to increase the Na–O bond distance.

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Registry No. $Na_{0.17}WO_{3.085}\cdot 0.19H_2O$, 138540-49-5; $Na_{0.17}WO_{3.085}\cdot 0.23D_2O$, 138540-48-4.

Photoelectron Transfer Mediated by Size-Quantized CdS Particles in Polymer-Blend Membranes

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Size-quantized cadmium sulfide (CdS) particles have been in situ generated in 300–400-Å-thick polymer-blend membranes (PBMs) prepared from mixtures of poly(styrenephosphonate diethyl ester) (PSP) and cellulose acetate (CA). Absorption spectroscopy of CdS particles in PBMs prepared from PSP:CA = 1:4, 1:1, 2:1, and 4:1 indicated bandgaps of 2.81, 2.63, 2.58, and 2.48 eV and, hence, size quantization. Mean diameters of CdS particles in PBMs prepared from PSP:CA = 1:4, 1:1, and 4:1 have been assessed from transmission microscopy to be 44, 58, and 82 Å. Excitation of CdS particles in PBMs at 400 nm resulted in observable emission spectra with maxima at 490 and 570 nm (PSP:CA = 1:4), 514 nm (PSP:CA = 1:1), 548 nm (PSP:CA = 2:1), and 580 nm (PSP:CA = 4:1). Emission of CdS particles embedded in PBMs was found to be quenched by methylviologen (MV^{2+}). Also, bandgap illumination resulted in photoelectron transfer to produce $MV^{\bullet +}$. More efficient photoelectron transfer was observed for smaller CdS particles than for larger ones.

Introduction

Preparation, characterization, and utilization of size-quantized semiconductor particles continue to be the subject of vigorous research activity.[3-9] Confinement of the electron and hole in a particle that is smaller than the exciton diameter in the bulk semiconductor (i.e., size quantization) often results in beneficial mechanical, chemical, electrical, and electrooptical properties.[10] Preparation and stabilization of nanosized semiconductor particles require, however, carefully controlled experimental conditions and/or the presence of a supporting matrix. In our laboratories, we have prepared and characterized size-quantized semiconductor particles in surfactant vesicles,[11] at the interfaces of monolayers[12-17] and bilayer lipid membranes,[18-20] and between the polar headgroups of Langmuir–Blodgett films.[21] Preparations at monolayers interfaces have been shown to be particularly useful since this method allowed a convenient morphology and dimensionality control and the transfer of the incipient semiconductor particles to slid support at different stages of their growth. In principle, a similar degree of control can be accomplished in ultrathin functionalized polymeric films.

Encouraged by the reported use of polymer films as matrices for semiconductor particles,[22-27] we have recently launched investigations into the formation of semiconductors in polymer-blend membranes (PBMs) prepared

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from cellulose acetate (CA) and poly(styrenephosphonate diethyl ester) (PSP).[28] PSP is an amorphous polymer which interacts with heavy-metal salts through its phosphoryl groups. Polymers with phosphonate ester functionality, $PO(OR)_2$, can chelate and dissolve large quantities (20–40 wt %) of metal nitrates within their matrices.[29-33] PSP and CA are a miscible polymer pair which can easily be cast into thin films.[32,33] Cast ultrathin PSP:CA PBMs provide matrices for the in situ formation of semiconductor particles. Exposure to hydrogen sulfate (H_2S) of $Cd(NO_3)_2$-equilibrated PSP:CA PBMs resulted in the formation of CdS particles.[28] The CdS molecules chelated less strongly than $Cd(NO_3)_2$; their nucleation apparently occurs within the PBM matrix. Growth properties of CdS particles in PBMs are the subject of the present report. Changes in the composition ratios of polymer blends are correlated with PBM properties and with CdS particle formation therein. Characterization of PBM-incorporated CdS particles by absorption, emission, and infrared spectroscopy, as well as by transmission electron microscopy and photoelectron transfer to aqueous methylviologen is reported in this paper.

Experimental Section

The following materials were used as received: $Cd(NO_3)_2$ (Fisher); methylviologen dichloride ($MVCl_2 \cdot 4H_2O$, Aldrich); benzyl alcohol (99%, Aldrich); CA (M_w = 29 000, Eastman Chemical Products, Inc.); 1,4-dioxane (spectroscopic grade, Aldrich); gaseous H_2S (99.5%, Matheson). Water was purified using a Millipore Milli-Q filter system provided with a 0.22-μm millistack filter at the outlet. The preparation, purification, and characterization of poly(styrenephosphonate diethyl ester) (PSP) have been described.[34]

Polymer-blend membranes (PBMs) were prepared by spreading a solution of 0.1 wt % PSP:CA (in the desired proportion of PSP:CA) in anhydrous dioxane over the entire surface (2.0 cm^2) of a dust-free glass slide. The dioxane was allowed to evaporate slowly (48 h) in an enclosed container and was subsequently separated from the glass slide by water. The PBM was then picked up from the water surface by a filter paper and dried.

