

# Synthesis and Characterization of CdS Nanocrystals Embedded on Solid Electrolyte Films

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**ABSTRACT:** In this article nano-sized CdS crystal embedded in a PEO matrix was successfully prepared by a complex transformation method that is universal for preparing nanosized compounds containing transition metals. The size of embedded CdS particles was in the nanoscale from 2 to 10 nm determined by X-ray diffraction. The nanosized CdS displayed the expected blue shift of the onset absorbance in the UV spectrum. The amount of blue shift depends upon the dipping time of the PEO–cadmium complex film in a sodium sulfide solution as well as its concentration. The most effective means for adjusting the size of CdS nanocrystals is to change the ratio of the oxygen along with the PEO chain to the cadmium ion in the complex film. The alkali salt in the film would contribute to the conductivity of the composite film. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1263–1268, 2002; DOI 10.1002/app.10459

**Key words:** polyethylene oxide; nanocomposites; metal-polymer complexes; conducting polymers

## INTRODUCTION

Nanocrystals of various direct-gap semiconductors exhibit unusual optical properties, which make them attractive as materials for nonlinear optical elements and luminescent devices.<sup>1</sup> Complexes of II–VI quantum-sized nanocrystals with organic polymers have attracted much attention because of their stable structures and controllable optical properties,<sup>2–4</sup> offering high potential for use in full-color displays. Organic polymers, used as a matrix and a passivation agent, allow the nanocrystals to be uniformly dispersed.<sup>5</sup> In the

previous work, we have successfully prepared nanosized CdS or ZnS embedded on chitosan,<sup>6</sup> polyacrylonitrile (PAN),<sup>7</sup> and polyvinyl alcohol (PVA),<sup>8</sup> by a complex transformation method. In this article, polyethylene oxide (PEO) is employed as a matrix for preparing the nanosized CdS, and for preparing a conductive composite film containing alkali salts.

PEO is a flexible hydrophilic polar polymer, which has a higher conductivity than most of other polymers. When PEO is doped with some alkali salts, it becomes a solid electrolyte conductor, which is a so-called fast ion conductor. This is because the alkali ion can be ionized efficiently in the PEO medium, and forms an ion–dipole complex with the oxygen atoms along with the polymer chain. The interaction of such an ion–dipole complex is not as strong as a covalent bond, allowing the alkali cation to transfer directionally in the electrical field through the progressive pro-

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cess of dissociation-forming–dissociation-reforming of the complex. By taking advantage of developments in the preparation and characterization of semiconductor nanocrystals, and of fast ion conductor polymers, we have now constructed a hybrid polymer/CdS complex to study its potentially novel optical and transport properties.

## EXPERIMENTAL

CdCl<sub>2</sub> and Cd(OAc)<sub>2</sub> (from Tingxin Chemical Plant, China) and Na<sub>2</sub>S (from Yizhi Chemical Plant, China) were analytical grade reagents, and were used without further purification. PEO, the number-average molar weight was 20,000, and was purchased from Shanghai Chemical Reagent Service Station.

Ten milliliters 0.70 mol/L CdCl<sub>2</sub> · 2.5H<sub>2</sub>O or Cd(OAc)<sub>2</sub> · 2H<sub>2</sub>O aqueous solution was added into a certain amount of PEO aqueous solution (0.70 mol unit/L). The coordination reaction was taken at 60–70°C for 2 h. Then a transparent colorless solution (I) was obtained.

Half of the solution (I) was used to cast a thin film on a cleaned glass or quartz plate. Excluding most of the water in the infrared drier box for 2 h gave a thin colorless soft film, which was subsequently dipped in 0.26 mol/L sodium sulfide ethanol solution for 1.0 min. Different concentrations and different dipping times were also taken to determine the effect of the reaction condition on the particle size. After allowing evaporative drying for 24 h, followed by vacuum drying for 8 h, a series of light yellow films were obtained. This complex transformation method is referred to as the “membrane method.”

