

Ultrasmall particles of cadmium selenide and cadmium sulfide formed in Nafion by an ion-dilution technique

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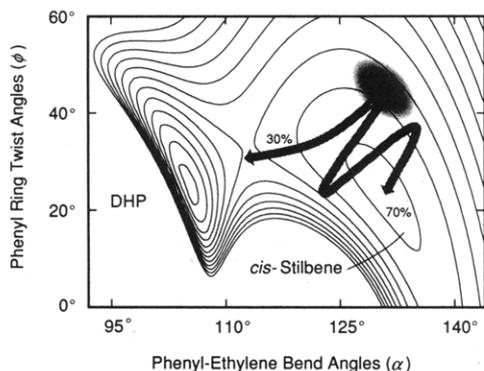


Figure 2. Conceptual picture of S_1 potential surface for *cis*-stilbene in the symmetric phenyl twist angle and central phenyl-ethylene bend angle coordinates. The position of the equilibrium configuration on the S_0 surface ($\phi = 43^\circ$; $\alpha = 129^\circ$)¹⁷ is marked by the shaded ellipse representing a wave packet where the isomerization dynamics is initiated. The gray lines indicate two dynamical pathways for pieces of this initial wave packet. Most of the wave packet will stay in the *cis*-stilbene side of the surface and eventually end up in the perpendicular intermediate configuration from which it decays radiationlessly to *cis*- and *trans*-stilbene. A smaller part of the wave packet finds its way over to the left side of the potential surface, where it becomes vibrationally excited dihydrophenanthrene (DHP). Some of this product decays to DHP while the rest internally converts to *cis*-stilbene.

effect of the cyclobutene ring on the 151.7-cm^{-1} mode shows that it has minor ethylenic torsional character. Finally, the observation of only two strongly coupled progressions with $\sim 31\text{-cm}^{-1}$ frequency for DBS is consistent with the bridging methylene group strongly restricting motion along ω_3 mode and strongly coupling ω_3 and ω_6 modes.

Proposed Mechanism for *cis*-Stilbene S_1 State Decay and Isomerization. The observation and assignment of the DPC-4 fluorescence excitation spectra provides new information on the *cis*-stilbene S_1 -state potential energy surface from which it is possible to reconcile formation of both *trans*-stilbene and DHP on a picosecond time scale. The gas-phase *cis*-stilbene S_1 -state lifetime⁸ corresponds roughly to one symmetric twist vibrational

period. The interaction between the phenyl groups is attractive when the phenyl ring configuration maximizes the p-orbital overlap between C_2 and $C_{2'}$, and it is repulsive when the $H_2-H_{2'}$ repulsion dominates. Thus, there is a narrow range of angles ϕ and α for which the barrier to DHP formation is low, as shown in Figure 2. When the repulsive interaction dominates, the symmetric phenyl twist couples with the ethylenic torsion, converting the initial phenyl twisting motion into ethylenic torsion leading to *cis*-*trans* isomerization. The quantum yield measurements by Fischer and co-workers imply that the branching ratio between *cis*-*trans* and DHP routes to nonradiative decay is 70:30.¹ This branching ratio is interpreted to be the fraction of configuration space that leads to DHP formation during one phenyl twisting vibration.

The nonradiative decay through phenyl twisting proposed in this work may be common to other molecules with vicinal, sterically hindered phenyl rings. For instance, Fox and co-workers found a strong dependence of the nonradiative decay rate on the phenyl twist for substituted tetraphenylethylenes whose phenyl rings were, to various degrees, constrained from twisting.³⁰ Other molecules such as diphenylamine are also known to form stable DHP-like photoproducts.^{2,22} From the viscosity dependence on the nonradiative decay rate, phenyl twisting has been implicated in triphenylmethane photochemistry.³¹ Further experimental and theoretical investigation of *cis*-stilbene photocyclization may provide a deeper understanding of nonradiative decay processes through the phenyl twisting motion.

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- (30) Shultz, D. A.; Fox, M. A. *J. Am. Chem. Soc.* **1989**, *111*, 6311.
 (31) Ben-Amotz, D.; Harris, C. B. *Chem. Phys. Lett.* **1985**, *119*, 305.

Ultrasmall Particles of CdSe and CdS Formed in Nafion by an Ion-Dilution Technique

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The transition of semiconductor chalcogenides from molecular CdX (X = Se, S) to bulk material has been observed in Nafion, a cation-exchange membrane. The two-phase structure of Nafion, consisting of a hydrophobic region and ionic clusters, has been utilized to form ultrasmall particles of CdS/Se by using a technique analogous to an inverted micelle microemulsion method, where the Cd ion/ionomer cluster ratio is controlled by diluting the cadmium-exchange solution with an inert ion (Ca^{2+}). The absorption onset for the cadmium chalcogenides formed can be tuned over a range of more than 3.5 eV by varying the $\text{Cd}^{2+}/\text{Ca}^{2+}$ ratio in the solution used to exchange the acidic form of the ionomer membrane.

We report here the synthesis of ultrasmall particles of CdS and CdSe, with sizes from monomolecular species through larger clusters to bulk materials, in the ion-exchange polymer Nafion as a matrix. These particles are formed by coexchanging Cd^{2+}

with an inert diluent ion (Ca^{2+}) followed by dehydration and reaction with H_2S or H_2Se . A large number of photoelectrochemical studies have been reported involving CdS (bandgap 2.4 eV) particle suspensions.¹⁻⁷ CdS showing bulk properties can

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(1) Harbour, J. R.; Hair, M. L. *J. Phys. Chem.* **1977**, *81*, 1791.

(2) Frank, S. N.; Bard, A. J. *J. Phys. Chem.* **1977**, *81*, 1484.

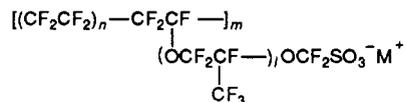
(3) Kalyanasudarm, K.; Borgarello, E.; Grätzel, M. *Helv. Chim. Acta* **1981**, *64*, 362.

