

Synthesis of Doped ZnS Nanoclusters within Block Copolymer Nanoreactors

R. S. Kane and R. E. Cohen*

Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

R. Silbey

Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Received July 1, 1998. Revised Manuscript Received September 18, 1998

We have synthesized Mn-doped and Tb-doped ZnS nanoclusters within the microphase-separated films of diblock copolymers containing carboxylic acid units on one of the blocks. The loading of metal ions can be monitored using inductively coupled plasma atomic emission spectroscopy. The impurity ion content of the acid-containing microdomains can be controlled by varying the concentration of the aqueous metal salt solutions or the time of exposure of the films to the aqueous salt solution. The doped ZnS nanoclusters are formed by subsequently treating the ion-loaded films with H₂S. The doped nanoclusters are optically active and show emission characteristic of the impurity ions (manganese or terbium). The universal nanocluster synthesis scheme could in principle be used with various combinations of metal salts to yield many different doped semiconductor nanocluster species.

Introduction

Semiconductor nanoclusters, i.e., particles with diameters between 1 and 10 nm,¹ have been the subject of numerous investigations in the past few years.^{2–12} The quantum size effect shifts the band gap of many semiconductors into the visible range and raises the possibility of applications for the nanoclusters in devices such as light-emitting diodes. Such practical applications of semiconductor nanoclusters have been hindered by surface defects and the concomitant surface-related nonradiative recombination, which lower the quantum yield of emission. The contribution from the surface states can be eliminated by passivating the semiconductor nanoclusters.¹⁰ Another method of increasing the quantum yield of emission reported by Bhargava et al.¹³

involves adding an impurity to a quantum dot, resulting in doped nanocrystalline materials.

Clusters of the mixed semiconductor Zn_xMn_{1-x}S were first synthesized by Wang et al.¹⁴ as an example of a dilute magnetic semiconductor quantum dot. Wang et al. also reported photoluminescence from these quantum dots, characteristic of the manganese ion. Mn-doped ZnS clusters have also been extensively studied by Bhargava et al.^{13,15,16} and Gallagher et al.¹⁷ These researchers have synthesized nanoclusters of Mn-doped ZnS with sizes ranging from 3.5 to 7.5 nm and have reported photoluminescence quantum yields as high as 18%.

We have been working on the synthesis of semiconductor nanoclusters with controllable sizes and narrow size distributions within processible block copolymer films prepared via ring-opening metathesis polymerization (ROMP). The utilization of block copolymers containing ROMP monomers with pendant hole-transport groups¹⁸ and electron-transport groups for cluster synthesis may provide us with electrical access to the nanoclusters for device applications. We have been making semiconductor nanoclusters by a universal scheme developed by Yue et al.¹⁹ Since doped nanoclusters are of interest because of their potential device applications, we decided to investigate whether our scheme could be modified to produce doped nanoclusters.

* To whom correspondence should be addressed

- (1) Henglein, A. *Chem. Rev.* **1989**, 89, 1861.
- (2) Lippens, P. E.; Lannoo, M. *Phys. Rev. B* **1989**, 39, 935.
- (3) Lippens, P. E.; Lannoo, M. *Phys. Rev. B* **1990**, 41, 6079.
- (4) Fischer, Ch.-H.; Weller, H.; Katsikas, L.; Henglein, A. *Langmuir* **1989**, 5, 429.
- (5) Eychmuller, A.; Katsikas, L.; Weller, H. *Langmuir* **1990**, 6, 1605.
- (6) Schooss, D.; Mews, A.; Eychmuller, A.; Weller, H. *Phys. Rev. B* **1994**, 49, 17072.
- (7) Wang, Y.; Herron, N.; Caspar, J. *Mater. Sci. Eng.* **1993**, B19, 61.
- (8) Bawendi, M. G.; Kortan, A. R.; Steigerwald, M. L.; Brus, L. E. *J. Chem. Phys.* **1989**, 91, 7282.
- (9) Bawendi, M. G.; Carroll, P. J.; Wilson, W. L.; Brus, L. E. *J. Chem. Phys.* **1992**, 96, 946.
- (10) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, 115, 8706.
- (11) Dabbousi, B. O.; Murray, C. B.; Rubner, M. F.; Bawendi, M. G. *Chem. Mater.* **1994**, 6, 216.
- (12) Kane, R. S.; Cohen, R. E.; Silbey, R. *J. Phys. Chem.* **1996**, 100, 7928.
- (13) Bhargava, R. N.; Gallagher, D.; Hong, X.; Nurmikko, A. *Phys. Rev. Lett.* **1994**, 72, 416.

