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SALT-INDUCED BLOCK COPOLYMER MICELLES AS NANOREACTORS FOR THE FORMATION OF CdS NANOPARTICLES

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ABSTRACT

A novel preparation method of CdS nanoparticles in the core or corona of micelles is presented. Poly(styrene-*block*-2-vinylpyridine) (PS-*b*-P2VP) and cadmium ions form aggregates of single micelles, called compound micelles, upon addition of the cadmium acetate salt into a solution of the block copolymer in tetrahydrofuran. The growth of CdS nanoparticles is confined to the core of single micelles after introduction of hydrogen sulfide gas into the solution. UV-visible spectroscopy, fluorescence spectroscopy, and transmission electron microscopy were employed to characterize the prepared core-embedded CdS nanoparticles. Corona-embedded CdS nanoparticles were prepared by dropping the core-embedded CdS nanoparticles into water with a low pH value. The location change of the CdS nanoparticles was accompanied by a structural change of the micelles, a change from compound micelles to single micelles. In a single micelle, CdS nanoparticles distribute randomly in the corona. The size of the nanoparticles increases slightly after the transition.

INTRODUCTION

The synthesis of semiconductor nanoparticles or clusters is emerging in the fields of materials science and colloid science because of their wide range of optical and electronic properties [1-5]. Many people have prepared nanoparticles in micelles formed by block copolymers [6-7]. A micelle core can be regarded as a nanosized reaction vessel, and the growth of colloidal particles can be limited to the micelle core. Recently in our group we prepared CdS nanoparticles in the core (core-embedded) and corona part (corona-embedded) of salt-induced micelles [8-9]. The size of CdS nanoparticles can be controlled by changing 2VP: Cd²⁺ molar ratio and block copolymer concentration in THF etc.

EXPERIMENTAL DETAILS

The synthesis of the PS-*b*-P2VP block copolymer was performed using sequential anionic polymerization. The molecular weight of the block copolymer is 25.5×10^3 g/mol (M_n) with a polydispersity of 1.30, measured by GPC relative to PS standards. The content of 2-vinylpyridine units in the block copolymer is about 35 mol% as measured by ¹H-NMR.

Preparation of core-embedded CdS nanoparticles: PS-*b*-P2VP block copolymer was dissolved in THF at different concentrations under vigorous stirring for 1 hour. Cd(Ac)₂·2H₂O dissolved in a mixture of methanol and THF (1:2 V/V), was added to the polymer solution. The light yellow solution of core-embedded CdS nanoparticles was prepared by introducing H₂S gas into the complex solution.

Preparation of corona-embedded CdS nanoparticles: Corona-embedded CdS nanoparticles were prepared by dropping varying amounts of core-embedded CdS nanoparticles solution into water with a low pH value and then removing THF in the solution under vacuum.

UV-Visible absorption spectra were recorded on a Shimadzu UV-Vis spectrophotometer (UV-2401PC), by scanning the CdS-containing solution in a 1-cm quartz cell. Steady-state fluorescence spectra were obtained on a SPEX Fluorolog spectrophotometer equipped with a 450W Xe arc-lamp and a PMT detector. The excitation wavelength was 350 nm and the bandwidths were 10 nm for excitation and emission. Fluorescence measurements were obtained on the colloidal suspensions contained in quartz cuvettes. Electron microscopy was performed on a Zeiss EM 10A transmission electron microscope operated at 100 kV. TEM samples were prepared by depositing a droplet of micelle solution or CdS-containing colloidal solution (<0.1 mg/ml) onto a copper grid which had been coated with Formvar/Silicon monoxide film.

RESULTS AND DISCUSSION

In a previous paper we have demonstrated that upon addition of cadmium ions into a solution of PS-*b*-P2VP block copolymer in THF, a solvent for both of the blocks, compound micelles form due to complexation of Cd²⁺ with the 2-vinylpyridine (2VP) units [8]. A compound micelle is an assembly of single micelles. A core of a single micelle is composed of Cd²⁺/2VP complexes and a corona is composed of PS blocks. The growth of a CdS nanoparticle is confined to the core of a single micelle.