Two different methods were used for the incorporation of cadmium ions into the ultrathin membranes. In the first method (method A), cadmium ions were incorporated into PBM by floating the membrane on an aqueous (1.0×10^{-3} M $Cd(NO_3)_2$) solution for 12 h (on each side). Particles of CdS were formed in the PBM by exposing the membranes to H_2S.[13] Specifically, the cadmium-ion-containing PBM was floated on the surface of the $Cd(NO_3)_2$ solution and placed in an airtight vessel into which 200 μL of H_2S was slowly infused. In the second method (method B), appropriate concentrations of $Cd(NO_3)_2$ were introduced into the membrane casting solution [$Cd(NO_3)_2$:PSP:CA = (0.045 or 0.0905):1:1 by weight; in dioxane, 1 wt %]. After the solution was stirred overnight, it was cast in a Teflon plate by a Doctor knife. The dioxane was allowed to evaporate slowly (~48 h) in a closed container. The thin film formed on the Teflon plate was carefully picked up with tweezers. The film was the placed in a quartz cell and exposed to stoichiometric amounts of H_2S. Method B led to thicker and more brittle PBMs than those prepared by method A. Prior to measurements, CdS-containing PBMs were well rinsed by distilled water and stored on solid substrates. The extent of CdS formation was monitored spectrophotometrically.

Table I. Properties of PSP, CA, and PSP:CA Membranes

membrane	$\bar{M}_v$[a]	T_g, °C	n	PO stretch, cm^{-1}
PSP	24 000	11[c]	1.483	1253
CA	29 000	185[c]	1.475	
PSP:CA = 1:4		127[c]	1.450	1234
PSP:CA = 1:1		67[c]	1.438	1238
PSP:CA = 2:1		60[c]	1.473	1244
PSP:CA = 4:1		36[c]	1.480	1247
PSP:CA:$Cd(NO_3)_2$ = 1:1:0.045[b]		135		1231
PSP:CA:$Cd(NO_3)_2$ = 1:1:0.0905[b]		181		1228

[a] Determined by viscosity measurements. [b] Method B. [c] Taken from ref 33.

Absorption spectra were taken on a Hewlett-Packard 8450 A diode-array spectrophotometer. Emission spectra were recorded on a Tracor Northern 6500 diode-array spectrophotometer. The membrane samples were securely positioned at a 45° angle to the incident excitation source and detector. A 450-nm cutoff filter was placed between the detector and cell.

Infrared spectra were recorded on a Nicolet 740 DX FTIR spectrometer with resolution of 2.0 cm^{-1} and 64 cumulative scans. Thin films were placed on a KCl plate window.

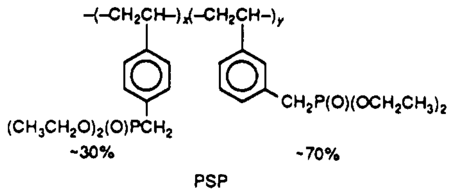
Intrinsic viscosities of PSP and CA were determined by an Ubbelohde viscosimeter. Glass transition temperatures of the membranes were determined by using a Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS data acquisition system. All of the measurements were conducted under a constant flow of nitrogen at a rate of 20 °C/min. The glass transition temperature value, T_g, was taken at the midpoint of the heat capacity change at glass transition.

Steady-state irradiation was carried out using a 200-W Xe lamp as the excitation source. The 1.0×1.0 cm optical cell was placed at a distance of 30 cm from the light source. A 400-nm cutoff filter was placed between the lamp and the cell. The quartz-supported, CdS-containing PBMs were placed in a 1.0×1.0 cm cell containing 3.0 mL of 4.0×10^{-4} M $MVCl_2$ and 0.01% (v/v) benzyl alcohol. The cell was sealed with a rubber cap, and argon gas was bubbled for 30 min before irradiation (in the dark). Full absorption spectra were taken every 5 min of irradiation, interrupting the irradiation by not more than 20 s. $MV^{\bullet+}$ concentrations were determined spectrophotometrically at 396 and 604 nm (extinction coefficients at 396 and 604 nm were 42 100 and 13 700 M^{-1} cm^{-1}, respectively).

Transmission electron micrographs were taken by a JEOL JEM-2000 EX 80-keV instrument. CdS-containing PBMs, floated on a water surface, were deposited onto 400-mesh copper grids by horizontal lifting and were dried in air at room temperature prior to electron microscopic measurements.

Results

Characterization of Ultrathin PSP:CA PBMs. The PSP used in this study was the product of radical polymerization of vinylphosphonate diethyl ester:[34]



PSP

Viscosity-averaged molecular mass, $\bar{M}_v$, and glass transition temperatures, T_g, of PSP, CA, and their polymers are collected in Table I. PSP was found to be completely miscible with CA. Formation of a homogeneous transparent thin membrane, with a single T_g, was observed over the entire composition range of PSP:CA. Increasing the fraction of CA in the PSP:CA mixture resulted in a progressive increase of T_g.

