preliminary test confirmed that the mixed emulsifier had the optimal hydrophilic–lipophilic balance (HLB) value (~6) for the water/toluene system. The aqueous phase, toluene and emulsifier were mixed ultrasonically for 5 min to form an emulsion, then heated at 60 °C for 1 h to initiate the reaction between $Zn(Ac)_2$ and TAA to form ZnS particles. After filtration, the precipitated ZnS was washed with ethanol and water, sequentially, to remove the emulsifier and unreacted reactants. X-ray diffraction (XRD) characterization indicated that the product was pure crystalline ZnS.

Fig. 1a and b shows the ZnS particles obtained from the water/toluene emulsions with emulsifier concentrations of 1.0% and 2.5% (w/v), respectively. Fig. 2 shows the ZnS particles obtained from the bulk aqueous solution containing the same concentration of reactants as that in the above emulsions. It can be seen that the ZnS particles obtained from the emulsions as reaction media, in comparison with those obtained from bulk aqueous solution, have a more regular, approximately spherical shape and a much smaller particle size, clearly demonstrating the compartmentalizing effect of the water droplets in w/o emulsions. Moreover, the particle size of the ZnS formed in emulsions showed a tendency to decrease as the concentration of emulsifier increased, consistent with the droplet size of the parent emulsions decreasing at higher emulsifier concentration.

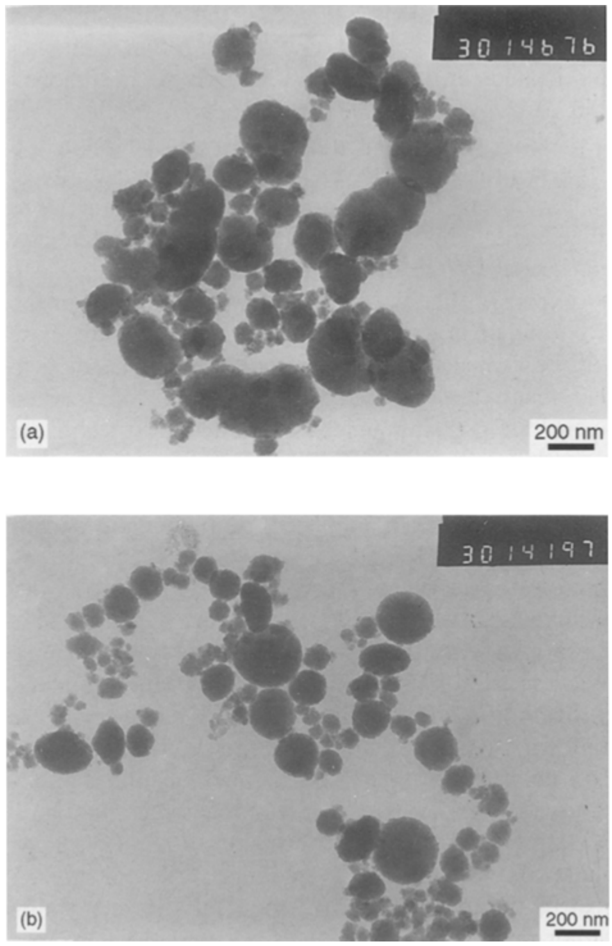

Figure 1 TEM micrographs of ZnS particles prepared in emulsion by heating in conventional manner; water/toluene ratio (v/v) = 1/3, $[Zn(Ac)_2] = 1\ mol\,l^{-1}$, emulsifier concentration: (a) 1% and (b) 2.5% (w/v).

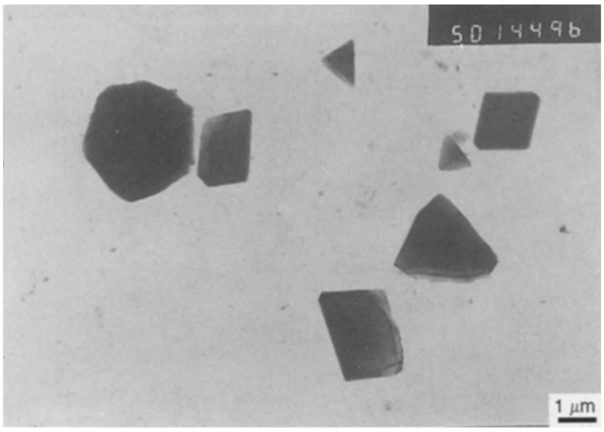

Figure 2 TEM micrograph of ZnS particles prepared in bulk aqueous solution, $[Zn(Ac)_2] = 1\ mol\,l^{-1}$.

