JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 5, May 2007, p. 1534 - 1539

The synthesis of luminescent nanoparticles from aqueous solutions

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The paper is an experimental study on obtaining method of nanocrystalline $Zn_xCd_{1-x}S$ from aqueous solution. The inorganic ternary compound is used as a pigment, phosphors and semiconductor material. We have investigated the dependence of $Zn_xCd_{1-x}S$ nanoparticles size and properties on composition, pH and concentration of the starting solution. The method consists in co-precipitation of $Zn_xCd_{1-x}S$ from $CdSO_4$/ $Cd(NO_3)_2$ and $ZnSO_4$/ $Zn(NO_3)_2$ solutions, by adding an exceeding amount of Na_2S at high pH of the solution. The precipitation reaction takes place in the presence of a chemical stabilizer as styrene-maleic anhydride or acrylic acid-maleic anhydride co-polymers. The stabilizer provides a colloidal state of the synthesized material and does not allow $Zn_xCd_{1-x}S$ nanoparticles to agglomerate. This ternary compound has a high conversion efficiency of the excitation energy into visible light, applied in photo and electroluminescent cells.

(Received November 14, 2006; accepted April 12, 2007)

Keywords: Luminescent nanoparticles, Zn-Cd-S, Energy conversion, Electroluminescent cell

1. Introduction

Ceramic films and coating are active fields of research and widely used areas of technology. The relatively high hardness and inertness of ceramic coatings make them interesting materials for protection of different substrates against corrosion, oxidation and wear resistance. The properties of ceramic films and coatings are applied in many electronic and optical devices. In the classic technologies, in order to improve the image quality and to remove the images formed by serigraphy, funds for cheaper methods have been allocated. Direct printing methods on plane surface were developed in different companies, yielding promising results.

The developing of the thermal technology of drops ejecting in laser and ink jet printers make possible to obtain a photographical quality and low cost of consumables. At present a cartridge made by thermal technology has 300-600 nozzles with 70 micrometers diameter. It is possible to eject drops of 8-10 picolitres, forming dots of 50-60 μm diameters. Nozzles density means 300-600 dpi resolution (dots per inch) which can be increased up to 1200 dpi. This technology uses CMY color system (cyan, magenta, yellow) which can reproduce high quality colored images. The use of the piezo method increases the image resolution up to 1440/720 dpi. The higher resolution, the smaller points should be formed on the substrate. Nowadays pigments for CMY system have particle size about 50 nm.

The synthesis of crystalline inorganic nanoparticles is very difficult because the composition and the particle size distribution must be controlled, simultaneously. The major problem which appears during the nanoparticles synthesis is the obtaining of the same size particles in every batch, taking into account that physical-chemical properties are dramatically modified when the particle dimension changes [1-3].

In this study we focused on crystalline pigments of zinc and/or cadmium sulphide [4-10] for which the modification of particle size distribution, colors and luminescence phenomena were studied.

In practice two principal ways are used to obtain [7] $Zn_xCd_{1-x}S$: methods by dried route and methods by wet route. As regards the chalcogenide matrix, it imposes an advanced purification in order to produce luminescence phenomena. Consequently, two synthesis methods have been selected. These methods lead to advanced reagents purification [14] before the chalcogenide matrix synthesis. The synthesis starts from zinc/cadmium salts, sodium thiosulphate and sodium sulphide.

When colloidal CdS is synthesized by "at drop" technique from $CdSO_4$ and Na_2S, efficient stabilizers can be used such as [1-3, 11-13]: styrene-maleic anhydride copolymer (1:1), acrylic acid-maleic anhydride (1:1), diarildimethil amonium-acrilamide chloride copolymer (1:1) etc. These ones are adsorbed on the surface of the colloidal particles blocking their increase.

2. Experiments

The precipitation of zinc and cadmium sulphides from sulphate solutions with sodium thiosulphate is a complicated synthesis method. One sulphate molecule (Me = Zn, Cd) can reacts with 1, 2, 3 or 4 thiosulphate molecules, depending on the reaction conditions [7].

$$MeSO_4 + Na_2S_2O_3 + H_2O \rightarrow MeS + Na_2SO_4 + H_2SO_4 \quad (1)$$

$$MeSO_4 + 2Na_2S_2O_3 \rightarrow MeS + 2Na_2SO_4 + SO_2 + S \quad (2)$$

$$MeSO_4 + 3Na_2S_2O_3 + 1/2H_2O + 1/2O_2 \rightarrow MeS + 3Na_2SO_4 + SO_2 + 2S \quad (3)$$

$$MeSO_4 + 4Na_2S_2O_3 \rightarrow MeS + 4Na_2SO_4 + 4S \quad (4)$$

On the other hand, secondary reactions appear and produce sulphur as by-product in $Zn_xCd_{1-x}S$ precipitate and decrease the reaction efficiency, depending on the reagents ratio and the reaction conditions [7].