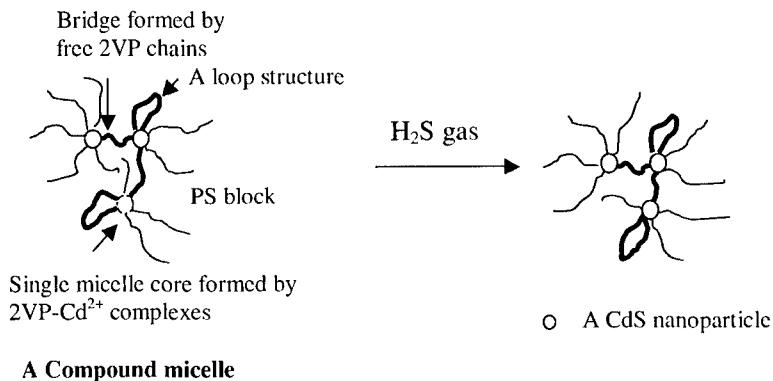


Figure 1 Schematic representation of the formation of a compound micelle, and preparation of CdS nanoparticles in a compound micelle.

Figure 2 are three UV-visible absorption spectra of nanoparticles prepared at different 2VP: Cd²⁺ molar ratios. The absorption edge of the curves shifts with the change of the molar ratio. When the molar ratio is 1:0.5, the absorption edge is at about 458 nm (particle diameter of 3.8 nm). However, when the ratio is 1:0.77 and 1:2.31, it red-shifts to 470 and 485 nm.

corresponding to particle diameters of 4.2 and 4.5 nm, respectively. This result indicates that larger nanoparticles can be prepared at lower 2VP: Cd²⁺ molar ratios.

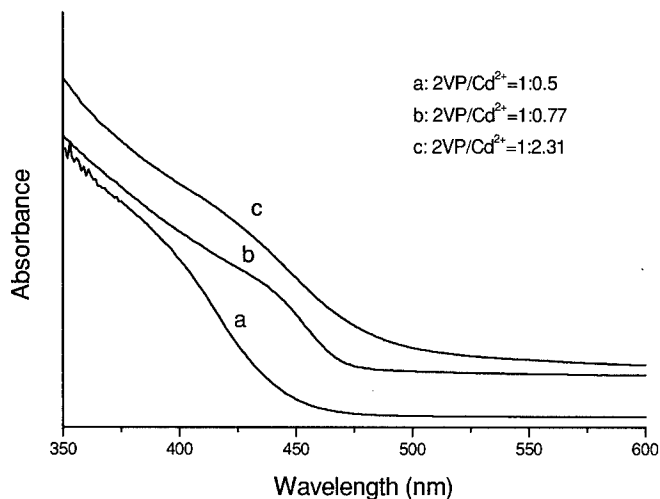


Figure 2 UV-visible absorption spectra of CdS nanoparticles in salt induced micelles at different 2VP : Cd²⁺ molar ratios. The concentration of the block copolymer in THF is 26.6 g/L.

Holding the 2VP: Cd²⁺ molar ratio constant (1:0.5), the effect of block copolymer concentration in THF on the size of CdS nanoparticles was investigated. Figure 3 shows three typical UV-Visible absorption curves of CdS nanoparticles prepared from the PS-*b*-P2VP-Cd²⁺ solutions with concentrations of 10, 2.5 and 1.0 g/L. It can be seen that the absorption edge blue-shifts with decreasing concentration. It is noted that a weak maximum develops at about 370 nm at low concentration. This maximum is characteristic of CdS nanoparticles with a comparatively small size and narrow size distribution.

The stability of CdS nanoparticles in solution was also investigated. The CdS nanoparticles prepared in the block copolymer micelle solutions are very stable if the 2VP: Cd²⁺ molar ratio is above 1:2. Precipitation was not observed even after storage of the solutions at room temperature for more than two months. UV-Visible absorption spectra shows that CdS-containing solutions measured after 12 days storage red-shifts 19 nm compared to freshly prepared CdS nanoparticles in solution. No further red-shift is observed after an additional 33 days of storage.