(14) Wang, Y.; Herron, N.; Moller, K.; Bein, T. *Solid State Commun.* **1991**, 77 (1), 33.

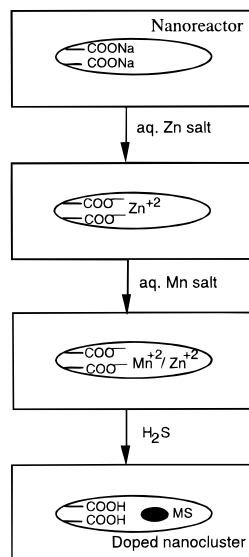
(15) Bhargava, R. N.; Gallagher, D.; Welker, T. *J. Lumin.* **1994**, 60 & 61, 275.

(16) Bhargava, R. N. *J. Lumin.* **1996**, 70, 85.

(17) Gallagher, D.; Heady, W. E.; Racz, J. M.; Bhargava, R. N. *J. Cryst. Growth* **1994**, 138, 970.

(18) Gratt, J.; Cohen, R. E. *Macromolecules* **1997**, 30 (11), 3137.

(19) Yue, J.; Cohen, R. E. *Supramol. Sci.* **1994**, 1, 117.

Scheme 1. Doped Nanocluster Synthesis Scheme

Our approach to doped nanocluster synthesis is shown in Scheme 1 and involves the selective sequestering of metals into the preformed microdomains of a block copolymer film. The scheme shows a cross section of a block copolymer film with a cylindrical morphology. Metals can be loaded from solutions of metal salts or by permeation of an organometallic compound. For producing doped clusters, the two metal ions can be loaded sequentially (by first treating the film with aqueous zinc acetate and then with aqueous manganese acetate) or directly from a mixture of aqueous metal salt solutions. Once loaded, these metal-containing domains serve as localized reaction sites for cluster synthesis. The spatially distinct domains can be thought of as nanoreactors within which nanoclusters are synthesized. Treatment with H_2S yields doped metal sulfide semiconductor clusters. In principle, this scheme can be used with various combinations of metal salts to yield many different doped semiconductor nanocluster species.

The purpose of this paper is to demonstrate the effectiveness of the block copolymer nanoreactor synthesis scheme for two cases: manganese-doped zinc sulfide nanoclusters and terbium-doped zinc sulfide nanoclusters. Photoluminescence spectroscopy was employed to demonstrate the formation of the doped nanoclusters.

Experimental Section

Hydrogen sulfide (H_2S , C. P. grade) was purchased from Matheson. Diblock copolymers of MTD (methyltetradecyldecene) and NORCOOH (2-norbornene-5,6-dicarboxylic acid) were synthesized by ROMP, inside a Vacuum Atmospheres nitrogen glovebox. Films of $(\text{MTD})_{500}(\text{NORCOOH})_{50}$ used for this work were static cast from THF. Details of the procedures used for the polymer synthesis, static casting, and reaction of the ion-loaded films with H_2S have been previously published.²⁰ Metal ion concentrations in aqueous solutions were measured with a Perkin-Elmer Plasma 40 inductively coupled plasma atomic emission spectrophotometer. Optical spectra of the polymer films were obtained on a Cary 5E UV-vis-NIR spectrophotometer using illumination from a tungsten halide

