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Ultrasound-assisted synthesis of highly disperse zinc sulphide powders

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Highly disperse zinc sulphide powders have been synthesized using an ultrasound-assisted reaction between zinc acetate and thioacetamide in aqueous solution. The synthesis was performed at 70°C, at different pH values, using variable reagent concentrations. All samples were characterized by infrared absorption spectroscopy (FT-IR), thermal analysis (TGA-SDTA), scanning electron microscopy (SEM) and photoluminescence spectroscopy (PL). A correlation between the preparation conditions and zinc sulphide characteristics was established.

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1. Introduction

Recently, II-VI semiconductor nanoparticles have been the subject of considerable interest because of their size-dependent (and thus tunable) photo- and electro-luminescence properties as well as their promising applications in optoelectronics. Among all II-VI semiconductors, ZnS is a rather interesting material because it has a high exciton binding energy (38 meV) and a wide band gap (3.7 eV), and has found many applications in various fields such as phosphors [1], solar cells [2, 3], infrared windows [4, 5], electroluminescence [6-8], ceramics [9-11] and photocatalysis [12]. Controlling the size of ZnS crystals may further lead to novel properties due to the quantum confinement effect.

ZnS nanoparticles can be prepared by a variety of methods, including sputtering [13], co-evaporation [14], sol–gel method [15-17], solid state reaction [18], gas-phase condensation [19], liquid-phase chemical precipitation [20], ion complex transformation [21], radiolysis [22], microwave irradiation [23-25], ultrasound irradiation [26] and biological synthesis [27]. From all these works, it has been found that the particle size and the properties of nanoparticles depend strongly on the specific preparation method and the applied experimental conditions.

Ultrasounds irradiation has been used extensively to generate novel materials with unusual properties, and they can induce the formation of particles with much smaller size and higher surface area than those reported by other methods [28]. The ultrasound chemical effects arise from acoustic cavitation, that is, the formation, growth and implosive collapse of bubbles in a liquid, which generate a transient temperature of approximately 5000 K, a pressure of approximately 1800 atm and a cooling rate in excess of 1010 K/s [29]. These extreme conditions can drive chemical reactions such as oxidation, reduction, dissolution and decomposition [30], which have been exploited to prepare nanoscale metals, metal oxides and nanocomposites [31–35]. In this paper, we report a convenient ultrasound assisted synthesis of highly disperse ZnS powders. The synthesized powders were characterized by infrared absorption spectroscopy (FT-IR), thermal analysis (TGA-SDTA), scanning electron microscopy (SEM) and photoluminescence spectroscopy (PL).

2 Experimental

Zinc acetate, thioacetamide and hydrochloric acid were purchased from Merck and used without further purifications. Isopropanol was purchased from Chimopar and used without further purifications. Deionized water was used in all the synthesis.

In a typical procedure, a homogeneous aqueous solution was obtained by mixing 0.05 M zinc acetate and 0.05 M thioacetamide (TAA) in a molar ratio between 2:3 and 1:3. The pH of the solution was adjusted to 2 or 3 using 6M HCl. The solution was transferred into a beaker covered with a watch glass, and then sonicated at 70ºC, with 35-kHz ultrasonic waves, at 360-kW output power. After 3 h sonication, the reaction mixture was cooled to 10ºC and left undisturbed for 24h. The resulting white powder was recovered by centrifugation, washed repeatedly with deionized water and isopropanol and then dried for 2h in vacuum, at 80ºC.

A JASCO 610 FTIR spectrophotometer was used to record the IR absorption spectra of the samples pelleted in KBr. A METTLER-TOLEDO TG//SDTA851 thermogravimeter was used for differential thermal analysis (DTA), thermal and differential thermal gravimetry (TG-DTG). The measurments were performed in alumina crucibles, in nitrogen or air flow (20 mL/min), with a heating rate of 5°C/min. The SEM images were obtained with a JEOL–JSM 5510LV electron microscope using Au-coated powders. The accelerating voltage was 20 kV. Photoluminescence spectra (PL) were registered with JASCO FP-6500 spectrofluorimeter (λ_{exc}=365 nm, with correction against MgO (Farbglasfilter WG 320-ReichmannFeinoptik).

