

SYNTHESIS OF MANGANESE-DOPED ZINC SELENIDE QUANTUM DOTS AND CORE-SHELL STRUCTURES USING MICROEMULSIONS AS TEMPLATES

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Summary

Doping of ZnSe Quantum Dots (QDs) with Mn^{2+} can be used to intentionally alter their optoelectronic properties. ZnSe:Mn QDs were synthesized in microemulsion droplets and capped with a ZnSe shell. The doping mechanism and Mn^{2+} incorporation efficiency were studied by monitoring the relative intensity of two fluorescence emission peaks, one resulting from exciton recombination at the ZnSe band edge and the other from an internal Mn^{2+} electronic transition. A transient analysis of Mn^{2+} incorporation into the ZnSe lattice was performed by correlating the intensity ratio of these peaks to the Mn^{2+} content of the nanocrystals during growth and subsequent annealing.

Keywords

Novel Functional Materials, Nanotechnology Applications, Materials for Energy Applications, High Value Added Products.

Introduction

The intentional doping of II-VI semiconductor nanocrystals (Quantum Dots or QDs) with transition metals enables tuning of their optoelectronic properties and can yield novel magneto-optical materials for spintronic applications. The doping efficiency of a certain metal ion depends on the size of the QD, its surface morphology, and the presence of surfactants in the growth solution¹. The typical method used for growing II-VI QDs, such as CdSe or ZnSe, and core/shell structures, such as CdSe/ZnS and ZnSe/ZnS, involves injection of a precursor solution into a hot (~300 °C) coordinating solvent, such as hexadecylamine or trioctylphosphine, and growth of nanocrystals as function of time in a small well-mixed batch reactor²⁻⁵.

We have developed a room-temperature technique for the synthesis of semiconductor nanocrystals that employs microemulsions or liquid crystals as templates to control both the size and the shape of the nanocrystals⁶⁻⁸. This technique eliminates time as the parameter controlling nanocrystal size. Instead, the size of the nanocrystals is controlled by the initial concentration of the precursor in the dispersed phase of the microemulsion. The technique has been used for growing ZnSe:Mn QDs and ZnSe:Mn/ZnSe core shell structures and enabled studies of the incorporation efficiency of the Mn^{2+} ion in the ZnSe lattice by monitoring the changes in the fluorescence emission peaks resulting from exciton recombination at

the ZnSe band edge and internal Mn^{2+} electronic transition.

Experimental Method

ZnSe:Mn QDs were synthesized inside the droplets of a microemulsion template formed by self-assembly of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) amphiphilic block copolymer at the interface between a p-xylene continuous phase and an aqueous dispersed phase⁸. These templates are very stable and exhibit very slow droplet-droplet coalescence kinetics, thus preventing particle aggregation and allowing precise control of particle size by changing the initial concentration of the reactant dissolved in the dispersed phase. The precursors dissolved in the aqueous dispersed phase were zinc- and manganese- acetate. The concentration of zinc-acetate in the dispersed phase determines the final size of the QDs. The initial concentration of manganese-acetate and the size and morphology of the QDs determine the dopant concentration in the nanocrystal, after chemical equilibrium with the surrounding solution has been established. The selenium precursor was hydrogen selenide gas, which was diluted in hydrogen and bubbled through the microemulsion. The Se precursor is assumed to be in excess during QD growth and doping.

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The technique operates at room temperature with nucleation of nanocrystals occurring via a spontaneous irreversible reaction between zinc-acetate and hydrogen selenide. ZnSe QDs grow first and the dopant ions subsequently chemisorb on their surface and are incorporated into the ZnSe lattice. A ZnSe shell was grown on the ZnSe:Mn QDs by adding a small amount of a concentrated aqueous solution of zinc-acetate to the microemulsion, followed by ultrasonic mixing. The additional amount of aqueous solution was such that the system remained in the microemulsion region of its phase diagram. Annealing of the core/shell nanocrystals was performed to study the kinetics of Mn^{2+} diffusion in the ZnSe lattice and the eventual expulsion of the Mn^{2+} ions from the ZnSe lattice, a phenomenon called self-purification of nanocrystals.

Results and Discussion

An analysis of the Mn^{2+} doping efficiency was performed by monitoring the two fluorescence emission peaks obtained after excitation of the ZnSe:Mn QDs with UV radiation.

The first peak originates from exciton recombination at the ZnSe band edge and its wavelength increases with the size of the ZnSe nanocrystals. The wavelength of this peak ranges from about 380nm to 460nm (UV-blue color), for nanocrystal sizes between 2nm and 9nm, respectively. Since the quantum confinement threshold of ZnSe is 9nm, any nanocrystal with size larger than this limit will emit at the bulk ZnSe emission wavelength of 460nm. The emission wavelength of this peak was used to estimate the size of the ZnSe QDs⁹ and to monitor the growth rate of the ZnSe shell. The second peak is attributed to an internal Mn^{2+} electronic transition and is fixed at 585nm (yellow-orange color). The ratio of the intensities of the two peaks is proportional to the number of Mn^{2+} incorporated in the ZnSe QD¹. This enables the use of fluorescence intensity measurements for the estimation of Mn^{2+} incorporation levels in the ZnSe lattice.

The fluorescence emission spectra indicate that ZnSe QDs are formed first and Mn^{2+} is slowly incorporated in the lattice. A kinetic model was developed that includes the following steps:

1. Mn^{2+} chemisorption onto the QD surface.
2. Mn^{2+} desorption that expels dopant ions from the surface of the QD back into the surrounding solution.
3. Irreversible Mn^{2+} incorporation into the ZnSe lattice.

The evolution of the Mn^{2+} emission intensity indicates that the Mn^{2+} incorporation step is rate determining, because this peak appears after a ZnSe QD has been formed and its intensity grows slowly with time. As a result, the first two steps can be assumed to be at equilibrium. Changes in the Mn^{2+} peak intensity can be directly correlated to Mn^{2+} incorporation in the ZnSe lattice. The mass balance of

Mn^{2+} ions is used to estimate the amount of Mn^{2+} incorporated into the QDs and the amount that remains in solution. This mass balance is also used to estimate the rate parameters of steps 1-3.

A similar mechanism describing chemisorption, desorption, and incorporation of Zn^{2+} ions was used to model the growth of a ZnSe shell on the ZnSe:Mn QDs. The observed red shift in the ZnSe emission wavelength was used to monitor the growth rate of the shell and connect it to the mass balance of Zn^{2+} ions, thus enabling the estimation of rate parameters.

Finally, the Mn^{2+} balance can be used to fit fluorescence emission data obtained from transient annealing experiments performed at elevated temperatures. These experiments lead to self-purification of ZnSe:Mn/ZnSe core/shell QDs resulting in pure ZnSe QDs. The rate of Mn^{2+} desorption can be estimated by monitoring the changes in the emission intensity of the peak at 585nm.

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