

pounds 15 and 17 were recrystallized from toluene, and compound 16 was purified by flash chromatography using dichloromethane as an eluent. 4-(Decyloxy)benzoyl chloride was prepared from commercially purchased 4-(decyloxy)benzoic acid (Frinton) using thionyl chloride.⁴

15: mp 106.1 °C, ¹H NMR (200 MHz, CDCl₃) δ 8.42 (s, 1 H), 8.08 (dd, *J*₀ = 9.0 Hz, *J*_m = 2.2 Hz, 2 H), 7.07 (dd, *J*₀ = 9.0 Hz, *J*_m = 2.2 Hz, 2 H), 7.05 (dd, *J*₀ = 9.0 Hz, *J*_m = 2.4 Hz, 2 H), 6.87 (dd, *J*₀ = 9.0 Hz, *J*_m = 2.4 Hz, 2 H), 4.11 (t, 2 H), 1.83-1.49 (m, 2 H), 1.34-1.29 (m, 14 H), 0.87 (t, 3 H); IR (Nujol) 3463, 1709, 1605, 1511, 1469 cm⁻¹.

16: C 136.0 °C N 148.5 I; ¹H NMR (300 MHz, CDCl₃) δ 8.2 (d, *J*₀ = 9 Hz, 2 H), 7.61 (d, *J*₀ = 8.3 Hz, 1 H), 7.6 (d, *J*₀ = 8.6 Hz, 1 H), 7.55 (d, *J*_m = 2.1 Hz, 1 H), 7.25 (dd, *J*₀ = 8.5 Hz, *J*_m = 1.5 Hz, 1 H), 7.06-7.02 (m 2 H), 6.99 (d, *J*₀ = 9 Hz, 2 H), 6.04 (s, 1 H), 4.05 (t, 2 H), 1.85-1.81 (m, 2 H), 1.48-1.28 (m, 14 H), 0.89 (t, 3 H); IR (Nujol) 3382, 1706, 1605, 1510, 1462, 1260 cm⁻¹.

17: C 130.8 °C I (I 111.8 N), lit.⁵ C 130.5-131.3 °C (N)*; ¹H NMR (200 MHz CDCl₃) δ 7.98 (d, *J*₀ = 9.0 Hz, 2 H), 7.30 (d, *J*₀ = 9.0 Hz, 2 H), 6.90 (d, *J*₀ = 9.0 Hz, 2 H), 6.74 (d, *J*₀ = 9.0 Hz, 2 H), 4.00 (t, 2 H), 2.41 (s, 1 H), 1.95-1.55 (m, 2 H), 1.25 (m, 14 H), 0.85 (t, 3 H); IR (Nujol) 3377, 1643, 1597, 1507, 1494 cm⁻¹.

The compounds 4-6 were prepared using a standard procedure⁴ from the corresponding hydroxy compound and decyl bromide in KOH/EtOH.

The phenols 5, 6, 10-12, and 15-17 were finally coupled with (*R*)-(+)-3-methyladipic acid using *N,N*-dicyclohexylcarbodiimide (DCC) as an esterification agent, 4-pyrrolidinopyridine (PPY) as a catalyst, and dried tetrahydrofuran (THF) as a solvent following

a method described in the literature.⁸ The corresponding elemental analysis, the most relevant IR data, and the [α]_D values are given in Table III. The ¹H NMR data for I-VIII are gathered in Table IV.

Conclusions

This new type of liquid crystal incorporating the chiral center in a flexible spacer between two identical mesogenic units shows ferroelectric behavior, although the values for *P*_s seem to be small. We were able to measure a response time of 1 ms for one of these compounds. Taking into account the data obtained for these compounds, we are working on the synthesis of new dimers with different flexible spacers which will hopefully have better ferroelectric properties. The results will be reported elsewhere.

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Synthesis of Cadmium Sulfide in Situ in Reverse Micelles: Influence of the Preparation Modes on Size, Polydispersity, and Photochemical Reactions

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We present results obtained by using reverse micelles of either sodium bis(2-ethylhexyl)sulfosuccinate (AOT) or mixed cadmium and sodium bis(2-ethylhexyl)sulfosuccinate (AOT/Cd(AOT)₂) to form CdS semiconductor particles. The control of size, polydispersity, and the photochemical reactions are compared by using various mode of synthesis of CdS. Three different reverse micellar systems have been used: the cadmium ions are solubilized in AOT reverse micelles either in the presence or in the absence of a protecting polymer such as HMP (Cd(NO₃)₂/±HMP/AOT/isooctane/water reverse micelles) or associated with bis(2-ethylhexyl)sulfosuccinate (Cd(AOT)₂/AOT/isooctane/water) reverse micelles. The size of the CdS particles is found to increase with the water content. The polydispersity strongly depends on the mode of CdS synthesis. At low water content, reverse micelles protect CdS semiconductors from photocorrosion. At higher water content, photocorrosion process depends on the *x* value, on the presence of HMP, and on the participation mode of cadmium ions (Cd(NO₃)₂ and Cd(AOT)₂) in the synthesis. The photoelectron-transfer reactions from CdS particles to different dialkyl viologens have been studied. The variation in the yield strongly depends on the relative value of the cadmium over sulfide ions concentrations and on the presence of sulfide clusters bound to the CdS at interface. It is possible to gelify the reverse micellar system and form semiconductors in isotropic gel using the various systems described previously.

Introduction

The use of dispersed media to solubilize or synthesize microparticles in situ has made considerable progress in the last few years: Langmuir-Blodgett films,¹ vesicles,²

polymerized vesicles,³ double layers,⁴ inert polymeric matrix,⁵ or reverse micelles⁶⁻¹⁵ have been used as the in-

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corporation media for microparticles, colloids, or semiconductors.¹⁶

Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) is the most commonly product used to form reverse micelles. The ternary system alkane/AOT/water present enormous advantages: these are spheroidal aggregates¹⁷ where water is readily solubilized in the polar core, forming a "water pool", characterized by the ratio of water to surfactant concentration ($w = [\text{H}_2\text{O}]/[\text{AOT}]$). In isooctane solution, the maximum amount of bound water in the micelle corresponds to a water-surfactant molar ratio about 10. Above a water content equal to 15, the water pool radius, R_w , is found to be linearly dependent on the water content ($R_w(\text{\AA}) = 1.5w$).¹⁸ Another important property of reverse micelles is their dynamic behavior: they can exchange the content of their water pools by a collision process.¹⁷ Such a process makes possible chemical reaction or precipitation between compounds solubilized in different droplets.

