Synthesis and Optical Properties of Mn\textsuperscript{2+}-Doped ZnS Nanoparticles in Solutions and Coatings

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Abstract. Mn\textsuperscript{2+}-doped ZnS nanoparticles with different Mn-doping concentrations stabilized by hydroxypropyl cellulose (HPC) have been synthesized in ethanolic solutions and coatings. Their optical and structural properties have been characterized by means of UV-vis spectroscopy, luminescence spectroscopy, high resolution transmission electron microscopy (HRTEM) and small angle X-ray scattering (SAXS). Solutions and coatings exhibit a strong luminescence at 590 nm when excited with UV light showing that Mn\textsuperscript{2+} is incorporated into the ZnS nanoparticles. The highest luminescence intensity is obtained with an Mn\textsuperscript{2+} concentration of 2 mol\%. HRTEM and SAXS investigations show that the particles are crystalline and are 3 ± 0.5 nm in size. Irradiation of the coatings with UV light leads to a photochemical oxidation of the particles, as shown by the decreasing absorption of the coating with irradiation time and a blue shift of the absorption maximum. Furthermore, the luminescence intensity first strongly increases and then decreases completely with UV-irradiation time. Both phenomena can be explained by the photochemical oxidation of the particles.

Keywords: zinc sulfide, nanoparticles, absorption spectroscopy, luminescence spectroscopy, coatings

1. Introduction

In recent years semiconducting nanoparticles have been investigated intensively because of their possible use in optoelectronic device materials [1–11]. Their optical properties depend on the particle size, producing for example fast relaxation times or changes in the electronic structure, respectively. On the other hand, their large surface area leads to a high chemical reactivity of the particles, which might give limitations in application.

Therefore, this paper addresses the chemical stability and the time dependence of the absorption and emission spectra of Mn\textsuperscript{2+}-doped ZnS nanoparticles during UV irradiation in a solvent-free environment. These particles are suitable model material to study the chemical stability by optical measurements, because the intensity of the luminescence of the Mn\textsuperscript{2+} center in the ZnS nanoparticles is very sensitive to chemical and structural changes of the host particles. It is known that micro sized Mn\textsuperscript{2+}-doped ZnS particles lose their luminescence properties within a few years under daylight UV irradiation [12]. In this paper, in the experimental section, it is shown that nanosized particles can degrade much faster due to their large surface area.

Considerable experimental work has been performed in the past in order to understand the physical and chemical properties of Mn\textsuperscript{2+}-doped ZnS nanoparticles. Bhargava et al. performed luminescence measurements on Mn\textsuperscript{2+}-doped ZnS nanoparticles as powders and in an organic polymer matrix [7, 13]. An increase in the luminescence intensity on irradiation with UV light was reported and it was hypothesized that passivation of the surface of the nanoparticles by photo-polymerization of the stabilizer (methacrylic acid) leads to a decrease of surface related nonradiative processes and therefore to an increased luminescence intensity [7, 8, 13]. An activation of the luminescence in Mn\textsuperscript{2+}-doped ZnS nanoparticles, stabilized with polymethylmethacrylate (PMMA) in ethanol was also detected by Jin et al. after UV irradiation for 1 h [14]. On the other hand, it has been shown by absorbance measurements on undoped ZnS-nanoparticles 2 to 3 nm
in size that the particles are oxidized in the presence of oxygen within several minutes under UV irradiation from a 450 W Xenon lamp at stand-off distance of 30 cm [4, 5].

Systematic investigation of these phenomena on Mn$^{2+}$-doped ZnS particles by measuring time dependent absorption and luminescence spectra have not been performed to date. To investigate this in detail, Mn$^{2+}$-doped ZnS nanoparticles have been synthesized in solutions and coatings, and their optical and structural properties are characterized in this paper. Hydroxypropyl cellulose (HPC) was used as a stabilizer and as a viscosity-increasing agent in order to obtain coatings with thicknesses in the micro range to investigate the spectroscopic properties in a solvent-free surrounding. Absorption and luminescence properties of the nanoparticles in the coatings were measured as a function of the UV-irradiation time and a model for the time dependent spectroscopical behavior is presented.

2. Experimental

A 50 ml solution with a constant total cation concentration of 0.01 M and 4.0 wt% HPC was prepared by dissolving Zn(CH$_3$COO)$_2$·2H$_2$O (Fluka), Mn(CH$_3$COO)$_2$·4H$_2$O (>99%, Aldrich) and HPC (Aldrich, average molecular weight 100,000) in ethanol, with stirring, at room temperature. Doping concentrations of 1, 2, 3, 4, 6, and 8 mol% Mn$^{2+}$ have been adjusted. Transparent solutions of Mn$^{2+}$-doped ZnS colloids were prepared by the injection of 15 ml H$_2$S gas from a 20 ml plastic syringe into the mixture within 2 min and during stirring. Coatings with thicknesses between 0.5 to 50 μm were obtained from the solutions by multiple dip-coating onto glass substrates. The coatings were dried at 120°C for 2 h in nitrogen atmosphere.

Absorption spectra were measured at room temperature using a Hitachi U3000 spectrophotometer and 2 mm fused silica cuvettes with air as a reference for the solutions. Emission spectra and excitation spectra were recorded with a Hitachi F-3010 fluorescence spectrophotometer. High resolution transmission electron microscopy (HRTEM) investigations were performed with a Philips CM 200 FEGTEM. Samples were prepared by dipping a copper grid coated with carbon film into the as-prepared solutions. The thickness of the coatings was measured with a Tencor P-10 surface profiler. UV irradiation of the samples has been performed under air using a Penray Hg-calibration lamp (Ultraviolet Products Inc; intense lines at 253, 312 and 365 nm; 14 W; 5 cm distance). Small angle X-ray scattering (SAXS) measurements were carried out under grazing incidence at the beam line D22 of the LURE synchrotron (Paris/Orsay) with an X-ray energy of 9500 eV. Details of the experimental setup and the data evaluation are described in [15, 16].

3. Results and Discussion

In Fig. 1 the absorption spectrum of a solution with a dopant concentration of 2 mol% is shown together with the spectra of the coatings before and after drying at 120°C. The spectra of the ZnS containing solutions have a peak at 273 nm, which can be assigned to an excitonic transition and proves the existence of ZnS nanoparticles [4, 5]. Compared with the solution, the peak measured for the coatings has a red shift of 0.11 eV and is broadened. As the absorption spectra of the coatings before and after heat treatment are nearly the same, it can be supposed that particles have slightly agglomerated during the dip coating. In addition, weak scattering effects of the HPC coating matrix have to be taken into account (see Fig. 1).