Synthesis and Characterization of Nanoscopic Entities Based on Poly(caprolactone)-Grafted Cadmium Sulfide Nanoparticles

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Nanosized CdS clusters have been synthesized using polyester chains with a thiol end group as a covalently attached colloidal stabilizer. Clusters were grown through the reaction of thiourea with cadmium acetate, which was in competition with surface stabilization due to the tethered poly(caprolactone) (PCL) chains. The kinetics of the CdS cluster growth in the presence of poly(caprolactone) ligands were compared with those obtained using a low molecular weight thiol. Control of the particle size was also achieved by varying the ratio of thiourea to PCL ligands. The resulting nanoscopic entities obtained in different solvents (DMF or THF), remained stable in solution for several months and could be cast into films. Homogeneous dispersions of CdS particles in a polymer matrix were obtained by solvent evaporation. The particle size and distribution were characterized using ultraviolet−visible and photoluminescence spectroscopies, and transmission electron microscopy.

Introduction

Owing to their size-dependent nonlinear optical, physical, and electronic properties, nanometer-sized semiconductor crystals have attracted wide interest in many areas of chemistry and physics.[1−3] The properties of the nanoparticles are substantially different from those of the bulk solids. They are strongly influenced by the surface structure owing to the relatively high proportion of surface atoms.[4] This large surface-to-volume ratio leads to enhanced catalytic properties.[5] Another important difference arises from the modification of the band structure in very small clusters (sometimes referred to as quantum particles or “Q-particles”), owing to severe spatial confinement.[6,7]

During the past decade, various methods of preparation of semiconductor nanoparticles such as cadmium or zinc sulfide have been investigated, and significant progress has been made in the preparation of colloid solutions using different thiol-functional molecules as stabilizers.[8−11] Competitive reactions between cadmium sulfide (CdS) core cluster growth and surface capping by thiol-containing ligands leads to clusters whose core is essentially CdS but whose reactive surface has been passivated by covalently attached ligands. Good control of the cluster size can be achieved by optimization of the kinetic trapping conditions.[12−14] The particle size distribution can be further refined by size classification using size exclusion chromatography or gel electrophoresis.[15]

At present, research interest is focused on the arrangement of individual particles in two- or three-dimensional superlattices.[16,17] Fine-tuning of interparticle spacing and hence interactions may permit exploitation of cooperative effects. Polymers have already been employed as steric stabilizers and as a means of controlling nanoparticle growth and spatial arrangement in films. Copolymer micelles[18−21] may be used as “nanoreactors” for the preparation of monodis-

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perse particles. However, micelles may rearrange on addition of a new reagent or a new solvent, or even on changes of temperature. Also the electrooptical effect associated with spatial confinement is offset by charge trapping in electronic surface states, which becomes significant owing to the large number of surface atoms and their weak interactions with the polymer micelles.[7,22] With stronger interactions, such as chemical bonds between ligands and particles, these effects may be suppressed.[23] Recently, stabilization of gold nanoparticles where the polymer chains are covalently bonded to the particle surface, has been reported.[24,25] CdS nanoparticles have also been passivated by thiol-containing polyphenolics after their synthesis in reversed micelles.[26]

Here we describe the controlled synthesis of distinct nanoscopic entities of several nanometers in size consisting of a CdS crystal core surrounded by covalently end-linked poly(caprolactone) (PCL) chains of controlled molecular weight. The polymer had three functions. First, thanks to its chemical structure, the soluble chain should make the particle dispersible and should prevent particle agglomeration. Second, due to its thiol functionality, it should act in similarity to a low molecular weight ligand and permit control of the particle size. Third, because of its well-defined length, it should control the spacing of the particles in solution cast solid films over length scales inaccessible by other techniques. This should also allow the analysis and manipulation of single CdS nanoclusters.

