STUDY OF PHOTOCATALYTIC ACTIVITY OF $Zn_xCd_{1-x}S$ QUANTUM DOTS IN DEPENDENCE ON THEIR COMPOSITION USING METHYLENE BLUE

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Abstract

$Zn_xCd_{1-x}S$ quantum dots (QDs) with the different composition *x* were prepared by precipitation of zinc and cadmium acetates with sodium sulphide in the presence of cetyltrimethylammonium bromide (CTAB) used for stabilization of their aqueous colloid dispersions. Transition energies of these quantum dots were determined from the UV-VIS spectra of QDs colloid dispersions and consequently used for calculation of the QDs sizes according to the Schrödinger equation. The $Zn_xCd_{1-x}S$ QDs size was found to be significantly influenced by their composition: the QDs size decreased with the increasing Zn content.

The photocatalytic activity of the $Zn_xCd_{1-x}S$ QDs was studied using the methylene blue decomposition under UV irradiation. Different photocatalytic activity depending on the composition *x* was observed and explained. The maximal photocatalytic activity was achieved for $x = 0.6$ when the energy of the irradiation photons was still sufficient to generate electron-hole pairs in majority of the QDs and at the same time the photocatalytic surface area was maximal.

Keywords: Quantum dots, $Zn_xCd_{1-x}S$, photocatalysis

1. NTRODUCTION

In past decades photocatalytic activity of different semiconductor nanoparticles (quantum dots) has been intensively studied. The main advantage of quantum dots is their large surface area which increases significantly their photocatalytic efficiency. However, quantum size effect, for QDs smaller than the exciton Bohr radius of given semiconductor, may also significantly influence their photocatalytic activity.

$Zn_xCd_{1-x}S$ is for a full range of compositions a direct band gap semiconductor with the gap energy between 2.4 eV (CdS) and 3.7 eV (ZnS) at 300 K [1-3]. Similarly to both binary semiconductors, ZnS and CdS, the ternary $Zn_xCd_{1-x}S$ is also known by their photocatalytic properties (see below). The advantage for $Zn_xCd_{1-x}S$ photocatalytic applications is the bigger exciton radius between 2.5 nm (ZnS) and 3 nm (CdS) in comparison with other known photocatalytic materials like TiO_2 or ZnO with the exciton Bohr radii close to 2 nm. This allows employing the quantum size effect to adjust required electron or hole energy for photocatalytic reactions in case that the QD radius is smaller than 3 nm. Another advantage is also decreased probability of radiative recombination of carriers for QDs with radius lower than 3 nm and composition closer to CdS [4] which can increase photocatalytic efficiency of such QDs. A disadvantage of this material is that only electrons can enter the photocatalytic reaction while holes do not have sufficient energy for oxidation of OH^- anions in aqueous solutions.

Synthesis and applications of $Zn_xCd_{1-x}S$ quantum dots have been already described. For instance, $Zn_xCd_{1-x}S$ composites with graphene and their hydrogen production performance were referred by Li and co-workers [5]. Mesoporous $Zn_xCd_{1-x}S$ nanoparticles in double hydroxides matrix were prepared and tested for the photocatalytic decomposition of methylene blue [6,7]. The highest photocatalytic activity was found for *x* =

0.20. In addition, $Zn_xCd_{1-x}S$ nanorods were prepared by shape-controlled synthesis from mixtures of zinc and cadmium ethylxanthates [8]. Laser ablation of CdS with thermal evaporation of ZnS was used for the preparation of nanoribbons [9]. $Zn_xCd_{1-x}S$ nanocrystals were synthesized in coordinating high boiling-point long-chain amines by reactions of metal salts and elemental sulphur [10]. Zinzag $Zn_xCd_{1-x}S$ nanowires were prepared by a one-step metal-organic chemical vapour deposition [11]. Other methods of synthesis and applications of $Zn_xCd_{1-x}S$ quantum dots have been reported in a comprehensive overview by Fang et al. [12].

In our previous works we tested ZnS and CdS nanoparticles for the photocatalytic reduction of carbon dioxide [13-15], for the photocatalytic decomposition of phenol [16] and combination of both binary semiconductors in core/shell CdS/ZnS nanostructures was studied by photocatalytic decomposition of methylene blue [17]. The aim of this work was to study the photocatalytic activity of $Zn_xCd_{1-x}S$ QDs depending on their composition *x*. For this purpose, the photocatalytic decomposition of methylene blue in the QDs aqueous dispersions under UV irradiation was investigated. $Zn_xCd_{1-x}S$ QDs were simply prepared by direct precipitation of mixtures of zinc and cadmium acetates with sodium sulphide in aqueous solutions of CTAB used for the stabilisation of resulting colloid dispersions against coagulation.