To prepare the composite conductive film PEO/CdS containing alkali salt, a “bulk method” was employed; 2.7 mL of 0.26 mol/L Na<sub>2</sub>S was dropwise added into the solution (I) containing  $7 \times 10^{-4}$  mol Cd<sup>2+</sup>, which was coordinated with PEO. The other samples were prepared using different amounts of different concentrations of Na<sub>2</sub>S, keeping the mol number of S<sup>2-</sup> equivalent to Cd<sup>2+</sup>. Still stirring sufficiently for 1 min after all the Na<sub>2</sub>S were dropped down, the solution was then casting on a glass or quartz plate with or without rinse by anhydrous ethanol to extract the alkali salt at the damp–dry state. The drying condition was similar to the membrane method described above.

The structure of the complexes was determined by IR spectroscopy. The crystal form and the size

of CdS in the PEO film were determined by XRD (D/MAX III X-ray diffractometer) patterns and UV (DMS-100s UV Spectrometer) spectra. The electric properties of the composite film containing alkali salt were measured by avometer (ZC-43, China) and megger (MY-63, China)

## RESULTS AND DISCUSSION

### Complex Transformation of Cd<sup>2+</sup> with PEO to CdS

Cd<sup>2+</sup>, like many other transition metal ions, may react easily with organic ligands to form a coordination bond. The oxygen atoms, contained in PEO chains, are good ligands due to their lone-pair electrons. The IR spectra give good evidence of the existence of such coordination bonds. The characteristic absorbance peak of C—O—C asymmetric stretch vibration was shifted from 1127 to 1150 after coordination with Cd<sup>2+</sup>, indicating that the bond had been formed.

According to the interface chemistry theory, the size of a precipitate from a reaction depends upon the concentrations of the reactants. If the concentration of both Cd<sup>2+</sup> and S<sup>2-</sup> are low enough, the product CdS should be nanoscaled. But the formation process of CdS nano-particles will also depend on the complex stability of the coordination bond. By contacting with a solution containing S<sup>2-</sup>, the Cd<sup>2+</sup> coordinated with PEO can be transformed to its sulfide compound because there is equilibrium between coordination and ionization reactions. The parameters of CdS and the complexes of Cd<sup>2+</sup> are listed in Table I, from which we can find that the solubility product of CdS is much smaller than that of the coordination bonds of cadmium. This indicates that CdS is extremely stable, and the PEO complexes of cadmium should easily change to CdS. Besides serving as a cadmium source from the complex, the polymer, PEO, can also be used as a stabilizer for the particles to protect the CdS particles from aggregating.<sup>9</sup>

### The Dependence on the Size of CdS

#### Size Determination

The typical X-ray diffraction patterns of CdS embedded in PEO matrix with and without alkali salt is shown in Figure 1, which compares the samples prepared by two different methods. Figure 1(a) shows that NaCl crystals are present in the composite sample prepared by bulk method;

**Table I** The Solubility Product of CdS and the Dissociation Constant of the Complexes of Cadmium<sup>10</sup>

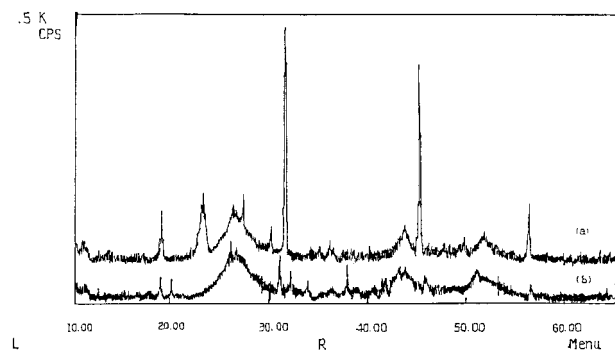
Cd(II)	lgk <sub>sp</sub> (Solubility Product)	The Dissociation Constant of Complex		
		pβ <sub>1</sub>	pβ <sub>2</sub>	pβ <sub>3</sub>
S <sup>2-</sup>	-26.1	/	/	/
Acetic acid	/	-1.5	-2.3	-2.4
Dicarboxyl	/	-3.52	-5.77	/
Acetylacetone	/	-3.84	-6.66	/
Dibenzoyl methane	/	-8.67	-16.63	/