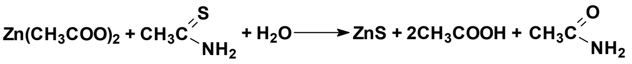
3 Results and discussion

Several zinc sulphide samples have been prepared by ultrasounds irradiation of a homogeneous aqueous solution of zinc acetate and thioacetamide (TAA) as the source of sulphide ions (Table 1).

Table 1. Synthesis conditions of some zinc sulphide powders obtained by ultrasonication

Code	Concentration (mol/L)		pH	Molar ratio	Yield %
	Zinc acetate	Thioacetamide			
C04	0.5	0.5	2	1.0:1.5	14.1
Co5	0.5	0.5	3	1.0:1.5	4.3
C06	0.1	0.1	2	1.0:1.5	0.3
C07	0.1	0.1	3	1.0:1.5	0.5
C08	0.5	0.5	2	1.0:3.0	53.1
C09	0.5	0.5	3	1.0:3.0	13.5
C10	0.1	0.1	2	1.0:3.0	20.4
C11	0.1	0.1	3	1.0:3.0	3.6

The chemical process can be described by the following overall chemical equation:



$$Zn(CH_3COO)_2 + CH_3C(=S)NH_2 + H_2O \longrightarrow ZnS + 2CH_3COOH + CH_3C(=O)NH_2$$

The thermal behavior of C08 sample in the 25-1200ºC range with N_2 and air flow respectively is plotted in Fig. 1. Up to about 380ºC the TG curves of the sample treated in N_2 and air are very similar. The corresponding three steps weight loss could be assigned to the desorption/elimination of the water and organic contaminants. The DTA curve shows no significant thermal effect for this weight loss. At about 900°C Zinc sulphide sublimation begin. However, the sample treated in air shows a major weight-loss (~15%) accompanied by an exothermal effect between 600-700ºC, assigned to the oxidation of ZnS to ZnO according to the following chemical equation:

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

According to the TG curves (fig. 2), ZnS samples can be divided in two categories:- samples that, up to 1200°C show a weight loss of about 10 %: C08, C10, C11.- samples that, up to 1200°C show a weight-loss of about 15%: C04, C05, C09.

The difference between ZnS samples could be correlated with the contamination level of the particles with different dimensions or surface area and also, with the variable sublimation rate, related with different dispersion degree of powders.

The FT-IR spectra of the samples C04-C11 (fig. 3) show only characteristic bands for the acetate, thioacetamide, acetamide and water contaminants ($\delta(H_2O)$+ ν(C=O acetamide)+ $\delta(NH_2)$ ~1625-1560 cm^{-1}, ν_{as}(COO) ~1457 cm^{-1}, ν_s(COO) ~1404 cm^{-1}, $\rho(CH_3)$ + $\rho(NH_2)$ ~1152-1010 cm^{-1}) [36].

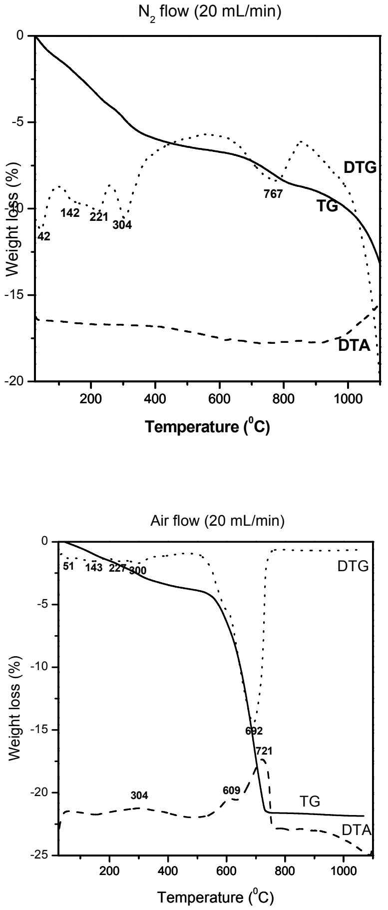


Fig. 1. TG, DTA and DTG curves obtained for the sample C08 treated in N_2 and air.

