SURFACE-MODIFIED BILAYER ULTRATHIN MEMBRANES

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Inspired by the ability of commercially available Nafion membranes to incorporate colloidal semiconductors and catalysts, we have developed functionalized, ultrathin, polymer-blend membranes (PBMs) as matrices for size quantized semiconductor particles. The polymer miscible blend offers an excellent membrane medium for the present application since micro- and submicrophases (clusters) can be induced in their matrix. The polymer pair chosen, PSP and CA, has been shown to interact well with each other. Mechanical integrity of the ultrathin membrane is provided by the semicrystalline CA fraction. Using the appropriate solvent (dioxane) leads to the creation of less than 100 Å diameter PSP clusters in the continuous CA-rich phase of the ultrathin PBM. Being a good chelating agent, the phosphoryl group (P → O) of PSP effectively complexes metal ions in the richly phosphorylated clusters of the PBM. Ultrathin PBMs were cast by carefully spreading a drop of anhydrous dioxane solution of PSP and CA (0.05 wt% PSP, 0.05 wt% CA) over the entire surface of a glass slide (1.0 x 2.0 cm x 5.0 mm thick; cleaned by soaking in chromic acid and copiously rinsing by dust-free water). Subsequent to the evaporation of the dioxane, the PBM was separated from the glass slide by immersion into water and was picked up from the water surface by a filter paper and dried. The PBM was then placed onto the surface of an aqueous 1.0×10^{-3} M $Cd(NO_3)_2$ solution and was allowed to soak for 12 hours on each of its two sides. Cadmium-ion incorporation into the PBM was established by FTIR spectroscopy. CdS particles were formed by the slow infusion of H_2S into the cadmium-ion-containing membrane.

The thicknesses of glass-slide-supported PSP membranes and PBMs were determined by a combination of refractive index and infrared interference fringe measurements to be 300 Å and 398 Å.

Absorption spectra clearly revealed the presence of CdS particles in the PBM (Figure 1). The observed band edge, 475 nm, corresponds to 70 Å diameter particles. Transmission electron micrograms (taken on a JEOL JEM-2000 EK, 120 keV instrument) confirmed the presence of 75-100 Å diameter CdS particles (see insert in Figure 1).

Excitation of the CdS-containing PBM at 400 nm resulted in a broad structureless band with an emission maximum at 560 nm which was quenched by methylviologen (MV^{2+}). Illumination with visible light (λ_{ex} > 400 nm) of the CdS-containing PBM in an aqueous, degassed solution which contained 4.0×10^{-4} M MV^{2+} (pH = 7.2) and 0.01% benzylalcohol (v/v) led to the development of a blue color (Figure 2). These results are explicable in terms of forming conduction-band electrons and valence-band holes in the band-gap excitation of the CdS:

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$$CdS \xrightarrow{h\nu} e^-_{CB} + h^+_{VB} \quad (1)$$

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

$$e^-_{CB} + h^+_{VB} \longrightarrow h\nu \quad (2)$$

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

$$e^-_{CB} + MV^{2+} \longrightarrow MV^{+\bullet} \quad (3)$$

and thus decreases the fluorescence yield (*i.e.*, quenching occurs). Benzylalcohol 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 mm and 604 mm) as a function of irradiation (Figure 2).

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.