In reverse micelles CdS particles can be formed by using either exchange micellar process among the micellar droplets or by bubbling hydrogen sulfide in a solution containing cadmium ions.^{6-8,10,12-15} A higher degree of monodispersity and smaller size has been obtained by using either very high concentrations of surfactant ($[\text{AOT}] = 0.5 \text{ M}$)⁷⁻¹² or a very small water content.^{10,13-15} By increasing the amount of water solubilized in reverse micelles, an increase in the average size of the particles and in the size distribution has been observed.

In a previous paper,¹⁹ we presented the data obtained by using functionalized reverse micelles ($[\text{Cd}(\text{AOT})_2/\text{AOT}/\text{isooctane}/\text{water}$ reverse micelles). Here, we choose to compare the CdS particles properties such as size, polydispersity, photocorrosion, and photoelectron-transfer process, by using various synthesis modes.

The total surfactant concentration and the relative amount of cadmium over sulfide ions concentrations are kept constant. The differences in the synthesis are due to the use of cadmium ions: either they are solubilized in the water pool of AOT reverse micelles in the presence or in the absence of a protecting polymer such as HMP ($\text{Cd}(\text{NO}_3)_2/\pm\text{HMP}/\text{AOT}/\text{isooctane}/\text{water}$ reverse micelles) or associated with bis(2-ethylhexyl)sulfosuccinate ($[\text{Cd}(\text{AOT})_2/\text{AOT}/\text{isooctane}/\text{water}$ reverse micelles).

Experimental Section

Products. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) is procured from Sigma and sodium sulfide (Na_2S) from Janssen. The synthesis of functionalized surfactant has been done according to a previously described procedure.¹¹ The various dialkyl viologens have synthesized as described elsewhere.²⁰

Synthesis of CdS in Reverse Micelles.^{9,11} Colloidal CdS particles were prepared by mixing two micellar solutions with the same water content value ($w = [\text{H}_2\text{O}]/[\text{AOT}]$), one containing the sulfide ions (Na_2S) and the other in which cadmium ions are present. The cadmium ions in the system are obtained from either cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$) solubilized in the water core or cadmium bis(2-ethylhexyl)sulfosuccinate ($\text{Cd}(\text{AOT})_2$).

The synthesis of CdS is realized by mixing rapidly variable volumes of the two reverse micelles solutions containing the ions (Cd^{2+} or S^{2-}) in the same concentration. Due to the dynamic properties of reverse micelles, reaction occurs rapidly. The overall (2-ethylhexyl)sulfosuccinate concentration is kept constant and equal to 0.1 M.

(i) **Use of cadmium nitrate in AOT reverse micelles:** The solutions were prepared with and without a protecting agent. In the first case, the protecting agent chosen is sodium hexametaphosphate, HMP. An aqueous solution of sodium sulfide and HMP was prepared previously. These solutions, which contain equimolar concentrations of the two solutes, are used in the formation of reverse micelle. The formation of cadmium sulfide is carried out by using the same procedure as that described earlier.

(ii) **Use of cadmium bis(2-ethylhexyl)sulfosuccinate ($\text{Cd}(\text{AOT})_2$) in mixed reverse micelles [AOT and $\text{Cd}(\text{AOT})_2$]:** The mixed reverse micelles are prepared by solubilizing AOT and $\text{Cd}(\text{AOT})_2$ in isooctane ($[\text{AOT}]_{\text{total}} = 0.1 \text{ M}$). Two modes of synthesis were used. The CdS synthesis were performed either by the method previously described (mixture of two micellar solutions) or by bubbling hydrogen sulfide, H_2S .

Preparation of Samples for Electron Microscopy Experiments. A water-acetone mixture is added to the mixed micellar solution containing CdS particles. A two-phase separation takes place, and the CdS particles migrate to the interface. A drop of the suspension of extracted CdS particles in acetone is spread on a copper grid with a carbon film. The solvent is evaporated under vacuum.

Apparatus. The small-angle X-ray scattering was done on a GDPA30 goniometer with copper $K\alpha$ radiation (1.54 \AA). The experimental arrangement²¹ used and the experimental pattern analysis^{18,22} has been described previously.

The absorption spectra were obtained with a Perkin-Elmer Lambda 5 and Hewlett-Packard HP8452A spectrophotometer, and the fluorescence spectra with a Perkin-Elmer LS5 spectrofluorimeter.

A transmission electron microscope (Philips CM 20 operating at 200 kV) was used to obtain electron micrographs of CdS particles, and diffractograms were obtained by selected area diffraction. The microanalysis technique of CdS particles is energy-dispersive X-ray spectrometry (EDXS).

Continuous irradiation was done by using a 1000-W Oriel lamp with a 20-cm water filter and 385-nm cutoff filter.

Flash photolysis experiments were performed using an Applied Photophysics apparatus.

Structural Study of Mixed Sodium-Cadmium Bis(2-ethylhexyl)sulfosuccinate (AOT and $\text{Cd}(\text{AOT})_2$). Using AOT reverse micelles, it has been shown^{17,18,22a} that these micelles are spherical and the water pool radius varies linearly with the water content ($R_w(\text{\AA}) = 1.5w$).

In the case of pure cadmium AOT reverse micelles, very strong changes in the phase diagram of $\text{Cd}(\text{AOT})_2$ -isooctane-water has been observed.²³ Using mixed micelles (sodium and cadmium AOT), the $\text{Cd}(\text{AOT})_2$ concentration is very low, so no major structural changes are observed when compared to AOT reverse micelles by small-angle X-ray scattering: the shape remains

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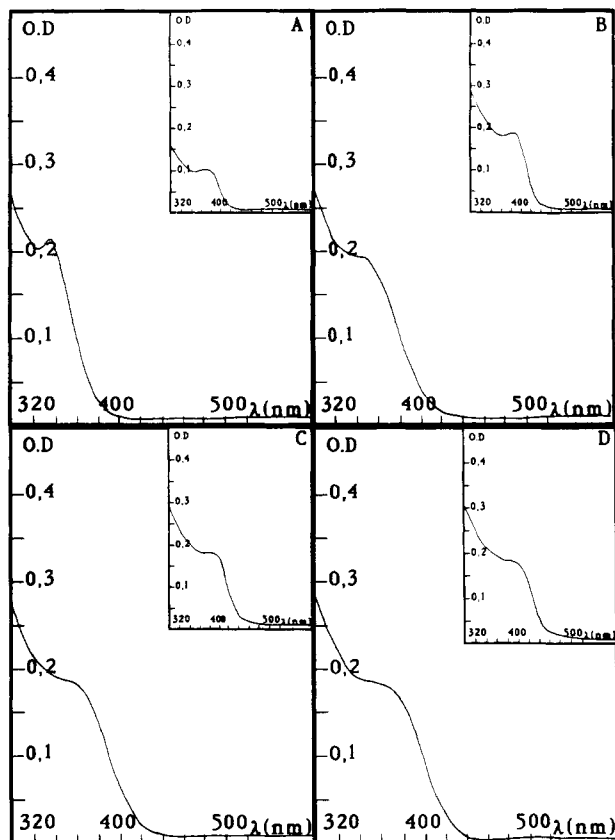