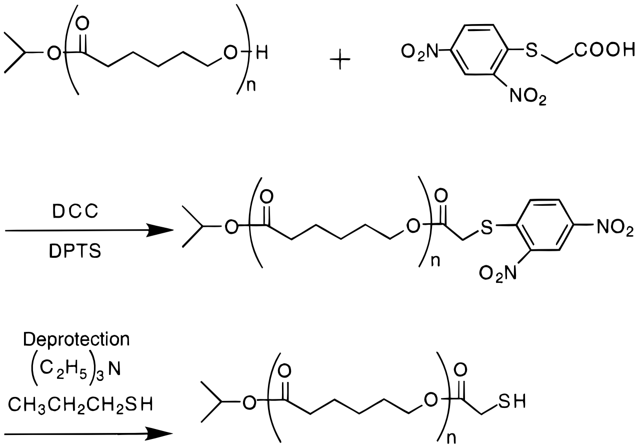
The method consisted of preforming thiol-functional poly(caprolactone) (PCL-SH) by ring-opening polymerization so that polymers with controlled molecular weight and narrow molecular weight distribution were obtained. The PCL-SH was then used as a ligand, capable of reacting in situ with the particles during synthesis. They thus became covalently bound to the cadmium surface ions, as previously demonstrated in the literature for low molecular weight thiols.[8,10,12,27] The synthetic approach is outlined in what follows, along with the characterization of the poly(caprolactone)-grafted cadmium sulfide (CdS-*g*-PCL) entities in solution and the morphology of solution cast films.

Experimental Section

Materials. Cadmium acetate (Cd(OAc)$_2$), thiourea, thioglycerol, and cadmium perchlorate (Cd(ClO$_4$)$_2$) were used as received from Aldrich. Dimethylformamide (DMF) and tetrahydrofuran (THF) were dried and deoxygenated by conventional techniques.

Preparation of CdS Clusters. The detailed synthesis of thiol-functionalized poly(caprolactone) (PCL-SH) has been described in previous papers[28,29] and will therefore only be briefly described here. Poly(caprolactone) (PCL) obtained from ring-opening polymerization (ROP) was functionalized by end functionalization or by use of a thiol-functional initiator. The first method consisted of esterifying the hydroxyl-terminated polyesters with mercaptoacetic acid protected by Sangers reagent (2,4-dinitrofluorobenzene). Subsequent deprotection could be carried out selectively under mild conditions to give the thiol-functional PCL (Scheme 1). A second technique involved the preparation of a protected thiol-functional alcohol, α-[(2,4-dinitrophenyl)thio]ethanol**,** which was used as initiator in the polymerization of ϵ-caprolactone after reaction with the aluminum isopropoxide. The deprotection reaction was then carried out to regenerate the thiol function. The PCL-SH used here had a molecular weight of 5400 g/mol and a polydispersity of 1.14.

Scheme 1. Thiol-Functional PCL Obtained by EndFunctionalization



The synthetic procedure given below was essentially the same for all the CdS cluster syntheses. The only differences between the various preparations were the solvent used, the cadmium precursor (Cd(OAc)$_2$ or Cd(ClO$_4$)$_2$) and the molar ratio of sulfide (thiourea) to the functional ligand (S/SH: 0.13, 0.5, 4, or 20).

A typical procedure using S/SH = $^1/_2$, was as follows: 0.1 g (0.43 mmol, 0.78 equiv) of Cd(OAc)$_2$ and 2.0 g of polymer (0.55 mmol, 1 equiv) were mixed in 100 mL of DMF at a temperature of 90 °C under argon flow in a 250-mL three-necked round-bottom flask fitted with a condenser. The desired amount of thiourea (0.5 equiv) in 1 mL of DMF was then added through a septum and the solution vigorously shaken. The solution rapidly became yellow (depending on the S/SH ratio) but remained clear. The reaction was monitored by taking aliquots for ultraviolet−visible (UV−vis) analysis, until no further changes were observed, at which point the reaction was judged to be complete (see next section).

Characterization. Optical absorption measurements were carried out using a Perkin-Elmer Lambda 900 UV−vis spectrometer and a quartz cuvette with a 2-mm path length. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded on a Hitachi FL-4500 fluorescence spectrometer equipped with a xenon high-pressure lamp as the light source and grating monochromators. The spectra were corrected according to the spectral response of the system.

Transmission Electron Microscopy (TEM) required films of less than 50 nm in thickness, cast from the solutions onto freshly cleaved mica surfaces and picked up on carbon-covered copper grids from distilled water. A Philips EM 430 operated at 300 kV and equipped with a low dose unit was used for the observations.