(4) Matsumura, M.; Sato, Y.; Tsubomura, H. *J. Phys. Chem.* **1983**, *87*, 3897.

also be formed in polymer matrices.⁸⁻¹² For example, when the perfluorinated cation-exchange polymer Nafion was treated with an aqueous solution of Cd²⁺ followed by exposure to H₂S or an aqueous solution of sulfide ions, yellow CdS particles were precipitated within the polymeric matrix.¹⁰ This material could be used for the photocatalyzed reduction of methylviologen,¹⁰ and in the presence of Pt (either chemically deposited throughout the membrane or sputter deposited) and a sacrificial donor, photochemical H₂ formation was observed.¹¹ A surface analysis of this semiconductor-incorporated polymer system showed that the CdS had bulklike properties and particle sizes (1–2 μm).¹⁰⁻¹² Wang and Mahler¹³ showed that much smaller CdS particles could be formed in Nafion, if the H₂S were reacted with dehydrated cadmium-exchanged Nafion in the gas phase. These quantum or Q-particles¹⁴ had larger bandgaps than the bulk material (up to 2.76 eV) and were identified with particles with diameters down to 50 Å.

Q-state semiconductors can also be prepared in a variety of matrices and media, including micelle microemulsions,¹⁶ zeolites,^{17,18} polymers,^{8,13,19} solutions,²⁰⁻²³ glasses,²⁴ and in Langmuir-Blodgett films.²⁵ These methods produce isolated small particles. A key principle in these methods is the use of a matrix to arrest Ostwald ripening. The method described here to produce even smaller particles is based on several new features. Cd²⁺ is exchanged into the Nafion membrane in the presence of a diluent ion, Ca²⁺ or Mg²⁺ with a similar ion-exchange constant, so that the amount and distribution can be controlled. This is followed by rigorous dehydration before gas-phase treatment with H₂S or H₂Se. By control of the inert ion/Cd²⁺ ratio, the absorption onset can be tuned over a range of greater than 3.5 eV. Continuous dilution of the Cd²⁺ resulted in a convergence of the onset to a value that we believe approaches that of molecular CdS. As we will show, this method can be considered an arrested (or static) micelle microemulsion technique. We also compare the spectra of particles formed in membranes treated with various dry non-aqueous solvents.

Nafion perfluorinated membranes have the following general chemical formula:



where n and m can be varied to produce materials of different ion exchange capacities and l is small. As in many ionomeric polymers, the ion-exchange sites in Nafion aggregate into clusters. Ion clustering in Nafion has been suggested by a number of techniques, including mechanical and dielectric relaxation, NMR, IR, transport experiments, electron microscopy, and X-ray studies.²⁶ Gierke and Hsu have derived a semiphenomenological expression for the diameter of ionic clusters in Nafion resins that correctly describes the observed variation in cluster diameter with water content, equivalent weight, and cation form.²⁷ Their theory also predicts that short channels connect adjacent clusters. A study of tracer self-diffusion coefficients for Na⁺ and Cs⁺ in Nafion by Yeager and Kipling support the Gierke model.²⁸ For a fully hydrated 1200 equiv wt polymer in the acidic form, the average cluster will contain approximately 70 ion-exchange sites and 1000 water molecules in a spherical domain resembling an inverted micelle with a diameter of about 40 Å. As the polymer is dehydrated, the cluster diameter and charge per cluster decreases. It is believed that the spherical clusters are connected by short channels approximately 10 Å in diameter in the swollen film. These channels are a controlling feature for transport in the membrane. Since the cluster diameter is dependent on overall swelling, it is possible that, below a certain degree of swelling, clusters are no longer connected by solution channels and diffusion is hindered.²⁸ Hence, Nafion can be considered an ensemble of inverted micelles connected by channels that can be opened or closed depending upon the extent of swelling or hydration of the polymer. By dilution of the ion of interest (e.g., Cd²⁺) with an inert ion, one can regulate the number of Cd²⁺ ions per cluster in the ionomer, thus enabling the synthesis of ultras-small clusters of CdX (X = S or Se) trapped in isolated regions of the polymer.

Experimental Section

Nafion 115 (1100 g/equiv, 5-mil thickness; E. I. duPont de Nemours, Inc., Wilmington, DE) was cleaned by boiling in concentrated HNO₃ twice, then rinsed in boiling milli-Q filtered water (Continental Water Systems, El Paso, TX) twice, and finally rinsed in milli-Q water. Reagent grade anhydrous CaCl₂ and CdCl₂·2H₂O were used without further purification to prepare 0, 1, 5, 10, 50, 75, and 100 mol % Cd²⁺ ion solutions with a total concentration (Ca²⁺ + Cd²⁺) of 1 M. The protonated Nafion samples were sonicated in these solutions for 7 h and rinsed in distilled water, and their surfaces were pat-dried with soft tissue paper (ChemWipes). The samples were then placed in quartz cells, which were attached to a vacuum line and heated to 140 °C for 5 h to dry. The samples were exposed to 1 atm of H₂S or H₂Se on the vacuum line for 10 h, and the gas was then pumped off. The absorption spectra taken were referenced to the same cell with either Ca²⁺-exchanged Nafion or clean protonated Nafion, depending on the mole percent of cadmium in the solution used to equilibrate the Nafion films. All absorption spectra were taken on a Hewlett-Packard Model 8451A single-beam diode array UV-vis spectrophotometer.

To ascertain how much Cd²⁺ was absorbed by the film when exposed to the exchange solutions, a 1.3 × 1.3 cm piece of Nafion film was exposed to the exchange solution. The absorbed Cd²⁺ was then extracted with three 5-mL aliquots of 0.2 M CaCl₂. KCl was added as a supporting electrolyte, the combined aliquots were diluted to 50 mL, and the Cd²⁺ was determined by square-wave polarography²⁹ using a BAS 100 (Bioanalytical System Inc.,

(5) Kuczynski, J. P.; Milosavljevic, B. H.; Thomas, J. K. *J. Phys. Chem.* **1983**, *87*, 3368.

(6) Meyer, M.; Walburg, C.; Kurihara, K.; Fendler, J. H. *J. Chem. Soc., Chem. Commun.* **1984**, 90.

(7) (a) Ueno, A.; Kakuta, N.; Park, K. H.; Finlayson, M. F.; Bard, A. J.; Campion, A.; Fox, M. A.; Webber, S. E.; White, J. M. *J. Phys. Chem.* **1985**, *89*, 3828. (b) Sobzynski, A.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallouk, T.; Webber, S. E.; White, J. M. *J. Phys. Chem.* **1987**, *91*, 3316.

(8) Meissner, D.; Memming, R.; Kastening, B. *Chem. Phys. Lett.* **1983**, *96*, 34.