In our experiments we used saturated $ZnSO_4$, $CdSO_4$ and $Na_2S_2O_3$ with 1/0, 2/1, 1/1, 1/2 and 0/1 Zn/Cd molar ratios, sulphate/thiosulphate molar ratios of 1/1, 1/2, 1/3 and 1/4, at room and boiling temperature. The precipitation rate at room temperature is too small in order to apply synthesis process at industrial scale. By increasing the solution temperature up to the boiling point, the precipitation rate significantly increases. Simultaneously, the reaction mechanism becomes complicated by increasing the weight of the secondary reactions and by forming of polithionates which contaminate the final product [7].

At the boiling point of the solution, the particle size of the precipitated sulphide increases. When zinc and cadmium nitrate solutions were used, we obtained smaller grain precipitates as compared to the grain size obtained from suphate solution as starting reagent. We obtained sulphides with average grain size between 1.1-2 μm by precipitation at the boiling point, for two hours, starting from sulphate solutions and 0.9-1.1 μm starting from nitrate solutions.

Zinc and cadmium sulphides precipitation, using sodium sulphide as reagent, represents a simple and rapid process which takes place at the room temperature. The average particle size is about 0.67 μm without any influence of Zn/Cd ratio.

$$MeSO_4 + Na_2S \rightarrow MeS + Na_2SO_4 \quad (5)$$

The decrease of the reagents concentration was experimented aiming at decrease the particle size of the final product. The previous experiments were repeated using 1M solutions of $ZnSO_4$, $Zn(NO_3)_2$, $CdSO_4$, $Cd(NO_3)_2$ and Na_2S. The anion effect was also investigated.

3. Results

Particles of 0.29 μm size were prepared at pH=7. It was observed that at low pH, precipitates with smaller particle size were obtained. The precipitation from nitrate solutions leads to smaller particle size as compared to the precipitation from sulphate solution (see Fig.1).

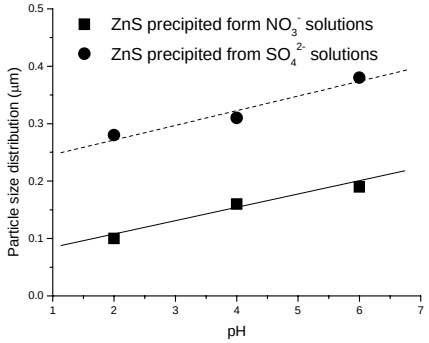


Fig. 1. pH and anion influence on the particle size distribution of $Zn_xCd_{1-x}S$ precipitate.

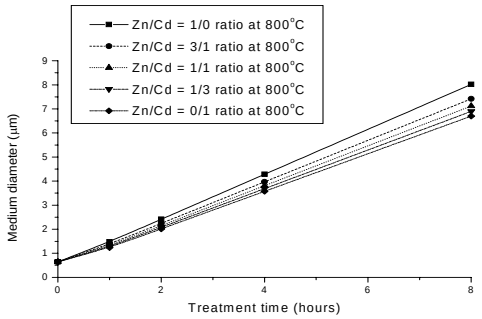


Fig. 2. The evolution of $Zn_xCd_{1-x}S$ (precipitated with sulphide) particle size distribution function of thermal treatment at 800 °C.

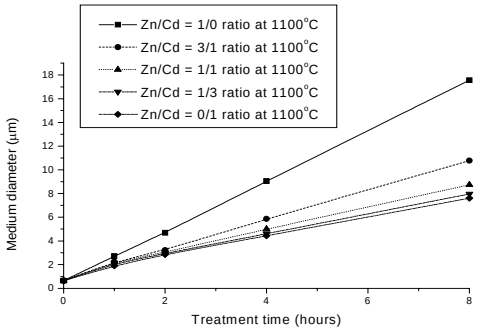


Fig. 3. The evolution of $Zn_xCd_{1-x}S$ (precipitated with sulphide) particle size distribution function of thermal treatment at 1100 °C.

The precipitated $Zn_xCd_{1-x}S$ powder was thermally treated at different temperatures in order to study the modification of the particle size distribution against the thermal treatment time.