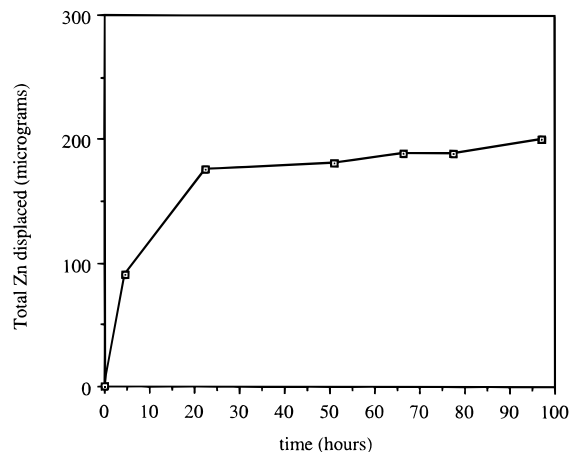


Figure 1. Ion exchange for a Zn-loaded film treated with 0.02 M aqueous manganese acetate.

lamp. Steady-state photoluminescence measurements were made on a SPEX Fluorolog Model FL212 spectrofluorometer equipped with a liquid nitrogen cooled CCD detector.

Results and Discussion

Metal Ion Loading. The first step in the doped ZnS nanocluster synthesis scheme involves the loading of zinc. This can be done by directly treating the static cast diblock copolymer films with a zinc acetate solution. However, it has been found that metal ion loading can be increased if the diblock copolymer films are pretreated with aqueous NaOH and the carboxylic acid groups are converted to the sodium carboxylate form.²¹ Our static cast films were therefore pretreated with a 0.1 M aqueous sodium hydroxide solution overnight. These films were washed with water and then soaked in a 0.01 M zinc acetate solution overnight. The zinc essentially displaces all of the sodium ions bound to the carboxylic acid groups. The binding of zinc is followed by a second wash step to remove any traces of the displaced sodium.

The next step involves partially displacing the zinc by the impurity atom (Mn or Tb). Displacement of the zinc by manganese can be achieved by treating the zinc-loaded films with an aqueous manganese acetate solution. The manganese displaces the zinc at a rate (and to an extent) depending on the concentration of the manganese acetate solution. The uptake of manganese can be monitored using inductively coupled plasma atomic emission spectroscopy (ICP-AES).²² As manganese displaces zinc, the zinc ions come out of the film into the aqueous solution. The amount of manganese loaded can be calculated by tracking the increase in the zinc ion concentration in the aqueous solution used for the loading. A typical curve is shown in Figure 1 for Mn loading from a 0.02 M aqueous manganese acetate solution. Almost complete manganese loading is achieved in 24 h. By varying the concentration of the manganese acetate solution, and the loading time, one can vary the ratio of bound Zn and Mn ions in the film and hence the level of doping in the final nanocluster.

It is possible to track the concentrations of both the zinc ions (leaving the polymer film) and the impurity

(20) Kane, R. S.; Cohen, R. E.; Silbey, R. J. *Chem. Mater.* **1996**, *8*, 1921.

(21) Clay, R. T.; Cohen, R. E. *Supramol. Sci.* **1998**, *5*, 41.

(22) Clay, R. T.; Cohen, R. E. *Supramol. Sci.* **1997**, *4*, 113.

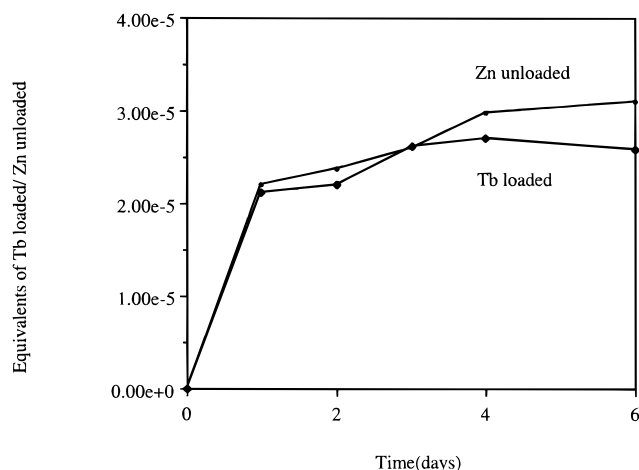


Figure 2. Stoichiometric displacement of zinc from a Zn-loaded polymer film by terbium.

