in full agreement with the ^{13}C NMR data recorded on such a sample where high-resolution spectra are obtained with a multiplicity of 2 at C1, C4, and C6.

The explanation of the diffraction diagram of the initial *Valonia* is less straightforward. From the analysis of the ^{13}C NMR spectrum of *Valonia* cellulose, Atalla and VanderHart[6,7,14] have demonstrated that *Valonia* was composed of two distinct crystalline phases: the dominant Iα and the minor Iβ. The above experiment has demonstrated that Iβ corresponds to a monoclinic phase. Therefore, the pure Iα diffraction diagram can be obtained by substracting the Iβ fraction from this diagram. Such substraction is, however, not very accurate as one does not know the exact proportion of the Iα and Iβ phases. Nevertheless, the Iα diffraction spectrum can be interpreted in at least two ways: (a) It may correspond to a two-chain triclinic cell with a = 0.954 nm, b = 0.825 nm, c = 1.036 nm, α = 90°, β = 57.0°, and γ = 96.6°. Such a cell would account for almost all the extra reflections arrowed in Figure 1D. (b) It may also correspond to an eight-chain triclinic cell similar to that of Honjo and Watanabe[2] with a = 1.584 nm, b = 1.644 nm, c = 1.036 nm, $\alpha = \beta$ = 90°, and γ = 97.3°. Our favor goes toward the first hypothesis, but unless a pure Iα form is prepared or pure Iα diagram is obtained, it is difficult to give a clear answer on the unit cell or crystal structure of Iα cellulose.

One may speculate as to why a highly crystalline native cellulose sample such as *Valonia* is found in the form of such a composite crystalline structure. It is likely that such occurrence results from the cellulose biogenesis mechanism. During such a biosynthetic process, cellulose is synthesized, spun, and crystallized almost simultaneously at a temperature far below the glass transition or the melting point of cellulose. This undoubtedly leads to a structure where strains and stresses are built in. We suggest that the triclinic Iα phase, which is more or less abundant depending on the specimen origin, corresponds to this strained crystalline form. The strains would be released when the tempertaure is raised, in particular, above the cellulose softening temperature, to give the relaxed monoclinic Iβ form.

The crystalline composite features observed for native cellulose are not unique in the world of either "nascent" or deformed crystalline polymers. This had been well documented in the case of crystalline polyethylene where a triclinic phase was also found in nascent samples, especially those prepared at a very low temperature.[15] Such a triclinic phase is also found in stretched polyethylene as for instance in the gel spun samples.[16] In both cases, the triclinic phase is metastable as opposed to the stable orthorhombic crystalline polyethylene. Upon annealing, the triclinic metastable form relaxes and disappears readily when the temperature of the specimen is brought in the vicinity of the melting point.[17] This is very similar to what happens in the present cellulose experiment.

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Size-Quantized, Semiconductor Particle Mediated Photoelectron Transfer in Ultrathin, Phosphonate-Functionalized, Polymer-Blend Membranes

Size and dimensionality reductions of semiconductor particles result in altered mechanical, chemical, electrical, electrooptical, and magnetic properties, which could be profitably exploited in a variety of applications, including solar energy conversion.[3-5] Carefully controlled experimental conditions are required, however, for the preparation and stabilization of ultrasmall colloidal semiconductor particles. Inspired by the ability of commercially available Nafion membranes to incorporate colloidal semiconductors and catalysts,[6-9] we have developed functionalized, ultrathin, polymer-blend membranes (PBMs) as matrices for size-quantized semiconductor particles. Our work shows that miscible polymer blends provide an excel-

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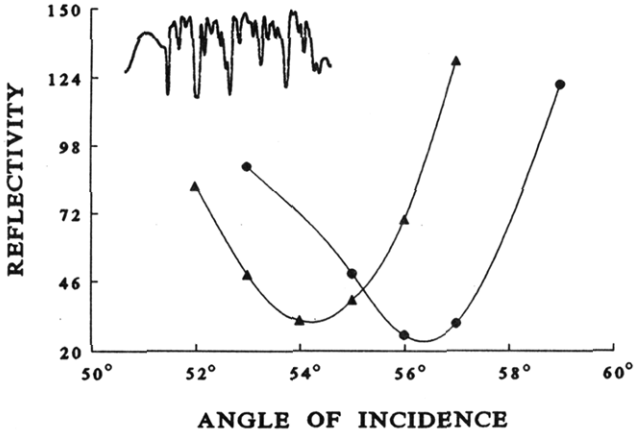

Figure 1. Plots of reflectivity for the empty (R_0; ▲) and PSP–CA blend membrane (R_{PBMa}; ●) against the angle of incidence. Intersection of curves R_0 with R_{PBM} gave the Brewster angle. The inset shows typical interference infrared bands.

