

MICROWAVE-ASSISTED PREPARATION OF 1D NCs FOR PHOTODEGRADATION PROCESS OF ORGANIC DYES

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Abstract

One-dimensional (1D) zinc sulphide (ZnS) manganese-doped and un-doped nanocrystals (NCs) were successfully fabricated in only 15-20 minutes by solvothermal reactions under microwave irradiation using ethylenediamine and hydrazine, respectively, as a stabilizer. The obtained NCs were systematically characterized in terms of structural and optical properties using X-ray diffraction (XRD), transmission electron microscopy (TEM), diffuse reflectance UV-Vis spectroscopy (DR UV-Vis), Fourier-transform infrared spectroscopy (FT-IR) analysis. The photocatalytic activity of the ZnS and ZnS:Mn NCs was evaluated by the degradation of Rhodamine 6G (R6G). The results show that the Mn-doped NCs samples had higher coefficient of degradation of organic dyes under ultraviolet irradiation (UV).

Introduction

Since 1972, when Fujishima and Honda reported [1] the photocatalytic water splitting by titanium dioxide (TiO₂) electrode, inorganic semiconductors have been considered a promising material for photocatalytic degradation of pollutants due to photocatalytic reactions [2], [3]. Due to their good properties, the materials like TiO₂, ZnO, ternary oxides such a CuWO₄, ZnFe₂O₄, CaFe₂O₄, CuBi₂O₄ and CuNb₃O₈ have been investigated as the best materials for photocatalytic application [2]–[6]. In the last decade, researchers have focused on the photocatalytic materials based on the II-VI group nanocrystals (NCs), for example sulphides of the metals from those groups [2], [3], [5], [7], [8]. One of the most investigated sulphides for photocatalytic application is cadmium sulphide (CdS). Due to its band gap, which is about 2.4 eV, CdS is considered a promising material for optoelectronic applications and also for the previously mentioned photocatalytic application, therefore many forms of CdS were synthesized and investigated [8]–[11]. Unfortunately, due to rapid recombination of electrons and holes, bare CdS semiconductors have a low efficiency of hydrogen production. Additionally, such materials, due to their high activity to light irradiation, lead to the corrosion of the semiconductors [12]. To avoid these problems, the CdS semiconductors are combined with other semiconductors. In such a case, the photogenerated electrons from the CdS semiconductors are transferred to electron levels of noble metals or are delocalized and transferred between the conduction bands of the semiconductors [2], [8], [9], [13], [14].

The second most popular metal sulphides used for photocatalytic application is zinc sulphide (ZnS) [2]. It is a non-toxic semiconductor from the II-VI group with the band gap of about 3.7 eV. Because of these characteristics, ZnS nanoparticles are considered promising materials for optoelectronic, electronic, photocatalytic and biomedical applications. There is a lot of examples of the synthesis of different forms with different dimensions of the ZnS NCs [15].

One example is a ZnS nanoribbon film obtained by Wang et al. [16]. They used their ZnS NCs for degradation of X-3B dye. After 100 min, even about 89% of dye was degraded with one sample of the ZnS nanoribbons. The most popular shape of the ZnS NCs used in the photodegradation are quantum dots and nanospheres [17]–[20][21]–[29]. For example, Sharma et al. [18] synthesized ZnS nanoparticles capped and uncapped with thioglycerol by chemical precipitation method and degraded bromophenol blue, crystal violet and reactive red with the obtained materials. To improve the photocatalytic properties, the ZnS NCs are doped with some metals, for example iron [30] and more popular copper [31]–[34], nickel [34], [35] and manganese [34]. The addition of such compounds influences the applicable surface of the photocatalyst and also accelerates the migration rate of electron/hole to the surface of the nanoparticles. These two phenomena increase the photocatalytic properties of the ZnS NCs.

