

# ***Microwave-assisted synthesis and the surface modification of 1-D dimensional ZnS:Mn nanocrystals for polymer applications***

Katarzyna Matras-Postolek \*, Svitlana Sovinska, Magdalena Wyrazik, Dariusz Bogdal

[matras@chemia.pk.edu.pl](mailto:matras@chemia.pk.edu.pl), Cracow University of Technology, Faculty of Chemical Engineering and Technology, Chair of Biotechnology and Physical Chemistry, Warszawska 24 St. 31-155 Krakow, Poland

## ***Abstract***

In recently years one-dimensional (1D) nanostructures (wires, rods, tubes) have received much attention because of two-dimensional quantum confinement effect and their potential application in optoelectronics devices, such as photovoltaic solar cells or light emitting diodes. In this context one of the most important is zinc sulfide (ZnS) nanocrystal materials. ZnS is a large band gap II-VI group compound, which has two structural polymorphs: cubic zinc blende (3.72 eV) or hexagonal wurtzite (3.77 eV). Typically one-dimensional ZnS nanocrystals are characterized by wurtzite structure. ZnS has been targeted as an efficient semiconductor host to dope different transition metal ions such as Mn or Cu. ZnS doped with Mn is a luminescent material well known for its photoluminescence, electroluminescence and cathodoluminescence. In this article we present the microwave solvothermal synthesis of 1D ZnS:Mn nanocrystalline and their surface modification for polymer application.

***Keywords:*** ZnS:Mn nanocrystals, one-dimensional, 1D, microwave irradiation, phase transfer

## ***1. Introduction***

Nowadays, the preparation of semiconductor nanocrystals (NCs) with different morphologies is very important part of materials sciences due to the possibility to explore the evolutions of materials properties with crystal size, shape and structure [1]. Dimensionality of nanocrystals plays a critical role in determining their optical and electrical properties. For instance, the sensor based on 1D ZnSe nanostructures has a better linear response of relative

humidity compare to their counterpart sensor based on 0D crystals. Moreover, the fabrication of hybrid polymer nanocomposite based on semiconductor NCs are interesting from a chemical and a technological point of view mainly because their potential application in optics and electronics. As the result, nanocomposite-based devices, such as light emitting diodes (LEDs), photodiodes, and photovoltaic solar cells have been fabricated and their properties were characterized [2-4].

From a scientific point of view ZnS:Mn nanocrystals dispersed in a polymeric matrix thus forming an inorganic/organic hybrid nanocomposite are of great current interest due to their unique optical and electronic properties. The main problem in the preparation of these materials is the process of phase separation promoted by the distinctly different chemical nature of both constitutive components of the composite. From practical point of view incorporation of inorganic nanoparticles NCs into polymer matrix without prior surface modification is in principle impossible. The ligand molecules on the surface of ZnS:Mn NCs can be replaced by others that can provide new functionality to the nanoparticles. Due to exchanging of the hydrophilic ligand with hydrophobic one inorganic NCs can be easily introduced into polymer or other organic system [5,6].

In this work we present the solvothermal synthesis of 1D ZnS:Mn nanorods and the ligand-exchange method on the surface for the polymer applications.

## ***2. Experimental***

### *2.1. Materials*

All chemicals were used without previous purification. Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), thiourea ( $\text{CS}(\text{NH}_2)_2$ ), manganese acetate tetrahydrate ( $(\text{CH}_3\text{OO})_2\text{Mn} \cdot 4\text{H}_2\text{O}$ ), ethylenediamine (EN), octadecylamine (ODA) and butylamine (BN) were purchased from Sigma-Aldrich.

### *2.2. Synthesis of ZnS:Mn NCs*

The preparation of 1D ZnS nanostructures generally requires high temperature, pressures and long-time synthesis (up to 24-36 h). Solvothermal reactions by conventional conditions, as described in the literature were performed within 8-24 hours [7]. In order to reduce the time of the reaction, the synthesis were performed under microwave irradiation. ZnS:Mn nanorods were synthesized in a microwave mineralizer Magnum II (Fig.1.A) at high pressure. The control of the reactor Magnum II was carried out by using software program

Magnum V2, which allows to control of the reaction conditions such as power, reaction temperature and pressure.

