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Spectral Cosensitization in Phthalocyanine-Porphyrin Photoelectrochemical Cells

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ABSTRACT

An organic multilayer photoelectrochemical cell was fabricated by sequential vacuum deposition of hydroxyaluminum phthalocyanine (PcAlOH) and hydroxyaluminum tetraphenylporphyrin (TPPAlOH). Absorption and action spectra of the NESA/PcAlOH/TPPAlOH/I_3^-/I^-/Pt cell cover the entire visible spectrum up to 900 nm. In the reverse deposition sequence, only NESA/TPPAlOH/PcAlOH/I_3^-/I^-/Pt photoelectrochemical cell with very thin organic layers showed a sensitization effect. The cosensitization effects are probably due to the porosity of the organic thin films, allowing the contact of the electrolyte with each semiconductor.

Since a few years, attention on organic semiconductors such as phthalocyanine has been put on the spectral response of photovoltaic and photoelectrochemical cells. Broadening of the action spectra has been noted for tri- and tetravalent metal phthalocyanine compared with divalent metal and H_2-phthalocyanine thin film photoelectrodes (1). An acid treatment leads to a spectral broadening and significant improvement of the photoelectrochemical characteristics of thin films of hydroxyaluminum phthalocyanine (PcAlOH) (2-4). However, the spectral response in these cells is still limited to the range 550-900 nm.

For a better match with the solar visible spectrum, one may consider association of two organic semiconductors, as in photovoltaic (5-7) or photoelectrochemical (8) p-n junctions. In some of these devices, n-type perylene derivative (7) or porphyrin (6, 8) were used in conjunction with p-type phthalocyanine compounds. But, as most of organic films exhibit p-type conductance (9), studies on organic p-n junctions are limited by the number of n-type organic semiconductors available.

Spectral cosensitization has been recently studied for a zinc tetraphenylporphyrin-zinc phthalocyanine photoelectrode (10); both organic semiconductors are of p-type, and the photocurrent broadening has been assigned to the formation of a p-p isotype junction between the two pigments. Such device showed photoresponse in the range 400-800 nm with a peak quantum yield of 1%. This present work describes an enlargement of these studies to other

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porphyrins and phthalocyanine, leading to an efficient solar-to-electrical conversion for an organic two-layer photoelectrochemical cell. Porosity of the films will be shown to contribute for a great part to the spectral cosensitization effects in very thin film configurations.

Experimental

Materials.—The hydroxyaluminum phthalocyanine (PcAlOH) was synthesized according to the method already described (3). The films were prepared by sublimation of the α-form thus obtained in a homemade bell jar evaporator under typical conditions of $P = 5 \times 10^{-6}$ torr and $T = 480°C$. The substrates used were NESA glass (P.P.G. Industries, sheet resistivity $\rho_s = 250\ \Omega/sq$). The conversion of the α-form PcAlOH thin films to the η-form has been reported elsewhere (3). It consists in dipping the films in a 0.1*M* potassium hydrogen phthalate aqueous solution for 15h. The acid treatment has no effect on porphyrin thin films.

The zinc tetraphenylporphyrin (ZnTPP) was prepared according to the method of Fuhrhop and Smith (11) from meso-tetraphenylporphyrin (TPP) purchased from Aldrich. The hydroxyaluminum tetraphenylporphyrin (TPPAlOH) was synthesized following the method described for the preparation of hydroxyaluminum octaethylporphyrin (12): three successive additions (1g) of $AlCl_3$ are made every 10 min to a suspension of TPP (300 mg) in carbon sulfide (200 ml). The mixture is then stirred in dried atmosphere at ambient temperature. TPPAlOH is obtained after dry column (Al_2O_3) chromatography and crystallization in methanol. The sublimation of porphyrins occurred at $T = 300°C$ under a pressure of 5×10^{-6} torr.

Two kinds of electrodes were fabricated: sublimation of PcAlOH onto NESA substrates followed by sublimation of a porphyrin film on the top of the phthalocyanine film, or the reverse sequence. The NESA electrodes ($2.5 \times 5.0\ cm^2$) were cleaned before sublimation by placing them in a detergent solution followed by subsequent rinsing with tap water, distilled water, and methanol (13). An insulating polymer was used to define a 1-2 cm^2 active area. The contact with the NESA was made with a copper wire and silver conducting paint (G.C. Electronics).