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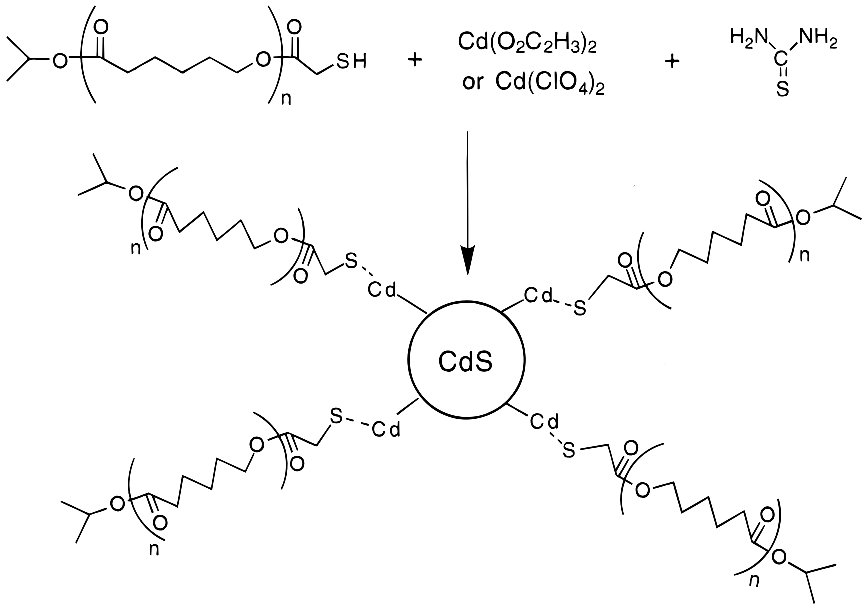
Scheme 2. Preparation of CdS-*g*-PCL Clusters



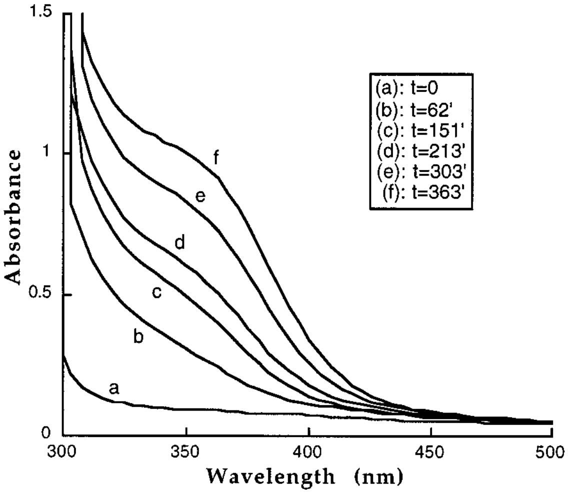


Figure 1. Evolution with time of the absorption spectra of the CdS particles stabilized with PCL-SH in DMF.

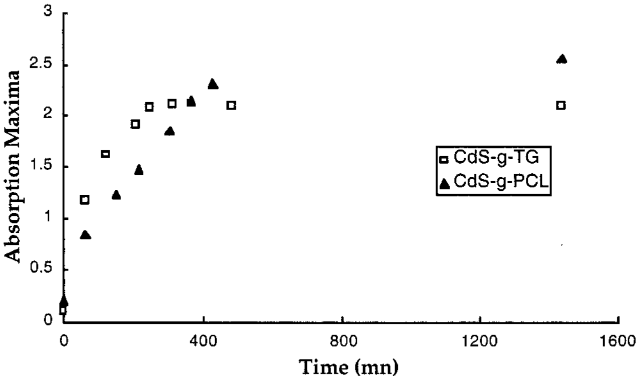


Figure 2. Absorbance of CdS nanoparticles in DMF stabilized with thioglycerol (CdS-*g*-TG) or PCL-SH ligands (CdS-*g*-PCL) versus reaction time ($S/SH = 0.5$, $Cd/SH = 0.78$, $T = 100$ °C), $\lambda = 350$ nm.

Results and Discussion

Reaction Kinetics: Comparison between Small Molecule and Macromolecular Ligands. Poly(caprolactone) obtained from ring-opening polymerization (ROP) have been end functionalized with a thiol, according to the reaction shown in Scheme 1. Reactions in DMF of the thiol-functional poly(caprolactone) (PCL-SH) with thiourea and cadmium acetate produced composites consisting of CdS nanoclusters embedded within the polymer matrix (Scheme 2).