Refractive indexes were determined by angle-dependent reflection measurements. The monochromatic reflectivity

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for the p-polarized incident light (514.5 nm, 50-mW Ar^+ laser) ws evaluated as a function of the incident angle, θ_0, for the uncoated (R_0) and the polymer-coated (R_p) glass slide. The angle at which the θ_0 vs R_0 curve crossed the θ_0 vs R_p curve was equated with the Brewster angle of the polymer film, θ_B. The refractive index, n, was assessed by

$$n = \tan \theta_B \qquad (1)$$

Refractive indexes of ultrathin PSP, CA, and PSP:CA PBMs are also provided in Table I. The refractive indexes of pure PSP (1.483) and CA (1.475) films were lower than those determined for their PBMs (1.500–1.480). This observation is entirely in accord with the strong intermolecular interactions and tight packing of the PSP and CA in the PBMs.[28,33]

The thickness (t) of a given PSP, CA, or PSP:CA membrane was assessed by measuring the distance between its neighboring infrared interference fringes, $\Delta\lambda$ (in nm), and substituting this value, along with that determined for n, into the following equation:

$$t = d\lambda/2n \qquad (2)$$

Values of t were found to range between 300 and 400 Å.

Cadmium Ion Incorporation into PBMs. The extent of cadmium ion incorporation into PBMs was controlled by casting dioxane solutions of $Cd(NO_3)_2$:PSP:CA = x:1:1 with increasing amounts of x (method B; see Experimental Section). For example, a maximum of 8.3 Cd^{2+} ions (per 100 P═O groups) could be introduced into the PBM, consisting of PSP:CA = 1:1. At this or higher amounts of Cd^{2+}, the membrane became opaque. Saturation of PBM by $Cd(NO_3)_2$ ($x = 0.095$) was also confirmed by monitoring the glass transition temperature (T_g) of the membrane by differential scanning calorimetry. Increasing the amount of salt in the membrane caused an elevation in T_g, but above 8.3% (relative to P═O) T_g remained constant at 181 °C (Table I).

Infrared spectroscopy (FTIR) shed some light on the nature of the interactions in PBMs. In the miscible blend, we detected rather large shifts in the phosphoryl stretching band [from 1253 cm^{-1} for PSP to 1238 cm^{-1} in PSP:CA (1:1)].[33] This was ascribed to the strong bond formed between P→O and the hydroxyl groups of CA. The P→O stretch for different compositions of the blend is collected in Table I. The different values represent bound and free phosphoryl groups and, therefore, the larger shift can be found in blend compositions which contain the lower fraction of PSP where most P→O are bound. Cadmium nitrate interactions with the phosphoryl groups of PSP yields a much larger shift. For example, equilibrating a PSP:CA (1:1) PBM to saturation with cadmium nitrate resulted in a stretching peak at 1228 cm^{-1} for P→O; while the uncomplexed PSP:CA (1:1) PBM displayed a stretching peak at 1238 cm^{-1} (Table I). The shift with cadmium nitrate is quite similar to that reported for complexations of the phosphoryl group with other heavy-metal salts (e.g., uranyl nitrate[31]) and corresponds to an interaction energy of ca. 8–9 kcal/mol.

CdS Formation and Characterization. Exposure of $Cd(NO_3)_2$-containing PSP and PSP:CA PBMs to H_2S resulted in the formation of CdS particles. CdS particle formation manifested in the appearance of light yellow domains at the membrane surface. In the absence of membranes, introduction of H_2S over an aqueous $Cd(NO_3)_2$ solution resulted in initial coloration and eventual precipitation of CdS.

Absorption spectrophotometry provided the most convenient and quantitative means of observation of the CdS particles, in situ generated in PBMs. In the absence of CdS, PSP:CA PBMs do not have measurable absorbances at wavelengths longer than 260 nm. Formation of CdS is signalled by the development of an absorbance in the visible region of the spectrum. At any given preparation and wavelength of observation, the absorbance due CdS was found to increase almost linearly with increasing amounts of infused H_2S up to a plateau value, beyond which the absorbance remained unchanged. Importantly, once formed, CdS particles did not leach out of the PBMs. The absorption spectrum of a given preparation remained unaltered after soaking it in water in the dark over a 10-day period.

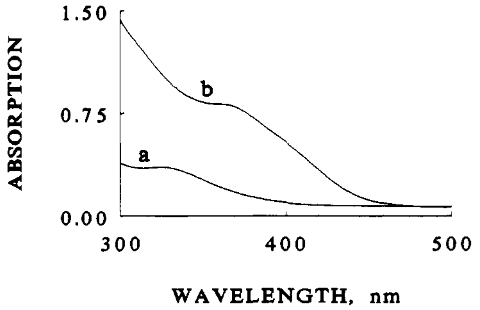

Figure 1. Absorption spectra of CdS particles in situ generated in ca. 300-Å-thick PSP:CA = 1:1 PBMs (method B). CdS particles were generated by the slow infusion of H_2S onto PBMs which contained 4.3 (a) and 8.7 (b) Cd^{2+} ions per P═O groups. Spectra were taken on quartz substrates.