In this work, we used microwave irradiation to obtain one dimensional ZnS NCs and ZnS NC synthesis with ethylenediamine and hydrazine, respectively, as a stabilizer. Both materials were obtained with and without Mn-doping. Due to the use of the microwave irradiation, the reaction time was only 15–20 minutes. The obtained materials were used to degrade organic dye – Rhodamine B under UV light.

Materials

All chemicals were used without further purification. The zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (>99%), thiourea ($\text{CH}_4\text{N}_2\text{S}$) (99%), manganese acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) (>99%), ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$) (>99%), hydrazine monohydrate (N_2H_4) (98%) and Rhodamine B (RhB) (99%) were purchased from Sigma-Aldrich.

Synthesis of the ZnS and ZnS:Mn NCs with hydrazine

The synthesis of the ZnS:Mn NCs was carried out in a vessel in a microwave reactor Magnum II (ERTEC, Poland) with a maximum applied power of 600 W and frequency of 2.45 GHz. In a typical procedure, zinc nitrate hexahydrate (1.25 mmol), thiourea (2.5 mmol) and manganese (II) acetate tetrahydrate (0.125 mmol) were dissolved in a solution of hydrazine monohydrate (20 ml) and distilled water (10 ml) in the PTFE vessel. The mixture was stirred at room temperature for 10 min. After that, the PTFE vessel was placed into the reactor and heated in various temperatures at 6-8 bar for 20 min. Next, the reaction mixture was cooled to room temperature. After cooling, the obtained materials were centrifuged and washed with methanol three times. Then, the nanoparticles were dried at 40°C in an oven for 24 h. In a typical reaction procedure, about 0.12 g of dry sample was obtained. The ZnS NCs were obtained as above without manganese acetate.

Synthesis of the ZnS and ZnS:Mn NCs with ethylenediamine

The synthesis of the ZnS:Mn NCs was carried out in a PTFE vessel in a microwave reactor Magnum II (ERTEC, Poland) with a maximum applied power of 600 W and frequency of 2.45 GHz. In a typical procedure, zinc nitrate hexahydrate (4 mmol), thiourea (8 mmol) and manganese (II) acetate tetrahydrate (0.04 mmol) were dissolved in a solution of ethylenediamine (20 ml) and distilled water (10 ml) in a PTFE vessel. The mixture was stirred at room temperature for 10 min. After that, the PTFE vessel was placed into the reactor and heated in various temperatures for 30 min. Next, the reaction mixture was cooled to room temperature. After cooling, the obtained materials were centrifuged and washed with methanol (with or without ultrasonic bath) three times. Then, the nanoparticles were dried at 40°C in the oven for 24 h. The ZnS NCs were obtained as above without manganese acetate.

Characterization and measurements of the nanomaterials.

All materials were characterized by XRD, FT-IR, S/TEM, UV-Vis analyses. The surface of the NCs was characterized with FT-IR. The morphology of the nanostructures was examined with transmission electron microscopy (TEM). The measurements were performed on a FEI Tecnai Osiris S/TEM. The crystallographic structure of the samples was investigated with an X-ray diffraction (XRD) method using Bruker D8 Phaser Diffractometer with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The surface of the NCs was confirmed with a Nicolet 6700 FT-IR spectrometer. The absorbance measurements of the powders were recorded using a Shimadzu UV-2700 spectrophotometer with ISR-2600 Plus Integrating Sphere Attachment. The emission and excitation of ZnS and ZnS:Mn NCs were characterized with Spectrofluorometer Fluorolog-3 from Horiba company.

Photocatalytic investigation of the nanomaterials

The photocatalytic activities of the ZnS and ZnS:Mn NCs were tested by the decomposition of RhB in water solution under ultraviolet (254 nm) (UV) irradiation. The appropriate amount of ZnS (ZnS:Mn) was dispersed in 60 ml of a Rhodamine B solution (concentration 5 mg/L). The solutions of dye with nanoparticles were placed under UV illumination for four hours. About 2 ml of the solution was taken every 20 minutes and characterized with UVVis-NIR (200-1100 nm) spectrometer from StellarNet Incorporation. The concentration of RhB in solutions was determined by monitoring the changes in the maximal absorbance at approximately 550 nm. The photocatalytic activities were implemented with a 6 W UV Spectroline lamp (Model ENF-260C/FE, 50 Hz, 0.17 AMPS, 254 nm). The blank control test without the ZnS or ZnS:Mn NCs was also made.