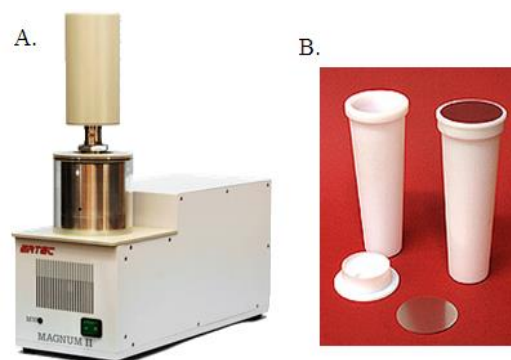


Fig. 1. Microwave mineralizer (A) and teflon containers (B)

In a typical ZnS:Mn NCs synthesis the appropriate amount of  $Zn(NO_3)_2 \cdot 6H_2O$ ,  $(CH_3OO)_2Mn \cdot 4H_2O$ ,  $CS(NH_2)_2$ , as well as appropriate volume of ethylenediamine or butylamine and water were applied to the container. The mixture was stirred for 10 min. Then the reaction mixture was transferred into a teflon container (Fig.1.B) and placed into the microwave reactor. After completion of the process, the samples were washed twice by ethanol and water and centrifuged. Finally, the powder was dried in a vacuum oven at  $60^\circ C$  for 4 h. The exact conditions of the synthesis and the quantities raw materials are shown below in Table 1.

**Table 1**

<b>Sample</b>	<b>Zn:S:Mn [n]:[n]:[n]</b>	<b>EN/BN</b>	<b>EN/BN:H<sub>2</sub>O [v]:[v]</b>	<b>Time [min]</b>	<b>Pressure [bar]</b>	<b>Temperature [°C]</b>
<b>ZnS-1</b>	1:3:0,07	BN	1:1	15	15-25	220-240
<b>ZnS-2</b>	1:3:0,07	BN	2:1	15	15-25	220-240
<b>ZnS-3</b>	1:3:0,07	BN	1:1	20	15-25	220-240
<b>ZnS-4</b>	1:3:0,07	EN	1:1	15	15-25	220-240
<b>ZnS-5</b>	1:3:0,07	EN	2:1	15	15-25	220-240
<b>ZnS-6</b>	1:3:0,07	EN	1:1	20	15-25	220-240

### 2.3. Ligand exchange

The phase transfer of the ZnS:Mn nanoparticles into organic solvent (hexane) using octadecylamine was carried out for a hydrophobic surface functionalization of NCs. The

aqueous dispersion of ZnS:Mn nanorods stabilized by ethylenediamine were mixed together with octadecylamine (ODA) and hexane at 70°C and constantly stirred for 1,5 hours. The molar ratio of ZnS:Mn nanorods and ODA was 1:5. After 12 hours the dispersion were washed twice with acetone and centrifuged. Next ZnS;Mn powder was dried in a vacuum oven at 60°C for 4 h.

#### 2.4. Characterization

Products were characterized by powder X-ray diffraction (Bruker D2 Phase). The morphologies of ZnS:Mn NCs were observed under SEM (Hitachi TM 3000, Denton Vacuum). FT-IR analysis and UV-VIS absorption of nanoparticles were recorded with a spectrophotometer Nicolet 6700 FT-IR and UV/VIS T80+ of PG Instruments Ltd Omc Envag company, respectively.

### 3. Discussion

Figure 2 shows the comparison of XRD results of the solvothermally fabricated of ZnS:Mn nanocrystals by using ethylenediamine and butylamine as a co-solvent and stabilizer.

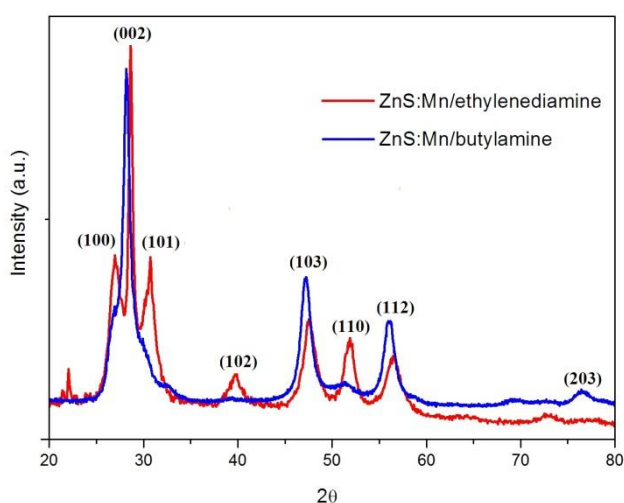


Fig. 2. XRD-patterns of ZnS:Mn NCs stabilized by ethylenediamine (red curve) and ZnS:Mn stabilized by butylamine (blue curve)