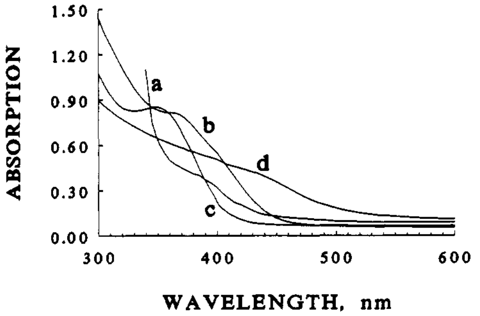

Figure 2. Absorption spectra of CdS particles in situ generated in ca. 300-Å-thick PSP:CA = 1:4 (a), 1:1 (b), 2:1 (c), and 4:1 (d) PBMs (method A). CdS particles were generated by the slow infusion of H_2S onto PBMs [soaked in $Cd(NO_3)_2$]. Spectra were taken on quartz substrates.

Table II. Properties of CdS Particles in PSP:CA PBMs

membrane	abs edge, nm	band-gap,[a] eV	mean diam,[a] Å	mean diam,[b] Å	emission max, nm
PSP:CA = 1:4[c]	440	2.81	40	44	490, 570
PSP:CA = 1:1[c]	470	2.63	50	58	515
PSP:CA = 2:1[c]	480	2.58	70		548
PSP:CA = 4:1[c]	500	2.48	80	82	580
PSP:CA:CdS = 1:1:0.045[d]	382	3.24			
PSP:CA:CdS = 1:1:0.0905[d]	460	2.68			
bulk CdS	>520	2.4			

[a] From absorption spectra using Henglein's published[6] absorption edge vs particle size curve. [b] From TEM. With estimated errors of ±10%. [c] Method A. With estimated errors of ±10%. [d] Method B.

Absorption edges of CdS particles, prepared by method B in PBMs (PSP:CA = 1:1) which contained 4.7 and 8.3 $Cd(NO_3)_2$ ions per 100 P═O groups, were determined to be 382 and 460 nm (Figure 1). These values allowed the assessment of CdS mean diameters and band gaps to be 22 and 45 Å and 3.24 and 2.68 eV (Table II) by using Henglein's published absorption edge vs particle size curve.[6] These CdS particles were in situ generated in PBMs by method A from PSP:CA mixtures in ratios of 1:4, 1:1, 2:1, and 4:1; had absorption edges of 440, 470, 480,

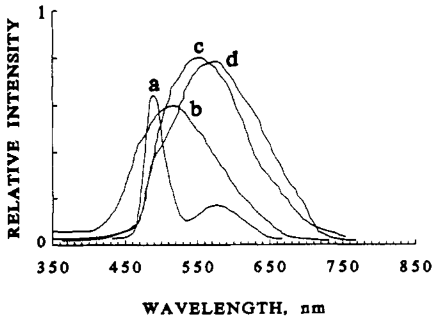

Figure 3. Fluorescence spectra of CdS particles in situ generated in ca. 300-Å-thick PSP:CA = 1:4 (a), 1:1 (b), 2:1 (c), and 4:1 (d) PBMs (method A). λ_{ex} = 400 nm. CdS particles were generated by the slow infusion of H_2S onto PBMs [soaked in $Cd(NO_3)_2$]. Spectra were taken on quartz substrates.

and 500 nm, respectively (Figure 2); and, hence, had 2.81, 2.63, 2.58, and 2.48-eV bandgaps and 40, 50, 70, and 80-Å mean diameters (Table II).

Fluorescence spectra of CdS particles, in situ formed in 1:4, 1:1, 2:1, and 4:1 PSP:CA PBMs (method A) are shown in Figure 3. In the absence of CdS, PBMs showed no fluorescence. Emission spectrum of CdS in the 1:4 = PSP:CA blend membrane showed a sharp peak at 490 nm and a weak broader band with a maximum at 570 nm. In the other PBMs, the emission maximum is seen to shift to lower energies with increasing amounts of PSP membranes.

Cellulose acetate is a semicrystalline polymer; when cast from a dioxane solution, the solid film contains 20–30% crystallites.[33] When blended with the PSP used in this study, crystallite formation was inhibited. Some crystallinity has been identified, however, when the CA fraction in the blend was higher than ~75%. For PSP:CA = 1:4, about 7% crystallinity was found. When the film was annealed above T_g, the crystallinity disappeared and the miscible blend became wholly amorphous;[32,33] however, the blends used in this study were not annealed. The crystallinity of the blend, as it pertains to the present study, relates only to the 1:4 composition, which might, therefore, contain crystalline domains of CA. Though crystallinity is limited, the amorphous composition of this blend should be viewed as slightly higher in PSP content (ca. 1:3.6 instead of 1:4). The existence of the crystallites should be considered as a separate domain which may be surrounded by a salt-absorbing interface.

Transmission electron micrographs of CdS particles prepared by method A in PSP:CA = 1:4 (a), 1:1 (b), and 4:1 (c) PBMs are shown in Figure 4. Size distributions of CdS particles in these media are illustrated in Figure 5. The number averaged diameters, d, of the CdS particles were calculated from

$$d = \sum n_i d_i / \sum n_i \qquad (3)$$

where n_i is the number of particles of diameter d_i. The calculated d values for CdS particles in PSP:CA = 1:4, 1:1, and 4:1 are 44, 58, and 82 Å, respectively, which agree well with the estimated values from their absorption spectra (Table II). Two sets of CdS particles were observable in PSP:CA = 1:4 PBMs (Figure 4a). A smaller sets of particles had mean diameters of 30 Å. The other set appeared to consist of four to five individual CdS particles aggregated into larger (50–70 Å) multiparticles. In contrast, PBMs prepared from PSP:CA = 1:1 and PSP:CA = 4:1 predominantly contained the larger aggregates of CdS multiparticles.