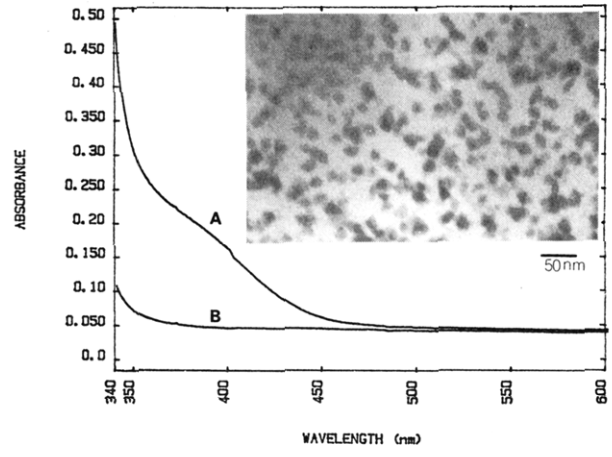

Figure 2. Absorption spectra of a CdS particle containing (A) and CdS-free (B) PBM (ca. 400 Å thick). A transmission electron micrograph is shown in the inset.

lent membrane medium for the present application since they can be easily tailored to contain micro- and submicrophases (clusters), which complex the metal ion precursor of the desired semiconductor particles.

The subject of the present paper is the in situ generation of monodispersed, 75–100-Å-diameter CdS particles in ultrathin PBMs (ca. 400 Å thick) and their utilization to mediate photoelectron transfer to methylviologen. Ultrathin PBMs were prepared from the miscible polymer pair poly(styrenephosphonate diethyl ester) (PSP; MW = 24 000; T_g = 11 °C) and cellulose acetate (CA; MW = 30 000; T_g = 185 °C). These polymers have been shown to interact well with each other, to form a homogeneous phase with a single T_g, and to be amenable for thin-film formation.[10-12] Phase segregation and formation of 75–100-Å, PSP-rich clusters in the CA-rich continuous phase of the ultrathin PBM can be induced by subjecting the membrane to a variety of conditions and/or casting it from the appropriate solvents (*p*-dioxane, for example).[10] In the PSP–CA blend system, the phosphoryl group (P → O) can chelate inorganic salts of transition elements and can also form strong hydrogen bonds with the residual hydroxyl groups of CA. The function of semicrystalline CA is to provide mechanical integrity for the ultrathin PBM.

The PBM was prepared by spreading a solution of 0.1 wt % PSP–CA (1:1 by weight) in anhydrous dioxane over the entire surface (2 cm²) of a dust-free glass slide. The dioxane was allowed to evaporate slowly for 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. In general, this procedure was found to be adequate for the formation of continuous CA-rich PBMs, which contained 75–100-Å-diameter, PSP-rich clusters.

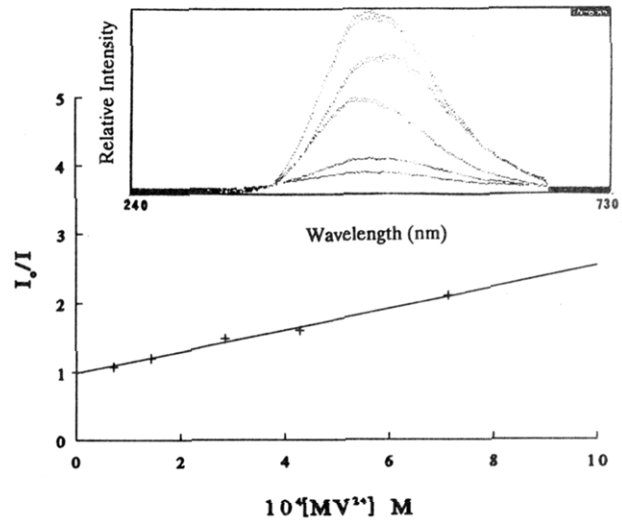

Figure 3. Emission spectra of a CdS-containing ca. 400-Å-thick PBM in the presence of increasing amounts of MV^{2+} in the solution soaking the membrane. λ_{ex} = 400 nm (inset). The resulting plot of relative fluorescence intensity vs [MV^{2+}] M indicates a linear Stern–Volmer behavior.

Cadmium ions were incorporated into the PBM by floating the membrane on an aqueous (1.0×10^{-3} M) $Cd(NO_3)_2$ solution for 12 h (on each side). The infrared spectra (KBr plate) of the phosphoryl stretching band revealed a significant downfield shift from 1251 to 1231 cm^{-1}, which is in accord with the expected change accompanying inorganic salt complexation to the phosphoryl group. Particles of CdS were formed in the PBM by exposing the membrane to H_2S. The cadmium ion containing PBM was floated on the surface of the $Cd(NO_3)_2$ solution and placed in an air-tight vessel into which 200 μL of H_2S was slowly infused. Penetration of H_2S into the membrane was ascertained by the visual observation of light yellow domains on both sides of the membrane surface. In contrast, opaque yellow coloration was observed on the water surface surrounding the PBM (which subsequently led to similar coloring of the subphase and to eventual precipitation of large CdS particles). Subsequent to the infusion of all of the H_2S, the CdS-containing PBM was removed from the surface of the $Cd(NO_3)_2$ solution, repeatedly rinsed in dust-free water, and used for further characterization and electron-transfer measurements. No leaching of CdS particles could be detected over periods of 10 days on soaking the CdS-containing PBMs in water.

