



Precipitation, stabilization and molecular modeling of ZnS nanoparticles in the presence of cetyltrimethylammonium bromide

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ABSTRACT

ZnS nanoparticles were precipitated in aqueous dispersions of cationic surfactant cetyltrimethylammonium bromide (CTAB). The sphere radii of ZnS nanoparticles calculated by using band-gap energies steeply decreased from 4.5 nm to 2.2 nm within CTAB concentrations of 0.4–1.5 mmol L⁻¹. Above the concentration of 1.5 mmol L⁻¹, the radii were stabilized at $R = 2.0$ nm and increased up to $R = 2.5$ nm after 24 h. The hydrodynamic diameters of ZnS-CTAB structures observed by the dynamic light scattering (DLS) method ranged from 130 nm to 23 nm depending on CTAB concentrations of 0.5–1.5 mmol L⁻¹. The complex structures were observed by scanning electron microscopy (SEM). At the higher CTAB concentrations, ZnS nanoparticles were surrounded by CTA⁺ bilayers forming positively charged micelles with the diameter of 10 nm. The positive zeta-potentials of the micelles and their agglomerates were from 16 mV to 33 mV.

Wurtzite and sphalerite nanoparticles with $R = 2.0$ nm and 2.5 nm covered by CTA⁺ were modeled with and without water. Calculated sublimation energies confirmed that a bilayer arrangement of CTA⁺ on the ZnS nanoparticles was preferred to a monolayer.

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1. Introduction

Semiconductors, such as metal oxides or metal sulfides, have specific physico-chemical properties, which make them interesting for fabrication of photosensitive materials [1]. By absorption of photons with energy equal to or higher than their band-gap energy, electrons are excited from valence to conduction bands and positive holes are generated. These types of semiconductors have been widely applied in photocatalysis and also in photonics, optoelectronics, etc. [2]. Nanosized semiconductors have large specific surface area that results in their high chemical reactivity. Unfortunately, freshly prepared nanoparticles tend to agglomerate and, therefore, must be stabilized by, for example, various polymers and surfactants [2].

Zinc sulfide is a semiconductor with wide direct band-gap energy of about 3.7 eV. It is a very good photocatalyst due to the rapid generation of electron–hole pairs by photoexcitation and highly negative reduction potentials of excited electrons. ZnS nanoparticles have been synthesized by precipitation of zinc ions with sulfide forming sphalerite (solubility product $K_s = 1.6 \times 10^{-24}$ at 25 °C) and wurtzite ($K_s = 2.5 \times 10^{-22}$ at 25 °C). Cationic surfactants like cetyltrimethylammonium bromide [3–6], sodium bis(2-ethyl-

hexyl) sulphosuccinate [7,8], L-cysteine and mercaptoethanol [9], hexamethylenetetramine [10] and other stabilizers were used to prevent the particles agglomeration keeping their size in the nanorange.

Some processes occurring in the systems of nanoparticles cannot be directly investigated in the experiment. Therefore, complementary methods such as molecular modeling can be used. For example, precipitation of ZnS nanoparticles and their structures were modeled in several studies [11–18].

In our previous study, we dealt with the preparation of ZnS nanoparticles in the presence of CTAB and montmorillonite [19]. We observed a high catalytic activity of ZnS nanoparticles for reduction of carbon dioxide. Since the reactivity of nanoparticles strongly depends on their size, it is very useful to develop some procedures for nanoparticles preparation with demanded size. Therefore, the main aim of this work was to investigate an influence of the stabilizing surfactant CTAB on ZnS nanoparticles growth in aqueous dispersions. Unlike other authors, who precipitated ZnS nanoparticles in the micellar dispersions of CTAB, we systematically studied the nanoparticles size in dependence on CTAB concentrations within the interval from 0.1 mmol L⁻¹ to 5 mmol L⁻¹. In addition, the research was also conducted to understand the stabilizing mechanisms of CTAB by molecular modeling methods. Although interactions between CTAB and various nanoparticles were modeled by several authors [20–24], interactions

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with ZnS nanoparticles and CTAB have not been simulated yet. Water molecules were considered in our models to simulate real colloidal dispersions.

2. Experimental

2.1. Chemicals

The used chemicals were of analytical reagent grade: Zinc acetate, sodium sulfide, cetyltrimethylammonium bromide (all from Lachema, Czech Republic). Water deionized by reverse osmosis (Aqua Osmotic, Czech Republic) was used for the preparation of all solutions.

2.2. Preparation of ZnS nanoparticles

In a typical procedure, 50 mL of the aqueous solution of Na₂S (15 mmol L⁻¹) and CTAB was added drop-wise to 250 mL of the aqueous solution of zinc acetate (Zn(OAc)₂) (2 mmol L⁻¹) under vigorous stirring. The S²⁻:Zn²⁺ ratio was kept at 1.5:1. The total concentrations of CTAB varied from 0.1 mmol L⁻¹ to 5 mmol L⁻¹. Wurtzite nanoparticles were prepared by the procedure referred in [19].

2.3. Instrumental methods

UV spectra of ZnS dispersions were measured in 1 cm quartz cuvettes by Lambda 35 (Perkin Elmer, USA) UV–VIS spectrometer. Dynamic light scattering at $\lambda = 633$ nm and zeta-potential were measured using ZEN 360 Zetasizer Nano ZS instrument (Malvern Instruments). This instrument is able to measure the particle size from 0.6 nm to 8.9 μ m and zeta-potential from -500 mV to +500 mV. The particle size was measured with RSD = 11% and zeta-potential with RSD = 3%.