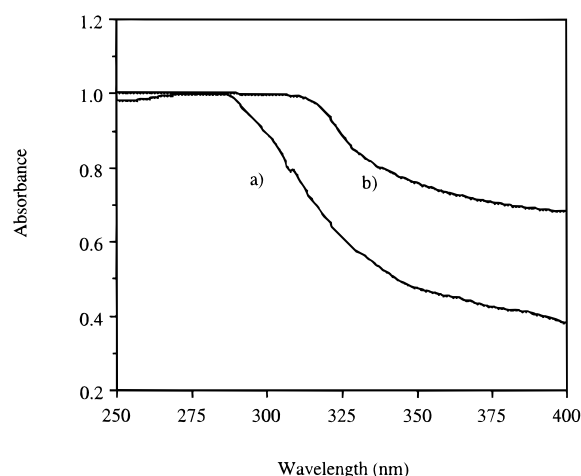


Figure 3. UV-vis spectrum for (a) (MTD)₅₀₀(NORCOOH)₅₀ polymer film and (b) (MTD)₅₀₀(NORCOOH)₅₀ polymer film containing Mn-doped ZnS nanoclusters.

ions in the aqueous solution. This is illustrated in Figure 2 for Tb loading from a terbium acetate solution. The displacement is seen to be stoichiometric—for each equivalent of zinc leaving the polymer film (unloading), 1 equiv of terbium enters the polymer film (loading).

The final step in the synthesis scheme involves treatment of the ion-loaded films with H₂S, which produces doped ZnS nanoclusters. Figure 3 shows the UV-vis spectrum for the block copolymer film before and after the formation of the doped ZnS nanoclusters. The increase in the absorption between 300 and 330 nm is consistent with the formation of ZnS nanoclusters.

Photoluminescence Spectroscopy. The formation of the doped ZnS nanoclusters was confirmed using photoluminescence spectroscopy. Doped nanoclusters should show optical activity characteristic of the impurity atom. Figure 4 shows the emission spectrum for a polymer film containing Mn-doped ZnS nanoclusters. The clusters were synthesized by treating the zinc-loaded film with a 0.002 M manganese acetate solution for 12 h (corresponding to a 2% Mn doping from ICP-AES experiments) and then with H₂S in the presence of methanol. The films were excited at 310 nm, and the characteristic manganese emission was seen as a broad peak centered at about 586 nm.

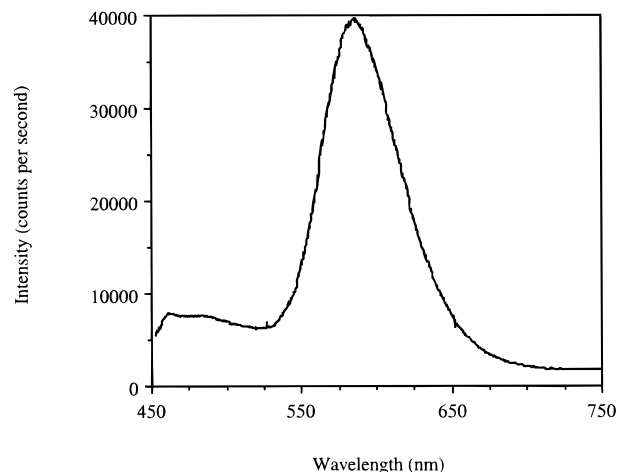


Figure 4. Photoluminescence emission spectrum for a polymer film containing Mn-doped ZnS nanoclusters.

