

Preparation of Nanosize Cadmium Sulfide Particles with a Silk Fibroin Membrane and Their Photocatalytic Activity

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ABSTRACT: We present a novel method for the synthesis of nanosize CdS particles with a silk fibroin membrane, which were characterized with UV spectrometry, X-ray diffraction (XRD), and atomic force microscopy. The UV spectra showed a clear blueshift in the absorption edge for the CdS particles prepared at different concentrations. XRD showed the prevailing crystal were the cube ZnS crystals formed. The particle sizes were calculated from the band

gaps with the effective mass approximate model, suggesting that they were dependent on the concentration of the precursors. Meanwhile, nanosize CdS had good photocatalytic activity throughout the photocatalytic degradation experiments. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2162–2166, 2006

Key words: silk fibroin membrane; band gap; photocatalytic

INTRODUCTION

Semiconductor nanoparticles that show quantum-size effects are defined as *quantum dots*. In the past decade, semiconductor quantum dots have drawn considerable attention because of their unique electronic,^{1,2} optical,^{3–5} catalytic,^{6,7} electrochemical,⁸ and enhanced nonlinear optical⁹ properties compared to those in their bulk forms. CdS nanoparticles have potential applications as optoelectronic devices,¹⁰ single-electron transistors,¹¹ lasers,¹² single-charge memories,¹³ electrochemical cells,¹⁴ fluorescent labelers of cell organelles,¹⁵ solar cells,¹⁶ and so on. Thus, the preparation of size-controlled, monodispersed semiconductor nanoparticles is of primary importance to these exciting applications.^{17,18} Several methods have been reported for the preparation of nanosize CdS particles, including the sol–gel method,¹⁹ solid-phase method,²⁰ and template synthesis.²¹ However, it is difficult to control the size of nanoparticles with these methods. Alternatively, membranes have been used as templates to synthesize nanosize CdS particles,^{22–26} which, however, could only synthesize one kind of size of the nanoparticles. For example, Manjunatha and Jayasheela²⁶ synthesized nanosize CdS particles with egg membrane, by which the average diameter of the grains was above 50 nm.

Bombyx mori silk fibroin is a fibrous protein that is one of the most extensively characterized silks. Be-

cause of their impressive properties combined with biocompatibility and relative environmental stability, *B. mori* silks have been used as an important set of material options in the fields of controlled release, biomaterials, and scaffolds for tissue engineering for decades, and also as textile materials.^{27–31}

Membranes prepared from *B. mori* silk fibroins are a kind of nonporous, homogeneous charged material. Silk fibroin membranes have been used as substrates for enzyme immobilization in biosensors^{27–29} and drug-delivery systems,^{32,33} among other applications.

In this article, a new application for the *B. mori* silk fibroin membrane is presented. A novel method was developed for the synthesis of CdS nanoparticles of a desired size with *B. mori* silk fibroin membrane. The prepared nanosize CdS particles with this method had good dispersity.

EXPERIMENTAL

Reagents and equipment

The following reagents and equipment were used: cadmium chloride [analytical-reagent (AR) grade, the Second Chemical Reagent Factory, Shanghai, China], thioacetamide (AR, Shanghai Chemical Reagent Co., Ltd., Shanghai, China), methyl alcohol and ethanol (AR, Hangzhou Changzhen Chemical Reagent Factory, Hangzhou, China), a Lambda900 UV/visibie/NIR spectrometer (PerkinElmer), a DDSJ-308A conductivity instrument (Shanghai Leici Co., Ltd., Shanghai, China), a 722S spectrophotometer (Shanghai Analysis Instrument Co., Ltd., Shanghai, China), a D-Max2400XRD instrument (Rigaku Co., Tokyo, Ja-

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pan), and a Nanoscope III atomic force microscope (Digital Instruments, Inc., Santa Barbara, CA).

Preparation of the silk fibroin membrane

The silk fibroin membrane was prepared according to the literature.³³ The disused cocoon was put in a mixed solution of fatty acid neutral soap [weight percentage (ω) = 0.02%] and sodium carbonate (ω = 0.001), degummed two times at 98°C (ca. 1 h each time), washed several times with deionized water, and dried, and the silk fibroin was prepared. Then, 3 g of the silk fibroin was put in a mixing solution (CaCl₂: C₂H₅OH : H₂O molar ratio = 1 : 2 : 8) at 70°C for 2 h. After the solution was filtered, it was put in a cellulose membrane to dialyze with deionized water for 3 days. Finally, the silk fibroin solution was put in a polystyrene box at 30°C for 3 days. After the membranes dried, they were immersed in a 75 wt % aqueous CH₃OH solution and kept for 2 h at 25°C to crosslink the silk fibroin membrane.

