

Synthesis and Characterization of ω -Sulfonated Polystyrene-stabilized Cadmium Sulfide Nanoclusters

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Abstract: We report an important and useful method for preparing ω -sulfonated polystyrene-stabilized cadmium sulfide (CdS) nanoclusters. The ω -sulfonated polystyrene ($M_n = 5000$ g/mol) was prepared successfully through chain-end sulfonation of poly(styryl)lithium using 1,3-propanesultone; the resulting polymer was used successfully as a polymeric stabilizing agent for the preparation of semiconductor CdS nanoclusters by reduction of cadmium acetate in a mixture of toluene and methanol (9:1, v/v). The nanoclusters that formed were characterized by a combination of transmission electron microscopy, X-ray diffraction, and UV/Vis spectroscopic analysis. The ω -sulfonated polystyrene-stabilized CdS nanoclusters synthesized in this study exhibited the cubic phase (zinc-blende phase) structure in the range of 2–8 nm.

Keywords: cadmium sulfide, chain-end sulfonation, nanoclusters, semiconductor, ω -sulfonated polystyrene.

Introduction

Most nano-sized transition metals or metal salts (nanoclusters) including semiconductors have received a great attention in academic as well as industrial fields because of their unique electronic and optical properties compared with those of the corresponding bulks due to the 'quantum-size effect'.^{1,2} Specifically, functionalized organic substances including polymers carrying thiol or amine groups were found to be the efficient materials for the preparation of stable nano-sized gold colloids.^{3,4} The recent important subject in the nanotechnology field is how to synthesize easily and cheaply stable nanoparticles or nanoclusters exhibiting narrow size distributions for their applications in a variety of fields of material science.³ Nano-sized II-VI semiconductor clusters may be used in a variety of technological fields such as light-emitting diodes, photodiodes, photovoltaic solar cells, or gas sensors.⁵ With this regard, it has been reported that cadmium sulfide (CdS) semiconductor can be readily synthesized by several reactions including in reversed micelles, organization of monodispersed nanoparticles in biological polymeric template, or specific interactions of the inorganic particles with a functional substance as a stabi-

lizer.⁵⁻⁷ Polymer-stabilized CdS nanocluster is expected to be utilized for an easy fabrication of self-assembled nanostructure via the 'bottom-up' process using block or random copolymers to produce useful nanodevices.^{3,4,7c,8} Although the CdS nanoclusters were not re-dissolved in organic solvents, telechelic polymers (α,ω -difunctionalized polymers) were found to be used as the polymeric stabilizers for nano-sized cadmium sulfide (CdS) prepared by the sol-gel process.⁶ Among many interesting methods, the sol-gel process is a good methodology to control the size of particles using polymeric surfactants including block copolymers or chain-end functionalized polymers.^{6,9}

In this article, we report the results for the synthesis of ω -sulfonated polystyrene and its use for the preparation of nano-sized CdS particles soluble in organic solvents.

Experimental

Toluene (DongYang Chem. Co., reagent grade) and methanol (DongYang Chem. Co., reagent grade) were used as solvents without further purification to synthesize cadmium sulfide nanoclusters. Cadmium acetate dihydrate ($\text{Cd}(\text{OAc})_2$; Aldrich Chem. Co., 98%) was used without further purification. In order to generate hydrogen sulfide (H_2S) gas, anhydrous sodium sulfide (Na_2S ; Strem Chem., 95%) was used as purchased. Benzene (DongYang Chem. Co., reagent

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grade) and tetrahydrofuran (THF; DongYang Chem. Co., reagent grade) were purified by following the procedures described in the literature.¹⁰ Styrene (DongYang Chem. Co.; reagent grade) and 1,3-propanesultone (Aldrich Chem. Co., 98+%) were purified by following the modified procedures described in the literature.^{10,11} *n*-Butyllithium was purchased and used as an anionic initiator without further purification.