Figure 1. Variation of the absorption spectrum of CdS in reverse micelles with the water content. $[AOT] = 0.1$ M, $[CdNO_3] = 2 \times 10^{-4}$ M, $[Cd^{2+}]/[S^{2-}] = 2$, $[HMP] = 10^{-4}$ M, insert $[HMP] = 0$; $w = 5$ (A); $w = 10$ (B); $w = 20$ (C); $w = 40$ (D).

spherical as in pure AOT reverse micelles and a linear relationship between the water pool and the water content ($R_w(\text{Å}) = 1.5w$) is also observed.²³

Results and Discussions

In aqueous solution, a mixture of solutions containing cadmium and sulfide ions induces a precipitation of CdS semiconductor. By adding a protecting polymer such as HMP in the solution, no precipitation is observed and a yellow solution remains optically clear, indicating the formation of CdS clusters. In reverse micelles similar behavior of the latter is observed. The synthesis of CdS in AOT reverse micelles obtained for various water contents ($w = [H_2O]/[AOT]$) and various values of the ratio of cadmium over sulfide ions concentrations ($[Cd^{2+}]/[S^{2-}]$).

(A) Intermicellar Synthesis. (1) Size Determination. Cadmium sulfide suspensions are characterized by an absorption spectrum in the visible range. In the case of small particles, a quantum size effect²⁴⁻³¹ is observed due to the perturbation of the electronic structure of the semiconductor with the change in the particle size. For CdS semiconductor, as the diameter of the particles ap-

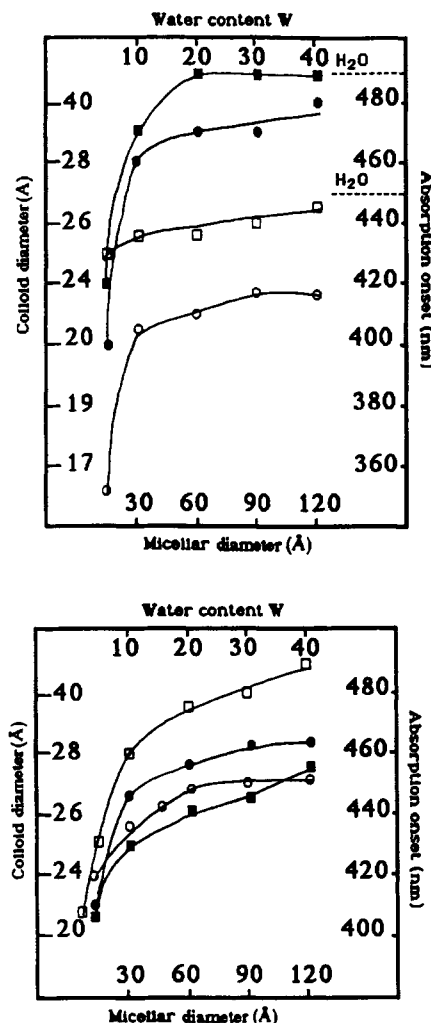


Figure 2. Variation of the size of the CdS particles and the absorption onset with the water content and with the size of the droplet. (A, top) $[AOT] = 0.1$ M, $[Cd^{2+}]/[S^{2-}] = 2$, $[CdNO_3] = 2 \times 10^{-4}$ M and for $[Cd^{2+}]/[S^{2-}] = 1/2$, $[CdNO_3] = 10^{-4}$ M. $[Cd^{2+}]/[S^{2-}] = 1/2$; $[HMP] = 0$ (■); $[HMP] = 2 \times 10^{-4}$ M (●). $[Cd^{2+}]/[S^{2-}] = 2$; $[HMP] = 0$ (□); $[HMP] = 10^{-4}$ M (○). (B, bottom) $[AOT] = 0.1$ M, for $[Cd^{2+}]/[S^{2-}]$ ratio equal to $1/4$, $1/2$, and 1, $[(AOT)_2Cd] = 1 \times 10^{-4}$ M and for $[Cd^{2+}]/[S^{2-}] = 2$, $[(AOT)_2Cd] = 2 \times 10^{-4}$ M. $[Cd^{2+}]/[S^{2-}] = 1/4$ (○); $[Cd^{2+}]/[S^{2-}] = 1/2$ (●). $[Cd^{2+}]/[S^{2-}] = 1$ (□); $[Cd^{2+}]/[S^{2-}] = 2$ (■).

proaches the excitonic diameter, its electronic properties start to change.^{24,29} This gives a widening of the forbidden band and therefore a blue shift in the absorption threshold as the size decreases. This phenomenon occurs as the crystallite size is comparable or below the excitonic diameter of 50–60 Å.^{29b} In a first approximation a simple “electron-hole in a box” model can quantify this blue shift with the size variation.^{24,29b,32} Thus the absorption threshold is directly related to the average size of the particles in solution.

