

Synthesis, Extraction and Surface Modification of (Zn,Mn)Se Nanocrystals Using Microemulsions as Templates

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ABSTRACT

We report the synthesis of ZnSe:Mn quantum dots (QDs) in the dispersed phase of a microemulsion template consisting of p-xylene as the continuous phase, water as the dispersed phase, and an amphiphilic block copolymer (Pluronic P105) as the surfactant. The Zn and Mn precursors were Zn-acetate and Mn-acetate, respectively, dissolved in the aqueous dispersed phase. Hydrogen selenide gas was bubbled through the microemulsion. A single ZnSe QD forms in each droplet of the microemulsion via an irreversible reaction between the precursors and coalescence of the resulting nuclei. Mn²⁺ ions slowly diffuse into the ZnSe lattice. The emission peak attributed to Mn²⁺ ions at 585 nm increases substantially with time eventually dominating over the ZnSe peak and reaching a plateau. The QDs were extracted from the template by adding water and inducing phase separation. They were subsequently capped with mercapto-undecanoic acid or dihydro-lipoic acid and dispersed in water.

Keywords: quantum dots, diluted magnetic semiconductors, synthesis, microemulsion template, zinc manganese selenide.

1 INTRODUCTION

Semiconductor nanocrystals or quantum dots (QDs) have size-tunable optical properties that make them excellent candidates for applications in clinical diagnostics, photovoltaics, optoelectronics, and spintronics[1, 2]. CdSe QDs that emit in the visible part of the spectrum have been the most widely studied system. ZnSe QDs emit in the blue and violet parts of the spectrum and are a less toxic alternative to CdSe for *in vivo* applications[3]. ZnSe QDs have a quantum confinement threshold of 9nm and tunable emission between 380 nm and 460 nm. Hines et al. reported a method for synthesizing highly luminescent ZnSe QDs using injection of organometallic precursors in a hot coordinating solvent[4].

Doping of II-VI semiconductors with transition metals yields diluted magnetic semiconductors (DMS), with materials having a chemical composition Zn^{II}_{1-x}Mn_xB^{VI} being the most widely studied compounds[5]. DMS-based nanocrystals have potential applications in spintronics and can be used to form QDs emitting at wavelengths that are longer than the wavelength corresponding to the gap emission of the original bulk semiconductor. Typical examples of such materials are ZnS:Mn[6], and ZnSe:Mn[7-10]. The introduction of the Mn²⁺ ion in the ZnSe lattice results in an emission peak at 585nm. In general, the doping of ZnSe nanocrystals with transition metals expands their emission range into the visible part of the spectrum and has additional advantages, such as the reduction of self-quenching and the elimination of the need to control the particle size for tuning the emission wavelength.[10]

In this paper, we report the synthesis of ZnSe:Mn nanocrystals using a microemulsion template. The technique is based on the templated growth of ZnSe nanocrystals reported by Karanikolos et al.[11-13] The microemulsion template consists of p-xylene as the continuous phase, water as the dispersed phase, and a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) block copolymer (Pluronic P105) as the surfactant. This template is very stable and has very slow droplet-droplet coalescence kinetics. Because of that, it minimizes particle aggregation and allows precise control of particle size by manipulating the concentration of the precursor in the dispersed phase. The technique is easy to scale up and employs less expensive chemicals compared to the hot injection method.

2 EXPERIMENTAL SECTION

Microemulsion templates were prepared by mixing 82.1 wt% p-xylene, 2.4 wt% aqueous solution of Zn- and Mn-acetate, and 15.5 wt% Pluronic P105 surfactant.[13] The concentration of Zn-acetate in the aqueous solution was used to control the final size of

the QDs. The typical Mn:Zn molar ratio in the solution was 1:9. Hydrogen selenide gas diluted in hydrogen was bubbled through the micro-emulsion to enable the formation of ZnSe QDs. The hydrogen selenide gas diffuses through the surfactant layer and reacts with Zn-acetate to form ZnSe. The Mn^{2+} ion is incorporated into the lattice through a slow diffusion process. The hydrogen selenide flow was kept on for 10 minutes to convert Zn-acetate to ZnSe. The microemulsion was subsequently purged with nitrogen and was analyzed using fluorescence spectroscopy. The extraction of particles from the microemulsion template was accomplished by adding water and inducing phase separation. Surface modification of the QDs with mercapto-undecanoic acid and dihydro-lipoic acid was performed. The surface modified QDs were dispersed in water.