2. EXPERIMENTAL

2.1 Materials and chemicals

All solvents and chemical used in this work were of analytical reagent grade: zinc acetate, cadmium acetate, sodium sulphide (all from Lachema, Czech Republic), cetyltrimethylammonium bromide (Sigma-Aldrich, USA). Water deionized by reverse osmosis (Aqua Osmotic, Czech Republic) was used for preparation of all solutions. Montmorillonite was purchased from the Source Clays Repository of the Clay Mineral Society (West Lafayette, USA).

2.2 Preparation of $Zn_xCd_{1-x}S$ quantum dots

All QDs were synthesized by precipitation reactions in mixtures of zinc and cadmium ions of different composition *x* with sulphide ions in the presence of CTAB. The concentration of CTAB was kept at about 4 $mmol^{-1}$ to form micelles and the molar ratios Zn(Cd) : S : CTAB was set at 1 : 1.5 : 2 [14].

2.3 UV-VIS and photoluminescence spectroscopy

UV-VIS absorption spectra of ZnS, CdS and $Zn_xCd_{1-x}S$ dispersions were measured in 1 cm quartz cuvettes by a UV-VIS spectrometer Lambda 25 (Perkin Elmer, USA) with the wavelength range of 200-800 nm.

2.4 X-ray powder diffraction analysis

X-ray powder diffraction patterns were recorded under CoKα irradiation (λ=0.1789 nm) using the Bruker D8 Advance diffractometer (Bruker AXS) equipped with a fast position sensitive detector VÅNTEC 1. Measurements were carried out in the reflection mode, powder samples were pressed in a rotational holder. Phase composition was evaluated using database PDF 2 Release 2004 (International Centre for Diffraction Data).

2.5 Photocatalytic decomposition of methylene blue

The phototcatalytic activity of colloidal dispersion of the ZnxCd1-xS QDs was evaluated based on the degradation of methylene blue in aqueous solutions under UV irradiation with the maximum emission wavelength at 365 nm (3.4 eV) (Hg lamp HSC-1L Pen-Ray, UVP, Germany) in a stirred batch reactor opened to the air. In a typical experiment the colloidal dispersion of ZnxCd1-xS QDs was added into the aqueous solution of MB; a total volume of the dispersions was 100 ml. The initial concentrations of MB and $Zn_xCd_{1-x}S$ were set at 8 x 10^{-3} $mmol \cdot l^{-1}$ and 2 $mmol \cdot l^{-1}$, respectively. Before the photocatalytic experiments

the MB solution was stirred in contact with the QDs for 10 minutes in the dark to reach the adsorption equilibrium and provide good homogenization of the dispersion. The temperature in the reactor was kept at 18 C in a thermostat.

3. THEORETICAL CALCULATIONS

The calculations of QD energy levels performed in our work were based on a spherical effective mass approximation. In the case of infinite potential barriers the energy of particle on *n-th* quantum level could be expressed by following expression:

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mR^2} \quad (1)$$

However, the more precise calculation supposes the presence of finite barriers with electrons and holes penetrating partly into the barrier region. In our case, the $Zn_xCd_{1-x}S$ QD represents the potential well region and water surrounding the QDs represents the barrier. The particle in a quantum potential well was described by the Schrödinger equation. Detailed explanation of the method used for calculation of quantum states energy in $Zn_xCd_{1-x}S$ QD can be found in [17].

4. RESULTS AND DISCUSSION

4.1 Characterization of QDs

The CdS, ZnS and $Zn_xCd_{1-x}S$ nanoparticles were prepared by precipitation reactions of zinc and/or cadmium ions with sulphide ions in the presence of stabilizing CTAB. For characterization by X-powder ray diffraction they were deposited on a clay mineral montmorillonite. X-ray diffraction patterns showed that prepared QDs were of hexagonal structures with the strongest (101) peak for zinc cadmium sulphide at 34.3°of 2 theta (PDF number: 00-04901302).