Results and discussion

The ZnS and ZnSMn NCs were synthesized in a microwave assisted synthesis with ethylenediamine or hydrazine as a synthesis stabilizer. The detailed information about the synthesis and the calculated bandgap of the samples are presented in Table 1.

The obtained ZnS and ZnS:Mn NCs were characterized and analyzed with XRD, TEM, ATR-IR, DR UV-vis measurements. The crystal structure of ZnS and ZnS:Mn was characterized with an X-Ray Diffractions method. The results are presented on Figure 1. All samples have a wurtzite structure. Figure 1 a shows that the materials synthesized with a microwave assisted heating method have all characteristic peaks for the ZnS wurtzite structure and crystal planes of (100) (002) (101) (102) (103) and (103) from the ZnS wurtzite JCPDS 96-110-0045 are present. The addition of manganese, different temperature and type of heating have no influence on crystal structure of the obtained ZnS NCs.

Table 1. Detailed experimental parameters for the synthesis of ZnS and ZnS:Mn and their band gap energy.

Sample	Zn ²⁺ :S ²⁻ :Mn ²⁺ molar ratio	Temperature [°]	Pressure [bar]	Stabilizer	Bandgap [eV]
H170Mn	1:1:0.01	170	6-8	hydrazine	3.80
H170	1:1:0	170	6-8	hydrazine	3.78
H160Mn	1:1:0.01	160	6-8	hydrazine	3.64
H160	1:1:0	160	6-8	hydrazine	3.64
H170\1:2	1:2:0.01	170	6-8	hydrazine	3.56
EN170	1:2:0	170	6-8	ethylenediamine	3.41
EN170Mn0.01	1:2:0.01	170	6-8	ethylenediamine	2.75
EN180	1:2:0	180	7-9	ethylenediamine	3.3
EN180Mn0.01	1:2:0.01	180	7-9	ethylenediamine	2.97
EN160	1:2:0	160	6-8	ethylenediamine	3.3
EN160Mn0.01	1:2:0.01	160	6-8	ethylenediamine	2.44
EN170Mn0.001	1:2:0.001	170	6-8	ethylenediamine	2.93
EN170Mn0.005	1:2:0.005	170	6-8	ethylenediamine	2.86
EN170Mn0.02	1:2:0.02	170	6-8	ethylenediamine	2.44
EN170Mn0.1	1:2:0.1	170	6-8	ethylenediamine	3.33

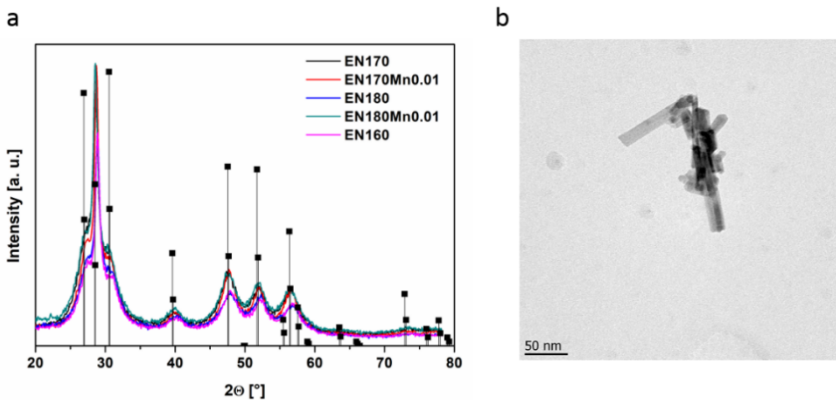


Fig. 1. XRD diffraction patterns of ZnS and ZnS:Mn of the samples obtained with ethylenediamine (a) compared to the ZnS wurtzite JCPDS 96-110-0045 and (B) TEM images.