no NaCl crystals are present in the samples prepared by the membrane method shown in Figure 1(b). Figure 1 indicates that the crystals of CdS are all β-face-centered cubic crystals. By assuming that the distribution curves of the sample fit the Cauchy function, while the standard diffraction curve fitted into the Gaussian distribution, the width due to the broadening effect could be approximately evaluated by the following equation.<sup>11</sup>

$$\frac{\beta}{B} = 1 - \left(\frac{b}{B}\right)^2, \quad (1)$$

where β is the real half-peak width of the sample due to the broadening effect, B is the apparent half-peak width, and b is the half-peak width of the standard diffraction peak, i.e., the width of the apparatus. If there was only the refining effect, the width of the diffraction peak caused by the refining effect could be substituted by β calculated from eq. (1).

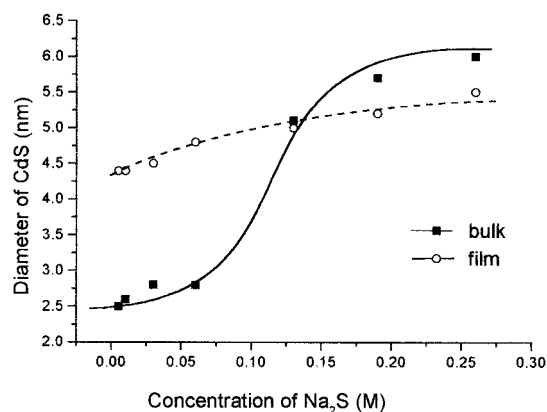
Then the diameter D of the CdS crystal could be calculated by the famous Scherrer equation,



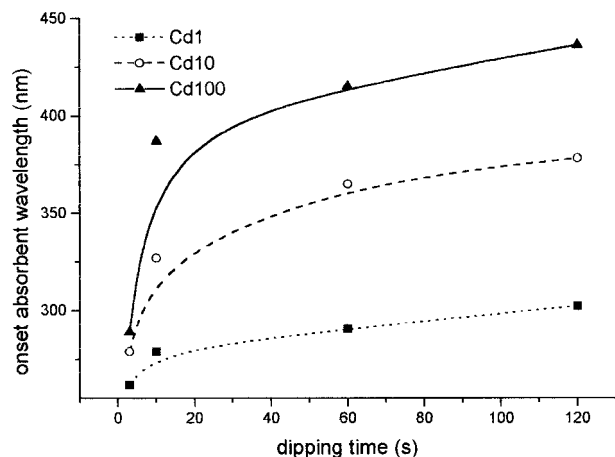
**Figure 1** X-ray diffraction pattern of CdS/PEO: (a) bulk method containing alkali salt; (b) membrane method without alkali salt.

$$D = \frac{k\lambda}{\beta \cos\theta}, \quad (2)$$

where *k* is Scherrer constant (geometrical factor of the crystal) being 0.89, λ is the X-ray wavelength of Cu K<sub>α</sub>, β is the half-peak width of the diffraction peak, and θ is the diffraction angle. The calculated value should correspond with that determined by AFM (atomic force microscopy) in the same order of magnitude that has been proven in the previous work.<sup>7</sup> The dependence of the diameter of CdS nanocrystal on the concentration of Na<sub>2</sub>S is shown in Figure 2. It was found that the size of CdS prepared by bulk method was smaller than that obtained by membrane method at lower concentrations of Na<sub>2</sub>S, while it was larger at higher concentrations. Bulk methods



**Figure 2** Particle size varying with the concentration of Na<sub>2</sub>S; reaction condition: Bulk method: a Na<sub>2</sub>S aqueous solution with a series of concentration was dropping slowly into 20 mL aqueous solution containing 1.6 g CdCl<sub>2</sub> and 1.84 g PEO under the ratio of S<sup>2-</sup> to Cd<sup>2+</sup> as 1. Membrane method: the casting film containing 6:1 of O:Cd<sup>2+</sup> was dipped in an Na<sub>2</sub>S solution of various concentrations for 1 min.