The thicknesses of PBMs were determined by combined refractive index and infrared interference fringe ($\Delta\lambda$) measurements. Optical reflectivity measurements followed previously described experimental procedures.[13] The monochromatic reflectivity for the p-polarized incident light (514.5 nm, 50-mW Ar^+ laser) was evaluated as a function of the incident angle, θ_0, for the uncoated (R_0) and the PBM-covered (R_{PBM}) glass slide (Figure 1). The angle at which the θ_0 vs R_0 curve crossed the θ_0 vs R_{PBM} curve (55.2°) was equated with the Brewster angle due to the PBM, θ_B. The corresponding refractive index, n, was assessed to be 1.439 from

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

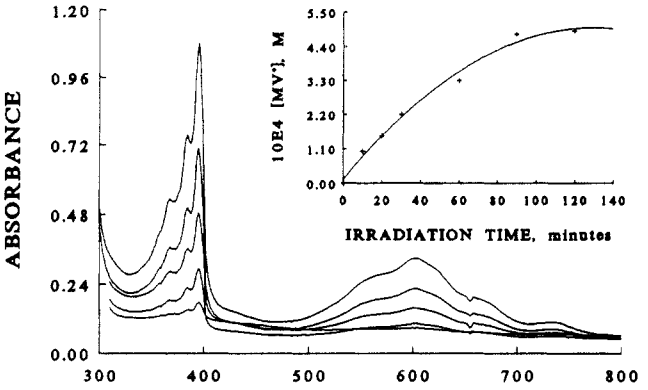

Figure 4. Absorption spectra of a CdS-containing ca. 400-Å-thick PBM in an aqueous, degassed solution, which contained 4.0×10^{-4} M MV^{2+} (pH = 7.2) and 0.01% benzyl alcohol (v/v) as a function of increasing irradiation time by a 200-W Hg–Xe lamp using a 400-nm cutoff filter. Increasing irradiation (time) resulted in the increasing absorbances with maxima at 397 and 604 nm. The amount of $MV^{\bullet+}$ produced (taking $\epsilon_{MV^{\bullet+}} = 13\,700$ M^{-1} cm^{-1} at 603 nm) as a function of irradiation time is shown in the inset.

Infrared interference fringe measurements yielded $\Delta\lambda$ values for the PBM (see the inset in Figure 1) from which the membrane thickness, d, was calculated by means of

$$d = d\lambda/2n \quad (2)$$

Substitution of the appropriate values into eq 2 led to 398 Å for the thickness of the PBM.

Absorption spectra[14] clearly revealed the presence of CdS particles in the PBM (Figure 2). The observed band edge, 475 nm, corresponds to 70-Å diameter particles.[5] Transmission electron micrograms (taken on a JEOL JEM-2000 EK, 120-keV instrument) confirmed the presence of 75–100-Å-diameter CdS particles (see inset in Figure 2). Importantly, the particles are well separated and uniform.

Excitation of the CdS-containing PBM at 400 nm resulted in a broad structureless band with an emission maximum at 560 nm (Figure 3).[15] Addition of increasing concentrations of methylviologen (MV^{2+}), a known electron acceptor, to the aqueous solution bathing the CdS-containing PBM (on a quartz support) progressively decreased the fluorescence and resulted in a linear Stern–Volmer plot (Figure 3). Illumination with visible light ($\lambda_{ex} > 400$ nm) of the CdS-containing PBM in an aqueous, degassed solution that contained 4.0×10^{-4} M MV^{2+} (pH = 7.2) and 0.01% benzyl alcohol (v/v) led to the development of a blue color (Figure 4). These results are explicable in terms of forming conduction-band electrons and valence-band holes in the band-gap excitation of the CdS:

$$CdS \xrightarrow{h\nu} e_{CB}^- + h_{VB}^+ \quad (3)$$

Recombination of a small fraction of the charged species results in fluorescence:

$$e_{CB}^- + h_{VB}^+ \rightarrow h\nu \quad (4)$$

MV^{2+}, an electron acceptor, competes with reaction 4 by

$$e_{CB}^- + MV^{2+} \rightarrow MV^{\bullet+} \quad (5)$$

and thus decreases the fluorescence yield (i.e., quenching occurs). Benzyl alcohol is a sacrificial electron donor whose function is to remove h_{VB}^+ and, thus, increase the yield of $MV^{\bullet+}$ and, hence, its absorbance (λ_{max} = 395 and 604 mm) as a function of irradiation (Figure 4).

Electron transfer has been shown to be more efficient from smaller than from larger CdS particles. The importance of PBMs is that they provide inert matrices for monodispersed, size-controlled semiconductor particles and, hence, allow the intimate investigation of the effects of size quantization on electron transfer.

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