TEM images of the ZnS and ZnS:Mn NCs were also taken. As we can see on Figure 1b, the ZnS:Mn NCs obtained with ethylenediamine in the microwaved assisted reaction at 170°C have one dimensional structures. As synthesized, the nanorods had a diameter of about 10 nm and the length of about 200 nm. Similarly, the ZnS and ZnS:Mn NCs synthesized with hydrazine have a one dimensional morphology and a wurtzite structure.

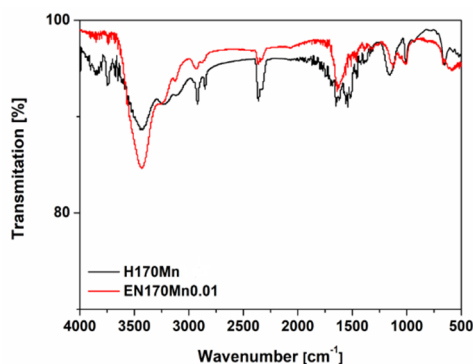


Fig. 2. FT-IR patterns of H170Mn0.01 and EN170Mn0.01

To investigate the surface of the ZnS and ZnS:Mn NCs, the FT-IR measurements were performed. Figure 2 shows that the FT-IR patterns of the ZnS:Mn NCs synthesized with ethylenediamine have a very similar FT-IR pattern to the ZnS:Mn NCs from the synthesis with hydrazine, indicating the presence of the stabilizer agent on the surface of the NCs. For $\nu = 2841 \text{ cm}^{-1}$ and 2924 cm^{-1} , the peaks are visible which correspond to the asymmetrical stretching vibrations of the methylene group. The peaks for scissoring and stretching vibrations of the amine group are observed at 1638 and 3443 cm^{-1} respectively. Peak at $\nu = 1142 \text{ cm}^{-1}$ correspond to stretching of the C-N bond and the peak visible at 670 cm^{-1} is from the C-H bond.

The photocatalytic activities of the ZnS and ZnS:Mn NCs synthesized with different capping agents were determined in the degradation of Rhodamine B under UV light. Figure 3 a and b demonstrates the changes of the concentration of Rhodamine B with the presence of the ZnS:Mn NCs stabilized with ethylenediamine (a) and hydrazine (b).

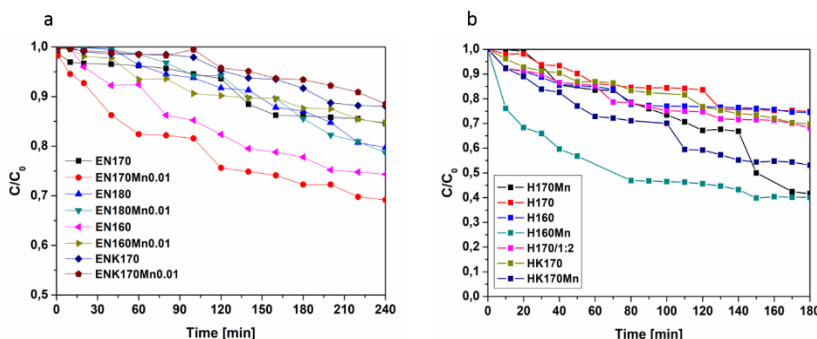


Fig. 3. Catalytic degradation of Rhodamine B with the ZnS and ZnS:Mn NCs from the synthesis with ethylenediamine (a) and hydrazine (b).

The curves present the dependence of the dye's normalized UV absorption at the maximum of absorbance versus illumination time. It can be seen that the degradation ratios for the microwave-assisted synthesis stabilized with hydrazine are bigger than the ZnS:Mn NCs stabilized with ethylenediamine. About 55% of the dye was degraded after 3 h, when the nanoparticles from the microwave-assisted synthesis with hydrazine were used. Also the addition of manganese improves the photocatalytic properties in both cases.

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