ω -Sulfonated polystyrene (PS) was synthesized by following the modified procedures in chain-end functionalizations of poly(styryl)lithium as described in the literature.¹¹ The resulting polymer was hydrolyzed with a mixture of the concentrated sulfuric acid/methanol/tetrahydrofuran (2 M in methanol/THF (5/95, v/v)). The synthesis of the ω -sulfonated PS-stabilized CdS nanoclusters were performed at room temperature. Both 10 mL of Cd(OAc)₂ (6.38×10^{-3} mol) in methanol and 90 mL of the ω -sulfonated polystyrene ($M_n = 5,000$ g/mol) (3.33×10^{-4} mol) in toluene were prepared with stirring. Again, the two stock solutions were mixed each other. The mixture of the stock solutions was directly reduced using H₂S gas obtained *in situ* through the reaction of Na₂S with dilute HCl. The H₂S gas was delivered until the color of the resulting product in the mixture of methanol/toluene (10/90, v/v) changed from white to yellow, followed by precipitation in excess methanol and filtration. Size exclusion chromatograms were obtained at a flow rate of 1.0 mL/min in THF at 30°C using a Wyatt Technology component system (OPTILAB DSP RI detector and miniDAWN) with a DIONEX P680 HPLC pump equipped with a five ultra- μ -Styragel columns (two 10⁵, and one each of 10⁴, 10³, and 500 Å) and a UV/Visible detector (Waters 490E Programmable Multi-wavelength Detector) after calibration with standard polystyrene samples (Polymer Laboratories). ¹H NMR spectroscopic analysis was performed using a Varian spectrometer (model; Gemini 200 (200 MHz)) in CDCl₃ at 25°C. The UV/Visible absorption spectra were obtained using a Hewlett-Packard 8453A Diode Array spectrophotometer. The X-ray diffraction (XRD) of the samples was obtained on a MacScience MXP18 diffractometer using Cu K α radiation at wavelength $\lambda = 1.5405$ Å. Diffraction patterns were measured in 40 kV and 100 mA with 1°/min scan speed. Transmission electron microscopic techniques (TEM, Philips CM) were employed to investigate the morphology and the microstructure of the CdS nanoclusters. The photoluminescence spectra with 1.0 g/L of the concentration were obtained using a 365 nm excitation line on a ISS PS-1 spectrofluorometer equipped with a 300 W-xenon arc lamp.

Results and Discussion

Synthesis of ω -Functionalized Polymers. Chain-end functionalizations of 'living' polymers prepared by alkyl-lithium-initiated polymerizations using a variety of electrophiles as the terminating agents can produce the

corresponding ω -functionalized polymers.¹² Practically, the ω -sulfonated PS was readily prepared by following the procedures described in the literatures.¹¹ The functionalization yields for ω -sulfonation in this experiment were over 98 mol-% on the basis of the result from ¹H NMR and thin layer chromatographic (TLC) analysis ($R_f = 0.0$ in toluene as an eluent for PS-SO₃H). As already mentioned in the case of α, ω -disulfonated PS,⁶ the resulting ω -sulfonated PS is also expected to be utilized as the polymeric stabilizer for the preparation of nano-sized CdS clusters.

Preparation of Semiconductor CdS Nanoclusters. The ω -sulfonated PS-stabilized CdS nanoclusters were prepared by following the same procedures described in the literature.⁶ The stock solution was first prepared in the mixture of methanol (10 mL) and toluene (90 mL) at room temperature by dissolving cadmium salt (Cd(OAc)₂) and the ω -sulfonated PS ($M_n = 5,000$), followed by reduction of the cadmium salt using H₂S gas delivered by a syringe with stirring. The optical color of the solution changed from no color to orange with addition of a proper amount of H₂S gas. However, no precipitate in the solution was observed unlike the case of preparation of the CdS nanoclusters using telechelic polymers.⁶ The transmission electron microscopic (TEM) image of the typical ω -sulfonated PS-stabilized CdS nanoclusters and the corresponding electron diffraction (ED) pattern are shown in Figure 1(a). The size of the CdS nanoclusters was in the range of 2~8 nm and the nanoparticles were homogeneously

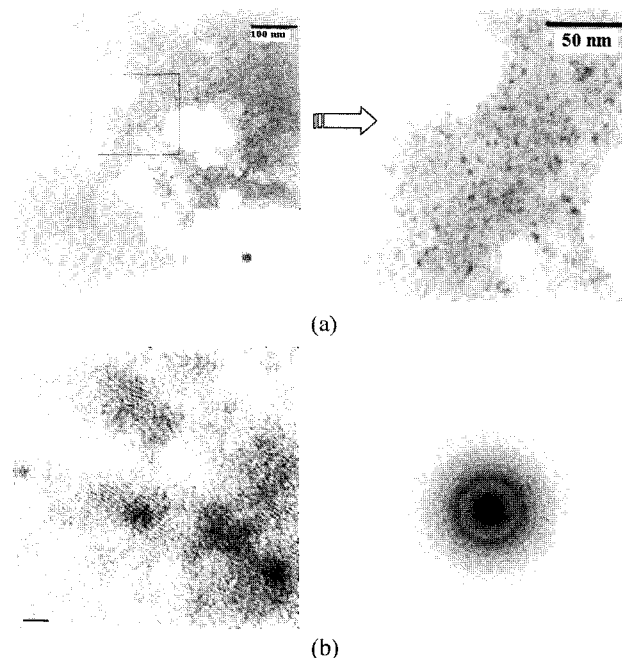


Figure 1. (a) The TEM image (inset electron diffraction pattern) and the TEM image enlarged of the ω -sulfonated polystyrene (PS)-stabilized CdS nanoclusters in toluene; (b) HRTEM image and electron diffraction pattern of the CdS nanoclusters (scale bar; 2 nm).