(9) Kuczynski, J. P.; Milosavljevic, B. H.; Thomas, J. K. *Chem. Phys. Lett.* **1984**, *88*, 980.

(10) Krishnan, M.; White, J. R.; Fox, M. A.; Bard, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 7002.

(11) Mau, A. W.-H.; Huang, C.-B.; Kakuta, N.; Bard, A. J.; Campion, A.; Fox, M. A.; White, J. M.; Webber, S. E. *J. Am. Chem. Soc.* **1984**, *106*, 6537.

(12) Kakuta, N.; White, J. M.; Campion, A.; Bard, A. J.; Fox, M. A.; Webber, S. E. *J. Phys. Chem.* **1985**, *89*, 48.

(13) Wang, Y.; Mahler, W. *Opt. Commun.* **1987**, *61*, 233.

(14) Brus, L. E. *J. Chem. Phys.* **1983**, *79*, 5566.

(15) Steigerwald, M. L.; Alivisatos, A. P.; Gibson, J. M.; Harris, T. D.; Kortan, R.; Muller, A. J.; Thayer, A. M.; Duncan, T. M.; Douglass, D. C.; Brus, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 3046.

(16) Youn, H.-C.; Baral, S.; Fendler, J. *J. Phys. Chem.* **1988**, *92*, 6320.

(17) Wang, Y.; Herron, N. *J. Phys. Chem.* **1987**, *91*, 257.

(18) Herron, N.; Wang, Y.; Eddy, M. M.; Stucky, G. D.; Cox, D.; Moller, K.; Bein, T. *J. Am. Chem. Soc.* **1989**, *111*, 530.

(19) Wang, Y.; Suna, A.; Mahler, W.; Kasowski, R. *J. Chem. Phys.* **1987**, *87*, 7315.

(20) Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 255.

(21) Fojtik, A.; Weller, H.; Henglein, A. *Chem. Phys. Lett.* **1985**, *120*, 6; **1985**, *120*, 552.

(22) Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 301.

(23) Nozik, A. J.; Williams, F.; Nenadovic, M. T.; Rajh, T.; Micic, O. I. *J. Phys. Chem.* **1985**, *89*, 397.

(24) Modes, S.; Llanos, P. *Chem. Phys. Lett.* **1988**, *153*, 351.

(25) Smotkin, E.; Lee, C.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallouk, T. E.; Webber, S. E.; White, J. M. *Chem. Phys. Lett.* **1988**, *152*, 265.

(26) Eisenberg, A.; Yeager, H. L. *Perfluorinated Ionomer Membranes*; ACS Symposium Series 180; American Chemical Society: Washington, DC, 1982, and references therein.

(27) Hsu, W. Y.; Gierke, T. D. *J. Membrane Sci.* **1983**, *13*, 307, 2528.

(28) Yeager, H. L.; Kipling, B. *J. Phys. Chem.* **1979**, *83*, 1836.

(29) Osteryoung, J.; O'Dea, J. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1986; Vol. 14, p 209.

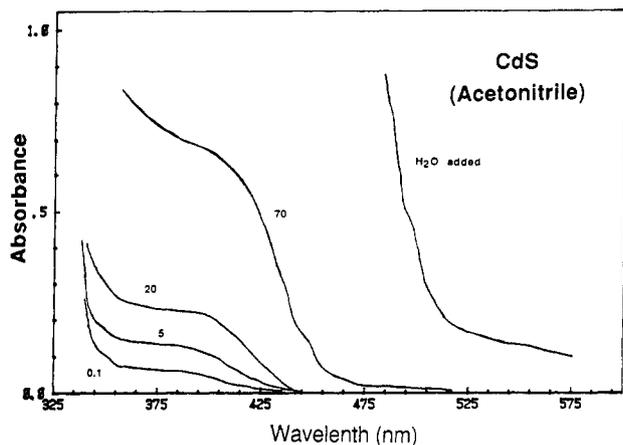


Figure 1. Growth of CdS in acetonitrile at time = 0.1, 5, 20, 70 min. Longest wavelength onset is seen after adding water.

Lafayette, IN) electrochemical system and a Princeton Applied Research Model 303 static mercury drop electrode. Energy-dispersive X-ray spectroscopy (EDS) was obtained on a JEOL JSM-35C system.

For electron microscopy of the Nafion films and CdS particles, thin films (less than 200 nm) of Nafion were cast onto 300-mesh Formvar-coated TEM grids. These films were then treated with Cd^{2+} , dried, and exposed to H_2S by aforementioned techniques. Observations of Nafion films and CdS particles were made with a Philips EM 420 transmission electron microscope operating at 100 keV. Graphitized carbon with its 0.34-nm lattice was used as a calibration standard. Electron images were captured by a yttrium/aluminum/garnet crystal that transmitted the respective photon images through a fiber optic system to a Gatan silicon intensified target diode video camera system. The images were then digitized and processed. Typical image processing routines included low-pass filtering and background subtraction, followed by scaling to achieve optimum contrast. Final images were captured from a high-resolution television monitor onto 35-mm film by using an Olympus OM-4 single-lens reflex camera.

Results and Discussion

CdS in Nafion Formed in MeCN. The absorption spectra of membranes containing CdS formed in dry MeCN solutions are shown in Figure 1. The dried Nafion membrane containing Cd^{2+} was immersed in MeCN, and H_2S was allowed to diffuse in from the head space of the cell. In all cases, a peak at 325 nm, due to dissolved H_2S , was seen. The first spectrum was taken seconds after injection of H_2S into the dry MeCN. Growth of clusters is indicated by the absorbance with an onset at 450 nm. The second and third spectra were taken 5 and 20 min after injection, respectively, showing continued growth of particles with the same absorption onset. The fourth spectrum was taken 70 min after injection of the H_2S . After 70 min, no further growth of particles was observed. The final spectrum was taken 15 min after 0.05 mL of water was added to the 3.0 mL of MeCN/ H_2S . A red shift, indicating growth of the particle size, occurs. In the absence of H_2S , particle growth upon addition water is very slow, as shown by the experiments in Figure 2. Curve 1 is the spectrum of a dry Nafion sample exchanged with Cd^{2+} in MeCN and treated with H_2S followed by removal of the H_2S and MeCN on a vacuum line. Curve 2 is the spectrum of the same sample after it had been immersed in water and sonicated for 5 min and then dried. The absorption onset did not shift to the bulk value. Curve 3 is the spectrum obtained after the sample was rehydrated and heated to 120 °C. Some particle growth was observed, as evidenced by the red shift in the onset. However, the spectrum does not rise sharply as does the spectrum of the bulk material in Figure 1, suggesting a broad distribution of sizes. We shall discuss possible mechanisms later.