All chemicals in this work were classified as high purity and used without further purification. They were dissolved in distilled water from a Corning Megapure water distillation system. The electrolytic solution contains 0.1*M* Na_2SO_4 and the optimized concentration of the redox couple ($[I_3^-] = 10^{-3}\ [I^-] = 10^{-4}M$ at *p*H 1.5 (adjusted with hydrochloric acid)) as reported before (14) was used.

Measurements.—Absorption spectra were recorded on a LKB 4050 spectrophotometer with an Apple IIe computer and Epson Dot Matrix printer.

A conventional three-electrode single-compartment cell was used for the electrochemical measurements. A saturated calomel electrode (SCE) served as the reference and a Pt foil (8 cm^2) as the counterelectrode. Electrolytic solutions were not deaerated and measurements were performed under ambient atmosphere. The working electrode was placed at about 2 mm from the cell window to minimize the light absorption by the solution. The organic film was always directly illuminated. The white light illumination ($W = 10\ mW \cdot cm^{-2}$) is given by the 300W ELH tungsten-halogen lamp of a Kodak Ektagraphic slide projector, Model AF2. Monochromatic illumination was performed using a monochromator H-20 (Instruments S.A.). All action spectra were converted for the same photon flux incident on the film at each wavelength ($N_{max} = 2.7 \times 10^{14}$ photons $\cdot\ cm^{-2} \cdot s^{-1}$) taking into account the measured light exponent, γ, at these energies (3). The light intensity was measured by a United Detector Technology 21A power meter equipped with a radiometric filter.

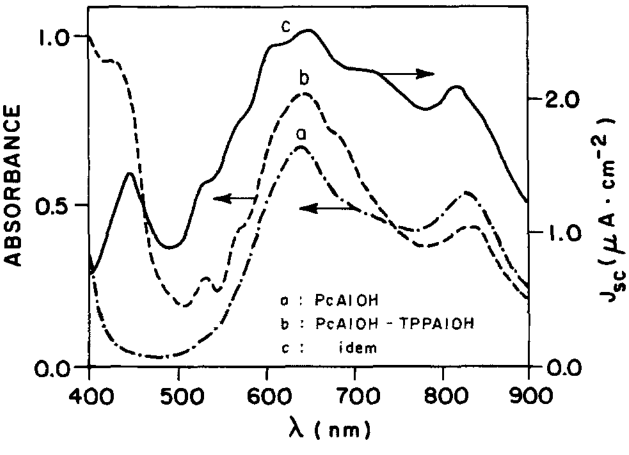

Fig. 1. Absorption spectra of PcAlOH (a) and PcAlOH-TPPAlOH (b) thin films on NESA. Action spectrum (c) of a NESA/PcAlOH-TPPAlOH/I_3^-/I^-/Pt cell.

All electrical measurements were performed in a Faraday cage. When used in the photogalvanic mode, the measurements were taken with a Keithley 616 electrometer; when used in the electrochemical and photoelectrochemical modes, the measurements were performed with a Model 362 potentiostat from Princeton Applied Research. The scanning rate was $V = 2\ mV \cdot s^{-1}$ for *J-V* measurements and $V = 50\ mV \cdot s^{-1}$ for cyclic voltammetry.

Results and Discussion

η-PcAlOH-TPPAlOH electrode.—Figure 1a shows the absorption spectrum of a PcAlOH thin film (400Å), which presents the two characteristic peaks of the η-form at 640 and 830 nm (2-4). Sublimation of a thin film (250Å) of TPPAlOH on the PcAlOH layer results in the appearance of new absorption peaks at 430 and 530 nm (Fig. 1b). The final spectrum then covered the entire visible region between 400 and 900 nm.