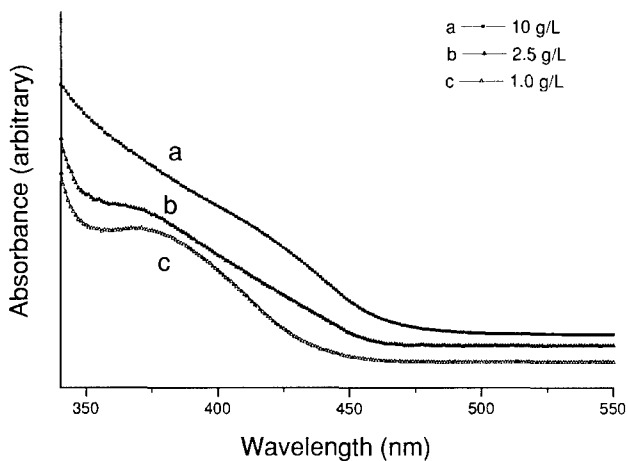


Figure 3 UV-visible absorption spectra of CdS nanoparticles in salt induced micelles prepared from PS-*b*-P2VP/Cd²⁺ in THF at different block copolymer concentrations. The 2VP : Cd²⁺ molar ratio is 1:0.5. The plots are shifted vertically for clarity.

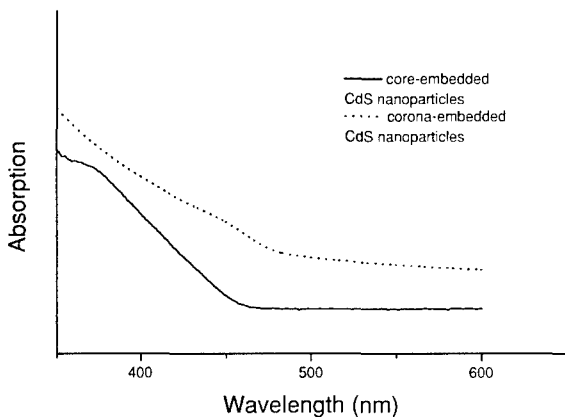


Figure 4 UV-Vis absorption spectra of core-embedded CdS nanoparticles and corona-embedded CdS nanoparticles. The concentration of the block copolymer in THF is 2.5 g/L and the molar ratio of 2VP units to Cd²⁺ is 1:0.5.

Figure 4 shows UV-vis spectra of core-embedded and corona-embedded CdS nanoparticles in THF. For the core-embedded CdS nanoparticles solution with a polymer concentration of 2.5 mg/ml, the absorption edge is at about 457 nm, however, the absorption edge red-shifted to 474 nm when the core-embedded CdS nanoparticles solution was dropped into water with a pH value of 3.3 (corona-embedded nanoparticles). The average diameter of the core-embedded CdS particles is about 3.7 nm, and after the transition it increases to about 4.4 nm, which indicates that some nanoparticles aggregated into bigger nanoparticles during the transition from core-embedded nanoparticles to corona-embedded nanoparticles.

Figure 5 is a TEM image of corona-embedded CdS nanoparticles prepared by dropping 1 ml of the core-embedded CdS nanoparticle solution into 20 ml of water with a pH value of 3.3. Examining the TEM image carefully, it can be found that there are more nanoparticles in the corona region. This morphology is just like a colloidal core-shell structure. This TEM image strongly proves that nanoparticles are located around the corona of the micelles and form a "red currant" morphology [10]. The diameters of the nanoparticles range from 2 to 5 nm.

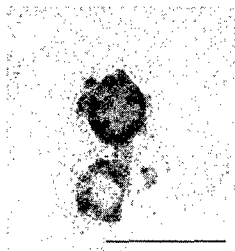


Figure 5 A TEM image of corona-embedded CdS nanoparticles prepared by dropping 1 ml of the core-embedded CdS nanoparticle solution into 20 ml water with a pH value of 3.3. The Scale bar on the TEM image represents 100nm.

ACKNOWLEDGMENTS

We would like to thank Dr. Jill Verlander Reed, and Ms. Melissa Ann Lewis, College of Medicine, electron microscopy core facility, University of Florida, for performing the TEM. and Prof. Kirk S. Schanze, Mr. Benjamin S. Harrison, Department of Chemistry, University of Florida, in fluorescence measurements and analysis. Financial support of the Center for Materials in Sensors and Actuators (MINSA, Grant No. DAAD19-00-1-0002) is gratefully acknowledged.

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