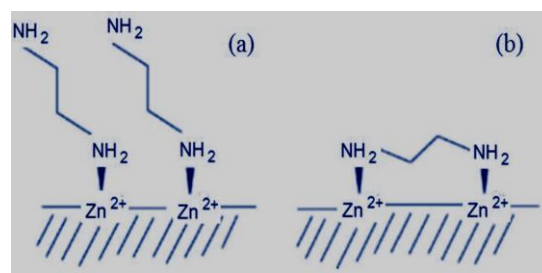


Fig. 3. Illustration of the possible coordination EN on the surface: (a) a monodentate ligand, (b) a multidentate ligand [8].

As we can see from Fig. 2, the ZnS:Mn synthesized by using varied co-solvents with the identical other conditions, have different crystal structures. XRD pattern of ZnS:Mn (sample ZnS-5) obtained at 220-240 °C with volume ratio of ethylenediamine to water 2:1 shows the presence of diffraction peaks corresponding to the crystal planes of typical hexagonal ZnS

structure. On the other hand, in case of ZnS:Mn synthesized with butylamine, XRD can be indexed to cubic zinc blende structure. The morphology of ZnS:Mn NPs stabilized by EN were simultaneously confirmed by SEM measurements (Fig. 4).

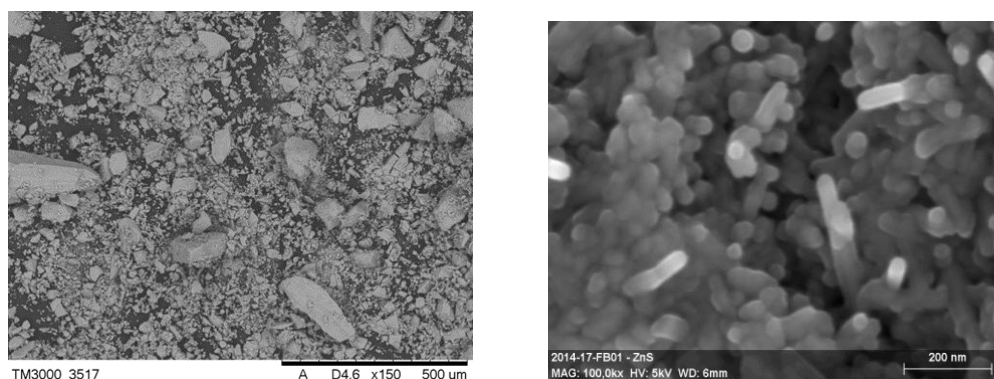


Fig. 4. SEM image of the ZnS:Mn NCs stabilized by EN

It became evident from the SEM images that obtained ZnS:Mn NCs are a 1D ZnS nanorods with the average diameter 40 -50 nm and uniform morphology. According to our results it was clear that 1D ZnS:Mn nanocrystals has been successfully prepared through a hydrothermal synthesis in microwave reactor in the presents of ethylenediamine, which provided high crystallinity of the samples. In our study, we have observed that in the solvothermal process the co-solvent plays the most crucial role in determining the size, shape and crystal structure of the final products. The use of ethylenediamine as nonaqueous reaction medium led to the formation of ZnS:Mn nanorods. However, in the case of using similar condition and parameters for the solvothermal process, but with butyloamine, we achieved ZnS:Mn crystals with a cubic zinc blende structure. Ethylenediamine molecules play an important role in the structure-directing nucleation process. Probably, ethylenediamine acts as template in a solvothermal route to direct the formation of nanorods through an accordion like folding process (Fig. 3) [8].