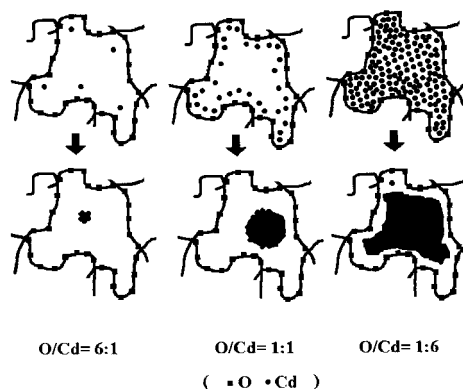
**Figure 3** Onset absorbent wavelength varying with dipping time: Cd1: O:Cd = 6:1; Cd10: O:Cd = 6:10; Cd100: O:Cd = 6:100.

would be expected to be strongly influenced by the concentration of the reactants.

### Dipping Time

Dipping time is one of the factors affecting the dimension of CdS particles (Fig. 3). It was found that the onset wavelength of UV absorption shifted from 516 nm to the blue range of all the samples. According to semiconductor theory, the efficient band gap would increase with the decrease of the size of the semiconductor when its size is close to the Bohr radius of the exciton, resulting in a blue shift of its absorbent spectrum. With the increase of dipping time the onset absorbent wavelength of the samples increased so that the blue shift amount was reduced, attributed to the increasing of the particle size.

From Figure 3 it was found that the curve could be divided into two steps. The onset absorbent wavelength ascended rapidly at the first step and then went down to a rather low speed. It stated that the initial reaction is very fast. In the film there is a certain number of free  $\text{Cd}^{2+}$ , which could be react with  $\text{S}^{2-}$  to form CdS particles. When the free  $\text{Cd}^{2+}$  was consumed, the coordinated  $\text{Cd}^{2+}$  would gradually dissociate to free ion due to the equilibrium process, causing the size increase sequentially. Because the dissociation rate of the coordination equilibrium and the penetration rate of the  $\text{S}^{2-}$  from the pure solvent district to the film affected the reaction, the conversion rate of CdS greatly diminished and reached a steady rate.

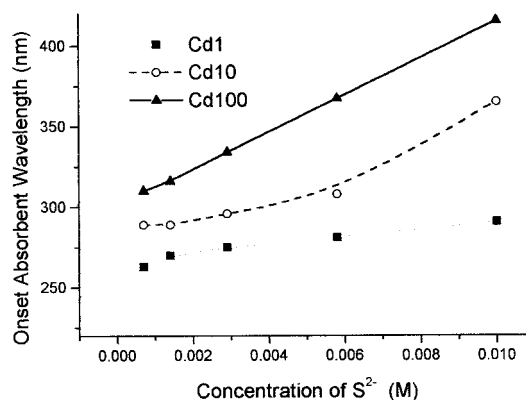


**Figure 4** The formation process of CdS crystal in the presence of PEO.

Figure 3 shows that there is great difference of the initial sizes of the CdS particles among the samples with different ratio of oxygen within PEO to  $\text{Cd}^{2+}$ . It is because that different ratio will cause different contents of  $\text{Cd}^{2+}$  in the film (Fig. 4), i.e., the less the ratio of O/Cd, the more free  $\text{Cd}^{2+}$  that would be present in the polymer film, leading to the larger initial size of CdS particles. It was found that the higher the content of  $\text{Cd}^{2+}$  in the film, the higher the initial rate of CdS formation. This result suggests that the content of cadmium ion can also affect the reaction.