CdS-Particle-Mediated Photoelectron Transfer in PBMs. Emission of CdS particles embedded in PBMs was found to be quenched in degassed aqueous methylviologen (MV^{2+}) solutions (Figure 6). In the concentration range of MV^{2+} investigated, the quenching of CdS fluorescence obeyed the Stern–Volmer relationship:

$$I_0/I - 1 = K_{SV}[MV^{2+}] \qquad (4)$$

where I_0 and I are emission intensities in the absence and presence of MV^{2+} and K_{SV} is the Stern–Volmer quenching constant. A plot of I_0/K against $[MV^{2+}]$ gave a straight line (Figure 6) from which K_{SV} was calculated to be 1.2×10^{-4} M^{-1}. This value indicates an appreciable electron transfer efficiency.[36]

Illumination of CdS particles embedded in PBMs and placed in an aqueous 4.0×10^{-4} M MV^{2+} solution (at pH = 7.2) containing 0.01% (v/v) M benzyl alcohol with visible light ($\lambda > 400$ nm) led to the development of a new species with absorption maxima at 396 and 604 nm (Figure 7). Increasing the irradiation time increased the amount of these absorbances (Figure 7). Significantly more efficient photoconversion was observed on using smaller rather than larger CdS particles.

Discussion

Miscible PSP:CA PBMs have been shown to provide eminently suitable media for the in situ generation of semiconductor particles. PSP binds the metal-salt precursor of the semiconductor while CA furnishes the mechanical integrity required for casting ultrathin PBMs. Infrared spectroscopy data indicate that cadmium nitrate, once absorbed into the blend, can compete successfully with the hydroxyl groups of CA for P→O. This can lead to polymer cluster formation and even to microphase separation. It should be recognized, however, that the PBM is in its glassy state at room temperature and that mobilities of the functional gruops of the polymer are restricted.

The PSP-rich clusters act as hosts for cadmium salts which are likely to complex to the P→O moiety in a manner analogous to that observed for other metal ions by X-ray diffractometry.[37] Indeed, uranyl nitrate was demonstrated to coordinate to PSP in the 1:2 ratio.[29] In the present work, up to eight phosphoryl groups were shown to complex one cadmium nitrate molecule in PSP:CA = 1:1. Presumably limited mobility of the functional groups of the polymer restricts the full involvement of all PSP in the complexation of cadmium ions. The PBM, soaked with cadmium nitrate, appeared to be homogeneous. However, upon exposure to H_2S, a drastic change occurred.

Exposure to H_2S resulted in the formation of small CdS particles which decomplexed from frozen PSP. The liberated, PSP segments (T_g = 11 °C, Table I) complexed with a second generation of $Cd(NO_3)_2$ molecules rather than with CA. This, in turn, led to the formation of clusters of CdS particles which continued to grow (see Figure 4) and which filled the available space in the PSP-rich clusters in the PBM. H_2S is likely to plasticize the PBM to a degree that allows some mobility to occur. A similar situation has been encountered in the behavior of uranyl nitrate in PSP:cellulose blends on treatment with other reagents.[35] CdS particles cannot be leached out by