One can observe (figs.2 and 3) that the evolution of the particle size is a linear function, depending on the time of thermal treatment and Zn/Cd ratio. Consequently, the heat treatment time for any temperature can be estimated in order to obtain a preset particle size distribution. The increase of

Zn content in the pigment implies an increase of the particle size of the heat treated final product.

The particle size distribution of the precipitated powders was investigated by Fritsch-Analisette 22/0.1-600 μm laser analyzer and by electronic microscopy. Transmission electronic microscopy (TEM) was performed with Philips CM 12 microscope having 2Å resolution. Scanning electronic microscopy (SEM) was performed with Hitachi S2600N. The fluorescence of the synthesized powders was investigated by FT-6500 Jasco spectrofluorimeter.

4. Discussion

$Zn_xCd_{1-x}S$ pigment was synthesized by precipitation experiments in 1/1 water-acetone environment and in 1/1/1 water-styrene-maleic anhydride environment. Initially, the precipitates are washed with unionized water and then with ethylic alcohol or acetone in order to stop the agglomeration and flocculation processes. The washed pigments are separated by sedimentation and dried in air at 80°C for 4 hours.

The grains dimensions increase during the thermal treatment and consequently, low heat temperatures and durations are recommended. The heat treatment time can be calculated using the presented graphics (figs.1 and 2) in order to obtain a desired crystalline structure with small size grains.

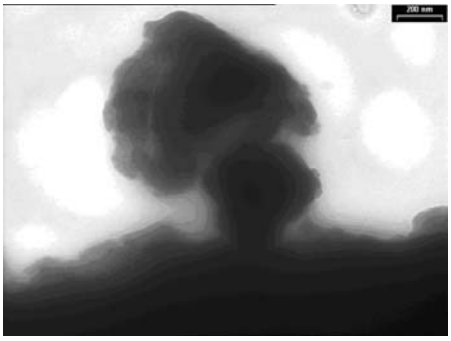


Fig. 4. TEMBF image of $Zn_xCd_{1-x}S$ sample, x=0; precipitated powder without heat treatment.

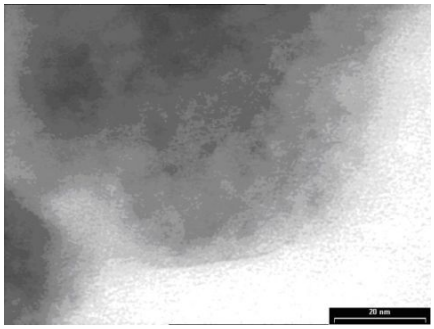


Fig. 5. TEM image (figure 4 detail).

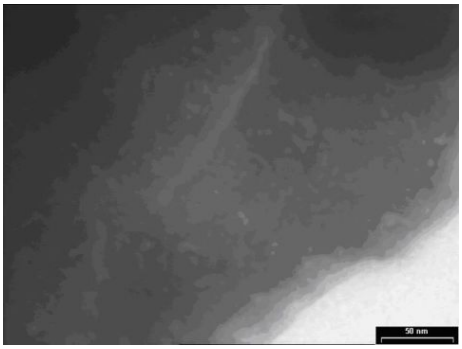


Fig. 6. TEMBF image (figure 4 detail).

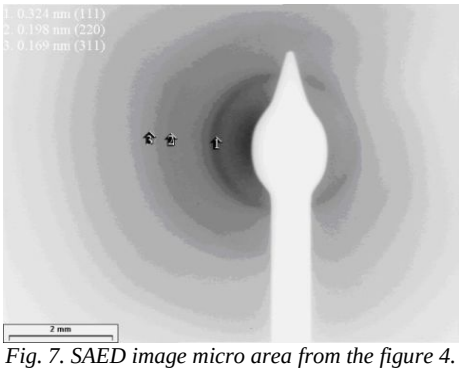


Fig. 7. SAED image micro area from the figure 4.

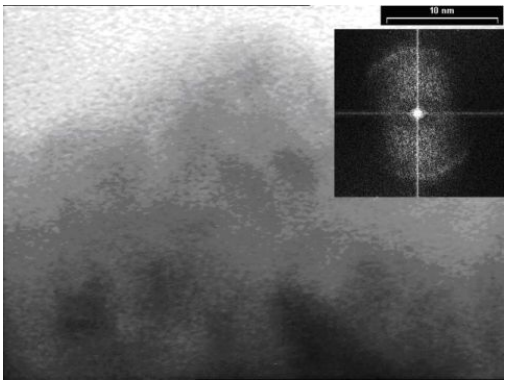


Fig. 8. HRTEM image and Fourier transform.