(i) AOT/Cd(NO₃)₂/isooctane/water reverse micelles in the presence and the absence of HMP: In the presence of an excess of cadmium ions, $[Cd^{2+}]/[S^{2-}] = 2$, Figure 1 shows the absorption spectra obtained at various water content, w , in AOT reverse micelles in the presence and in the absence (insert) of HMP. A red shift in the absorption spectra is observed by increasing w . For a given w value, a blue shift in the presence compared to the absence of HMP is observed. As has been described in the literature,^{24,29b,32} the average size of the particles can be

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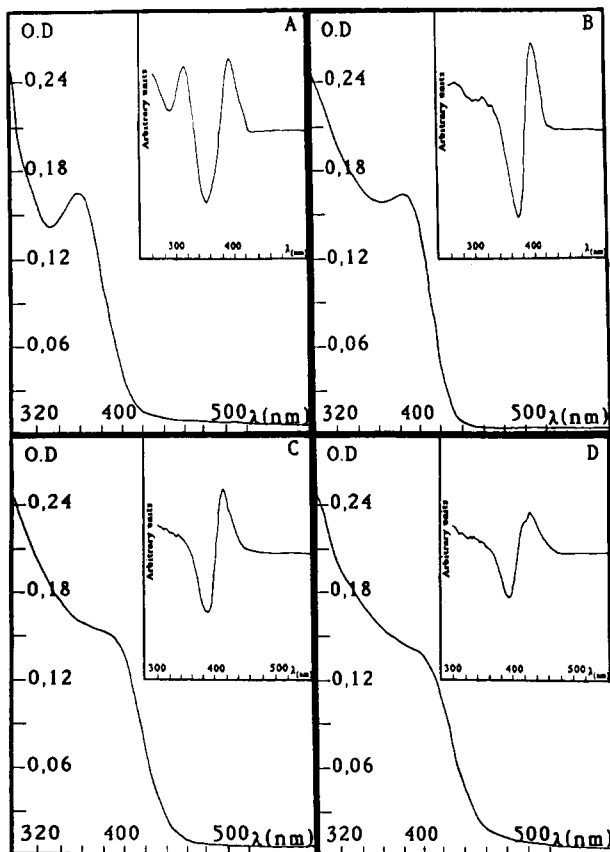


Figure 3. Variation of the absorption spectrum of CdS in reverse micelles with the water content. $[AOT] = 0.1 \text{ M}$, $[(AOT)_2Cd] = 2 \times 10^{-4} \text{ M}$, $[Cd^{2+}]/[S^{2-}] = 2$. A ($w = 5$); B ($w = 10$); C ($w = 20$); D ($w = 40$); insert, second derivative of the photoabsorption, the minimum indicates the excitonic peak.

deduced from the absorption onset. Figure 2A shows the absorption onset and the CdS diameter obtained at various water contents in the presence and in the absence of HMP. It can be seen that the size of the particles increases with the water content, w . The size of the semiconductor is always less than that obtained in aqueous solution. The presence in reverse micelles of HMP as a protecting agent allows a reduction in the size of the particle.

In the presence of an excess of sulfide ion, $[Cd^{2+}]/[S^{2-}] = 1/2$, and in the absence of any protecting agent such as HMP, the absorption threshold of the cadmium sulfide particles reaches that of the particles obtained in aqueous solution⁹ (490 nm) and the presence of HMP makes it possible to obtain smaller particle sizes, (absorption threshold of the order of 470 nm). These data confirm the protecting effect of HMP and AOT which plays a role in limiting the growth of the particles.¹¹

(ii) **Using mixed reverse micelles ($Cd(AOT)_2/AOT/isooctane/water$):** For the presence of an excess of cadmium ions, $[Cd^{2+}]/[S^{2-}] = 2$, Figure 3 shows a behavior similar to that observed in AOT reverse micelles in the presence of HMP. An increase in the average size with the water content is observed. Below the absorption onset several bumps are observed (Figure 3) and can be clearly recognized in the second derivative (insert Figure 3). These weak absorption bands correspond to the excitonic transitions. This clearly shows a narrow size distribution.³³ At low water content the first excitonic peak is well resolved and is followed by a bump. The second

derivative shows a very high intensity of this bump (insert Figure 3A). With a small crystallite, according to the data previously published,³⁴ several bumps due to several excitonic peaks are expected. The insert in Figure 3A shows only one bump. This is due to the very small size of the particles, so the others bumps are blue shifted and are not observable under our experimental conditions. By increasing the water content, that is to say, by increasing the size of the particles, several bumps are observed (insert, Figure 3B). This confirms the fact that, at $w = 5$, the bumps are blue shifted and indicates a very narrow distribution in the size of the particles. The intensity of these bumps decreases with increasing the water content w (inserts, Figure 3), indicating a decrease in the number of excitonic transitions when the size of the particle increases. This is in agreement with the theoretical calculations previously reported for Q particles.³⁴

Electron microscopy has been performed using a sample synthesized at $w = 10$, $[Cd^{2+}]/[S^{2-}] = 2$, and characterized by a 430-nm absorption onset which corresponds to a CdS diameter equal to 25 Å. The microanalysis study (Figure 4A) shows the characteristic lines of sulfide and cadmium ions, indicating that the observed particles are CdS semiconductor crystallites. The micrograph (Figure 4B) shows spherical particles with the average size in the range $40 \pm 20 \text{ Å}$. The electron diffractogram shows concentric circles which are compared to a simulated diffractogram of bulk CdS. A good agreement between the two spectra is obtained, indicating the particles keep zinc blende crystalline structure (fcc) with a lattice constant equal to 5.83 Å. The radius of the particle deduced from the line widening of the diffraction signals is 41 Å.¹⁹ The differences in the size of the particles deduced from the absorption onset and obtained from electron microscopy are probably due to the extraction of CdS particles from the droplets with formation of aggregates.

In the presence of an excess of sulfide ions, $[Cd^{2+}]/[S^{2-}] = 1/2$, a strong change in the absorption spectra at low water content is observed compared to that obtained for a ratio $[Cd^{2+}]/[S^{2-}] = 2$. By increasing the water content, the sharp peak disappears and a behavior similar to that for the case of excess of cadmium is observed, i.e., a red shift in the absorption spectrum. The sharp peak observed at low water content increase with the relative amount of sulfide ions.¹⁹ This peak could be attributed to sulfide clusters³⁷ formed on the CdS particles because of the high local concentration of sulfide ions. The disappearance of this peak by increasing the water content could be explained by the fact that sulfide clusters with negative charges are repelled to the center of the droplets and redissolve themselves inside the water pool.