However, the ZnS particles obtained from emulsions still show a relatively large particle size in the submicrometre range and a rather broad size distribution. This is probably due to the inhomogeneity of the reaction temperature in the interior of the emulsion and the frequent mass interchange between the water droplets of the emulsion during the long heating time. In order to diminish the undesired influences of the above factors, heating by microwave was used to initiate the reaction between $Zn(Ac)_2$ and TAA in the w/o emulsions. To do this, the same emulsions obtained after ultrasonication were put into a closed thick-wall Teflon container and heated for 4 min in a microwave oven (National, 750 W, 2.45 GHz). The formed ZnS particles were worked up in a similar manner as described above. It is known that microwaves have a strong capability to penetrate into media and cause only polar media to be heated, while nonpolar media are substantially unaffected by the microwave field. Therefore, it can be expected that the separated water droplets in the w/o emulsions with nonpolar oil as continuous phase will be heated rapidly and simultaneously, leading to the occurrence of a large number of ZnS crystal nuclei almost simultaneously, hence this technique should favour the formation of ZnS particles with small and uniform size. Fig. 3a and b shows the ZnS particles formed in emulsion with emulsifier concentrations of 1% and 2.5% (w/v), respectively, by microwave heating. It can be seen that the ZnS particles obtained in this manner have a particle size substantially in the nanometre range (40–100 nm), much smaller than that of the ZnS particles obtained by heating in a conventional manner, and a relatively uniform size distribution. It may be noted that the ZnS particles formed by microwave heating demonstrate a somewhat blurred periphery, which may be a consequence of the rapid formation of ZnS particles under microwave heating leading to irregular crystal growth through insufficient time for the recrystallization process.

Since nanosized ZnS particles can be prepared in conventional emulsions by using microwave heating, the combination of using compartmentalized liquids as reaction media and microwave as the heating method may provide a promising technique for preparing ultrafine particles.

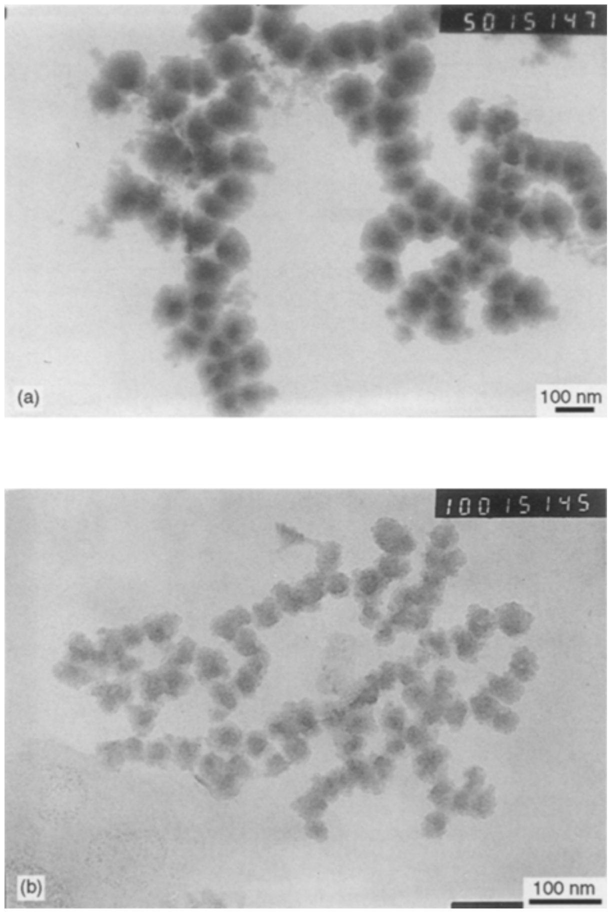

Figure 3 TEM micrographs of ZnS particle prepared in emulsion under microwave heating; water/toluene ratio (v/v) = 1/3, $[Zn(Ac)_2] = 1\ mol\,l^{-1}$, emulsifier concentration: (a) 1% and (b) 2.5% (w/v).

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References
1. D. SEGAL, in "Chemical synthesis of advanced ceramic materials" (Cambridge University Press, Cambridge, 1989).
2. M. A. LOPEZ-QUINTELA and J. RIVAS, *J. Colloid Interf. Sci.* **158** (1993) 446.
3. S. BHANDARKAR and A. BOSE, *ibid.* **139** (1990) 541.
4. E. C. O'SULLIVAN and A. J. L. WARD, *Langmuir* **10** (1994) 2985.
5. M. P. PILENI, *J. Phys. Chem.* **97** (1993) 6961.
6. M. AKINC, ASTIA document A185140, 1987.
7. W. SAGER, H. F. EICKE and W. SUN, *Colloids Surf. A* **79** (1993) 199.

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