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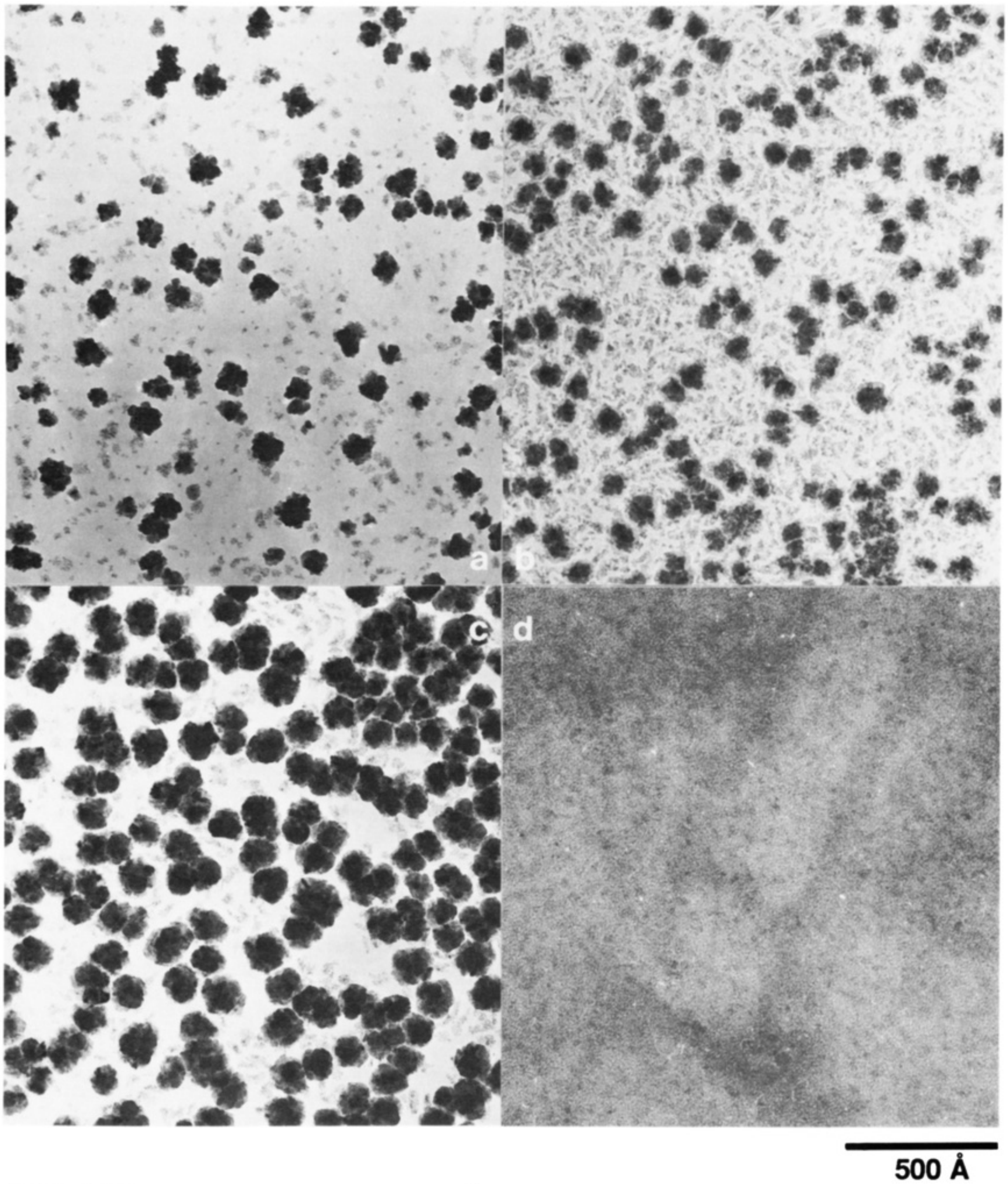

Figure 4. TEMs of CdS particles in situ generated in ca. 300-Å-thick PSP:CA = 1:4 (a), 1:1 (b), and 4:1 (c) PBMs (method A). For the sake of comparison, a TEM of a PSP:CA = 1:1 PBM (in the absence of CdS) is shown in d. CdS particles were generated by the slow infusion of H_2S onto PBMs [(soaked in $Cd(NO_3)_2$]. TEMs were taken on copper grids as substrates.

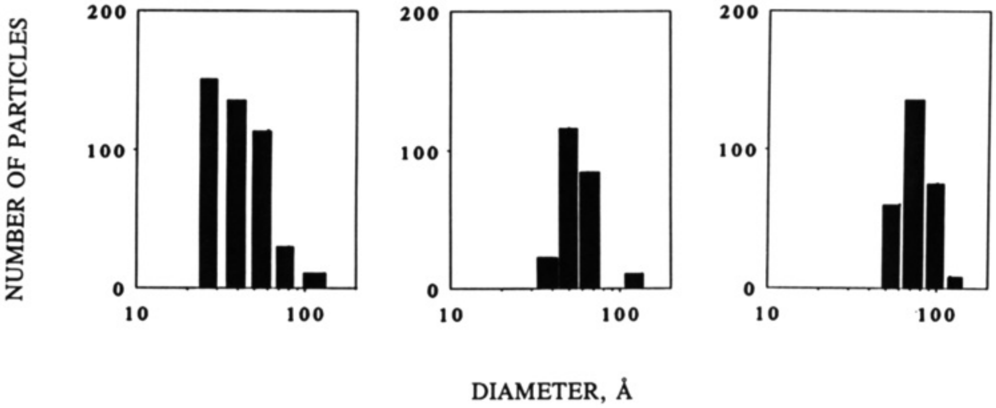

Figure 5. Size distribution of CdS particles in PSP:CA = 1:4 (a), 1:1 (b), and 4:1 (c) PBMs (method A); see Figure 4 legend.