The image from the fig. 4 shows particle agglomerations up to tens nanometers. Details presented in the Figs. 5 and 6 show inhomogeneous particles groups of nanometer size. SAED image presented in the fig.7 shows diffraction diffuse rings which indicate a crystalline order on nanometer scale. The corresponding interlayer distances have small deviations from the displayed values on the image. These distances correspond to ZnS particles with cubic crystalline structure (cfc). HRTEM image from the fig.8 shows that dark crystalline clusters (about 5 nm) are dispersed in a thin film which seems to be an amorphous material. However, Fourier transform shows high level of local disorder.

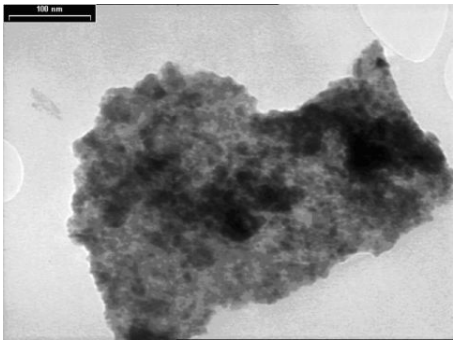


Fig. 9. HRTEM image of $Zn_xCd_{1-x}S$, x=1; precipitated powder without heat treatment.

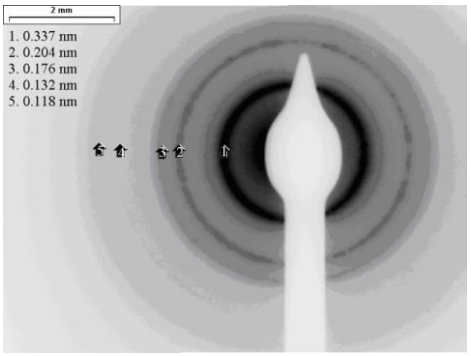


Fig. 10. SAED image for micro area from the Fig. 9.

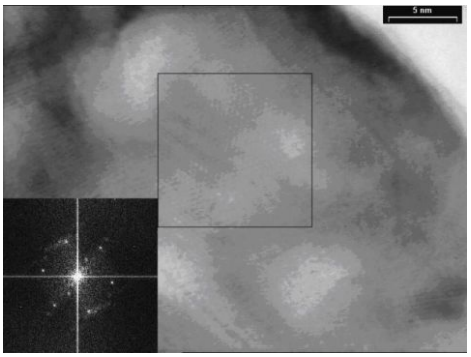
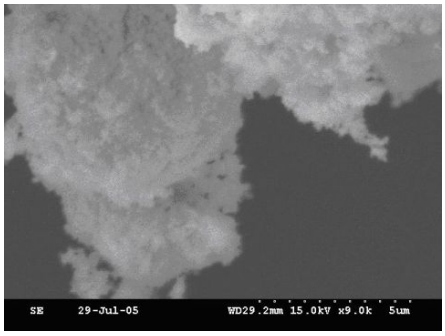
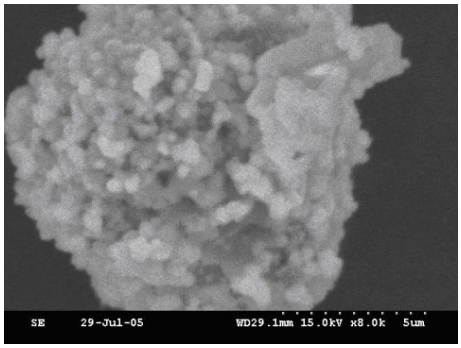


Fig. 11. HRTEM image and Fourier transform of image area marked as square.

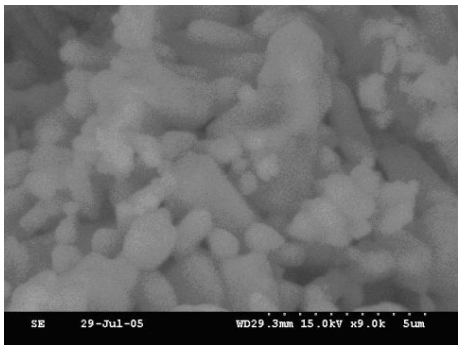
The image from the Fig. 9 exhibits an agglomeration of tens nanometers. Electron diffraction pattern from the Fig. 10 presents some pronounced diffraction rings which certifies the existence of a small size crystalline phase. The interplanar distances between the diffraction rings indicate the presence of CdS compound with cubic crystalline structure. The crystalline plane families have Miller index (111), (220), (311), (331), (422), in accordance with CdS compound. HRTEM images exhibit crystallites of 10 nm dimensions.