The UV-VIS absorption spectra of the resulting dispersions were recorded immediately after the precipitation. The typical UV-VIS absorption spectra of CdS, ZnS and $Zn_xCd_{1-x}S$ nanoparticles are shown in Figure 1. The measured UV-VIS spectra of the prepared QDs were used for evaluation of the gap energy by the Tauc equation, which involves plotting *(εhv)1/p* against *(hv)* shown in e.g. [13]

$$\varepsilon h\nu = C(h\nu - E_t)^p \quad (2)$$

where ε is the molar extinction coefficient, which can be obtained from the Lambert-Beer law, $h\nu$ is the energy of incident photons, C is a constant, E_t is the transition energy of the material and the parameter p depends on the type of transition. For direct semiconductors like ZnS and CdS p = 1/2.

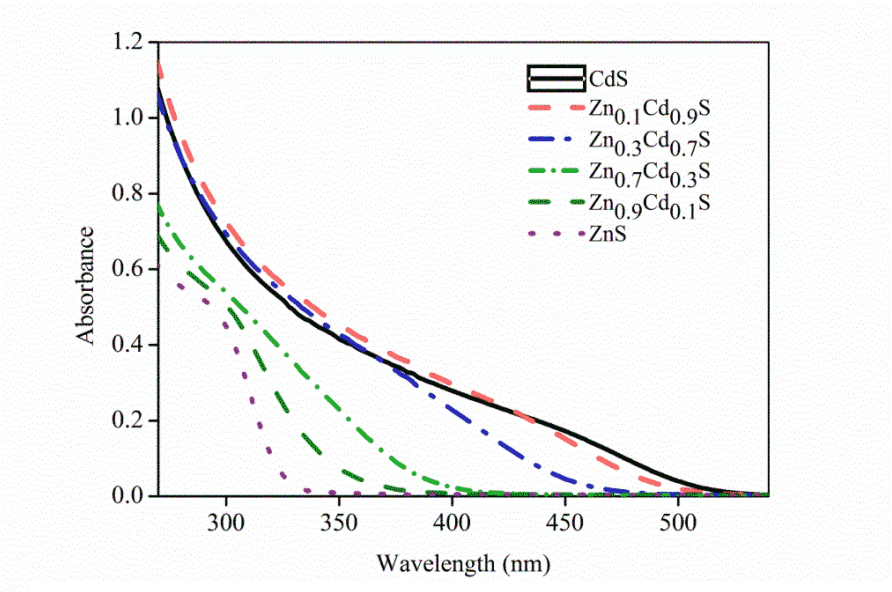

Fig. 1 UV-VIS absorption spectra of ZnS, CdS and $Zn_xCd_{1-x}S$ colloid dispersions

4.2 Photocatalytic decomposition of methylene blue

Photocatalytic efficiency of CdS, ZnS and $Zn_xCd_{1-x}S$ QDs was investigated using the photodecomposition of methylene blue. The decomposition reaction rate *r* of MB can be described by the Langmuir-Hinshelwood equation [17] as follows

$$r = k_{pp} K_{MB} c_{MB} = k_{obs} c_{MB} \quad (3)$$

where k_{app} is an apparent kinetic parameter depending on irradiation intensity, mass and nature of the solid phase (catalyst), k_{obs} is the observed kinetic constant, K_{MB} and c_{MB} are the adsorption constant and concentration of remaining MB, respectively. The reaction rate constant k_{obs} was calculated by fitting measured data by the integrated rate equation of the first order kinetics ($ln\ c_0/c = k_{obs}t$, where c_0 and c are the concentrations of MB at time $t = t$ and $t = 0$, respectively). The same photocatalytic experiments were performed with CdS and ZnS nanoparticles for comparison and also without any nanoparticles to observe the MB photolysis, which was found to be negligible.