CdS and CdSe in Nafion Formed by Coexchange. Even smaller particles could be produced by coexchanging the Cd^{2+} with an

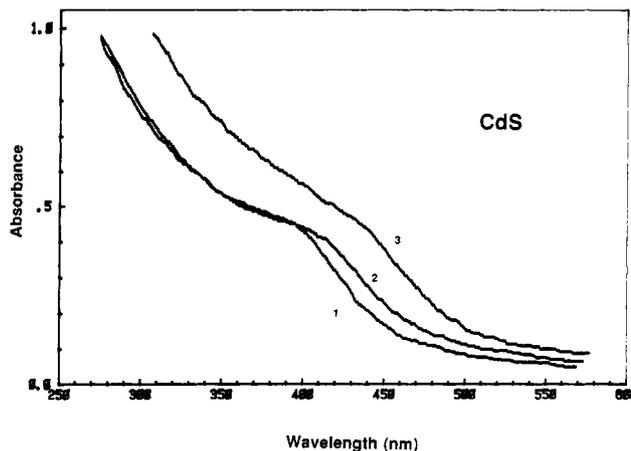


Figure 2. Stability of Q-particles in water. 1. Spectrum of particles formed in acetonitrile after solvent and H_2S have been removed. 2. Spectrum after sonication in water. 3. Spectrum after annealing in water.

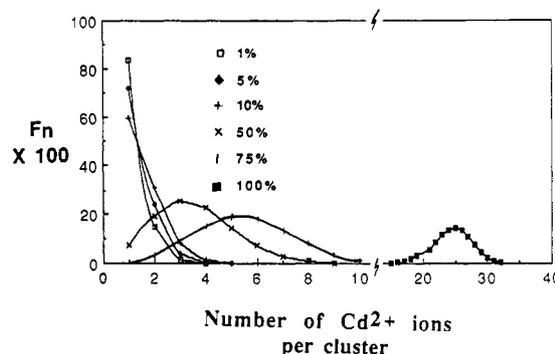


Figure 3. Distribution of total Cd atoms (%) as a function of the number of Cd atoms in a cluster, assuming 70 sulfonate sites (35 Cd^{2+} ions) per cluster and all sites equally probable.

TABLE I: Amount of Cd^{2+} in Nafion 115 as a Function of Soaking Solution Concentration

Cd, ^a mol	solution ^b mole fraction, %	wt of Nafion, g	% total sites occupied
1.39×10^{-7}	1	0.0588	0.52
<i>c</i>	5.0		0.97
3.80×10^{-7}	10	0.0550	1.52
1.90×10^{-6}	50	0.0557	7.54
3.45×10^{-6}	75	0.0568	13.35
1.72×10^{-5}	100	0.0566	67.0

^a Determined by extracting Cd^{2+} from membrane and analysis by square-wave polarography. ^b Total concentration ($\text{Cd}^{2+} + \text{Ca}^{2+}$), 1 M. ^c The 5% data were obtained by interpolation.

inert diluent ion such as Ca^{2+} or Mg^{2+} . To determine the amount and distribution of the Cd^{2+} ions in the clusters, the Cd^{2+} was extracted from the Nafion and determined by square-wave polarography. In Table I, the total moles of Cd^{2+} in a 1.3×1.3 cm film of Nafion (0.83 mequiv/g) immersed in solutions with various mole fractions of Cd^{2+} with Ca^{2+} as the diluent ion are tabulated along with the percentage of ionic sites in the Nafion occupied by Cd^{2+} ions. By assuming 70 SO_3^- per cluster, all of which can be exchanged with equal probability, we can apply eq 1 to calculate the probability, p_n , of finding n Cd^{2+} ions in a cluster,

$$p_n = [35! / (35 - n)!n!] f^n (1 - f)^{35-n} \quad (1)$$

where n is the number of Cd^{2+} in the cluster and f is the fraction of sites occupied by Cd^{2+} ions as determined polarographically. The fraction of Cd^{2+} ions existing in clusters of size n , F_n , can be calculated from the probabilities as shown in eq 2. Figure

$$F_n = np_n / \sum_{i=1}^{35} n_i p_i \quad (2)$$

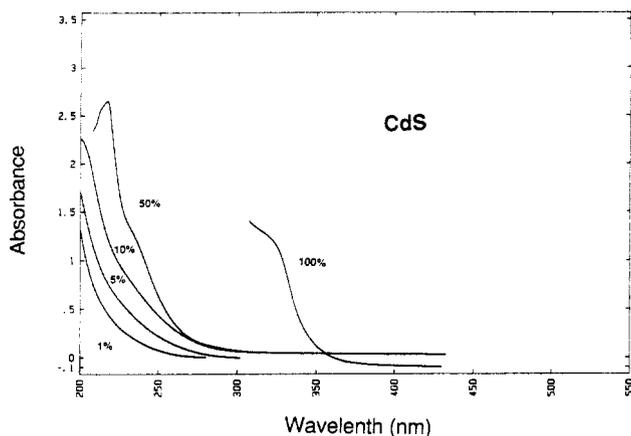


Figure 4. Absorption spectra of CdS in Nafion. Spectra of wavelengths lower than 300 nm are of samples made by equilibrating Nafion with solutions of 1, 5, 10, and 50 mol% CdCl₂ with CaCl₂. These spectra are referenced to Nafion exchanged with Ca²⁺. The spectrum with onset at 350 nm is from Nafion equilibrated with 100 Cd²⁺ solution. This spectrum was referenced to clean Nafion. All solutions were 1 M overall.

3 is a plot of F_n vs n for Q-particles formed in Nafion-exchanged in Cd²⁺/Ca²⁺ solutions. One can see that the films immersed in 1, 5, and 10 mol % Cd²⁺ solutions should produce predominantly monomers, while the 50% solution should yield mostly trimers. These results are only semiquantitative. In fact, the clusters are probably somewhat smaller when the samples are exposed to the chalcogenide because the films are dehydrated. The distribution diagram is probably most accurate when considering the location of the Cd²⁺ ions before reacting with gas-phase H₂S or H₂Se. Migration during the reaction will cause deviation from the calculated distribution, and this migration undoubtedly occurs to some extent.

