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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/cluster ratio is controlled by diluting the cadmium-exchange solution with an inert ion (Ca*). The absorption onset for the cadmium chalcogenides formed can be tuned over a range of more than 3.5 eV by varying the Cd2*/Ca2+ 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 Cd2+ with an inert diluent ion (Ca2+) followed by dehydration and reaction with H2S or H2Se. A large number of photoelectrochemical studies have been reported involving CdS (bandgap 2.4 eV) particle suspensions.\(^7\) CdS showing bulk properties can

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also be formed in polymer matrices. For example, when the perfluorinated cation-exchange polymer Nafion was treated with an aqueous solution of CdS followed by exposure to H$_2$S or an aqueous solution of sulfide ions, yellow CdS particles were precipitated within the polymeric matrix. This material could be used for the photocatalyzed reduction of methyliodide and in the presence of Pt (either chemically deposited throughout the membrane or sputter deposited) and a sacrificial donor, photochemical H$_2$S formation was observed. A surface analysis of this semiconductor-incorporated polymer system showed that the CdS had bulklike properties and particle sizes (1–2 μm).

A Q-state semiconductor can also be prepared in a variety of matrices and media, including micelle microemulsions, zeolites, polymers, glasses, and in Langmuir–Blodgett films. 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. CdS is exchanged into the Nafion membrane in the presence of a diluent ion, Ca$^{2+}$ or Mg$^{2+}$ 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 H$_2$S or H$_2$Se on the vacuum line for 10 h, and the gas was then pumped off. The absorption spectra taken were referenced to the same polymer. By dilution of the ion of interest (e.g., Cd$^{2+}$) with an inert ion, one can regulate the number of Cd$_2^+$ ions per cluster in the ionomer, thus enabling the synthesis of ultrasmall clusters of CdX (X = S or Se) trapped in isolated regions of the polymer.

Nafion perfluorinated membranes have the following general chemical formula:

\[ \text{[I(CF$_2$CF)$_n$-CF$_3$]} \]

where \( n \) and \( m \) can be varied to produce materials of different ion exchange capacities and \( l \) is small. As in many inorganic 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. Gierke and Hsu have derived a semphenomenological expression for the diameter of ion clusters in Nafion that correctly describes the observed variation in cluster diameter with water content, equivalent weight, and cation form. Their theory also predicts that short channels connect adjacent clusters. A study of tracer self-diffusion coefficients for Na$^+$ and Ca$^{2+}$ in Nafion by Yeager and Kipling support the Gierke model. 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. 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., Cd$^{2+}$) with an inert ion, one can regulate the number of Cd$_2^+$ ions per cluster in the ionomer, thus enabling the synthesis of ultrasmall 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 HNO$_3$ twice, then rinsed in boiling milli-Q filtered water (Continental Water Systems, El Paso, TX) twice, and finally stored in milli-Q water. Reagent grade anhydrous CaCl$_2$ and CdCl$_2$•2H$_2$O were used without further purification to prepare 0, 1, 5, 10, 50, 75, and 100 mol % Cd$^{2+}$ ion solutions with a total concentration (Ca$^{2+}$ + Cd$^{2+}$) 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 H$_2$S or H$_2$Se 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 Ca$^{2+}$-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 Cd$^{2+}$ 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 Cd$^{2+}$ was then extracted with three 5-mL aliquots of 0.2 M CaCl$_2$. KCl was added as a supporting electrolyte, the combined aliquots were diluted to 50 mL, and the Cd$^{2+}$ was determined by square-wave polarography using a BAS 100 (Bioanalytical System Inc.).

Ultrasmall Particles of CdSe and CdS

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 CdSe, dried, and exposed to H2S 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 CdSe was immersed in MeCN, and H2S was allowed to diffuse in from the head space of the cell. In all cases, a peak at 325 nm, due to dissolved H2S, was seen. The first spectrum was taken seconds after injection of H2S 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 H2S. After 70 min, no further growth of particles was observed. The final spectrum was taken 15 min after 0.05 M H2S was added to the 3.0 mL of MeCN/H2S. A red shift, indicating growth of the particle size, occurs. In the absence of H2S, particle growth upon addition of water is very slow, as shown by the experiments in Figure 2. Curve 1 is the spectrum of a dry Nafion sample exchanged with Cd2+ in MeCN and treated with H2S followed by removal of the H2S 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 Cd2+ with an inert diluent such as Ca2+ or Mg2+. To determine the amount and distribution of the Cd2+ ions in the clusters, the Cd2+ was extracted from the Nafion and determined by square-wave polarography. * Table 1 to calculate the probability, \( p_n \) of finding \( n \) Cd2+ ions in a cluster, assuming 70 sulfonate sites (35 Cd2+ ions) per cluster and all sites equally probable.