### Concentration of $\text{Na}_2\text{S}$

As the X-ray results showed, the size of CdS was hardly affected by the concentration of  $\text{Na}_2\text{S}$  at the ratio of O to Cd equal to 6. The same phenomenon appeared in the UV spectrum (Fig. 5). At the molar ratio of O to  $\text{Cd}^{2+}$  equal to 6:1, the amount



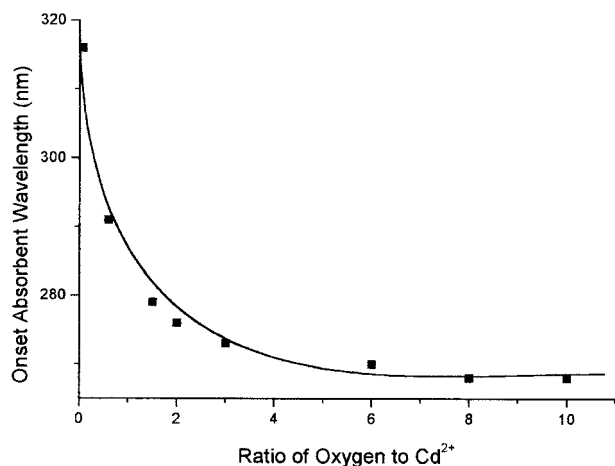
**Figure 5** Effect of concentration of  $\text{S}^{2-}$  on onset absorbent wavelength (dipping time: 1 min): Cd1: O:Cd = 6:1; Cd10: O:Cd = 6:10; Cd100: O:Cd = 6:100.

of blue shift was almost equal for these samples, indicating that the size of CdS varied little in the practical concentration range of  $S^{2-}$ . When the content of Cadmium in the film increased, the influence would be gradually obvious. At the ratio of 6:10, the onset absorbent wavelength had hardly changed until the  $S^{2-}$  reached over 0.005 M. At the ratio of 6:100, the dependence of the onset wavelength on concentration was close to linearity.

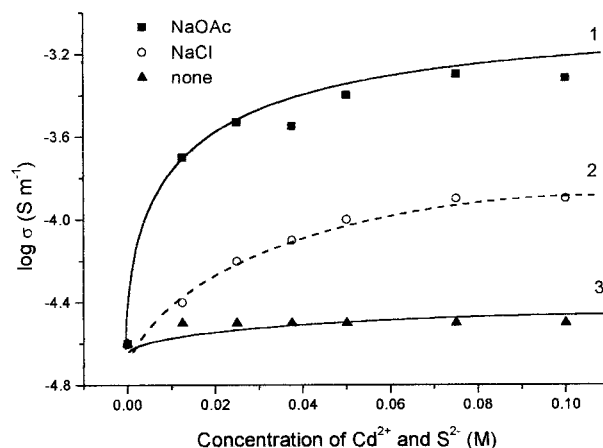
When the ratio of O to Cd is 6:1, the content of Cd in the polymer network is small, and almost all of the  $Cd^{2+}$  is coordinated; the amount of free  $Cd^{2+}$  in the polymer network available for conversion to CdS is very small. The conversion rate depends on the dissociation rate of the coordination bond as well as the penetration rate of the  $S^{2-}$ . The surrounding concentration of the  $S^{2-}$  only affects the penetration rate but hardly influences the size of the CdS particles formed.

When the ratio of O to  $Cd^{2+}$  was decreased to 6:10, there were many free  $Cd^{2+}$  ions in the solution. When these free  $Cd^{2+}$  ions contact the  $S^{2-}$  ions, CdS is formed. The conversion rate depends on the diffusion rate of  $S^{2-}$  in the film. The magnitude of this rate usually depends on the concentration of  $Cd^{2+}$  in the polymer network.