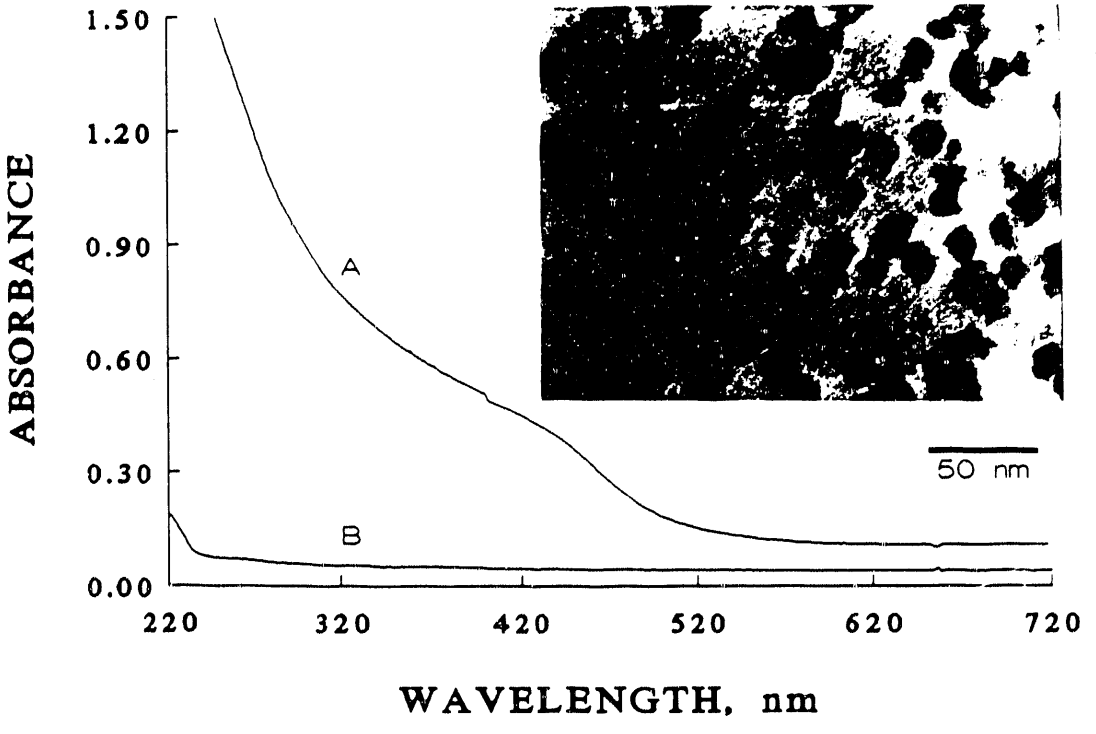

Figure 1. Absorption spectra of a CdS-particle-containing (A) and empty 400 Å thick PBM. A transmission electron microgram is shown in the insert.

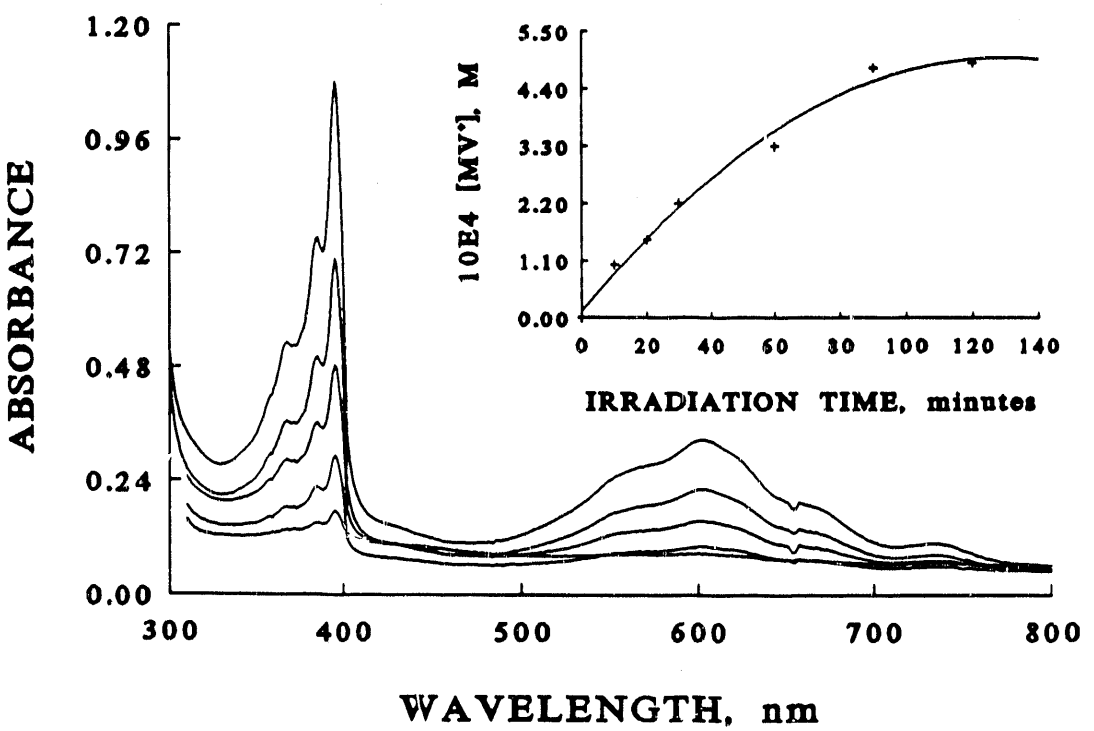

Figure 2. Absorption spectra of a CdS-containing, *ca.* 400 Å thick PBM in an aqueous, degassed solution which contained 4.0 x 10^{-4} M MV^{2+} (pH = 7.2) and 0.01% benzylalcohol (v/v) as a function of increasing irradiation time by a 200 W Hg-Xe lamp using a 400 nm cut-off filter. Increasing irradiation resulted in the increasing absorbances with maxima at 397 nm and 604 nm. The amount of $MV^{+\bullet}$ produced as a function of irradiation time is shown in the insert.

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