Figure 4 shows the absorption spectra of the CdS formed with Cd²⁺ mole fractions of 0.01, 0.05, 0.10, 0.50, and 1 in the equilibration solutions used to exchange the Nafion films, respectively. The 1, 5, 10, and 50% samples were referenced to calcium-exchanged films (in these cases Cd²⁺ occupies 0.5–7.5% of the available sites), while the rest were referenced to clean Nafion in the proton-exchanged form. While a rigorously correct reference would require a careful sulfide analysis of the sample, in all cases the absorbance of the reference sample in the region of interest, i.e., in the Q-particle absorption onset region, was minimal. At wavelengths shorter than 200 nm, the absorbance of the Nafion reference samples exceeds one, and the subtracted spectra are therefore less reliable.

Ostwald ripening occurs upon exposure of the CdS/Nafion samples to water and water + H₂S, as demonstrated in Figure 5. The spectrum with the onset at about 270 nm is the 50% sample. After the H₂S was removed on a vacuum line, the sample was immersed in water, yielding the spectrum with an onset at about 440 nm. Without dissolved sulfide, the absorption onset did not shift to the bulk value. Addition of Na₂S to the water resulted in an instant shift of the onset to about 470 nm. This is similar to the results obtained in MeCN. The lowest energy spectrum is the result of exposing a 100% sample to air for 6 months. Similar ripening of the 1, 5, and 10% samples occurred in water, although the results were not reproducible, possibly because of loss of CdS to the aqueous phase.

An analogous set of samples can be prepared for the selenides by using the same Cd²⁺ exchange solutions as those used for the sulfide samples. In Figure 6, the spectra for the 1, 5, 10, 75, and 100% samples are shown. When the 75% sample was exposed to water, the onset shifted to about 600 nm. Addition of Na₂Se resulted in the spectrum with the onset at highest wavelength. As expected, the results have the same trend as the sulfide data but are all red shifted (CdSe has a smaller bandgap (1.7 eV)).

The distribution diagram suggests that 100% percent samples (CdS or CdSe) should have no overlap in the onset area with the smaller clusters. This is what is observed in Figures 4 and 6. The

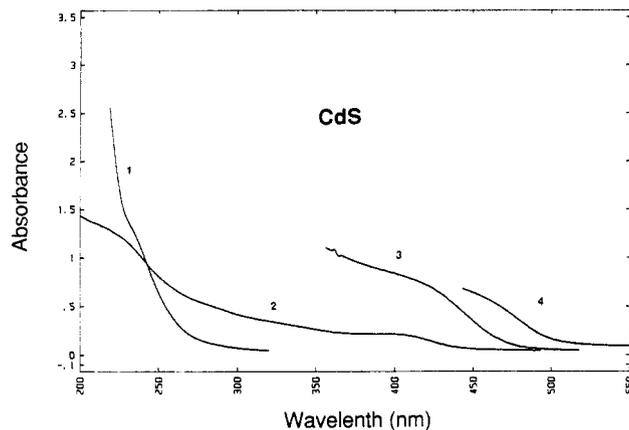


Figure 5. Effect of water on CdS clusters in Nafion: (1) the 50% sample from Figure 4; (2) the spectrum of the 50% sample after immersion in water and sonication for 5 min followed by drying on the vacuum line without heat; (3) the spectrum of the 50% sample exposed to water and excess sulfide; (4) the spectrum of a 100% sample after exposure to air for 6 months.

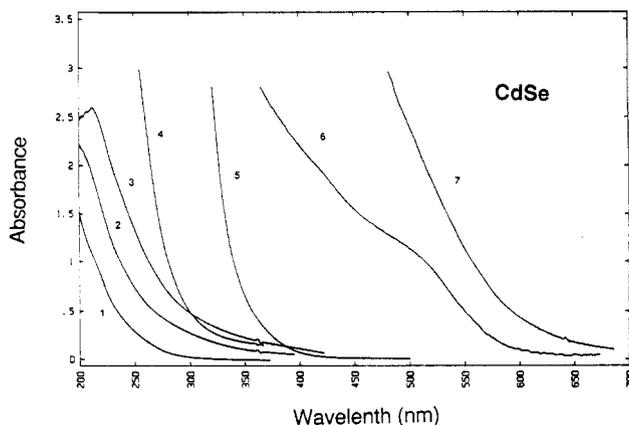


Figure 6. CdSe in Nafion. Curves 1, 2, 3, and 4 are spectra of CdSe prepared by exposure of Nafion to solutions of 1, 5, 10, 75 mol % CdCl₂ (referenced to Nafion exchanged with Ca²⁺). Curve 5 corresponds to sample made with 100 mol % Cd referenced to clean Nafion. Curve 6 is spectrum of particles formed by exposing the 75% sample (curve 4) to water and sonicating for 5 min. Curve 7 is CdSe formed by exposing the sample yielding curve 6 to Na₂Se in water.

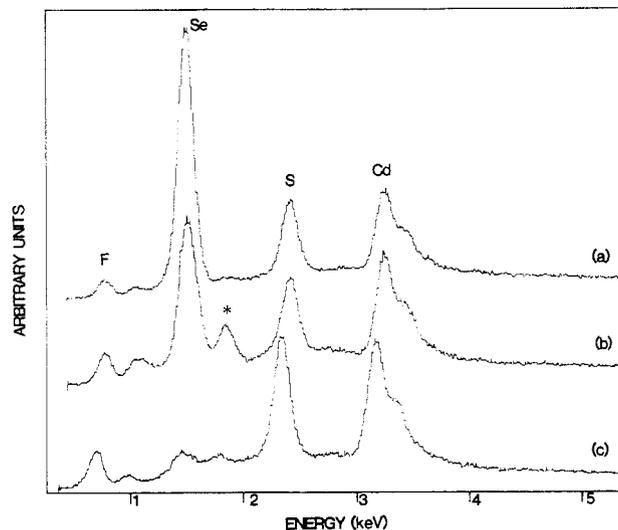


Figure 7. EDS spectra of a 100% CdSe/Nafion sample. In (a) Nafion sheet. In (b) and (c), the sheet was cut and mounted on edge, spectrum (b) was obtained with the beam focused on a spot within 1 μm of the surface, and spectrum (c) was obtained from a 1-μm spot in the middle of the sample. (Asterisk: silicon peak from sample holder.)