The action spectrum of the corresponding NESA/η-PcAlOH/TPPAlOH/I_3^-/I^-/Pt photoelectrochemical cell (Fig. 1c) presents current density maxima at 450, 650, and 815 nm. The shape of the action spectrum indicates that cosensitization effects occur between the phthalocyanine and the porphyrin, as noted for an ITO/ZnPc/ZnTPP photoelectrode by Harima and Yamashita (10). This behavior had been attributed to the formation of a p-p junction, efficient for cathodic currents generation, between the two organic semiconductors. Moreover, in our case, a photoresponse exists over the 400-900 nm region of the visible and near infrared region, although photocurrents given by the TPPAlOH itself are lower than the PcAlOH contribution.

The quantum efficiency, ϕ, defined as the number of electrons actually collected divided by the number of photons incident on the solid-liquid interface, is given by the equation (14)

$$\phi(\%) = 100\ J_{sc}/qN \qquad [1]$$

where J_{sc} is the short-circuit current density, *q* the electronic charge, and *N* the photon flux ($N = 2.7 \times 10^{14}$ photons $\cdot\ cm^{-2} \cdot s^{-1}$).

From the action spectrum, we can obtain $\phi = 5.73\%$ at $\lambda = 650$ nm, $\phi = 4.83\%$ at $\lambda = 815$ nm, and $\phi = 3.36\%$ at $\lambda = 450$ nm. These values are very high compared with those reported for an ITO/ZnPc/ZnTPP photoelectrode in O_2 solution, which had a peak quantum yield of 1% (10). This improvement can be attributed in our cell to the high photoactivity of η-PcAlOH with the I_3^-/I^- redox couple (2-4).

Figure 2 represents the current-voltage characteristics of the same cell in the dark (curve a) and under white light irradiation (curve b). The dark *J-V* curve shows a reasonable rectification with I_3^-/I^-, as seen by the value of the rectification ratio, which is 45 when measured at 0.2V. Both anodic and cathodic photocurrents can be delivered by the cell, depending on the applied potential. The anodic photocurrent appearing at $V \leqslant 0.17\ V/E_{red}$ is certainly a contribution of the porphyrin film, as no anodic currents are seen in NESA/η-PcAlOH/I_3^-/I^-/Pt photoelectrochemical cells (3-4).

From the *J-V* curve under illumination, one can calculate (14) the short-circuit current density $J_{sc} = 58\ \mu A \cdot cm^{-2}$, the open-circuit voltage $V_{oc} = 106$ mV, the fill factor $ff = 0.49$, for a conversion efficiency $\eta = 0.03\%$.

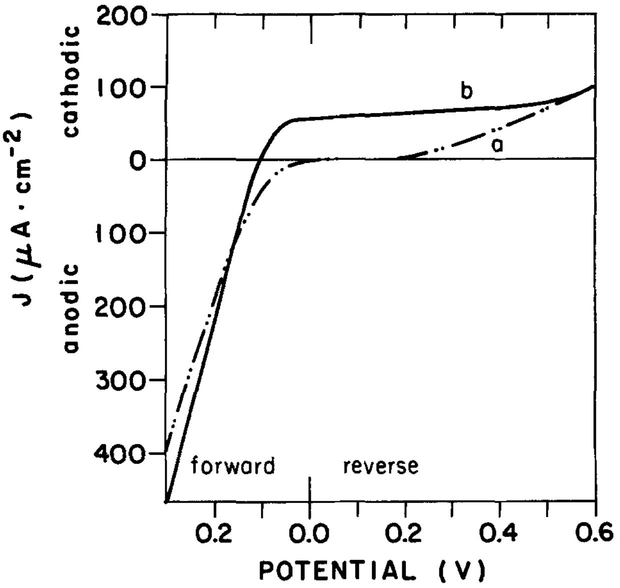

Fig. 2. *J-V* characteristic of a NESA/PcAlOH-TPPAlOH/I_3^-/I^-/Pt cell in the dark (a) and under illumination (b).