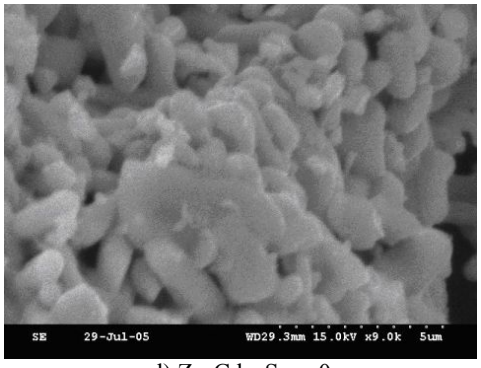
a) $Zn_xCd_{1-x}S$; x=1



b) $Zn_xCd_{1-x}S$; x=0.75



c) $Zn_xCd_{1-x}S$; x=0.25



d) $Zn_xCd_{1-x}S$; x=0

Fig. 12. Scanning electronic microscopy (SEM) images of $Zn_xCd_{1-x}S$ samples (a, b, c, d), treated at 800 ℃ for 0.5 hours.

SEM images point out that laser granulometry method detect only the agglomerated particles dimensions (Fig. 12).

The influence of (SO_4^{2-}, NO_3^- etc) anions and pH on the particle dimensions [5], must be taken into account in the case of Na_2S precipitation method.

The preparing of nanometer $Zn_xCd_{1-x}S$ particles is not so complicated, but it is very difficult to maintain the particle size distribution during the thermal treatment of the precipitated product.

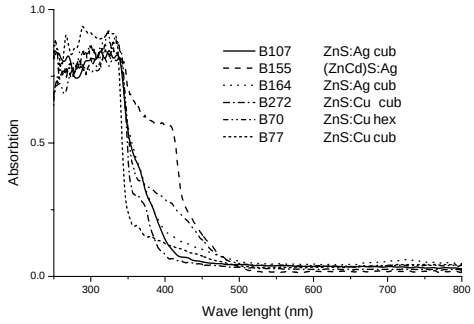


Fig.13. The optical absorption spectra of different synthesized luminescent powders.

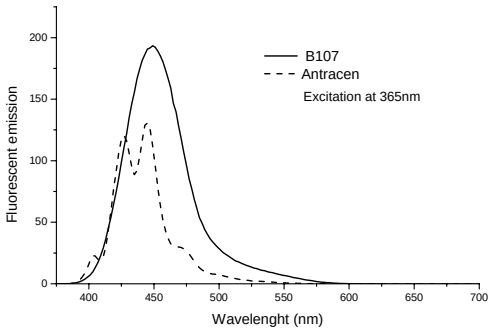


Fig. 14. The fluorescence emission of synthesized $Zn_xCd_{1-x}S$:Ag; x=1.

In the Fig. 13 we present the optical absorption spectra of different luminescent powders synthesized in our work. It can be seen that the absorption domain is ranged between 200 and 450 nm depending on the crystalline structure and the type of the dopant. Thus, these materials can be used as phosphors active in the natural light.

The fluorescence of the synthesized sample (B 107) was analyzed by comparison with a reference antracen sample (fig.14). It can be noticed a higher luminescence emission at about 450 nm and a conversion efficiency higher than the reference sample.

5. Conclusions

The agglomeration process of $Zn_xCd_{1-x}S$ particles can be controlled using different flocculation agents. This process is important for usual pigments synthesis but it is not desired in the case of the nanometer pigments synthesis. Thus, the synthesis process will be guided to avoid the particles agglomeration phenomena.

The experimental data shows that $Zn_xCd_{1-x}S$ crystals of 5-20 nm size are synthesized by precipitation from various starting solutions and the thermal treatment (800°C, for 30 min) increase the crystal size up to 50 nm.

The pigment grains dimension increase during the thermal treatment and for this reason the classical method of pigments obtaining is not suitable for the digital decoration pigments synthesis.

Based on this study, we proposed to use half-finished ceramic nanometer pigments into stabilized colloidal suspensions for digital decoration. Further on, the pigment was thermally treated together with the ceramic substrate. Thus, the grains growth during the thermal treatment does not disturb the digital decoration process.

The obtaining of $Zn_xCd_{1-x}S$ nanometer ternary compound into stabilized colloidal suspensions allows the achievement of luminescent coatings by deep-coating method. This ternary compound has a high conversion efficiency of the excitation energy into visible light, applied in photo and electroluminescent cells.

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