distributed in the ω -sulfonated PS. The ED pattern in the inset of Figure 1 informs that the CdS nanoclusters exhibit a crystal structure in the ω -sulfonated PS matrix under these experimental conditions. Clearly, high resolution TEM of the CdS nanoclusters as shown in Figure 1(b) also indicates that the nanoclusters shows a crystal structure with 2~8 nm of size. The X-ray diffraction (XRD) patterns of the ω -sulfonated PS and the ω -sulfonated PS-stabilized CdS nanoclusters are shown in Figure 2. It has been reported that the corresponding peaks in the XRD pattern of the cadmium ion disappeared in the small-angle X-ray diffraction region of 0~15° with sulfidation by exposure of H₂S gas leading to the formation of the CdS nanoclusters.^{7b} In this respect, the peaks at the relatively low angle range of 10~20° may be attributed to the diffractions arising from an association of the ω -sulfonated polystyrene chains leading to the formation of crystal-like structures as shown in Figure 2(a). On the other hand, the two peaks at 27.9 and 45.5° in X-ray diffraction pattern at high angle must be attributed to the diffraction of (111) and (220) lattice planes of the cubic (zinc-blende phase) CdS nanostructures in Figure 2(b).¹³ The broad phase structure seems to be due to a broad size distribution of the CdS nanoparticles or an incomplete conver-

sion of cadmium ion to CdS salt.^{13c}

Most ω -sulfonated PS-stabilized CdS nanoclusters are very stable in air and can be readily re-dissolved in the hydrocarbon or polar solvents such as toluene, tetrahydrofuran (THF), or chloroform. It has been reported that the polymer-stabilized semiconductor CdS nanoclusters exhibit not only a weak electronic spectral absorption controlled in the wavelength range of 300~500 nm depending upon the environmental condition but also the photoluminescent (PL) property in the range of 500~600 nm.^{13b,c,14} Specifically, the adsorption edge of the CdS nanoparticles in tri-*n*-octylphosphine has been reported to be 478 nm which is a blue shift in relation to that of the bulk material (515 nm).^{14f} It has been reported that the CdS nanoclusters prepared in isopropanol as a non-aqueous solvent exhibited an absorption edge near 400 nm while the CdS bulk band gap was 510 nm.¹⁵ The polystyrene-based ionomer carrying carboxylic acid groups-stabilized CdS nanoclusters showed the adsorption edge near 390 nm.¹⁶ An important point has been found that the absorption edge increases with the length of the side chain in the ionomer.¹⁶ Usually, the luminescence spectrum of bulk CdS was reported to exhibit a broad emission in the 500 to 700 nm region.^{14f} The edge luminescence usually shifts to higher energy in smaller particles because of shallow traps blue-shifting with the conduction band in smaller crystallites.¹⁵ Furthermore, it has been reported that not only the ratio of the matrix to Cd²⁺ + S²⁻ increases the emission spectra shift toward the blue but also the shapes of the emission spectra are dependent of the concentration of the matrix.^{14b} In this experiment, the UV/Visible spectra of bare ω -sulfonated PS and CdS/ ω -sulfonated PS nanoclusters and the PL spectrum of the corresponding CdS nanocluster in THF are shown in Figure 3. No absorption maximum of the electronic spectrum of the ω -sulfonated PS in organic solvents such as toluene, chloroform, or THF was observed over the range of 300 nm as shown in the inset of Figure 3. In the case of polystyrene-ionomer as the matrix,¹⁶ analogously no absorption behavior having the absorption edge near 300 nm was observed. Concerning the absorption onset of the CdS particles greatly dependent of the size, the concentration, and the kind of the surfactant stabilizing the particles,^{7b,14b,17} the absorption edge near 450 nm of the ω -sulfonated PS-stabilized CdS nanoclusters in this experiment may also correspond to relatively small CdS particles exhibiting a 'quantum size effect' compared with that of the bulk CdS (510 nm).^{7b,18} Especially, upon the excitation with light at a wavelength of 360 nm, the bands edge luminescence (BEL) emission spectrum at about 405 nm may be attributed to a narrow size distribution of very small CdS nanoclusters (2~8 nm). The broad PL peak of the ω -sulfonated PS-stabilized CdS nanoclusters may be attributed to recombination of charged carriers trapped in the surface.^{7c,14} The transition absorption at 405 nm is expected to arise from the formation of S⁻ at the semiconductor surface undergoing chemical changes at the smaller CdS particle