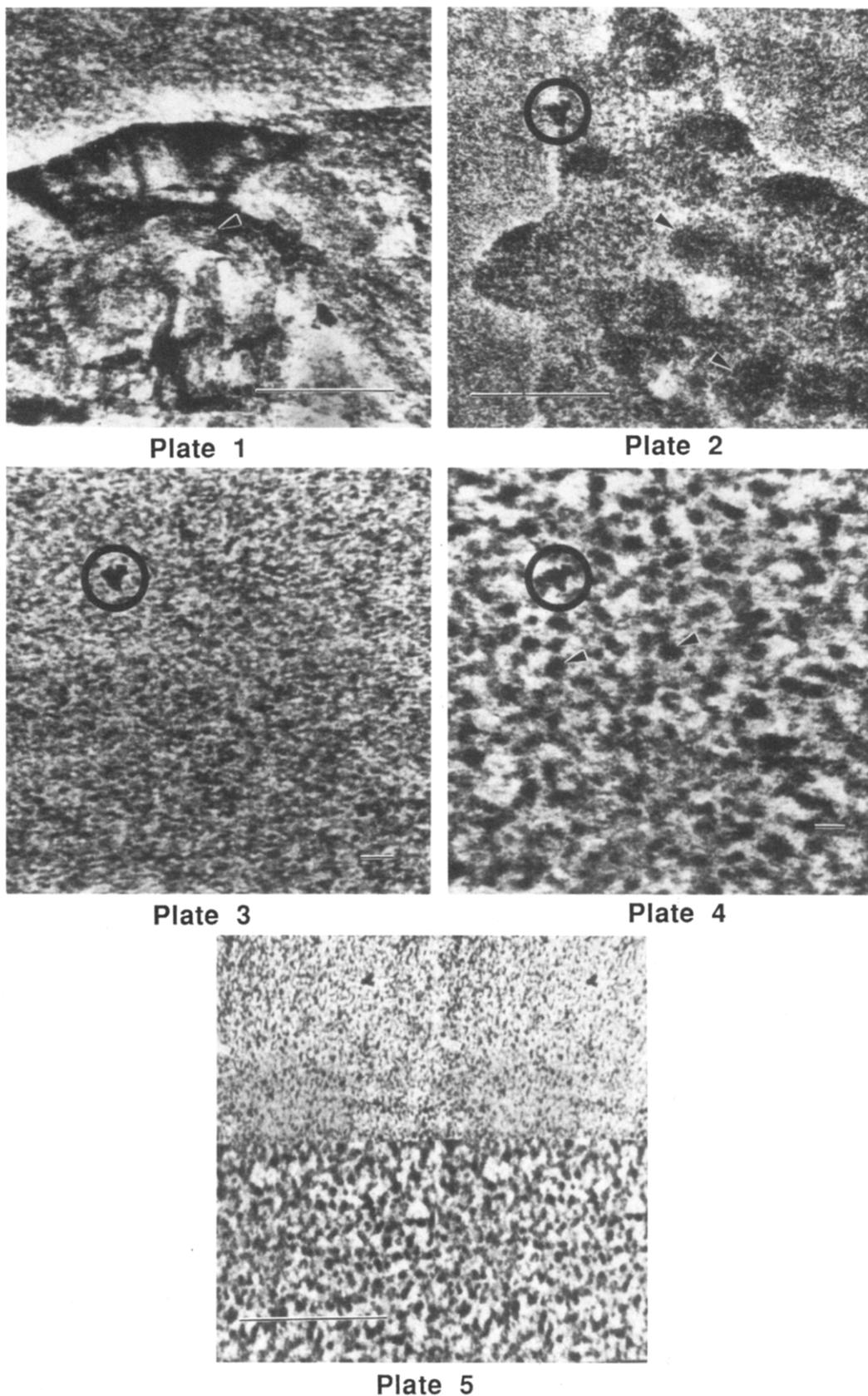


Figure 8. Transmission electron micrographs of graphitized carbon, Nafion films, and CdS particles formed by 100% Cd²⁺ exchange. The encircled object in plates 2–4 is a defect in the vidicon screen. Plate 1: (bar = 10 nm) graphite lattices 250 000 \times . Plate 2: (bar = 10 nm) area of Nafion overlaying the Formvar coating. Electron-dense areas (arrows) within the Nafion represent CdS particles. Plate 3: (bar = 10 nm) granular image of clean Nafion (without CdS), 45 000 \times . Plate 4: same magnification as plate 3, a more granular pattern, typical of CdS particles (arrows). Plate 5: raw images of plates 3 and 4, demagnified to 22 500 \times , spliced together, and processed together to maximize contrast.

1, 5, and 10% samples should be predominantly monomers. The overlap in the onset area of these spectra is consistent with the distribution diagram, since these samples contain predominantly

monomers. One would expect some overlap of the 50 and 75% samples with the 1, 5, and 10% samples as all of these samples have monomers to pentamers. The distribution diagram suggests

that the 50 and 75% samples should have little overlap with the onset area of the 100% samples. All of these predictions are consistent with the experimental data. The absorption onsets for these monomeric and oligomeric CdS particles are significantly blue-shifted, compared to those characterized previously. For example, colloidal CdS with an average particle diameter of 41 Å has an absorbance onset at ca. 475 nm.³⁰ Isolated Cd₄S₄ clusters grown within the sodalite cages of zeolite Y have an absorbance onset at 350 nm,^{17,18} which shifts to 400–425 nm as they become electronically coupled to form "superclusters" and ultimately to 520 nm for strongly coupled Cd₄S clusters confined to the analogous face-sharing cages in borolite.³¹ By comparison, the 100% Cd²⁺-exchanged CdS/Nafion sample, which contains on average 25 Cd/cluster, has an absorbance onset at ca. 370 nm (Figure 4). The 1, 5, and 10% samples, which should contain predominantly isolated Cd²⁺, have absorbance onsets in the 250–270-nm range. Preliminary analysis of Se EXAFS data from similarly prepared dry CdSe/Nafion and ZnSe/Nafion samples show fewer than two Se atoms in the second coordination shell, supporting the conclusion that monomers or oligomers of low nuclearity have been produced; surprisingly, this is so even in the case of the dry 100% Cd²⁺-exchanged samples. These data will be discussed in detail in a separate paper.³²