Scanning electron microscopy was performed on a Jeol JEM 1230 microscope operated at 80 kV. Freshly prepared samples of ZnS nanoparticles stabilized by CTAB were placed on a copper grid (400 mesh) coated by a film of 1.5–3% of polyvinylformaldehyde in chloroform, dried by blotting paper and analyzed after 2 days. A contrast of micrographs was improved by 1% solution of ammonium molybdate added to the samples.

2.4. Molecular modeling

Molecular modeling simulations were carried out in the Cerius² and Materials Studio 4.3 modeling environment [25]. The most occurring crystal structures of ZnS can be found in the wurtzite and sphalerite form, and their structure data were used for building ZnS nanoparticles. The crystallographical data for wurtzite and sphalerite are the following: wurtzite space group P6₃mc, $a = b = 0.382$ nm, $c = 0.626$ nm; sphalerite space group F43m, $a = 0.54$ nm [26]. According to experimental data, a nanocluster in the shape of a sphere with radii of 2.0 nm and 2.5 nm was created from both wurtzite and sphalerite crystal structures. The CTA⁺ ion was built in the 3D sketcher module and its geometry was optimized in the Compass force field [27] in vacuum with partial charges assigned by the force field.

ZnS nanoparticles of wurtzite and sphalerite structures were surrounded by various amounts of optimized CTA⁺ (10, 30, 50, 70, 90 and 100 CTA⁺) in the form of monolayer and bilayer arrangement. Optimized alkyl chains of CTA⁺ in the Compass force field were straight and placed perpendicular to the surface of ZnS nanoparticle. The geometry of micelles consisting of ZnS nanoparticle and CTA⁺ for monolayer and bilayer CTA⁺ arrangements without water was optimized in Universal force field [28]. The cutoff (1.55 nm) and spline (0.1 nm) were used to calculate the Coulom-

bic energies. The Van der Waals energy was calculated by the Lennard-Jones potential. The charges of CTA⁺ were assigned by the Compass force field and the ones for the ZnS nanoparticle were calculated by the QEq method [29]. All atomic coordinates in the system were variable.

The micelles with optimized geometry were surrounded by an envelope of water in the form of a sphere layer, in all cases consisting of the same amount of water molecules in order to be able to feasibly compare interactions in the systems. The charges for water molecules were taken from the Compass force field.

All the optimized models were refined up to by 300 ps of a quenched dynamics. One step was 1 fs. Since the geometry of ZnS nanoparticles was nearly rigid, the atomic coordinates of the nanoparticles were kept fixed and the atomic coordinates of all other species were variable.

3. Results and discussion

3.1. UV absorption spectra study

In aqueous solutions, ZnS nanoparticles were stabilized by CTAB in the concentration range of 0.4–5 mmol L⁻¹. The UV spectra of stable slightly blue transparent dispersions of ZnS and CTAB were recorded. At the concentrations <0.4 mmol L⁻¹, ZnS particles rapidly settled. It is known that the onset of absorption (absorption edge) depends on semiconductor nanoparticle sizes as a result of quantum size effect. Compared to bulk ZnS having the absorption edge at about 340 nm, the absorption onset was blue-shifted to about 315 nm [19]. This phenomenon is generally considered to be an evidence of the presence of nanoparticles. The band-gap energies (E_{bg}) were evaluated using the Tauc equation [30] from the obtained UV spectra:

$$\varepsilon h\nu = C(h\nu - E_{bg})^r \quad (1)$$

where ε is the absorption coefficient, $h\nu$ is the energy of incident photons, and r is the power, which characterizes the electronic transition during absorption processes. The parameter C depends on the transition probability that can be considered as a constant within the optical frequency range. For direct semiconductors like ZnS, r is 1/2. An usual method for the estimation of E_{bg} involves plotting $(\varepsilon h\nu)^{1/r}$ against $(h\nu)$ [19].

Besides stabilizing properties, CTAB is also considered as a shape-directing agent because of its preferential adsorption on specific crystal planes [34]. In our previous work, spherical ZnS nanoparticles prepared in the presence of CTAB were observed by HRTEM [19]. In this study, the radii of spherical ZnS nanoparticles were calculated by means of the Brus equation [31] describing the quantum size effect:

$$E_{bg}(nano) - E_{bg}(bulk) = \frac{h^2}{8R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \left(\frac{1.8e^2}{4\pi\varepsilon_r\varepsilon_0R} \right) \quad (2)$$

where $E_{bg}(bulk)$ and $E_{bg}(nano)$ are the band-gap energies of bulk and nanosized semiconductors, respectively, h is the Planck's constant, m_e and m_h are the effective masses of electron and hole, respectively, and ε_r and ε_0 are the dielectric constants of material and vacuum, respectively, R is the radius of spherical nanoparticle, and e is elementary charge. Here, $m_e = 0.42m_0$ and $m_h = 0.61m_0$, where m_0 is free electron mass, $\varepsilon = 8.76$ [32] and $E_{bg}(bulk) = 3.70$ eV.

Fig. 1 shows the dependences of R on the total concentrations of CTAB. The radii R were calculated from $E_{bg}(nano)$ immediately after precipitation and after 24 h. One can see that the radii of ZnS nanoparticles steeply decreased from 4.5 nm to 2.2 nm with increasing concentrations up to about 1.5 mmol L⁻¹, which is close to the critical micelle concentration of CTAB [33]. At the higher concentrations, the radii slightly decreased at 2.1 nm. After 24 h, the radii

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