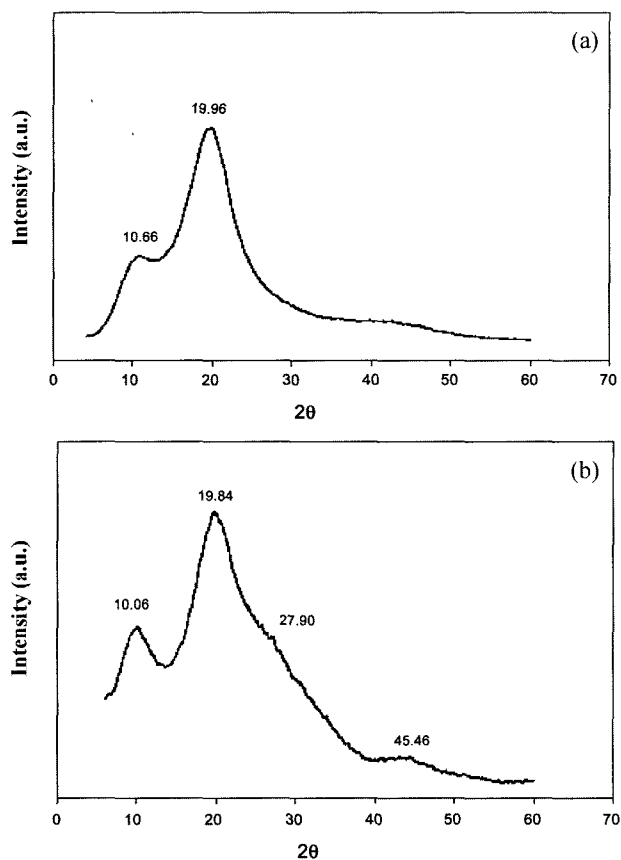


Figure 2. The X-ray diffraction pattern of the (a) ω -sulfonated polystyrene and (b) the ω -sulfonated PS-stabilized CdS nanoclusters isolated from methanol.

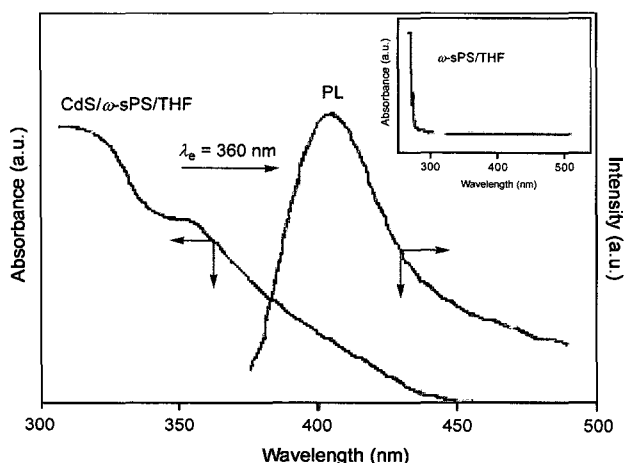


Figure 3. The UV/Visible spectrum of the ω -sulfonated PS and the ω -sulfonated PS-stabilized CdS nanoclusters and the photoluminescence (PL) spectrum of the ω -sulfonated PS-stabilized CdS nanoclusters in THF upon the excitation with light at a wavelength of 360 nm.

surface compared with the bulk CdS particle.^{14c} Concerning the solution behavior of the ω -sulfonated PS-stabilized CdS nanoclusters soluble in common organic solvents such as toluene, THF, or chloroform, there is no change of photochemical behaviors of the formed ω -sulfonated PS-stabilized CdS nanocrystal occurred irrespectively of environmental change. Furthermore, the ω -sulfonated PS-stabilized CdS nanoclusters were very stable even in air for at least 6 months.

Conclusions

Although there are many reports for the useful methodology to synthesize the CdS nanoclusters-stabilized by using functional polymers, there is few report for the preparation of the CdS nanoclusters using ω -functionalized polymers. We report a simple synthetic method to produce the ω -sulfonated PS-stabilized CdS nanoclusters soluble in common organic solvents. The formed CdS nanoclusters in this experiment exhibited the cubic phase (zinc-blende phase) crystal structure in the range of 2~8 nm. This result informs us that ω -functionalized polymers may be utilized as the polymeric stabilizers for the preparation of nano-sized transition metal or metal salt clusters via a sol-gel process. Concerning the 'bottom-up' technique for an easy fabrication of nano-patterned structures, further application studies for the resulting nanoclusters will be our future works.

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