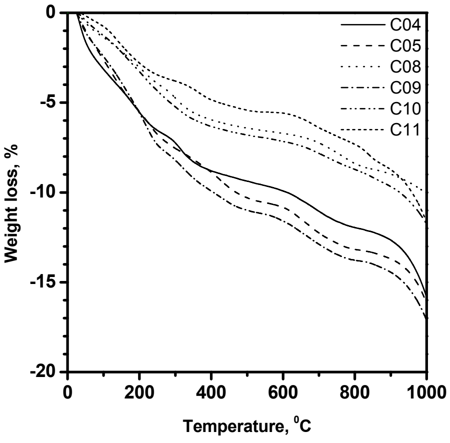


Fig. 2. TG curves of several ZnS samples.

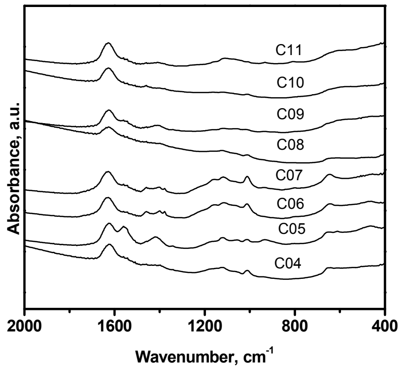
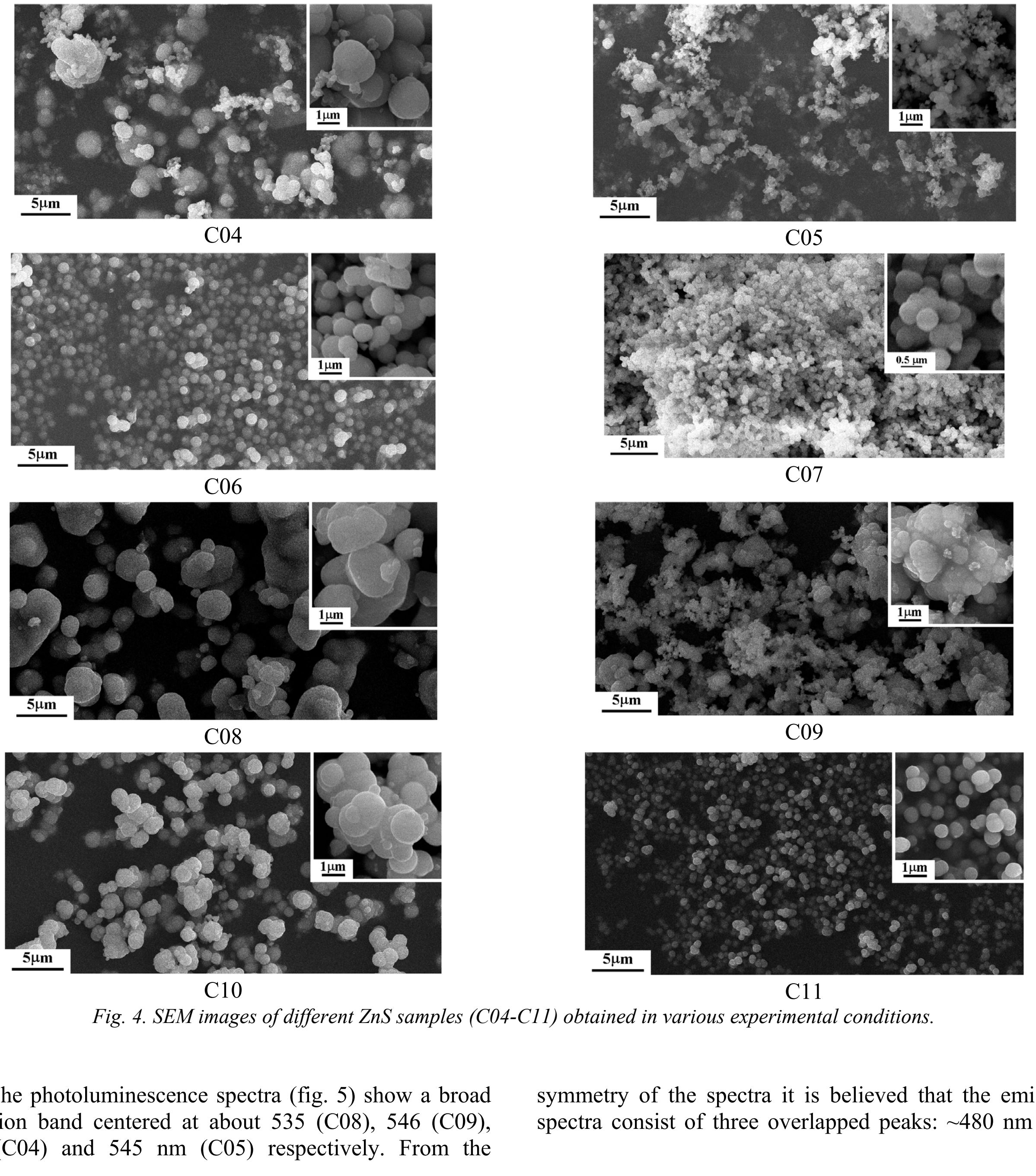