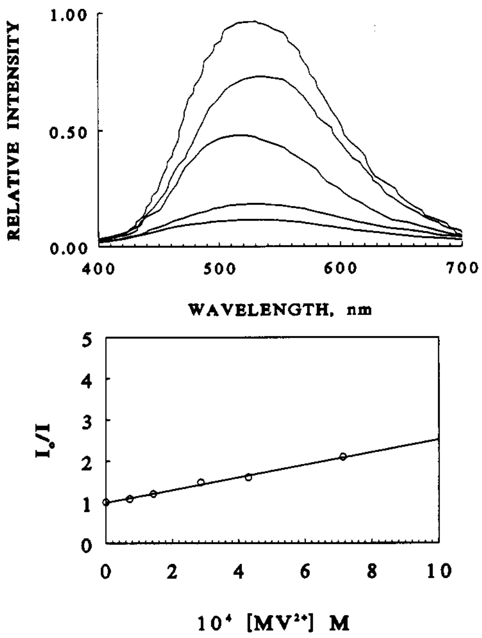

Figure 6. Top: emission spectra of CdS particles in PSP:CA = 1:1 PBMs (method A) in the aqueous (1–7) × 10^{-4} M MV^{2+} at pH = 7.2. λ_{ex} = 400 nm. CdS particles were generated by the slow infusion of H_2S onto PBMs [soaked in $Cd(NO_3)_2$]. The PBM on a quartz substrate was securely positioned at a 45° angle to the incident excitation and detector in a rectangular cell which contained appropriate concentrations of the aqueous MV^{2+}. The MV^{2+} solution was deoxygenated by argon bubbling for 30 min. Bottom: plot of the data according to eq 4.

washing the membrane as can be clearly seen in Figures 4a–c.

In general, $Cd(NO_3)_2$ complexation can be written as

$$\alpha[(RO)_3P{=}O] + \beta[Cd(NO_3)_2] \rightleftharpoons \alpha[(RO)_3P{=}O]{\cdot}\beta[Cd(NO_3)_2]$$

$$Cd^{2+} + 2NO_3^- \rightleftharpoons Cd(NO_3)_2 \qquad (5)$$

and nucleation occurs at selected PSP sites upon injection of H_2S:

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$\alpha[(RO)_3P{=}O]{\cdot}\beta[Cd(NO_3)_2] + \beta[HS^-] \rightleftharpoons \alpha[(RO)_3P{=}O]{\cdot}\beta[(CdS)] \qquad (6)$$

which provides the seed for particle growth:

$$\alpha[(RO)_3P{=}O]{\cdot}\beta[(CdS)] + \mu[Cd(NO_3)_2] \rightleftharpoons \alpha[(RO)_3P{=}O]{\cdot}\mu[Cd(NO_3)_2]{\cdot}\beta[(CdS)] \qquad (7)$$

$$\alpha[(RO)_3P{=}O]{\cdot}\mu[Cd(NO_3)_2]{\cdot}\beta[(CdS)] + \sigma[HS^-] \rightleftharpoons \alpha[(RO)_3P{=}O]{\cdot}\sigma[(CdS)]\beta[(CdS)] \qquad (8)$$

$$\alpha[(RO)_3P{=}O]{\cdot}\delta[Cd(NO_3)_2]\sigma[(CdS)]\beta[(CdS)] + \delta[HS^-] \rightleftharpoons \alpha[(RO)_3P{=}O]{\cdot}\delta[(CdS)]\sigma[(CdS)]\delta[(CdS)] \qquad (9)$$

where α, β, μ, σ, and δ represent different aggregation numbers.

Limited availability of space and finite amounts of $Cd(NO_3)_2$ are responsible for controlling the growth of semiconductor particles. At the PSP:CA ratios investigated (Table I), the diameters of CdS particles varied between 40 and 100 Å. As expected, the smallest particles formed in PBMs which contained the least amount of PSP (see Figure 4). The 40–80-Å diameter CdS particles are distributed within the entire matrix of the 300–400-Å-thick PBM. Most of them are partially embedded, but some of them are partially exposed at the surface and some of them are "buried" in the interior of the PBM. Given the thinness of the polymer, some CdS particles may even connect and, thus, span the membrane.

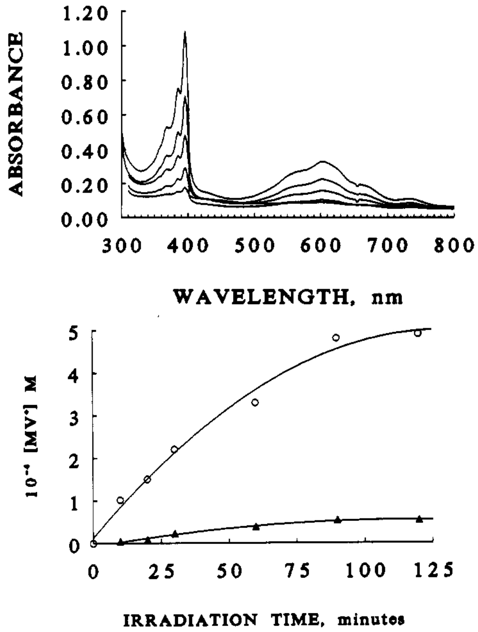

Figure 7. Top: absorption spectra of a CdS-particle-containing PSP:CA = 1:1 PBM (method A) on a quartz support, positioned in a spectrophotometric cell which was filled by a deoxygenated (argon bubbling for 30 min), aqueous 4.0 × 10^{-4} M MV^{2+} (pH = 7.2) and 0.01% (v/v) benzyl alcohol solution. Spectra were taken subsequent to 10, 20, 30, 60, and 90 min of increasing irradiation by a 200-W xenon lamp. Bottom: the change of absorbance at 603 nm (i.e., the development of $MV^{\bullet+}$) with irradiation times for CdS particles embedded in PSP:CA = 1:1 (a) and 4:1 (b) PBMs.