As previously, the size of CdS particle, the average radius is deduced. Figure 2B shows a change in the size of the particle with the molar ratio of cadmium and sulfide ions concentration. The largest size particles are obtained for $[Cd^{2+}]/[S^{2-}] = 1$, and the smallest for $[Cd^{2+}]/[S^{2-}] = 2$. It can be noticed that the size of CdS is always smaller when one of the two reactants are in excess ($[Cd^{2+}]/[S^{2-}] = 1/4, 1/2, 2$). This confirm that the crystallization process is faster when one of the reacting species is in excess.³⁸

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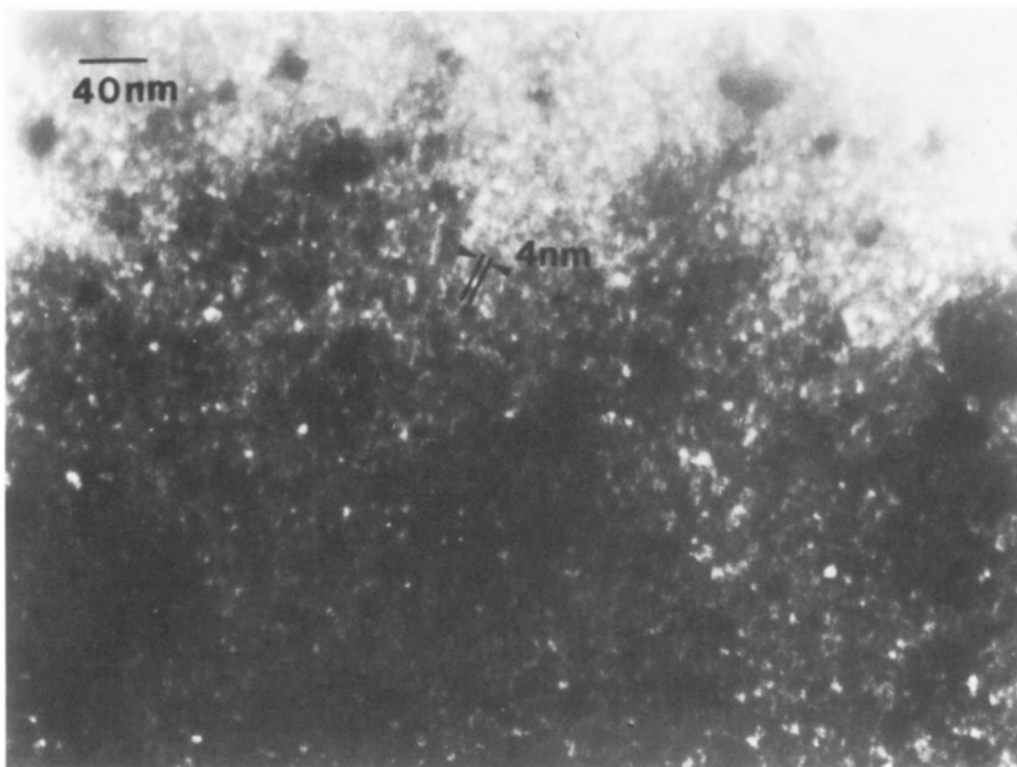
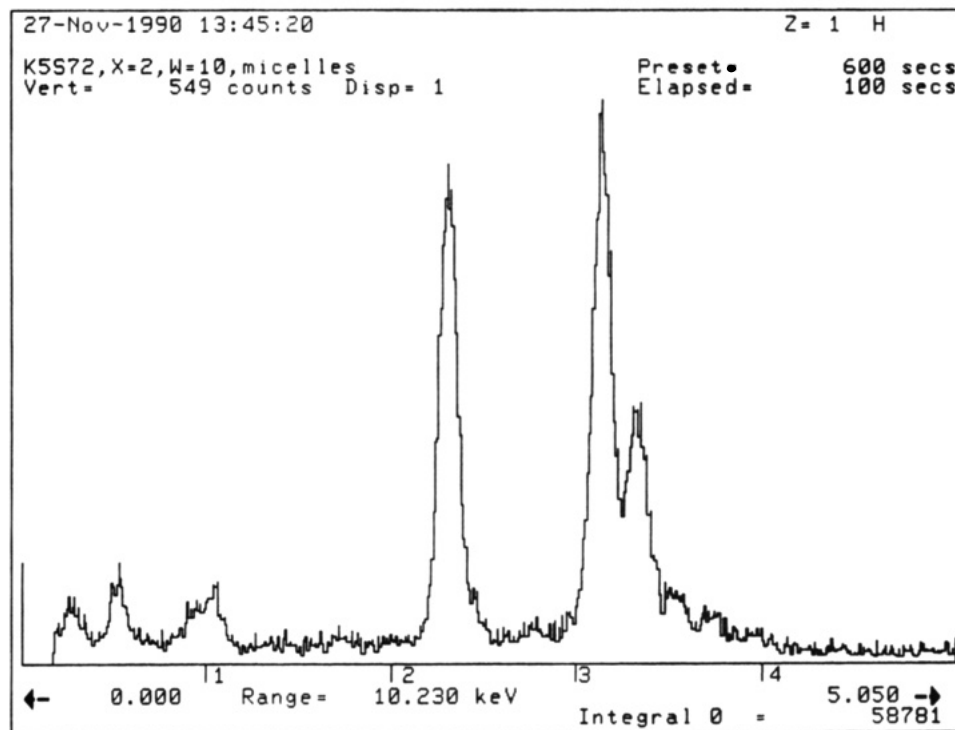


Figure 4. (A, top) X-ray microanalysis of CdS particles after extraction from a micellar solution. (B, bottom) Electron microscopy of a sample after extraction from a micellar solution.

(2) Polydispersity. The fluorescence of cadmium sulfide is strongly dependent on the particle size and the presence or absence of sulfide vacancies.^{8,39} The fluorescence of cadmium sulfide particles observed in solution in water^{32,40} and in acetonitrile solution³⁹ is dependent on the particle method of preparation of CdS particles:

(i) Two types of fluorescence spectra are observed in aqueous solution and in the presence of an excess of cadmium ions. In the absence of any stabilizer the fluorescence is characterized by two very weak bands,⁹ one centered at 450 nm, and attributed to the direct recombination of charge carriers⁴¹ from shallow traps, and the other very broad at about 650 nm which is not clearly attributed. The presence of a stabilizing agent, such as HMP,⁴⁰ makes it possible to increase the sulfide vacancies at the surface

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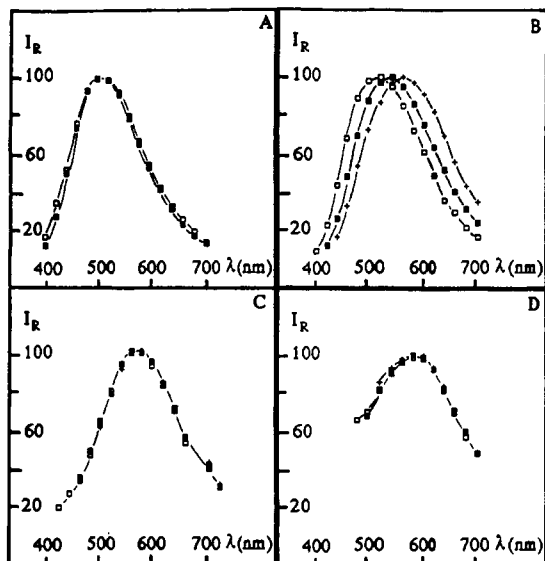