Different syntheses of CdS clusters were carried out in DMF using either PCL-SH or thioglycerol as the stabilizer under equivalent reaction conditions, using a S/SH ratio of 0.5 and a concentration of cadmium acetate ($Cd(OAc)_2$) of 1 mg/mL or 5 mg/mL. The reaction consisted in mixing the polymer or the thioglycerol, with $Cd(OAc)_2$ followed by the addition of thiourea. Aliquots were taken from the reaction medium at different times and analyzed by UV–vis spectroscopy as shown in Figure 1. The relative absorbance corresponding to the absorption peak is proportional to the number of particles formed, allowing the degree of conversion to be estimated.[30] Thus the evolution of the absorbance with time could be used to deduce the reaction kinetics.

In Figure 2, the absorbance is given as a function of time for both types of stabilizer (thioglycerol or PCL-SH). The initial rapid increase observed in both cases is attributed to the rapid nucleation following the dissociation of the thiourea. Subsequent growth of the CdS particles is in competition with surface capping by the ligands or macroligands.[31] This is termed the "propagation step" by analogy with a polymerization process. Propagation was faster when using thioglycerol and the threshold was reached earlier (300 mn instead of 450 mn, see Figure 2). This may be attributed to a relatively fast diffusion compared with that of PCL-SH, resulting in a rapid termination of the particle growth.

The particle sizes in the two cases were nevertheless very similar as deduced from the position of the absorption peak (~2 nm). However, the presence of sharper

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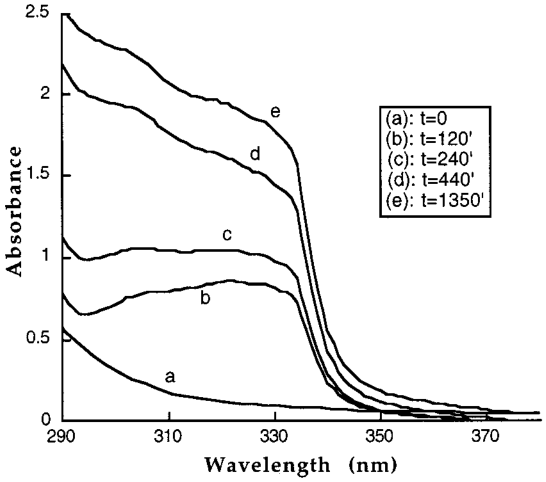

Figure 3. Evolution with time of the absorption spectra of the CdS particles stabilized with PCL-SH in THF.

absorption bands suggests the particle size distribution to be narrower for the thioglycerol stabilizer.[32,33] This may be related to the faster termination. For long reaction times, the absorption maximum was higher for the PCL-SH-stabilized particles, which is indicative of a larger number of particles. We attribute this to the slower growth process and to the small number of chains involved in the stabilization of each CdS particle. The polymer attached to the surface of the particles reduces the space available for further grafting. Therefore, a larger number of particles can be formed and a higher degree of conversion can be obtained for a given initial number of thiol functional groups, when using a polymeric thiol rather than a low molecular weight ligand.

Influence of the Solvent. The reaction to form the poly(caprolactone)-grafted cadmium sulfide (CdS-*g*-PCL) nanocomposites was also carried out in THF. The reaction was again monitored by UV−vis absorption measurements (Figure 3). For both solvents, the final particle-containing suspensions were stable for months and after solvent evaporation the yellow powder could readily be redispersed in other solvents such as dichloromethane, benzene, or chloroform.

As shown in Figure 1, a slight red-shift was observed in the UV−vis absorption spectrum of the CdS clusters in DMF as the reaction proceeded, indicating an increase in particle size, even in the presence of the macroligands.

However, no shift was observed in THF even after long reaction times and the particles were inferred to have remained small (Figure 3). This indicates that the stabilization provided by the macroligands was more effective in the presence of THF. Owing to its higher polarity, DMF is a poor solvent for the PCL chains and it may interact preferentially with the CdS surface, limiting the stabilizing effect of the polymer with respect to further particle growth.