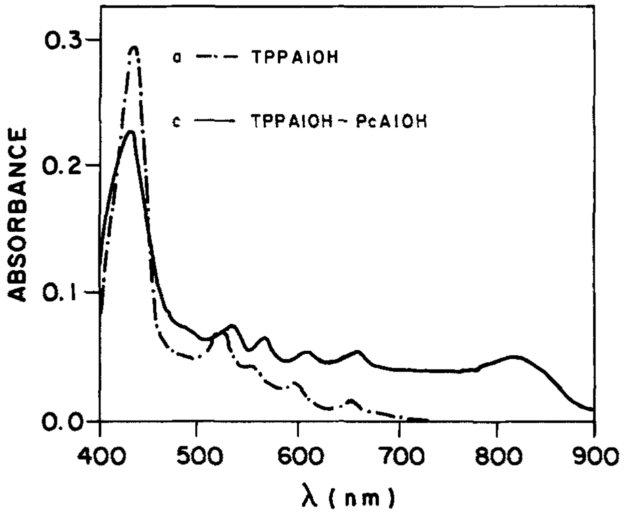

Fig. 4. Absorption spectra of TPPAlOH film (a) and TPPAlOH-PcAlOH film (c) on NESA.

TPPAlOH-η-PcAlOH electrodes.—Two kinds of electrodes were investigated in this configuration: electrodes with relatively thicker organic films (*ca.* 500-600Å) and electrodes with very thin films (50-100Å). The photoelectrochemical behavior of these two types of electrode was quite different: no sensitization was seen with thick films, while the action spectrum of the thin film cell shows a sensitization effect.

Thus, absorption (A) and action (B) spectra (*i*) of films of various porphyrins (thickness 600Å): TPP, ZnTPP and TPPAlOH (curves a) and (*ii*) films of porphyrin-phthalocyanine (curve b) are depicted in Fig. 3. Cathodic currents present several peaks between 400 and 700 nm, and a maximum around 450 nm for the three porphyrins (Fig. 3B). After deposition of 500Å layer of α-PcAlOH and its transformation into the η-form, current given by the cells falls (curves b, Fig. 3B). Contrary to the NESA/η-PcAlOH/TPPAlOH electrode, no spectral cosensitization effect is found at electrodes with the phthalocyanine as top layer. This has been already noted for ZnTPP-ZnPc films with the ZnPc layer as thin as 70Å, ascribable to unfavorable position of the energetics of the phthalocyanine and the porphyrin (10). In our case, however, the behavior of electrodes coated with very thin organic films is quite different.

Figure 4 depicts the absorption spectrum of a thin film (*ca.* 100Å) of TPPAlOH (curve a) and the same film coated with a thin layer (*ca.* 50Å) of η-PcAlOH (curve c). A small decrease of the absorption peak at 450 nm of the porphyrin layer was observed after PcAlOH coating, probably due to change in light scattering effect. This phenomenon is common for the preparation of all porphyrin-PcAlOH electrodes. Typical absorption peaks of the TPPAlOH and the η-PcAlOH are present in the final spectrum (curve c).

Action spectra of the NESA/TPPAlOH/I_3^-/I^-/Pt (curve a) and NESA/TPPAlOH/η-PcAlOH/I_3^-/I^-/Pt (curve c) cells are presented in Fig. 5. The action spectrum of the final electrode looks similar to that of the electrode where the organic layers were inversed (Fig. 1c); characteristic peaks of the TPPAlOH (λ = 432 nm) and the η-PcAlOH (λ = 660 and 820 nm) are also seen in the final spectrum.

J-V curves of NESA in the dark (a), NESA/TPPAlOH in the dark (b) and under illumination (c), and NESA/TPPAlOH/η-PcAlOH in the dark (d) and under irradiation (e) are presented in Fig. 6. Anodic photocurrents can be present with the porphyrin electrode for an applied voltage higher than 0.05 V/E_{red}. The illuminated *J-V* curve for the TPPAlOH-η-PcAlOH sequence (Fig. 6e) looks like that of the η-PcAlOH-TPPAlOH sequence (Fig. 2b), but no anodic current was observed in the forward region of the applied potential, despite the fact that the porphyrin contribution is important, as seen in the action spectrum (Fig. 5c). The NESA/TPPAlOH (100Å)/η-PcAlOH (50Å)/I_3^-/I^-/Pt cell under illumination produces J_{sc} = 37.5