Fig. 3. FT-IR spectra of C04-C11 ZnS samples.

The SEM images of samples C04-C11 are shown in fig. 4. The samples C04 and C08, prepared from 0.5M solutions of zinc acetate and thioacetamide at pH 2, show a broad size distribution ranging from 80 to 3600 nm. The increase of the pH results in a more narrow size distribution as observed for the samples C05 and C09 (100 – 800 nm). The samples prepared in more diluted medium are much more homogenous having most of the particles size of about 500 nm (C06), 300 nm (C07).



C04 C05 C06 C07 C08 C09 C10 C11

Fig. 4. SEM images of different ZnS samples (C04-C11) obtained in various experimental conditions.

The photoluminescence spectra (fig. 5) show a broad emission band centered at about 535 (C08), 546 (C09), 544 (C04) and 545 nm (C05) respectively. From the symmetry of the spectra it is believed that the emission spectra consist of three overlapped peaks: ~480 nm selfactivated ZnS, ~505 nm oxygen impurities and ~545 nm other impurities.

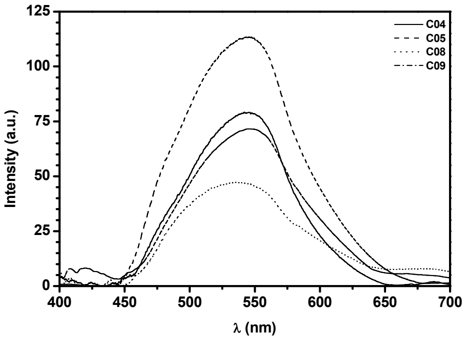


Fig. 5. The PL spectra of some ZnS powder samples obtained in various experimental conditions.

4. Conclusions

There is a strong dependence between experimental conditions and the morphology and size of the ZnS particles. The samples obtained using 0.1 M solutions of zinc acetate and thioacetamide show a narrow size distribution of spherical particles. Increasing the concentration of the reagents results in a broad distribution of size and morphology (spheres and platelets), whereas the increase of the pH results in smaller particles. Further experiments are in progress.

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