This evolution in particle size was also reflected by photoluminescence (PL) measurements (Figure 4). The PL spectra exhibited a strong peak, which was assigned to emission from holes and electrons traps.[27] Traps are frequently located at the surface as a result of the perturbed bonding forces.[22] At the beginning of the reaction, when the particles are small, this peak occurs at relatively short wavelengths. As the reaction proceeded in DMF, the red-shift was even more pronounced than that observed in the UV−vis absorption spectra. On the other hand, the PL spectra obtained from THF solutions, showed only slight variations with time.

TEM of the cast films permitted resolution of individual particles in all the samples, broadly confirming the results from the spectroscopic measurements. However films obtained by drying doctor bladed or spun DMF solutions (Figure 5) showed highly nonuniform spatial dispersions of the particles, indicating segregation from the nongrafted polymer above a certain critical concentration (drops of the solutions were also observed to become cloudy during drying). Nevertheless, relatively uniform dispersions could be obtained in films cast from THF. The second image in Figure 5 reflects not only the uniform dipersion of the particles in this case, with a projected interparticle separation of about 10 nm, but also their narrow size distribution. Several factors may contribute to this. Under ambient conditions, THF evaporates faster than DMF, which may impede phase separation. Also, THF is a better solvent for PCL than DMF so that phase separation may be delayed to higher concentrations, or even suppressed. Finally, as mentionned previously, particle stabilization is more effective in THF, possibly as a result of a greater density of grafted chains.

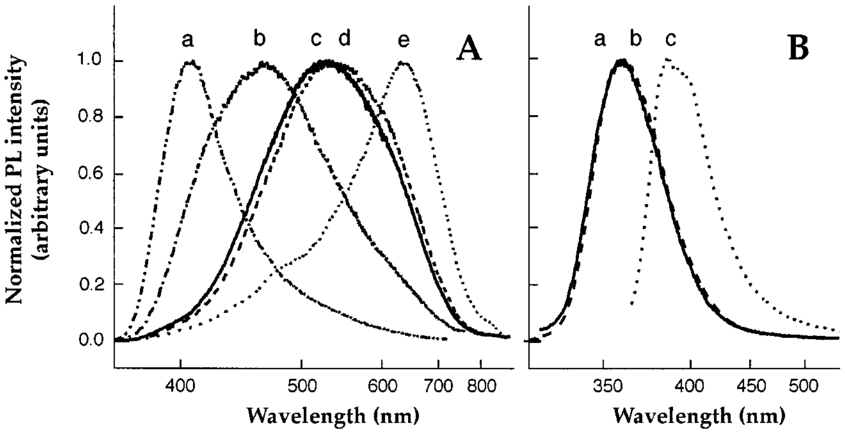

Figure 4. Photoluminescence spectra for CdS particles stabilized with PCL ligands after different reaction times in DMF (left, (a) $t = 0$; (b) $t = 62$ min; (c) $t = 151$ min; (d) $t = 213$ min; (e) $t = 1320$ min) and THF (right, (a) $t = 0$; (b) $t = 120$ min; (c) $t = 1350$ min).

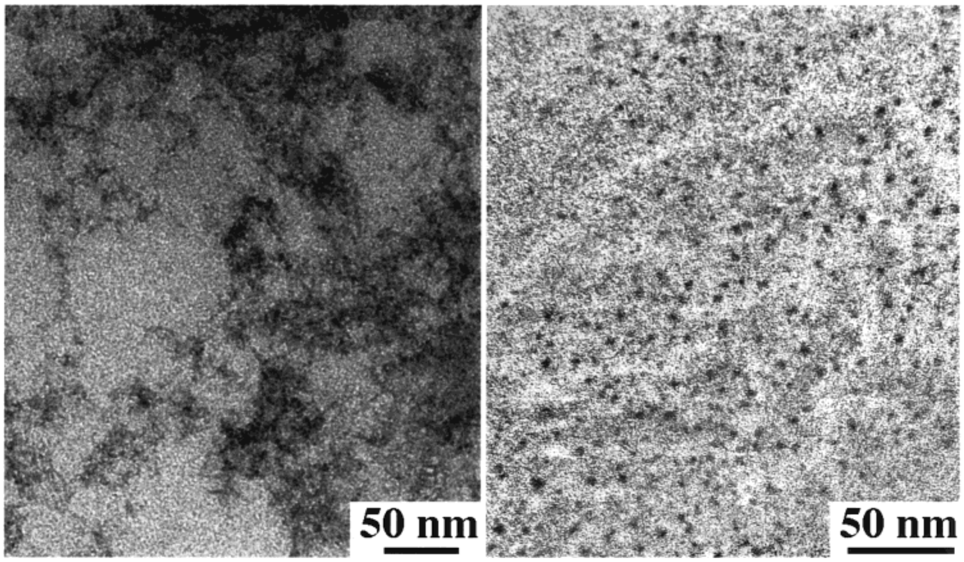

Figure 5. TEM micrographs of CdS particles (black contrast) with PCL ligands cast from DMF (left) and THF (right).