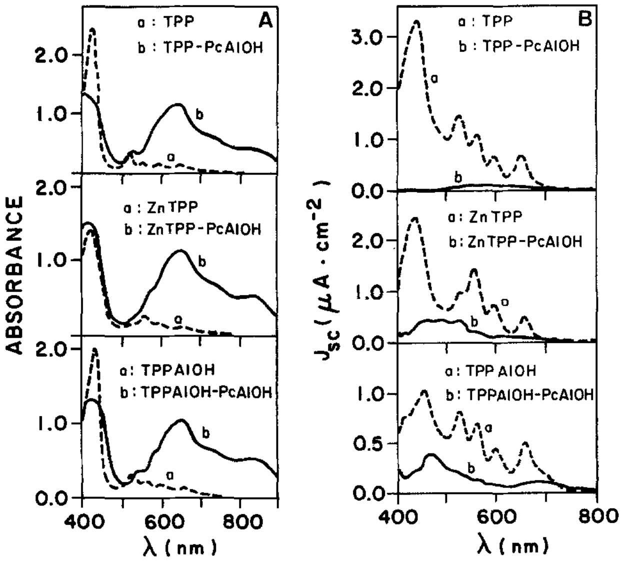

Fig. 3. A. Absorption spectra of porphyrin films (a) and porphyrin-phthalocyanine films (b) on NESA. B. Action spectra of porphyrin films (a) and porphyrin-phthalocyanine films (b) with I_3^-/I^- redox couple.

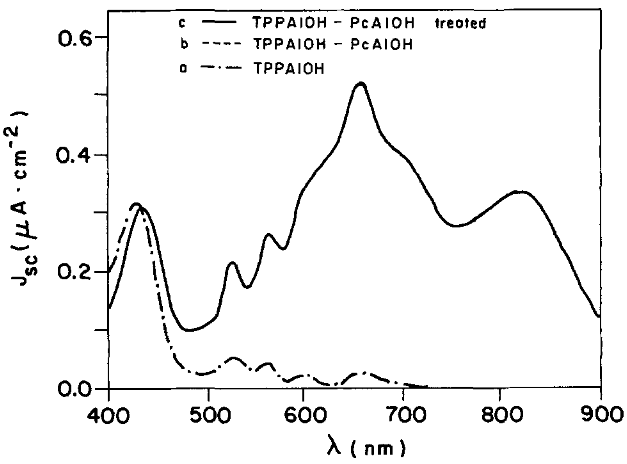

Fig. 5. Action spectra of TPPAlOH film (a) and TPPAlOH-PcAlOH film (c) with I_3^-/I^- redox couple.

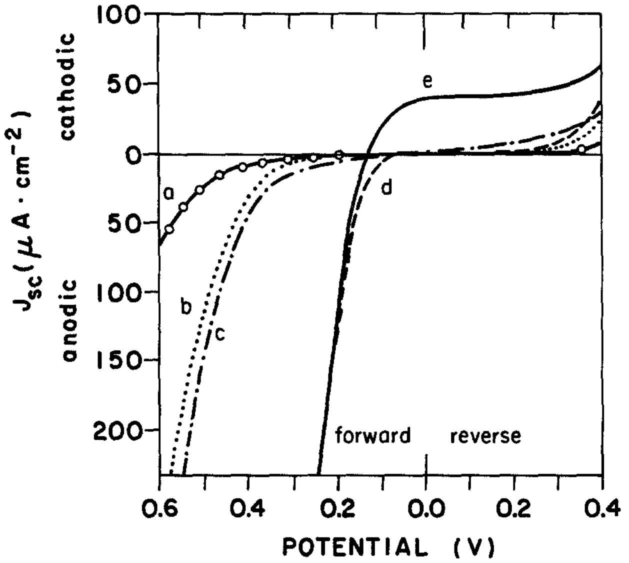

Fig. 6. Redox system: I_3^-/I^-. J-V characteristics of NESA in the dark (a), NESA/TPPAlOH in the dark (b) and under illumination (c), and NESA/TPPAlOH/η-PcAlOH in the dark (d) and under illumination (e).