Figure 5. Variation of the relative fluorescence spectra (normalized at the emission maximum) with the water content at various excitation wavelength; [AOT] = 0.1 M, $[Cd^{2+}]/[S^{2-}] = 2$. (A) $[CdNO_3] = 2 \times 10^{-4}$ M, [HMP] = 10^{-4} M, $w = 10$ (λ_{exc} : (□) = 370 nm; (■) = 400 nm). (B) $[CdNO_3] = 2 \times 10^{-4}$ M, [HMP] = 10^{-4} M, $w = 30$ (λ_{exc} : r = 370 nm; n = 400 nm; + = 420 nm). (C) $[(AOT)_2Cd] = 2 \times 10^{-4}$ M, $w = 10$ (λ_{exc} : r = 380 nm; n = 400 nm; + = 420 nm). (D) $[(AOT)_2Cd] = 2 \times 10^{-4}$ M, $w = 30$ (λ_{exc} : r = 380 nm; n = 410 nm; + = 430 nm).

resulting in a more intense fluorescence band, centered in the region of 550 nm. This band is attributed to the recombination of charges previously trapped at the surface in sulfide vacancies.⁴² As the energy of these deeper traps is related to the particle size,³⁹ the shift with excitation wavelengths of the emission maxima to longer wavelengths is explained by the increase in the size of the colloids, which brings about a decrease in the energy of these traps.³⁹

(ii) In the presence of an excess of sulfide ions two fluorescence emissions are observed. The first is centered at 450 nm and is attributed to the direct recombination of charge carriers. The second emission band, observed at around 650 nm, depends on the particle size. This second emission band is very weak and is very often quenched by the presence of species adsorbed at the interface. By analogy it could be attributed to cadmium ion vacancies.

As the fluorescence is dependent on the size of the particles,³⁹ a shift of the excitation threshold with the emission wavelength indicates the presence of particles of different sizes in the solution which shows polydispersion of the aggregates.^{9,11} In the case where this excitation spectrum is analogous to the absorption spectrum, the threshold is a measure of the average size of the emitting particles.

The change of the fluorescence maximum with the excitation wavelength gives a qualitative measure of the polydispersity.²⁹

(i) **AOT/Cd(NO₃)₂/isooctane/water reverse micelles in the presence and in the absence of HMP:** For the presence of an excess of cadmium, $[Cd^{2+}]/[S^{2-}] = 2$, Figure 5A,B shows the fluorescence spectra obtained at various water content and various excitation wavelength. The spectra are normalized at the maximum of emission. At low water content the fluorescence spectra are centered

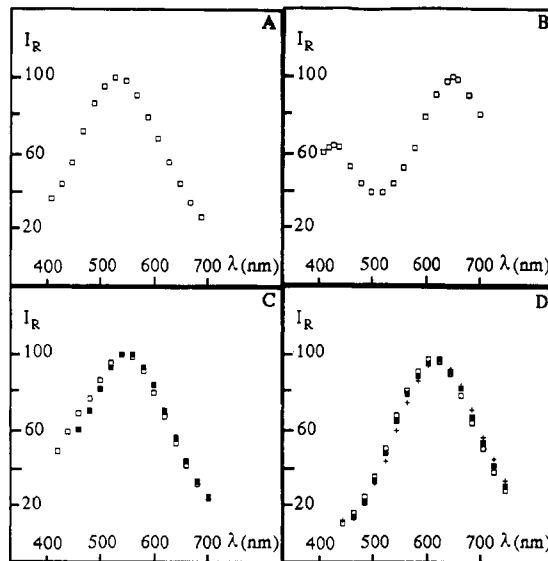


Figure 6. Variation of the fluorescence spectra with the water content at various excitation wavelength. The intensities are normalized to the emission maximum. [AOT-Na] = 0.1 M, $[Cd^{2+}]/[S^{2-}] = 1/2$. (A) $[CdNO_3] = 10^{-4}$ M, [HMP] = 2×10^{-4} M, $w = 5$ (λ_{exc} : (□) = 350 nm). (B) $[CdNO_3] = 10^{-4}$ M, [HMP] = 2×10^{-4} M, $w = 10$ (λ_{exc} : (□) = 370 nm). (C) $[(AOT)_2Cd] = 10^{-4}$ M, $w = 5$ (λ_{exc} : (□) = 380 nm; (■) = 400 nm). (D) $[(AOT)_2Cd] = 10^{-4}$ M, $w = 10$ (λ_{exc} : (□) = 380 nm; (■) = 400 nm; + = 425 nm).

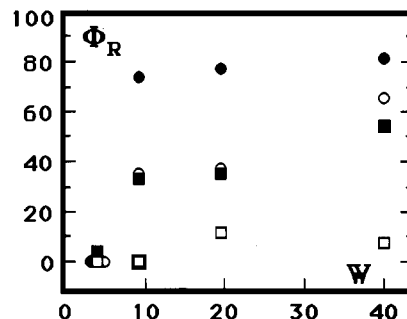


Figure 7. Variation of the relative yield of photocorrosion of CdS particles with the water content. (■) $[CdNO_3] = 10^{-4}$ M, [HMP] = 2×10^{-4} M, $[Cd^{2+}]/[S^{2-}] = 1/2$. (□) $[CdNO_3] = 2 \times 10^{-4}$ M, [HMP] = 10^{-4} M, $[Cd^{2+}]/[S^{2-}] = 2$. (○) $[(AOT)_2Cd] = 10^{-4}$ M, $[Cd^{2+}]/[S^{2-}] = 1/2$. (●) $[(AOT)_2Cd] = 2 \times 10^{-4}$ M, $[Cd^{2+}]/[S^{2-}] = 2$.

at 500 nm. The emission maxima are not changed with the excitation wavelengths ($\Delta\lambda = 10$ nm). By increasing the water content, a red shift of the fluorescence spectra due to the emission of biggest particles is observed and the emission maxima strongly depend on the excitation wavelength ($\Delta\lambda = 40$ nm). This indicates polydispersity among the particles. This is confirmed from the excitation spectra observed at various emission wavelength: at low water content ($w = 10$), the fluorescence excitation threshold is not drastically changed ($\lambda = 405 \pm 2$ nm), whereas at high water content ($w = 30$), a shift in the fluorescence excitation threshold is obtained by changing the emission wavelength ($\lambda = 415 \pm 10$ nm).