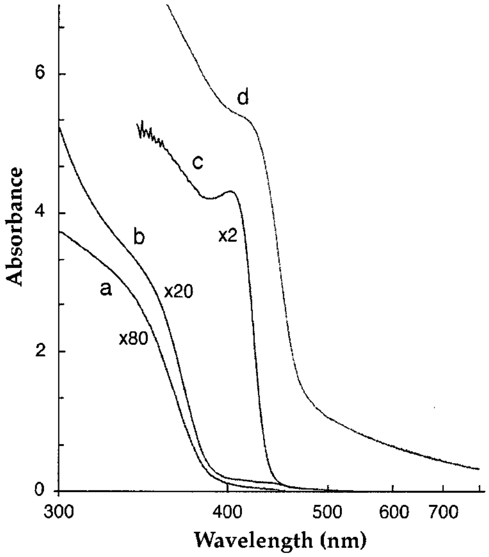

Figure 6. Absorption spectra of the CdS nanoparticles with PCL ligands for various S/SH ratios in DMF: a, 0.13; b, 0.5; c, 4; d, 20.

Table 1. Experimental Compositions of CdS-*g*-PCL Clusters

sample	PCL-SH M_n	PCL-SH in feed (g/mL)	$Cd(OAc)_2$ in feed (mg/mL)	S/SH	solvent
a	5600	0.01	0.2	0.13	DMF
b	5600	0.01	0.5	0.5	DMF
c	5600	0.01	2.2	4	DMF
d	5600	0.01	10	20	DMF

Chemical Control of Particle Size. CdS-*g*-PCL entities were synthesized using different molar ratios of thiourea to PCL-SH (S/SH ratio), as indicated in Table 1. The UV−vis absorption spectra corresponding to the different samples are shown in Figure 6. These may be linked to the particle size by analysis of the absorption onset.[22] The evolution of the absorption spectra reflects shifts in the electron energy levels with decreasing particle size, consistent with model calculations of quantum confinement effects on the band structure.[34] The position of the absorption peak in the UV spectrum may be calculated, and Weller and coworkers have published a curve giving the absorption of CdS as a function of particle size.[34]

High relative concentrations of PCL-SH led to absorption at low wavelengths. With a small amount of thiourea (sample a, Figure 6), the absorption onset (associated with the lowest energy exciton) showed a shoulder at about 330 nm, indicating the presence of very small particles of about 1−2 nm, according to Weller's model.[34] The same reaction, but with addition of a slightly larger amount of thiourea to the reaction mixture resulted in a shift of the shoulder to longer wavelengths (sample b). Samples c and d, with higher S/SH ratios, showed even stronger red-shifts in the absorption, due to the formation of larger particles, consistent with a decrease in surface stabilization. Although the solutions were colorless for lower S/SH ratios they became yellow as S/SH increased, as observed for small thiol ligands.[12,14,35] Sample c (S/SH = 4) showed a clear absorption peak, indicative of a narrow particle size distribution. This is consistent with the observation of Reiss who showed how growth by combination of particles can result in production of highly monodisperse colloidal dispersions from systems that initially are polydisperse.[36] A similar peak was obtained for sample d (S/SH = 20), but light scattering below the absorption threshold suggested that agglomeration had taken place. Finally, a reference synthesis in the absence of PCL-SH or in the presence of nonfunctional PCL led to precipitation of CdS in the form of large particles or agglomerates.