All of the CdS and CdSe samples, whose spectra appear in Figures 4 and 6, respectively, with absorption onsets at shorter wavelengths than 410 nm were formed by reaction of gas-phase H₂S or H₂Se with Cd²⁺ ions in dehydrated Nafion on a vacuum line. Under these conditions, there is minimal swelling, and it is reasonable to conclude that transport between clusters via channels is severely hampered.²⁸ Hence, Ostwald ripening, yielding larger particles, cannot occur. Ripening can be induced by hydrating the Nafion, thereby opening up the channels between the ionomer clusters. This is demonstrated in the case of the 50% CdS sample in Figure 5, in the MeCN samples of Figure 1, and in Figure 6 for the 75% CdSe sample. The samples of Figures 5 and 6 were exposed, in the absence of H₂S and H₂Se, to water and sonicated for 5 min. The samples were then dried on the vacuum line, yielding spectra with onsets red shifted, yet still at significantly shorter wavelengths than the bulk values. Although the channels are opened with the swelling of the hydrated Nafion, the ripening process is limited. A more dramatic example of this effect can be seen in the 100% samples. After removing the excess H₂S on a vacuum line, when the cell was opened to the humid air, and the film changed from a clear colorless film to a clear yellow film in minutes. We have observed the same effect with PbS samples as well.

In the presence of both H₂S and water, the red shift that accompanies ripening is rapid, taking only seconds. In addition to the opening of channels between the ionomer clusters, caused by swelling of the film, Wang and Herron have suggested that excess H₂S can act as a transport agent for CdS.³³ They attribute this to the following equilibrium:



The higher solubility product of Cd(HS)₂ leads to increased mobility of cadmium ions between the ionomer clusters, thereby assisting in the ripening process.

In summary, fast ripening occurs in samples made from concentrated Cd²⁺-exchanged Nafion (i.e., the 100% sample) when exposed to water. The absorption onsets shift to the bulk values in the absence of excess S²⁻ or Se²⁻. In samples prepared with the diluent ion, Ca²⁺, the ripening process is slower, and sharp bulk onsets are not attained for the dilute samples even in the presence of water. In the presence of both excess S²⁻ or Se²⁻ and water, the ripening process is faster in all samples. Hence, the kinetics of the ripening process appears to depend on the avail-

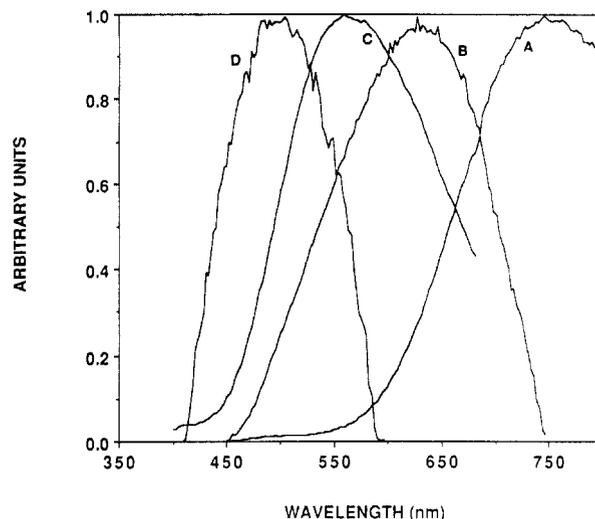


Figure 9. Emission spectra of CdS/Nafion films: (A) bulk CdS; (B) sample prepared from a 50% Cd²⁺/50% Ca²⁺ solution and exposed to aqueous sulfide; (C) sample prepared from a 100% Cd²⁺ solution, reacted with gas-phase H₂S; (D) same as (C) but prepared from a 90% Cd²⁺/10% Ca²⁺ solution. Excitation wavelength: 260 nm.

ability of open channels through which migration can occur, the availability of excess chalcogenide ions (presumably yielding more soluble species, e.g., Cd(HX)₂), and the concentration of the Cd²⁺ ions in the Nafion film.

Energy-Dispersive X-ray Spectroscopy (EDS) of CdSe in Nafion. EDS of a sample of CdSe (100% exchange solution) with a beam 90° to the surface of the film showed that the average ratio of the Cd to Se was 1.32 ± 0.12 near the surface. The ratio of Cd to Se throughout the bulk was determined by X-ray absorption measurements, to be described elsewhere,³² to be about 10:1, suggesting an inhomogeneous distribution. A sample was sliced and placed edge-up on the SEM sample stage. Figure 7a is the spectrum resulting from a beam normal to the surface. The S and F peaks are background from the Nafion. Figure 7b is the spectrum resulting from directing the beam normal to the edge approximately 1 μm from the surface. One can see that while the Cd concentration is unchanged the Se content is diminished. In Figure 7c one can see that while the Cd concentration is constant throughout the film, there is no Se in the center region. Hence, most of the CdSe is located near the surface of the film with most of the Cd in the bulk unreacted. This implies that diffusion of H₂Se into the dry Nafion film is sufficiently slow that uniform penetration at room temperature is not attained in 10 h. Recent studies on the preparation of FeS₂ in Nafion indicate however that heating a dry film at 120 °C for 16 days does lead to complete permeation of H₂S.³⁴

Transmission Electron Microscopy (TEM) of CdS Particles in Nafion. TEM pictures of a thin (<200 nm) film cast from soluble Nafion are shown in Figure 8. Plate 1 (bar = 10 nm) is the image of the graphite lattice taken at the instrument magnification of 250 000×. Note that the 0.34-nm interplanar distance of the lattice (arrow) is clearly evident and can be used to calibrate other plates presented. In plate 2 the electron-dense areas (arrows) within the Nafion represent the CdS particles. These individual particles range from 2 to 4 nm in diameter. Plate 3 (bar = 10 nm) taken at an instrument magnification of 45 000× shows the granular image of clean Nafion (without CdS), while plate 4 (bar = 10 nm) depicts at the same instrument magnification a more granular pattern, typical of the CdS particles (arrows).

To verify that these observations are not artifacts of the image processing, the raw images of plates 3 and 4 were demagnified to an instrument magnification of 22 500× and then spliced together. The composite plate 5 (bar = 100 nm) was then processed

(30) (a) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 5649. (b) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.