3 RESULTS AND DISCUSSION

Figure 1 shows the evolution of fluorescence emission spectra from a microemulsion containing ZnSe:Mn QDs with increasing time in storage. For this case the initial concentration of Zn-acetate precursor in the dispersed phase was 0.1 M and the Mn:Zn molar ratio in that solution was set at 0.1. The initial spectrum exhibits a single peak at 393nm that corresponds to ZnSe QDs. The spectra obtained after 3, 4 and 5 days in storage exhibit two major peaks, one at 393 nm that corresponds to ZnSe and one at 585 nm that corresponds to the Mn^{2+} ion. The relative intensity of the Mn^{2+} peak with respect to the ZnSe peak increases with time in storage, most probably due to the diffusion of the Mn^{2+} ion into the ZnSe lattice, until equilibrium with the surrounding solution is established. Initially, the ZnSe emission peak is dominant, but the Mn^{2+} peak eventually dominates. These observations suggest that ZnSe QDs are formed first, and Mn^{2+} diffuses slowly into them to replace Zn^{2+} in the crystal lattice.[5] It has been reported that for a single ZnSe:Mn QD, the emission intensity ratio should be directly proportional to the number of Mn^{2+} ions incorporated into the nanocrystal.[8] In Figure 2, the intensity ratio of the Mn^{2+} and ZnSe peaks is plotted as a function of storage time. The emission intensity ratio increases with time in storage at room temperature and reaches a plateau after about 20 days.

The effects of varying the Mn to Zn ratio in the precursor solution, while keeping the initial Zn-acetate concentration constant at 0.3M, were also studied. The observed emission intensity that corresponds to the Mn^{2+} peak is plotted in Figure 3 as

function of time in storage. The data shows that when the Mn^{2+} concentration in the precursor solution is increased, the evolution of the Mn^{2+} peak emission intensity from the ZnSe:Mn QDs is slower. This is counter-intuitive and suggests that the rate of incorporation of Mn^{2+} into the ZnSe QD is not simply proportional to the Mn^{2+} concentration in the surrounding solution. An investigation of the underlying Mn^{2+} incorporation mechanism is currently underway in our laboratory.

4 CONCLUSIONS

We report the synthesis of ZnSe:Mn QDs in microemulsion templates using aqueous solutions of Zn-acetate and Mn-acetate, and hydrogen selenide gas. The reaction takes place at room temperature and the size of the particles is controlled by the concentration of Zn-acetate in the dispersed phase. The ratio of the emission peak intensity at 585nm attributed to the Mn^{2+} ion to the emission peak attributed to ZnSe increases with time in storage until a plateau is reached. This indicates that ZnSe QDs are formed first and the Mn^{2+} ion subsequently diffuses into the ZnSe lattice.

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6 FIGURES

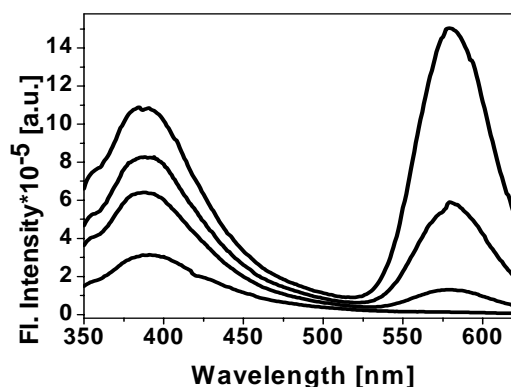


Figure 1: Fluorescence spectra of ZnSe:Mn QDs after 2, 3, 4, and 5 days in storage in the microemulsion. The emission intensity increases with time.

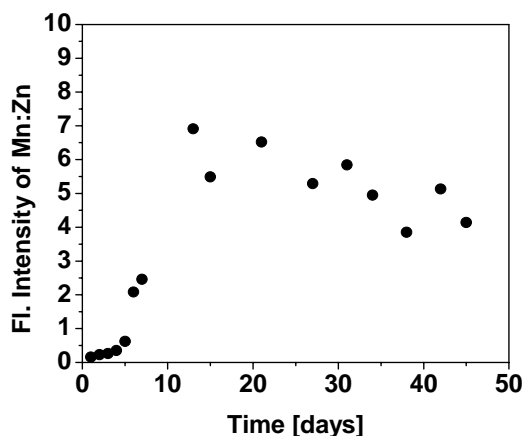


Figure 2: Evolution of Mn^{2+} to ZnSe fluorescence emission intensity ratio in ZnSe:Mn QDs with time in storage in the microemulsion.

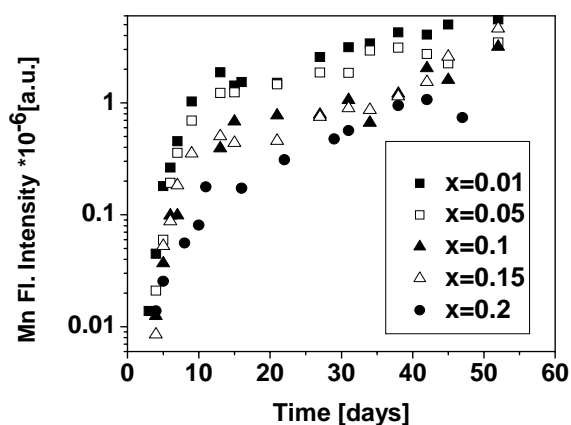


Figure 3: Evolution of Mn^{2+} peak fluorescence emission intensity from ZnSe:Mn QDs for various Mn to Zn molar ratios in the initial precursor solution.

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