Additional information on the degree of conversion may be obtained by normalizing the absorption with respect to the cadmium or sulfur concentrations. As stated previously, the absorbance of the lowest energy exciton is a measure of the relative particle concentra-

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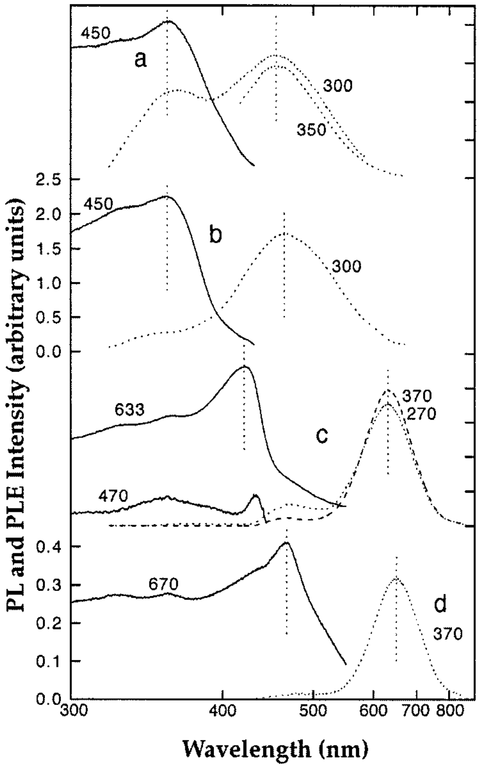

Figure 7. Photoluminescence spectra (dotted lines) and photoluminescence excitation spectra (solid lines) for particles prepared using PCL-SH in DMF with different S/SH ratios. The respective excitation and emission wavelengths are given in nanometers.

tion.[30] These concentrations can be calculated from the molar absorption coefficients of the particles given as a function of their size in the work of Vossmeyer and coworkers.[30] Lower concentrations are determined in samples a and b (7.25 and 8.3 mmol/L, respectively) compared to the concentrations of sample c and d (15 and 20 mmol/L), so that a low conversion rate may be assumed for a and b. This is attributed to the low thiourea content, which limited particle growth.

The photoluminescence excitation (PLE) spectra in Figure 7 showed similar trends to the UV−vis absorption spectra. The PLE band was again blue-shifted with increasing PCL-SH concentration, indicating reduced cluster sizes. Moreover, the excitation peak associated with the lowest energy exciton was red-shifted with respect to the absorption peak of the same sample. PLE was always most efficient when the lowest energy state was used for excitation. (This is why the excitation wavelength can be used for size-selective spectroscopy of the nanoparticles[37]).

Investigation of the emission spectra using different excitation wavelength allows one to distinguish between different recombination mechanisms characteristic of different particle size ranges or surface defects (Figure 7). As the size of the particles increases, the luminescence emission peak moves to higher energy.[38,39] This size-dependent shift of the luminescence spectrum has been observed before. Two types of emission peaks could be identified in the spectra. First, in all the samples, the PL emission spectra from Figure 7 showed a large peak which was found to be strongly red-shifted with respect to the absorption edge. Second, the three samples containing the smaller particles showed an additional, weaker peak, which was only slightly red-shifted with respect to the absorption edge. The first peak (at longer wavelengths) is due to emission from trapped states, whereas the second characteristic emission at higher energy has been attributed to recombination from the excitonic state in the crystallite interior.[9,40] The wavelengths indicated alongside the emission spectra in Figure 7 are the excitation wavelengths. It may be seen from the figure that changing the excitation wavelength affected the intensity ratio of the two peaks in the emission spectrum, but not their positions.

Several parameters influence the intensity of the excitonic fluoresence. For example, it has been found to decrease with increasing ambient dielectric constant and in protic solvents.[27] Also, trapping of holes by surface sulfur anions may lead to a weakening of the direct excitonic fluorescence. The binding conditions at the particle surfaces, however, would be expected to be similar for all samples in the present study, so this was not thought to be responsible for the observed intensity differences. The decrease in direct excitonic fluorescence can be due to the increase of the dielectric constant in the surrounding of a particle in case of agglomeration, which permits the exciton wave function to extend into this region. Bawendi and co-workers showed that energy transfer occurs via Förster mechanism when the particle are close together.[41] This leads to increased trapping in the particle surface region, as observed in sample d, where this type of fluorescence was absent. In this case the particles were also relatively large, as indicated by the UV−vis absorption spectra, with fewer polymer ligands grafted to the surface, presumably leading to weaker stabilization.