(31) Stucky, G. D.; MacDougall, J. E. *Science* **1990**, *246*, 669.

(32) Felton, R.; Hoener, C.; Bard, A. J.; Campion, A.; Fox, M. A.; Mal-louk, T. E.; Webber, S. E.; White, J. M., manuscript in preparation.

(33) Wang, Y.; Herron, N. *J. Phys. Chem.* **1987**, *91*, 5005.

(34) Zen, J.-M.; Chen, G.; Fan, F.-R.; Bard, A. J. *Chem. Phys. Lett.* **1990**, *169*, 23.

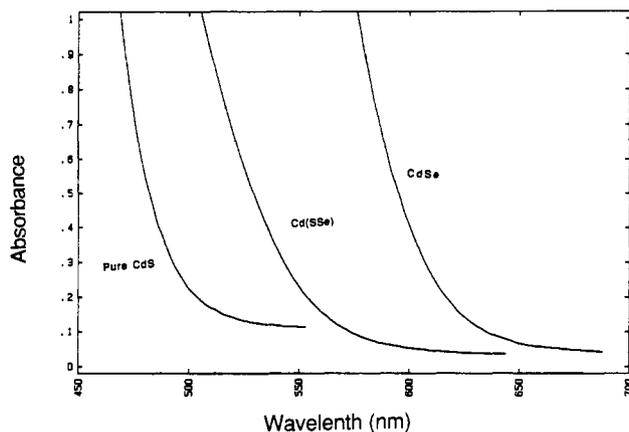


Figure 10. Formation of mixed chalcogenides by exposure of CdS to H_2Se .

to achieve maximum contrast, and the results clearly show that the presence of the CdS is correlated with the particulate structure, which averages 2–4 nm. While a cluster of 25 CdS (predicted from the distribution diagram, Figure 3), should be considerably smaller than this, the TEM film samples are extremely thin and can quickly equilibrate with water from the air. These samples were handled in air prior to obtaining the images in Figure 8. Hence, it is likely that ripening occurred to produce much larger particles than are formed under dry conditions.

Fluorescence Spectra of Q-CdS in Nafion. The fluorescence spectra of bulk CdS, a 50% sample exposed to aqueous sulfide, a 100% gas-phase sample, and a 90% gas-phase sample (in descending order of emission maxima) are shown in Figure 9. The excitation wavelength is 260 nm. Spectra obtained with emission maxima at lower wavelengths were unreliable as emissions in these regions were observed even in the clean Nafion.³⁵ One can see that the emission maxima blue shift corresponds with the blue shifting of the absorption onset.

(35) Lee, P. C.; Meisel, D. *J. Am. Chem. Soc.* **1980**, *102*, 5477.

CdS_xSe_{1-x} Mixed Q-State Particles in Nafion. We have observed that the exposure of Q-state particles of CdS in Nafion to H_2Se results in exchange of sulfide in the lattice by selenide. The standard free energy (ΔG°) of reaction for the exchange is -9 kcal/mol with bulk CdS and CdSe. As expected, CdSe in Nafion is essentially unreactive toward H_2S . Upon exposure of CdS to H_2Se , the shift of the spectrum to that of CdSe is gradual. Hence, quenching of the reaction prior to complete exchange results in the formation of mixed chalcogenides. The spectrum of pure CdS shows an absorption onset of about 520 nm (Figure 10). Exposure of the sample to H_2Se (1 atm) for 10 min resulted in the mixed chalcogenide, yielding a spectrum with an onset at 580 nm. Exposure of the same sample for 10 h to H_2Se yielded a spectrum with an onset at 650 nm. Neither further exposure to H_2Se nor exposure of the CdSe material to H_2S had an effect on the absorption spectrum. The absorption onset of the CdSe spectrum in Figure 10 is blue shifted from the bulk value by 0.20 eV. Possibly, the CdS particles were of a size intermediate between Q-state particles and bulk CdS. Exchange of the sulfide for selenide resulted in particles of similar size but with smaller effective electron and hole masses, pushing the system deeper into the Q-state regime. Further studies on mixed Q-state particles in Nafion are in progress.

Conclusions

A simple method has been devised to synthesize molecular clusters of CdS and CdSe in a cation-exchange membrane by controlling the number of sites available in the ionomer clusters of Nafion by blocking exchange sites with Ca^{2+} . Ostwald ripening can be controlled by dehydrating the film and hampering inter-cluster diffusion. In principle, this technique, involving the dilution of the cation used in the synthesis, could be applied to many types of reactive cations exchanged into Nafion.

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Aggregation and Solvent Interaction in Nonionic Surfactant Systems with Formamide

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The self-association and solvent interaction of some polyethylene glycol alkyl ether surfactants (C_xE_y) in formamide have been studied via determinations of phase diagrams and NMR self-diffusion measurements. For $C_{12}E_3$ and $C_{12}E_4$, small micelles but no liquid crystalline phases form. Increasing the alkyl chain length to hexadecyl ($C_{16}E_4$, $C_{16}E_6$, and $C_{16}E_8$), mesophase formation occurs analogously to the corresponding aqueous system. No aggregate growth occurs in the micellar phase, neither at high temperatures and high surfactant concentrations nor when approaching the lower consolute temperature. The solvent diffusion was analyzed within the cell diffusion model, and a concentration-independent amount of 1–5 and probably not more than 3 formamide molecules was found to interact with each ethylene oxide group. Furthermore, the calculations indicated a polymer-like state of the micellar headgroup shell, with a slight decrease of the formamide content therein at a raised temperature. In conclusion, the behavior of C_xE_y /formamide systems is qualitatively similar to that of the corresponding aqueous systems.

Introduction

The aggregation of surfactants in nonaqueous, polar solvents has during the past few years been intensely scrutinized.^{1,2} It

has been established that amphiphiles such as lecithin^{3,4} and, recently, also normal single-chain surfactants^{5–7} form liquid

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(1) Friberg, S. E.; Liang, Y. C. In *Microemulsions*; CRC Press: Cleveland, OH, 1988; Chapter 3, p 79.

(2) Evans, D. F. *Langmuir* **1988**, *4*, 3.

(3) Moucharafieh, N.; Friberg, S. E. *Mol. Cryst. Liq. Cryst.* **1971**, *49*, 231.

(4) Bergenstahl, B.; Stenius, P. *J. Phys. Chem.* **1987**, *91*, 5944.