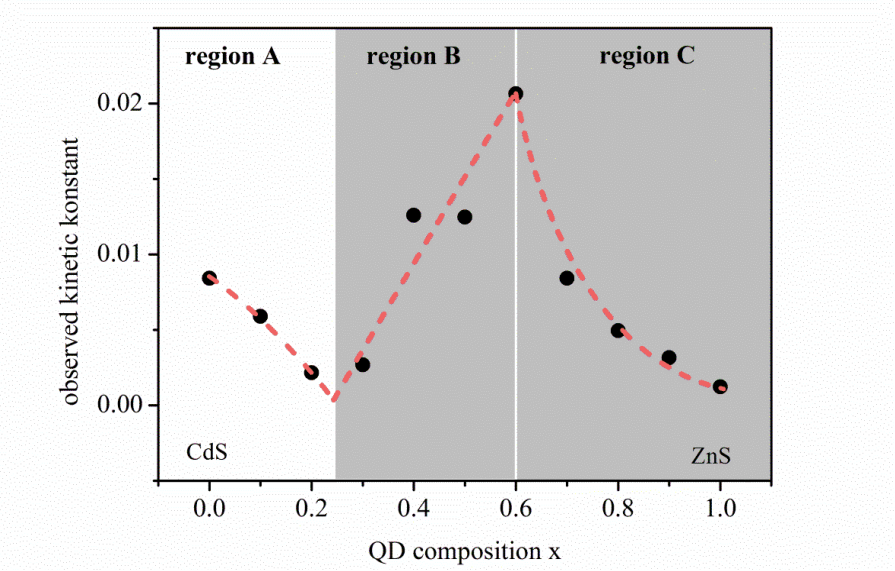

Fig. 2 Kinetic constants of photocatalytic decomposition of MB in aqueous dispersions of $Zn_xCd_{1-x}S$ QDs

The evaluated kinetic constants of the photocatalytic decompositions are shown in Figure 2. It was expected that the increasing Zn content in $Zn_xCd_{1-x}S$ QDs would increase their photocatalytic activity due to the increased energy of electrons. However, three distinct regions with different dependence of photocatalytic activity on the QDs composition were observed. In the region A for $x \leq 0.3$ the photocatalytic efficiency decreased with the increasing Zn content. An increase of photocatalytic efficiency was observed in the region B reaching its maximum for $x = 0.6$ and then decreased continually with the increasing content of Zn in the region C.

In order to explain this behaviour the quantum dots radii were derived from the measurements of transition energies determined and summarized in Table 1. This transition energy is equal to the transition energy between the ground and (1st) electron and hole levels E_{t1}. The calculated $Zn_xCd_{1-x}S$ QDs radii were found to decrease with the increasing Zn content.

Table 1 Measured and calculated parameters of $Zn_xCd_{1-x}S$ QDs

$Zn_xCd_{1-x}S$ composition x	Transition energy (eV)	E_g (bulk) (eV)	QD radius (nm)	Kinetic constant (s^{-1})
0	2.583	2.4	2.71	0.00843
0.1	2.707	2.53	2.52	0.00590
0.2	2.818	2.66	2.46	0.00216
0.3	2.945	2.79	2.29	0.00268
0.4	3.155	2.92	1.76	0.01260
0.5	3.238	3.05	1.84	0.01248
0.6	3.435	3.18	1.53	0.02066
0.7	3.594	3.31	1.29	0.00843
0.8	3.735	3.44	1.30	0.00495
0.9	3.792	3.57	1.40	0.00317
1.0	3.924	3.7	1.34	0.00124

CONCLUSION

A set of 11 colloid solutions of the $Zn_xCd_{1-x}S$ QDs were prepared by the precipitation method. From the measurement of transition energies between the first electron and hole quantum levels we found that the QD size was significantly influenced by the $Zn_xCd_{1-x}S$ composition: the QDs size decreased with the increasing Zn content.

The photocatalytic activity of $Zn_xCd_{1-x}S$ QDs was not simply increasing with the increasing Zn content as was expected. The maximal photocatalytic decomposition of MB was observed for x = 0.6 when the irradiation with the photon energy of 3.4 eV (365 nm) was used for photocatalytic experiments. From comparison of the calculated transition energies in the $Zn_xCd_{1-x}S$ QDs with the kinetic constants we obtained the following explanation of the QDs photocatalytic activity.

For QDs with the low Zn content and the radii of above 2.5 nm for x = 0 – 0.2 (region A) the photons with the excitation energy of 3.4 eV had sufficient energy to generate electron-hole pairs in two quantum states, ground and first excited quantum states, but the number of the QDs in which both quantum states can be excited by incident light was decreasing with increasing x. In the region B for x = 0.2 – 0.6 with radii in the range between 1.7 nm and 2.5 nm the photon energy could be absorbed in the QDs but was sufficient only for electron-hole generation in ground quantum state. For the QDs in this composition range the photocatalytic efficiency was increasing with the increasing Zn content because the QDs size was decreasing, which increased the photocatalytic surface area and also penetration of electrons from the QDs into the solution. The maximal photocatalytic efficiency was reached for x = 0.6. Above this value of the QDs composition (region C) the transition energy became higher than energy of exciting photons. Photon energy was insufficient to generate electron-hole pair in majority of the QDs.

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