Preparation of nanosize CdS

The solution pH value can affect the velocity of ions crossing a silk fibroin membrane because the isoelectric point of the silk fibroin is about pH 4.5.³³ The velocity of the ions increases with pH value from 6 to 7. However, no significant difference was observed when the data were compared at pH 7 and pH 8 (Table I). Moreover, the solubility of the silk membrane increases when the pH value is above 9,³³ so the following experiments were carried out at pH = 7.

CdCl₂ (250 mL, 0.1 mol/L) and CH₃CSNH₂ (250 mL, 0.15 mol/L) aqueous solutions (pH = 7.0) were prepared and put into the right room and the left room of the membrane reactor [Fig. 1(a)], respectively; they were then stirred at room temperature for 24 h. When the pH value of the aqueous solution was higher than the isoelectric point (pI), the silk fibroin membrane became negatively charged. In this case, the Cd²⁺ ions in the right room crossed the silk fibroin membrane and reacted with CH₃CSNH₂ to crystallize the nanosize CdS particles [Fig. 1(b)]. For comparison, the same experiments were carried out at concentra-

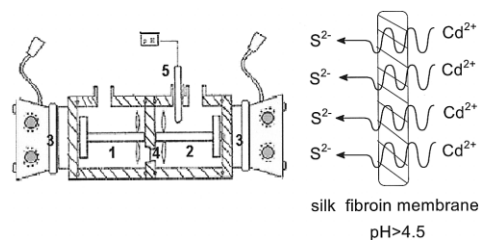


Figure 1 (a) Schematic diagram of the membrane reactor and (b) the expanded silk membrane that the Cd²⁺ ions crossed to react with S²⁻ and form CdS particles: (1) left room, (2) right room, (3) magnetic stirrer, (4) silk membrane, and (5) pH electrode.

tions of 0.5 mol/L for CdCl₂ and 0.6 mol/L for the CH₃CSNH₂ aqueous solution.

The reaction solution in the left room was then taken out every 4 h for UV absorption on the Lambda900 UV/visible/NIR spectrometer, measured at wavelengths of 310–450 nm. The band gap of nanosize CdS particles was calculated according to the following equation:³⁴

$$E_g = \frac{1240}{\lambda_0} \quad (1)$$

where E_g is the absorption band gap of the semiconductor nanosize grains (eV) and λ_0 is the maximum absorption wavelength (nm).

The particle size of nanosize CdS was calculated according to the following equation (effective mass approximate model):^{35,36}

$$E_{(\gamma)} = E_{g(\gamma=\infty)} + \frac{\hbar^2 \pi^2}{2\mu\gamma^2} - \frac{1.768e^2}{\epsilon\gamma} - 0.248E_{Ry}^* \quad (2)$$

$$\mu = \left[\frac{1}{m_e^{-1}} + \frac{1}{m_h^+} \right]^{-1}$$

$$E_{Ry}^* = \frac{\mu e^4}{2\pi^2 \hbar^2}$$

where $E_{(\gamma)}$ is the absorption band gap in nanosize form, $E_{g(\gamma=\infty)}$ is the absorption band gap in the block form, \hbar is Planck's constant, e is the electronic charge, m_e^{-1} is the effective mass of the electrons, m_h^+ is the effective mass of the electron holes, μ is the converted mass of the particle, ϵ is the dielectric constant of the medium, γ is the radius of the particle, and E_{Ry}^* is the finite Rydberg constant.

When the colorless solution in the left room of the membrane reactor gradually became a yellowish milk solution, a small amount of milk liquid was diluted to the proper concentration with deionized water. A slice of glass was ultrasonically cleaned, and a membrane was made with the diluted proper concentration of

TABLE I
A Remaining Concentration of the Ca²⁺ Reactant at Different pH Values

pH	0		5						
	min	min	1 h	4 h	8 h	12 h	16 h	20 h	
6	0.10	0.085	0.070	0.065	0.055	0.041	0.038	0.034	
7	0.10	0.078	0.060	0.050	0.043	0.029	0.025	0.022	
8	0.10	0.075	0.057	0.045	0.042	0.028	0.023	0.021	

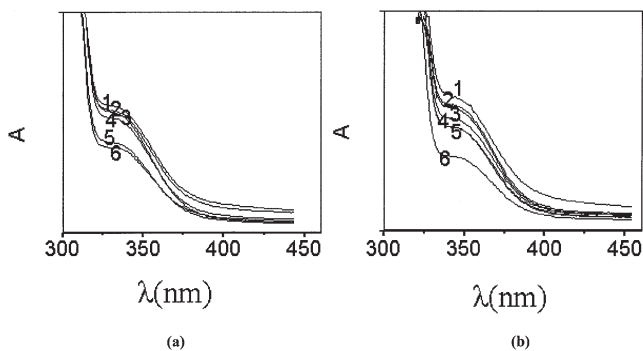


Figure 2 UV absorption (A) spectra of CdS particles prepared at Cd^{2+} concentrations of (a) 0.1 and (b) 0.5 mol/L: (1) 4, (2) 8, (3) 12, (4) 16, (5) 20, and (6) 24 h.

nanosize CdS, and the distribution situation of the nanosize CdS was then characterized with the Nano-scope III atomic force microscope (Fig. 4, shown later).