The phase transfer of ZnS:Mn nanorods into organic system were conducted exclusively on nanocrystals stabilized by EN. Figure 6 shows photographs of ZnS:Mn NCs stabilized by ethylenediamine in the aqueous and hexane phase before and after phase transfer. The dispersion were excited with UV lamp with light wavelength of 254 nm.

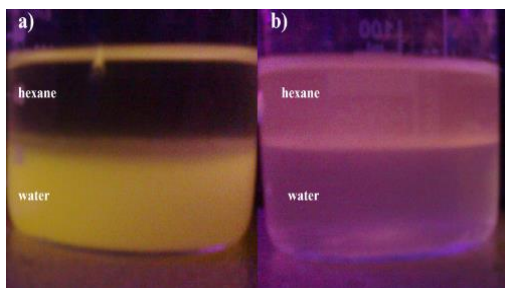


Fig. 5. Photographs of the phase transfer experiments using ZnS:Mn NCs: a) ZnS:Mn NCs stabilized by ethylenediamine before phase transfer, b) ZnS:Mn NCs after ligand-exchange with octadecylamine in hexane

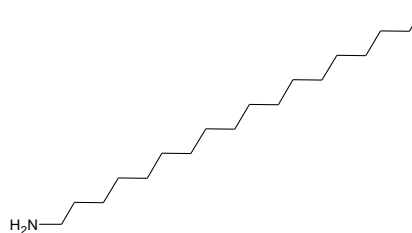


Fig. 6. The hydrophobic ligand molecule (octadecylamine)

From these pictures it is clear that ZnS:Mn nanorods were successfully transferred into the hexane phase after the ligand-exchange reaction with octadecylamine. Unfortunately, still some ZnS:Mn NCs were remained in water phase. This suggested, that phase transfer process should be carried out longer than 1.5 h. ZnS:Mn nanocrystals after ligand exchange process were characterized by XRD, UV-VIS and FT-IT spectroscopy. The UV-VIS absorption of the ZnS:Mn NCs before and after phase transfer is shown in Fig. 8. Maximum absorption of ZnS:Mn stabilized by long-chain stabilizers is at 285 nm. In the literature, the maximum absorption of ZnS:Mn NCs also occurs near 240-320 nm [10].

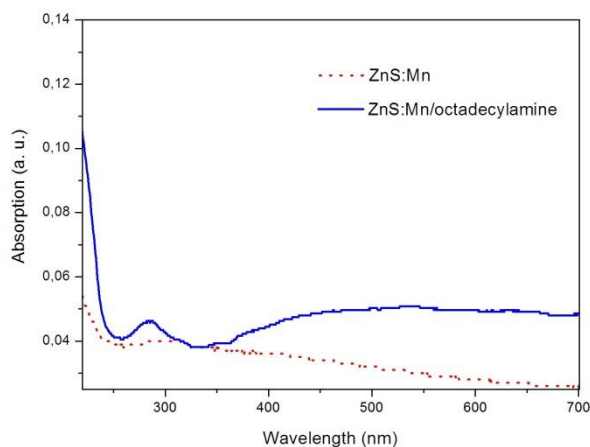


Fig. 7. UV/visible spectra of ZnS:Mn with different ligand molecules.

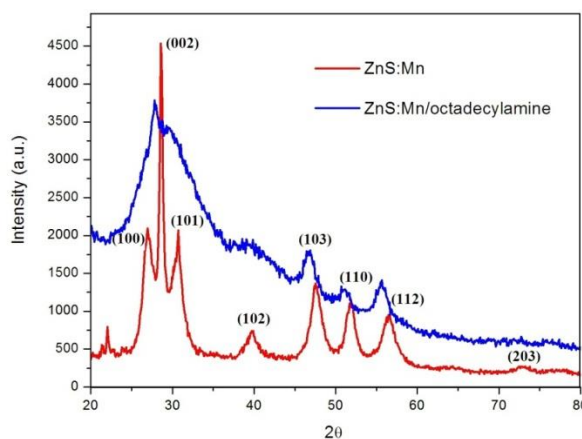


Fig. 8. XRD-patterns of ZnS:Mn NCs stabilized by ethylenediamine (red curve) and ZnS:Mn stabilized by octadecylamine (blue curve).