**Table 1:** Amount of Cd2+ in Nafion 115 as a Function of Soaking Solution Concentration

* Determined by extracting Cd2+ from membrane and analysis by square-wave polarography. * Total concentration (Cd2+ + Ca2+), 1 M.

\[
\text{Cd}^{2+} \text{mol} \quad \text{solution}^a \text{ mole fraction, g} \quad \text{wt of Nafion,} \quad \% \text{ total sites occupied} \\
1.39 \times 10^{-7} \quad 1 \quad 0.0588 \quad 0.52 \\
3.80 \times 10^{-7} \quad 0.0550 \quad 1.52 \\
1.90 \times 10^{-4} \quad 0.0557 \quad 7.54 \\
3.45 \times 10^{-5} \quad 0.0568 \quad 13.35 \\
1.72 \times 10^{-5} \quad 100 \quad 0.0566 \quad 67.0 \\
\]

where \( n \) is the number of Cd2+ in the cluster and \( f \) is the fraction of sites occupied by Cd2+ ions as determined polarographically. The fraction of Cd2+ ions existing in clusters of size \( n \), \( F_n \), can be calculated from the probabilities as shown in eq 2.

\[
F_n = \frac{p_n}{\sum_i p_i} \\
\]
The distribution diagram suggests that 100% percent samples have 3 is a plot of F, vs n for Q-particles formed in Nafion-exchangedCdS/Cd2+ 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 Ca2+. 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 equilibrium 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
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. Isolated CdS particles are thought to grow within the sodalite cages of zeolite Y because they have an absorbance onset at 350 nm, which shifts to 400-425 nm as they become electronically coupled to form "superclusters" and ultimately to 520 nm for strongly coupled CdS clusters confined to the analogous face-sharing cages in boralite. By comparison, the 100% Cd-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 CdS+, 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% Cd-exchanged samples. These data will be discussed in detail in a separate paper.

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. 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, caused by 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 or H2Se 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. They attribute this to the following equilibrium:

\[
\text{CdS} + \text{H}_2\text{S} \rightarrow \text{Cd(HS)}_2
\]

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 dilute 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 bulk onsets, the ripening process is faster in all samples. Hence, the kinetics of the ripening process appears to depend on the availability of open channels through which migration can occur, the ability 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, 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 that heating a dry film at 120°C for 16 days does lead to complete permeation of H2S.

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 250,000X. 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 45,000X 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 22,500X and then spliced together. The composite plate 5 (bar = 100 nm) was then processed...
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% sample exposed to aqueous sulfide, a 100% gas-phase sample, and a 90% gas-phase sample (in de-
scending 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. One can see
that the emission maxima blue shift corresponds with the blue
shifting of the absorption onset.


**CdS_{x}S_{1-x} Mixed Q-State Particles in Nafion.** We have observed that the exposure of Q-state particles of CdS in Nafion
to H_{2}Se results in exchange of sulfide in the lattice by selenide.
The standard free energy (\Delta G^o) of reaction for the exchange is
\(-95\) kcal/mol with bulk CdS and CdSe. As expected, CdSe in
Nafion is essentially unreactive toward H_{2}S. Upon exposure of
CdS to H_{2}Se, 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_{2}Se (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_{2}Se yielded a
spectrum with an onset at 650 nm. Neither further exposure to
H_{2}Se nor exposure of the CdSe material to CdS 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_{E}E) in formamide have been studied via determinations of phase diagrams and NMR self-diffusion measurements. For C_{12}E_{3} and C_{16}E_{3}, 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_{E}E/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. It
has been established that amphiphiles such as lecithin and, recently, also normal single-chain surfactants form liquid

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