In the presence of an excess of sulfide ions, $[Cd^{2+}]/[S^{2-}] = 1/2$, the fluorescence spectra strongly depend on the water content (Figure 6A,B). At $w = 5$, one fluorescence band centered at 520 nm is observed. When the water content is increased, the two characteristic fluorescence bands usually observed in aqueous solution appear (Figure 7B).

(ii) **Using mixed reverse micelles (Cd(AOT)₂/AOT/isooctane/water):** For the presence of an excess

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of cadmium ions, $[Cd^{2+}]/[S^{2-}] = 2$, Figure 5C,D shows the fluorescence spectra at various water content. The unchanged spectra with the excitation wavelengths indicate more monodispersity of the particles formed in mixed reverse micelles than that obtained in case of Cd-(NO₃)₂/±HMP/AOT/isooctane/water reverse micellar system. The shift of the emission maximum with the water content, w , can be related to the increase of the average size of the particles. For a sample synthesized for a given experimental condition (fixed w and ratio $[Cd^{2+}]/[S^{2-}]$) the fluorescence excitation spectra are unchanged with the emission wavelengths. This confirms the monodispersity in the size of the CdS particles.

In the presence of an excess of sulfide ions, $[Cd^{2+}]/[S^{2-}] = 1/4$ and $1/2$, one fluorescence band centered at 550 nm is observed at low water content ($[H_2O]/[AOT] = 5$, Figure 6C). This band is red shifted by increasing the water content (Figure 6D). This behavior differs from that observed in the case AOT reverse micelles in the presence of HMP: the two fluorescence bands usually obtained in the presence of an excess of sulfide ions are observed only in AOT reverse micelles at high water content (Figure 5B). At low water content in AOT (Figure 5A) and in mixed (Figure 5C,D) reverse micelles, one fluorescence band is observed. This effect can be explained in term of location of the CdS particles: by increasing the water content, CdS particles containing an excess of sulfide anion are expelled to the water pool with a microenvironment similar to the bulk aqueous phase. As has been said before, the first fluorescence band centered at 450 nm is attributed to the direct recombination of charge carriers. From these data, it can be concluded that the location of CdS particles close to the interface creates a local environment which prevents a direct recombination of charge carriers.

(iii) **Remark:** In the presence of an excess of cadmium ions and at a given water content ($w = 5$), the maximum of fluorescence is red shifted by using a functionalized surfactant (560 nm) instead of a mixture of cadmium ions in the presence of HMP (500 nm). This difference can be attributed to a change of 2 Å in the particle radius.

(3) **Photochemical Reaction.** (i) **Photocorrosion:** Photocorrosion, observed in the presence of oxygen, is due to the photodissolution of CdS particles. The main photochemical reaction is the following:⁴³



Such processes can be blocked by trapping the holes, h^+ , formed during the irradiation of the particles. The reduction of the hole takes place either by adding an external electron donor or by the presence of an excess of sulfide ions.

The yield of photocorrosion is determined from the initial slope of the disappearance of the absorption spectrum with time. To determine the relative yield of photocorrosion we choose to measure to the optical density with time at 300 nm. Figure 7 shows the increase of the relative photocorrosion yield with the water content. In the presence of an excess of sulfide ions ($[Cd^{2+}]/[S^{2-}] = 1/2$) a shift of the absorption threshold to longer wavelengths is observed showing an increase in the size of the aggregates. This phenomenon favoring the formation of large particles corresponds to a greater thermodynamic stability (Ostwald's ripening⁴⁴). Similar behavior is also observed using either Cd(NO₃)₂/HMP/AOT/isooctane/water or

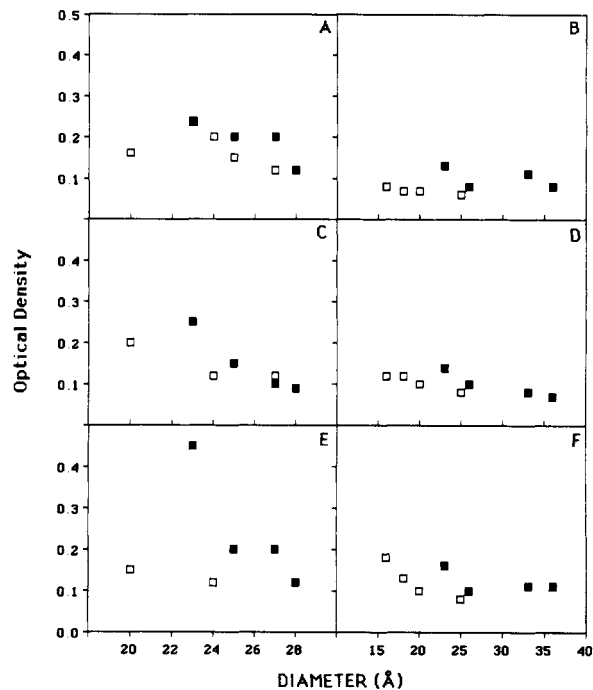


Figure 8. Variation of the yield of reduced dialkylviologens with the size of CdS particles; in mixed reverse micelles (A, C, E) (Δ): Cd(AOT)₂/AOT/isooctane/water) and AOT micelles ((B, D, F) Cd(NO₃)₂/AOT/isooctane/water) at $[Cd^{2+}]/[S^{2-}] = 2$ (\square) and $1/2$ (\blacksquare). The length of dialkyl viologen chain is respectively equal to C₁ (A and B), C₈ (C and D), and C₁₂ (E and F).

Cd(AOT)₂/AOT/isooctane/water reverse micelles. Because of the excess of sulfide ions at CdS interface, the reduction of holes formed by UV irradiation prevents CdS dissolution and does not depend on the synthetic mode of the CdS particles. The poor efficiency of the protecting polymer (HMP) in these experiments can be explained in term of electrostatic repulsion between CdS particles containing cadmium vacancies and HMP, both negatively charged.

In the presence of an excess of cadmium ions, $[Cd^{2+}]/[S^{2-}] = 2$, the photocorrosion process strongly depends on the mode of CdS synthesis (Figure 7): With Cd(NO₃)₂/HMP/AOT/isooctane/water reverse micelles, the photocorrosion yield is close to zero at water content below $w = 20$ and is not strongly affected by the increase in the water content. This could be explained in terms of strong electrostatic attractions between the negatively charged polymer (HMP) and CdS particles containing sulfide vacancies. On the contrary, using functionalized surfactants [Cd(AOT)₂/AOT/isooctane/water solution], the photocorrosion yield is very high at $w \neq 5$.