The XRD-patterns in the Fig. 8 shown comparison of XRD ZnS:Mn NCs before and after phase transfer process. As we can see from XRD results, the ZnS:Mn NCs stabilized by

octadecylamine has almost the same XRD patterns, indicating that the structure of nanocrystals does not change significantly. But this results need to be confirm also by SEM measurement.

In order to investigate the surface properties of the ZnS:Mn nanoparticles the FT-IR spectra were recorded (Fig. 9). The two sharp peaks at  $2918\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$  correspond to the stretching vibrations of N-H groups. Moreover,  $\text{NH}_2$  groups appear in the  $1582\text{ cm}^{-1}$  and  $1147\text{ cm}^{-1}$ . Stronger bands demonstrate the weaker interactions. The sharp peak at  $515\text{ cm}^{-1}$  correspond to the stretching vibrations of  $-\text{CH}_2-$  groups. CH groups appear in  $720\text{ cm}^{-1}$  and  $1467\text{ cm}^{-1}$ . Observed the two sharp peaks at  $1010\text{ cm}^{-1}$  and  $1717\text{ cm}^{-1}$ , which characterized stretching of  $-\text{C}-\text{C}-$  groups. All features of the FT-IR indicate that the octadecylamine successfully passivate the surface of the ZnS:Mn NCs.

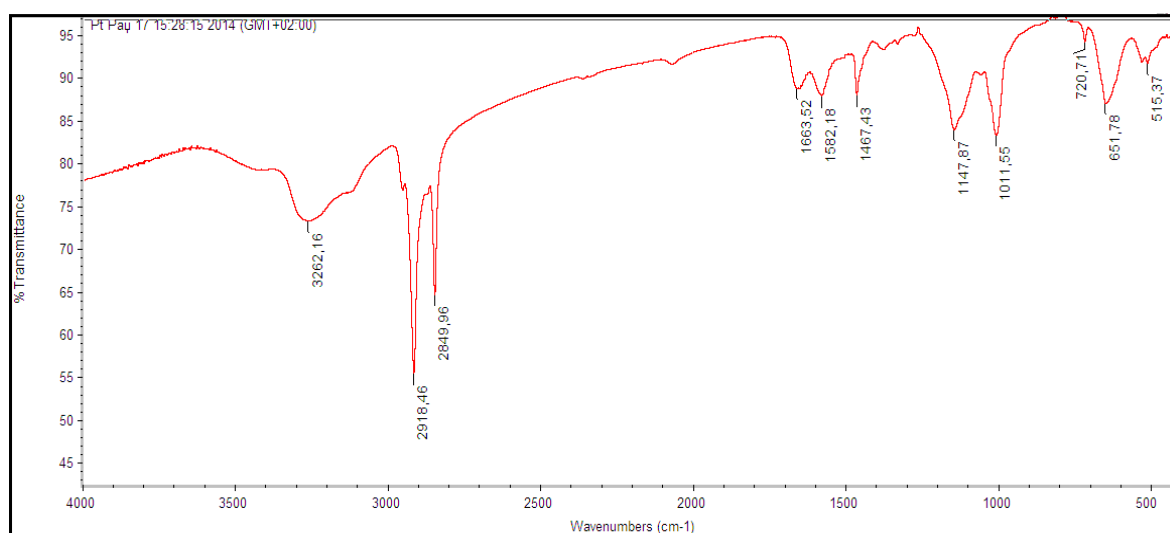


Fig. 9. FT-IR spectrum of ZnS:Mn NCs stabilized by octadecylamine

## 5. Conclusions

In conclusion, ZnS:Mn nanorods with wurtzite structure have been successfully synthesized by simple solvothermal route in relatively short time using ethylenediamine as co-solvent and stabilizer. The XRD and SEM measurements determined that obtained ZnS:Mn NCs are a 1D nanorods with the average diameter 40 -50 nm and uniform morphology nanocrystals. Functionalization with octadecylamine transfers the particles into organic phase allows for the integration into polymer system.

## 6. Acknowledgment

The work was financially supported by the Foundation for Polish Science (FNP, grant HOMING PLUS/2012-6/5), co-financed from the European Union's Regional Development Fund within the Operational Programme Innovative Economy.

## 7. Literature

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