Finally, the CdS particles in the left room were washed 5–6 times with deionized water, dried at 50°C , and then characterized with X-ray diffraction (XRD).

The photocatalytic activity of 4 mg of prepared nanosize CdS was put into 25 mL of a 50 mg/L solution of the reactive dye KD-8B ($\lambda_{\text{max}} = 542 \text{ nm}$). The solution was taken out at different times, and the dye fade ratio (D) was tested according to the following equation:

$$D = \frac{E_0 - E_i}{E_0} \times 100\% \quad (3)$$

where D is the dye fade ratio, E_0 is the optical density of the reactive dye before sunlight and E_i is the optical density of the reactive dye in different sunlight period.

RESULTS AND DISCUSSION

Analysis of nanosize CdS with UV spectroscopy and atomic force microscopy (AFM)

Generally, if the size of a semiconductor particle is small enough, that is, several nanometers, band gap widening and the quantum-size effect will occur.^{35,36} The quantum-size effect has the most direct effect on the blueshift of the border for the absorption spectrum of nanosize particles. Figure 2 shows the variation of optical absorptions at different reaction times at Cd^{2+} concentrations of 0.1 and 0.5 mol/L, where an obvious blueshift was observed. Particularly interesting was that the wavelength of the UV absorption spectrum increased when the Cd^{2+} concentration increased. However, at the same concentration, the wavelength of the absorption spectrum of CdS did not increase with reaction time. This indicated constant fresh nucleation rather than the growth of initially formed nuclei as more cadmium ions diffused across the

membrane and were available for the reaction. The band gaps as shown in Figure 2 were 3.10 and 2.89 eV. The band gap of CdS was a function of particle size within the nanosize range under both tight binding and effective mass approximation. Therefore, the particle sizes were calculated to be 3.5 and 8 nm, respectively, at Cd^{2+} concentrations of 0.1 and 0.5 mol/L on the basis of the band gap variation with size data under effective mass approximation.

Figure 3 shows the XRD data of prepared CdS. Both samples had three strong diffractive peaks (111, 220, and 311), which suggested that the prepared nanosize CdS was mainly cube ZnS crystals formed according to XRD standard cards. Although the literature³⁷ has reported that the crystal form of nanosize CdS is a mixture with cube ZnS and hexahedron ZnS, the crystal form of our prepared CdS was more close to the cube ZnS. The width of the three diffractive peaks of the samples was big, due to the ultrafine nature of the CdS powders. The halfwidth values of the strongest diffractive peaks of both samples were measured, and the particle size of the nanosize CdS particles was calculated according to eq. (1).^{37,38} The particle sizes were calculated to be 3.7 and 7.8 nm, respectively, at Cd^{2+} concentrations of 0.1 and 0.5 mol/L; this was in good agreement with the size determined from the effective mass approximate calculations:

$$R = \frac{0.89\lambda}{\beta \cos\theta} \quad (4)$$

where R is the radius of the particle, λ is the wavelength of the Cu atoms of $\text{K}\alpha$ X-ray lines (0.154 nm), β is the halfwidth value of the diffractive peaks (rad), and θ is the half diffractive angle.

Figure 4 shows the AFM data of prepared CdS. The prepared nanosize CdS had good dispersity and di-

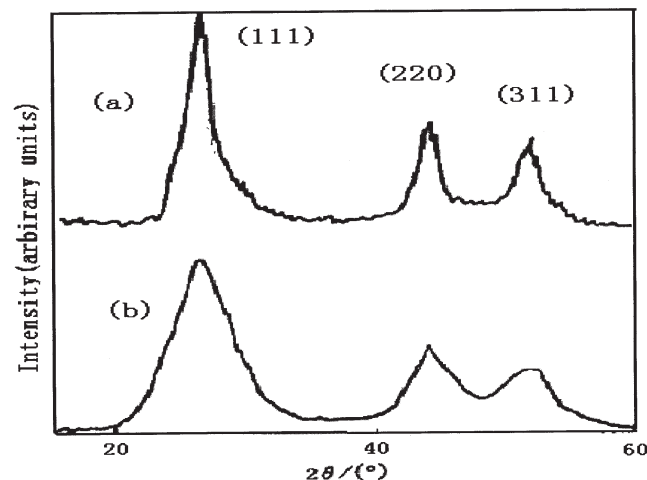


Figure 3 XRD images of CdS particles prepared at Cd^{2+} concentrations of (a) 0.1 and (b) 0.5 mol/L.