At low water content ($w = 5$), no photocorrosion process is observed in different synthetic modes of CdS particles as shown Figure 7. This is due to the fact, that, at low water content, the CdS particles and water pool sizes are comparable and the CdS particles are totally surrounded by surfactant molecules which in turn plays the role of a protecting agent.

(ii) **Photoelectron transfer:** The reduction of viologens in aqueous solution using CdS particles as a photosensitizer have been well developed during past few years.^{9,45-47} Our purpose is to compare the efficiency of

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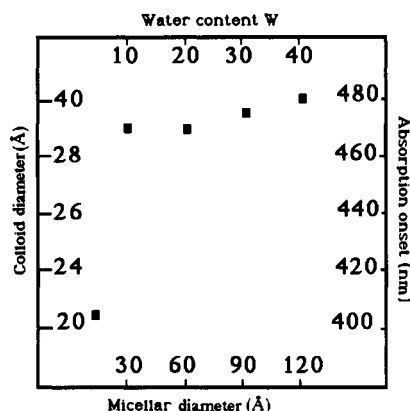


Figure 9. Variation of the absorption onset and the CdS radius with the water content, w , obtained by bubbling H_2S [$AOT-Na$] = 0.1 M, $[(AOT)_2Cd]$ = 2×10^{-4} M.

the photoelectron transfer from CdS particles synthesized under different conditions to various dialkyl viologens. Figure 8 shows the variation of the yield of reduced viologen with the size of CdS particles in the various experimental conditions. Except at low value (around 16-Å diameter in the presence of an excess of cadmium) and for a long chain of viologen (C_{12}), the size of the particles does not strongly affect the yield of reduced viologen. For a given particle size, the yield of reduced viologen is higher using cadmium AOT instead of cadmium nitrate. At $[Cd^{2+}]/[S^{2-}] = 1/2$, the yield strongly increases for relatively low size of the particle (between 20 and 25 Å). However, for similar sizes at $[Cd^{2+}]/[S^{2-}] = 2$ no changes in the yields can be observed. From these data it can be concluded that when the size of CdS particles is between 15 and 40 Å, a change in the yield of reduced viologen is not due to the length of alkyl chains and can be mainly attributed to interfacial effect (excess of sulfide ions). As a matter of fact, in the case of an excess of sulfide ions ($[Cd^{2+}]/[S^{2-}] = 1/2$), the yield of reduced viologen strongly decreases by increasing the CdS size. This can be related to the fact that under the same experimental conditions, the absorption spectra of CdS particles show a sharp band attributed to the formation of sulfide clusters at the CdS surface. Such clusters could give an electron to the hole formed by CdS excitation and then prevent the back electron transfer reaction.

(4) **Gelation of Reverse Micelles.** Gelatin can be solubilized in an AOT–isooctane reverse micellar solution and form a transparent, stable gel. A model of spherical droplets containing water and part of the gelatin has been proposed.^{22b} These water-in-oil microemulsions droplets are connected by the gelatin, arranged in helical strands but not covered by surfactant. For this system of interconnected spheres, the droplet structure, characteristic of the water/AOT/isooctane system, is retained during all of the gelation process. Similarly optically transparent gels have been obtained by replacing AOT by mixed cadmium–sodium AOT with the same overall surfactant concentration.

The CdS absorption spectra obtained for various $[Cd^{2+}]/[S^{2-}]$ values in reverse micelles and in gels are

unchanged (10% of gelatine; $w = 45$; $[AOT] = 0.25$ M), indicating no changes on the size of the particles by gelifying the system.

(B) **Intramolecular Synthesis. Synthesis in Mixed Micelles by Bubbling Hydrogen Sulfide.** This gives a relatively high concentration of CdS (up to 10^{-3} M). The bubbling of H_2S is continued until there is no further changes in the CdS absorption spectrum, resulting in an excess of sulfide ions in the solution. The size of the CdS particles increases with the CdS concentration formed and with the water content (and, thus, with the size of the water pool of the reverse micelles). Above $w = 10$ only large aggregates are obtained (Figure 9). At $w < 10$ the water is essentially water of hydration of the polar heads,¹⁷ the percentage of sulfide ions formed should be much smaller than that obtained at high water concentrations ($w > 10$). This could explain the very clear break between the size of colloids above and below $w = 10$. The essential interest using H_2S , lies in the significant increase in concentration at small w values corresponding to a factor between 4 and 20, depending on the size of the micelles.

The comparative study of the size of particles as a function of the method of synthesis shows that the method plays an important role in the size of the semiconductor obtained. The use of hydrogen sulfide gas results in the formation of the largest particles. This is probably due to the fact that the formation of the semiconductor is intramolecular. The reverse micelle acts simply as a microreactor. In the first method of synthesis (addition of sodium sulfide), the formation of the semiconductor is controlled by the exchange process between water pools, which should, probably, contribute to the limitation of the growth of the particles. However it can be noticed a similar value of the particle radius ($r = 22 \pm 1$ Å) is obtained at low water content ($w = 5$) by using various synthetic modes. This indicates a micellar effect on the synthesis of semiconductors.

Conclusion

We compared the effect in controlling in CdS particle size, the polydispersity and the photochemical reactions CdS particles synthesized “in situ” in reverse micelles by using different modes.

With functionalized micelles, the particles formed are more monodisperse than those obtained by using cadmium nitrate in the absence and in the presence of a protecting polymer. However, in the latter case, it is possible to reach smaller particles.

In the presence of an excess of sulfide ions, the photocorrosion yield does not change with the mode of synthesis of CdS particles. On the contrary, at w up to 5, in the presence of an excess of cadmium, the photocorrosion yield is very low with a protecting polymer and very high with mixed micelles, indicating that the photocorrosion process is strongly increased by using monodispersed particles. The photoelectron transfer efficiency of CdS particles to viologens cannot be directly related to a size effect of the crystallites but mainly to the localization of the particles at the interface. The presence of a protecting polymer decreases the yield of the photoelectron transfer by a factor of 2.

Registry No. NaAOT, 20542-42-1; $[Cd(AOT)_2]$, 124461-79-6; HMP, 68915-31-1; $Cd(NO_3)_2$, 10325-94-7; H_2O , 7732-18-5; Cd^{2+} , 22537-48-0; S^{2-} , 18496-25-8; H_2S , 7783-06-4; CdS, 1306-23-6; O_2 , 7782-44-7.

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