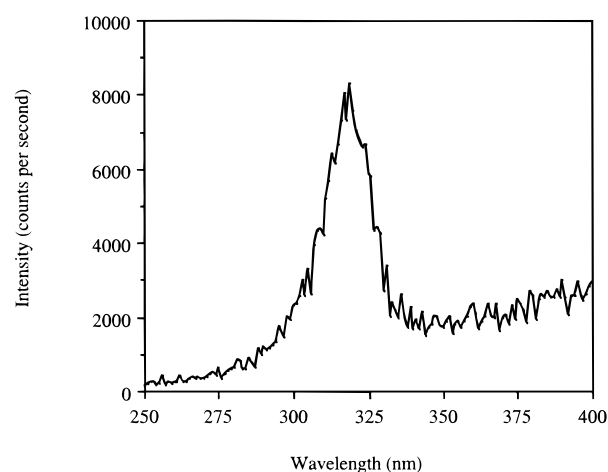


Figure 5. Photoluminescence excitation spectrum for a polymer film containing Mn-doped ZnS nanoclusters.

Although the manganese emission is evident in the emission spectrum, one still needs to prove that this emission is a result of a transfer of energy from the ZnS nanocluster to the manganese ion. This can be demonstrated by excitation spectroscopy. Figure 5 shows the photoluminescence excitation spectrum for a polymer film containing Mn-doped ZnS nanoclusters. In this case, the intensity of the emission at 586 nm (the peak of the manganese emission) was measured as a function of the excitation wavelength. As the wavelength of the incident radiation decreases below 330 nm, ZnS nanoclusters begin to absorb light, and a corresponding increase in the intensity of manganese emission is seen. Below 320 nm, however, the intensity of the emission begins to drop, resulting in a peak in the excitation spectrum. This decrease in the intensity of manganese emission is a result of the absorption of light by the polymer film at these shorter wavelengths. We have thus shown that excitation of ZnS in the region of 330 nm results in Mn emission at 586 nm, while excitation in the region of strong polymer absorption (i.e. below 320 nm) fails to result in Mn emission. This proves that energy transfer from ZnS to Mn is taking place, evidence that the Mn is doped within the ZnS cluster.

Emission characteristic of the impurity ions is also observed in Tb-doped ZnS nanoclusters. Figure 6 shows the photoluminescence emission spectrum for a film

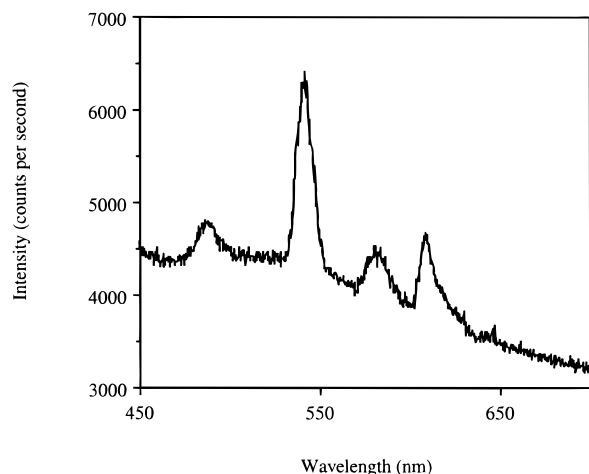


Figure 6. Photoluminescence emission spectrum for a polymer film containing Tb-doped ZnS nanoclusters.

containing Tb-doped ZnS nanoclusters. The clusters were synthesized by treating the zinc-loaded film with a 0.002 M terbium acetate solution for 2.5 h and then with H_2S in the presence of methanol. Four peaks

characteristic of terbium emission are seen in the emission spectrum.

Conclusions

We have synthesized Mn-doped and Tb-doped ZnS nanoclusters within diblock copolymer nanoreactors. The loading of metal ions can be monitored using ICP-AES, and the level of doping in the nanoclusters can be varied. The clusters synthesized are optically active and show emission characteristic of the impurity ions (manganese or terbium). The universality of the block copolymer nanoreactor approach may enable the facile synthesis of other technologically relevant doped or mixed semiconductor nanoclusters and allow their incorporation in light-emitting devices.

Acknowledgment. The authors thank Prof. Mouni Bawendi and Ken Kuno for useful discussions. R.S.K. thanks the NSF for his graduate fellowship. This research was supported by NSF primarily under grant no. CHE-9312413 and in part by grant no. DMR-9022933. CM980468P