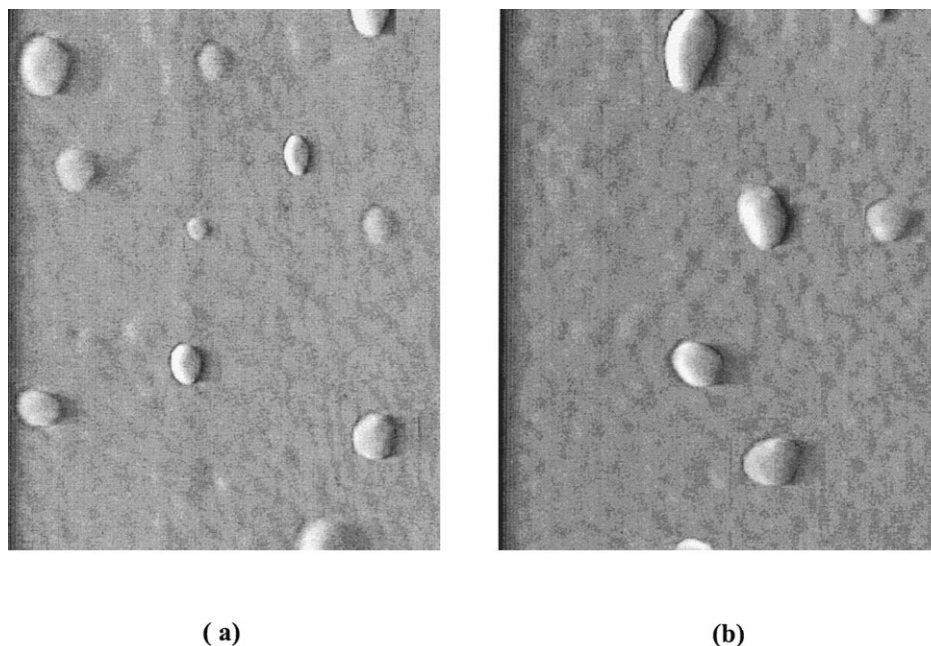


Figure 4 AFM images of CdS particles prepared at Cd^{2+} concentrations of (a) 0.1 and (b) 0.5 mol/L. The scan size was $50 \times 50 \text{ nm}^2$.

mensional uniformity. The average size of the nanosize particles prepared from the Cd^{2+} concentration of 0.1 mol/L was less than that prepared from the 0.5 mol/L concentration, although both were less than 10 nm. This was in good agreement with the size determined from our calculations.

The absorption spectrum of prepared CdS through the silk fibroin membrane took on blueshift and presented the quantum-size effect; it showed that the nanosize CdS was prepared successfully. Meanwhile, this result was confirmed by XRD and AFM. This showed that old cores were not increased, but new cores were formed constantly when Cd^{2+} through the silk fibroin membrane reacted with CH_3CSNH_2 , with to the same concentration gaining the same size nanosize particles. This could help with the preparation of smaller size and better dispersity nanosize particles.

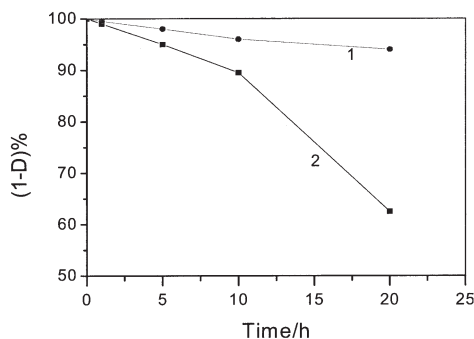


Figure 5 Photocatalytic degradation of the active dye KD-8B (1) without nanosize CdS and (2) with nanosize CdS.

So smaller sized and better dispersity nanosize CdS could be prepared with silk fibroin membranes.

Photocatalytic activity of nanosize CdS

When the energies of the photons are greater or equal to that of the band gap of nanosize CdS, the electron of valence band was excited to a conduction band, which produced electrons holes and made nanosize CdS have strong catalytic activity. As shown in Figure 5, the remaining rate ($1 - D$) of the reactive dye KD-8B with nanosize CdS reduced more quickly than that without nanosize CdS, which showed that the photocatalytic activity of nanosize CdS might have effectively degraded the dyestuffs. This photocatalytic performance could be used to deal with low-concentration organic wastewater in the textile industry, such as dye pollutants.

CONCLUSIONS

Nanosize CdS was synthesized with silk fibroin membranes, and the size of the CdS particles was only related to the concentration of the reactants, that is, CdCl_2 and CH_3CSNH_2 . High concentrations of reactants led to larger size CdS particles; this was independent on the reaction period. Nanosize CdS had good photocatalytic activity throughout photocatalytic degradation experiments.

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