μA cm^{-2} and V_{oc} = 131 mV, with a fill factor of 0.47 for a conversion efficiency η = 0.023%.

Morphology and porosity of the films.—Harima and Yamashita found no cosensitization effects in their ITO/porphyrin/phthalocyanine cell, even for phthalocyanine layers as thin as 70Å (10). This is also the case with our relatively thick multilayer films,, but cosensitization occurs for the same configuration when the organic layers are very thin. The cited authors gave no discussion on the morphology or the porosity of their films. Porosity, however, seems to play a significant role in our work, as pointed out by the means of scanning electron microscopy and cyclic voltammetry.

Surface morphology of thick and thin films are radically different, as seen on scanning electron micrographs. The TPPAlOH and PcAlOH thick films appeared very compact, in opposition to thin films seen in Fig. 7A for a 100Å TPPAlOH film and Fig. 7B for the same film coated with a 50Å η-PcAlOH layer. In this case, the large TPPAlOH platelets and the PcAlOH "noodles" are likely very porous and this is confirmed by the cyclic voltammetry results.

The technique of cyclic voltammetry has been used for characterizing phthalocyanine films as to their degree of porosity (15-16). In these cases, the organic layers were deposited on Au or Pt substrates and the $Fe(CN)_6^{3-/4-}$ redox couple was used as a probe, reacting reversibly when reaching the substrates. Previous studies on PcAlOH show that this organic semiconductor is rather porous when deposited by sublimation in our system, due to the formation of "noodles" crystallites (16).

Cyclic voltammogram of bare Pt electrode is shown in Fig. 8a. When a 200Å TPPAlOH is sublimed onto the Pt electrode, no change either in the shape or in the value of the peak current is visible (Fig. 8b), indicating that the film is very porous. If a thin layer (200Å) of PcAlOH is sublimated on the TPPAlOH film, the cyclic voltammogram becomes that of Fig. 8c; the TPPAlOH-PcAlOH thin film electrode is then rather porous to the electrolyte. It has to be noted that PcAlOH films are even more permeable to the I_3^-/I^- redox couple (16). Figures 8d and 8e show cyclic voltammograms of a Pt electrode coated by a 500Å TPPAlOH layer (Fig. 8d), and this electrode with a 500Å PcAlOH film on the top (Fig. 8e); in this case, the organic film seems to be only slightly porous.

Conclusion

Results presented here for NESA/η-PcAlOH/TPPAlOH/I_3^-/I^-/Pt and NESA/various TPP/η-PcAlOH/I_3^-/I^-/Pt thick film photoelectrochemical cells show that a spectral cosensitization may be expected between a porphyrin and a phthalocyanine in the sequence ohmic contact/phthalocyanine/porphyrin/electrolyte. This conclusion is in full agreement with the results of Harima and Yamashita, who proposed a mechanism for photocurrent generation at the p-p electrodes (10). Their model is based upon the fact that the Fermi level of the ZnTPP solid before contact lies above that for the ZnPc. It would be of interest to discuss this point, but there are only few reports dealing with Fermi levels or work functions in porphyrins and phthalocyanines. Moreover, a large discrepancy exists between the Fermi levels when determined by physical measurements or photoelectrochemical measurements, especially for porphyrins (ZnTPP) (10, 17). In our case, the Fermi levels, as determined by measurements of the flatband potential, lie at 5.07 eV for TPPAlOH and 5.21 eV for η-PcAlOH; these values are too close to permit important discussion on energy bands at the interface porphyrin-phthalocyanine.