Figure 8 shows TEM micrographs obtained from films cast from each preparation (with S/SH ratios ranging from 0.13 to 20). Since the synthesis was carried out in DMF, the particle spacial distributions were nonuniform on solvent evaporation, owing to the phase separation referred to previously. TEM also confirmed the size differences resulting from the different preparations.

Work currently in progress suggests that the phase separation may be suppressed by the use of a higher weight ratio of cadmium to polymer. This is thought to lead to an increase in the number of grafted chains, and preliminary results indicate the particles to be more regularly distributed in cast films. Chromatography analyses are at present being performed to estimate the graft density from the proportion of nongrafted chains.

Conclusion

The aim of the present work has been to explore a novel strategy for the regular organization of quantum-sized semiconductor CdS particles in an organic matrix.

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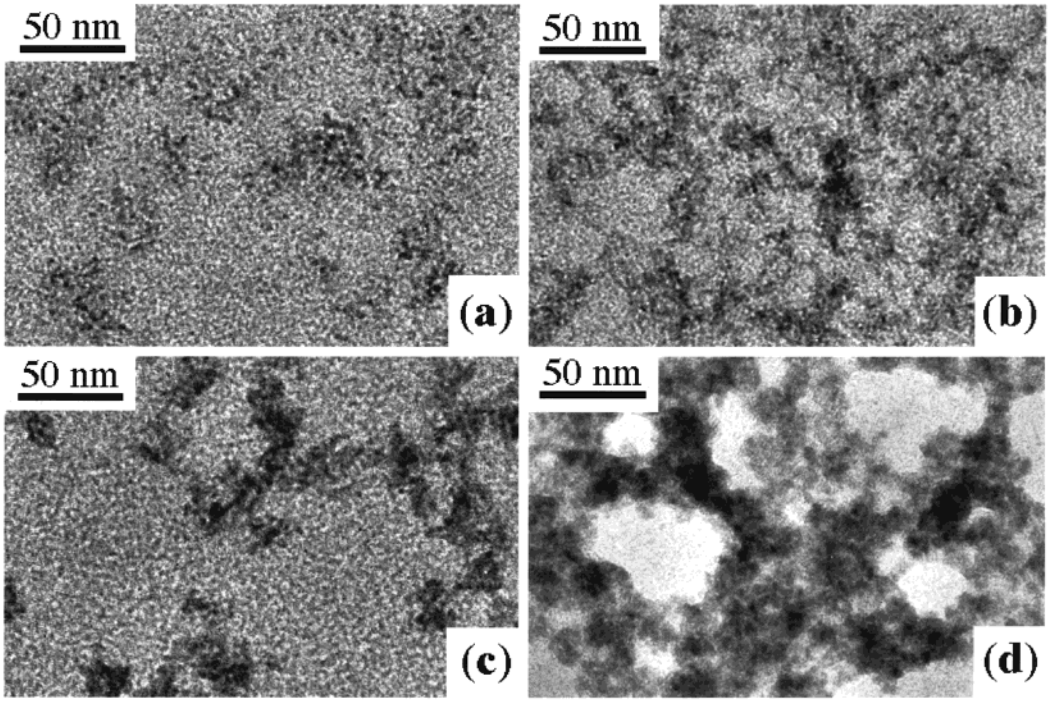

Figure 8. TEM micrographs of CdS clusters obtained from DMF solutions using PCL-SH ligands for different S/SH ratios: a, 0.13; b, 0.5; c, 4; d, 20.

A new synthetic approach yielding nanoscopic CdS-*g*-PCL entities has been developed with the use of thiol-functionalized poly(caprolactone) as a “macroligand”. Creation of a covalent bond between the polymer chains and the CdS surface provided particles which were highly stable in solution and which could be cast into films and redissolved. Homogeneous dispersions of CdS particles in a polymer matrix have been obtained after solvent evaporation. Although the cluster concentration could be controlled by the reaction kinetics, their size was determined by the S/SH ratio. Clearly the cluster size is being determined by the relative rate of propagation/termination reactions and in turn by the relative concentrations of the initiating (sulfide) species and the terminating polymers (PCL-SH) in the “polymerization” solution. Thiol-functional polymers had the additional advantage over low molecular weight ligands in that they could be used to cast films in which the interparticle distance could be controlled.

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