Size quantization is the consequence of confining the semiconductor particles within the PSP-rich clusters whose diameters are shorter than the exciton length in bulk CdS. The exciton length of CdS is in the order of 80–100 Å.[4-6] Size quantization has manifested in appreciable shifts of the absorption edge to higher energies (Figures 1 and 2) and in the appearance of characteristic fluorescence spectra (Figure 3). CdS particle emission with maxima in the 520–580-nm region is attributable to energy transition involving defect states.[38] Interestingly, the fluorescence spectrum of the smallest CdS particles, generated in the PSP:CA = 1:4 PBM, showed two maxima, one with a relatively sharp emission band, close to the absorption onset, at 488 nm and one with a broad band with an emission maximum centered at 580 nm (Figure 3). The sharp emission band at the higher energy may be due to excitonic fluorescence.[39,40] It was previously indicated that PSP:CA PBMs (1:4) may have two regions for CdS particle incorporation: the region of the homogeneous amorphous blend and the interface between the CA crystallites and the blend. Shifts in the absorption edge and changes in emission spectra of CdS may originate from a delicate balance between the different types of particles present in the class of polymer blends under investigation.

Bandgap irradiation of CdS particles results in the formation of conduction band electrons, e^-_{CB}, and valence band holes, h^+_{VB}:

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$$CdS \xrightarrow{h\nu} e^-_{CB} + h^+_{VB} \qquad (10)$$

Although most of e^-_{CB} recombines with h^+_{VB}, some are trapped. Recombination of a small fraction of the charge species, generated either by bandgap irradiation (eq 10) or from those subsequently detrapped, results in fluorescence. MV^{2+} removes some electrons competitively:

$$MV^{2+} + e^-_{CB} \rightarrow MV^{\bullet +} \qquad (11)$$

and thus decreases the fluorescence yield (Figure 6). The absorption spectra seen in Figure 7 corresponds to $MV^{\bullet +}$, the product of reaction 11. The function of benzyl alcohol is to remove h^+_{VB} and, thus, increase the yield of $MV^{\bullet +}$. Significantly, size quantization has not only manifested in bandgap shifts and in the appearance of exciton fluorescence but has also affected photoelectron transfer efficiencies.

In summary, ultrathin membranes prepared from carefully selected polymer blends provide, therefore, unique matrices for the in situ generation of uniform size-quantized semiconductor particles and for the examination of vectorial photoelectron transfer therein.

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NMR Chemical Shift Tensors and Peak Assignments for the 6H Polytype of Silicon Carbide

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^{29}Si and ^{13}C chemical shift tensors have been determined for single crystals of 6H SiC and are assigned to each of the crystallographically distinct sites (three silicon and three carbon) on the basis of symmetry arguments. The tensor components are dramatically dependent upon the number and geometrical arrangement of second neighbors but are not appreciably affected by the very slight variations in bond distances among the different sites.

Our magic angle spinning (MAS) NMR studies of silicon carbide polytypes[1,2] showed that the different polytypes, and crystallographically distinct silicons (and carbons) within the same polytype, give distinctive isotropic chemical shifts. The range of chemical shifts in the 6H polytype is roughly 10 ppm for ^{29}Si and 8 ppm for ^{13}C. These chemical shift differences among lattice sites seem remarkably large, considering that the chemical environments appear to be practically identical, the range of bond distances in the Si–C tetrahedra is less than 0.01 Å, and the bond angles are all 109.4–109.5°.[3] The simplicity of the silicon carbide structure combined with the range of NMR chemical shifts make silicon carbide an excellent compound for exploring the general problem of chemical shifts in network solids.

Silicon carbide polytypes have layer-type structures in which the layers are identical but the stacking sequences of the layers differ.[4-7] Thus, although the first-neighbor surroundings of each Si (or C) are quite similar, the second-neighbor surroundings can be different, depending on the stacking sequences of the layers. We[1,2] and others[8,9] proposed that the number of NMR peaks is related to the ways that layers can be stacked about a central atom. There are only four independent stacking sequences within a 5-Å radius, denoted as types A–D. Figure 1 shows diagrams of the four types, with an SiC_4 tetrahedron embedded in the second-neighbor polyhedron. Of the crystallographically independent silicons in 6H SiC, one is type A, one is type B, and one is type C, corresponding to the three equal-intensity peaks in the ^{29}Si MAS NMR spectrum. The carbon atoms in any polytype are isostructural to the silicon atoms, so the ^{13}C spectrum of the 6H polytype also has three equal-intensity peaks corresponding to type A, type B, and type C carbons. O'Keeffe's topological approach to site classification gives similar results.[9]

However, unambiguous assignment of NMR peaks to specific sites in the crystal lattice has proved elusive.[2,8,10] Additional interactions beyond the 5-Å radius must have appreciable effects on chemical shift, since the 15R polytype, which has five crystallographically distinct carbon sites but with only types A–C represented, has four rather than three ^{13}C peaks.[2] Also the recently reported[10] ^{29}Si and ^{13}C chemical shifts of the 4H polytype (with only types B and C represented) are distinctly different from chemical

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