When the ratio of O to Cd reaches 6:100, the majoring cadmium ions are free, rather than coordinated. Thus, the content of cadmium on the surface of the film is sufficiently high that high conversion rates will be observed. The conversion amount of  $Cd^{2+}$  to CdS on the surface depends on the concentration of the  $S^{2-}$  ion in the solution; the higher the concentration of  $S^{2-}$ , the faster the



**Figure 6** Effect of the ratio of oxygen to  $Cd^{2+}$  on crystal size.



**Figure 7** The conductivity of the composite films: 1—with NaOAc; 2—with NaCl; 3—without alkali salt.

conversion of  $Cd^{2+}$ . But it should be noted that, even at very low concentration of  $S^{2-}$ , the size of the CdS particle observed was still larger than expected, probably due to the lower restriction effect by the polymer chain on the surface. In contrast, the penetrated  $S^{2-}$  in the film would react with the inner  $Cd^{2+}$ , causing smaller sized CdS particles to be produced in the film. So that in this case the size distribution would be wide.

#### Molar Ratio of Oxygen to Cadmium Ion

As analyzed above, the size of CdS depends on the dipping time and the concentration of  $S^{2-}$ , especially depending on the ratio of oxygen to Cd.

Figure 6 gives the effect on crystal size of the ratio of oxygen within the polymer chain to  $Cd^{2+}$ . There is a strong dependence of the size of CdS particles and the ratio of oxygen to Cd. With decreasing the O:Cd ratio, the onset wavelength declined rapidly until the ratio was equal to 2. At ratios greater than 4, the curve went down to a plateau being about 268 nm, which implied that the size tends to invariableness. It may be concluded that at the ratio above 2, the formation of CdS only depends on the dissociation rate of the coordinated  $Cd^{2+}$ , so it can be implied that 2 is the coordination number of PEO complex with  $Cd^{2+}$ .

#### Electric Conductivity

The conductivity of CdS/PEO/alkali salt tri-system was shown as Figure 7. The conductivity of PEO without added CdS or alkali salt was only 1

$\times 10^{-5}$  S/m. It was found that the conductivity increased rapidly and towards a plateau.

Because the concentration of  $\text{Cl}^-$  or  $\text{OAc}^-$  was twice that of  $\text{Cd}^{2+}$ , and the concentration of  $\text{Na}^+$  was twice that of  $\text{S}^{2-}$ , the concentration of NaCl or NaOAc should be twice of that of CdS. When all the coordinated  $\text{Cd}^{2+}$  was transformed to CdS, the oxygen atom originally coordinated with  $\text{Cd}^{2+}$  would be liberated and free to interact with  $\text{Na}^+$  and produce a solvent separated ion pair. This effect would result in increasing conductivity in this system.

Different alkali salts would lead to different conductivity levels. Figure 7 shows that the composite film containing NaOAc has higher conductivity than that with NaCl. It may be that the interaction between the cation and the anion in the film affects the motility of the alkali ion that contributes to the conductivity. The dissociation energy of Na–Cl (410 kJ/mol) is greater than that of Na–O (e.g., 256 kJ/mol for diatomic molecule Na–O),<sup>10</sup> so that greater ion pair separation is expected in the PEO/CdS/NaOAc than in the NaCl containing system.

## CONCLUSION

A complex transformation method is effective for preparing nanosized compounds containing transition metals. XRD results indicated that the CdS particles embedded in polyethylene oxide film were in the nanoscale from 2–10 nm. The size of CdS depends on the dipping time of the PEO–Cd complex film in the  $\text{Na}_2\text{S}$  aqueous solution and its concentration. The longer the dipping time and the higher the concentration of  $\text{Na}_2\text{S}$  are, the larger the size of CdS particles and the wider the distribution of the size are. The most effective means for adjusting the size and its distribution

of CdS particles is to change the ratio of the oxygen along with the PEO chain to the cadmium ion in the complex film. The alkali salt combined in the film would be dissociated to free movable ions through the interaction with PEO chain that contributed to the conductivity of the composite film PEO/CdS/alkali salt. The conductivity of the film containing NaOAc of lower dissociation energy is higher than that containing NaCl.

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