Porosity of the films seems to be of crucial importance for the cosensitization. Varying the thickness of the organic layers in the NESA/TPP/Pc photoelectrode configuration allows the induction of a spectral cosensitization for very thin organic films. The SEM picture (Fig. 7A) of the very thin film of TPP shows lots of voids. During the deposition of the Pc layer some of it may fill the voids. Lots of NESA/TPP/Pc junctions are formed on microscopic scale and the very thin Pc present on top of TPP would permit the electrolyte to reach TPP, and hence the cosensitization

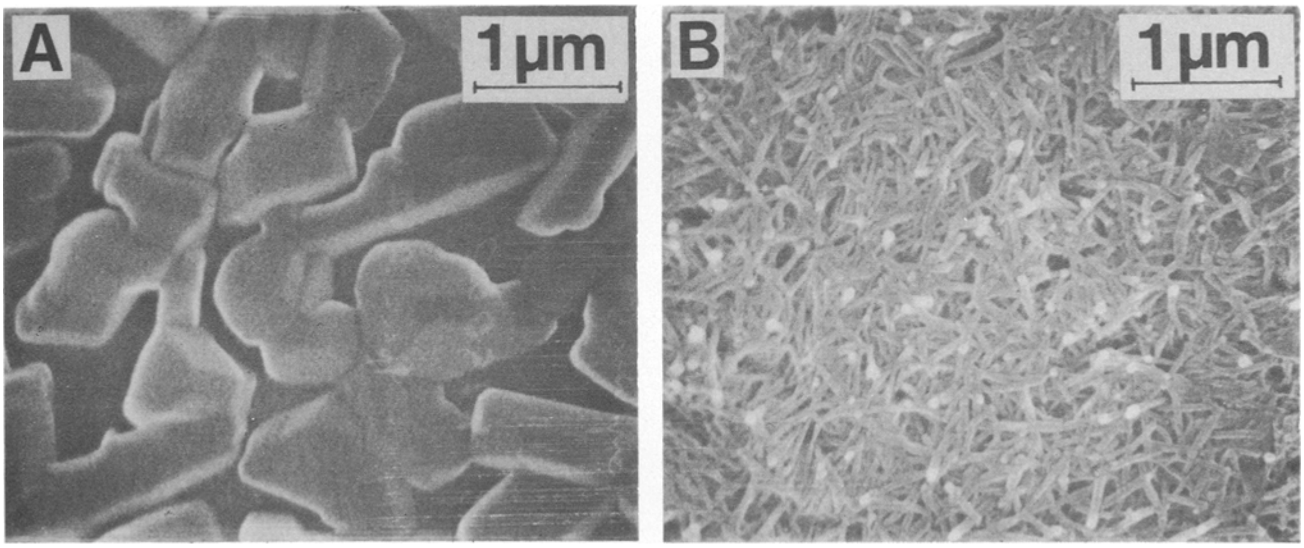

Fig. 7. A. SEM of a TPPAlOH film (100Å). B. SEM of a TPPAlOH-PcAlOH film (100 and 50Å)

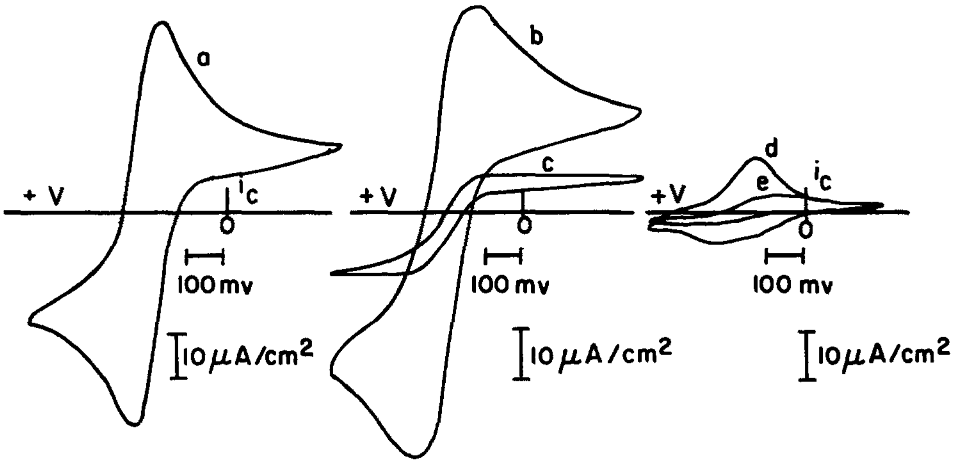

Fig. 8. Cyclic voltammogram with $Fe(CN)_6^{3-/4-}$ redox couple of Pt electrode (a): TPP-AlOH film (200Å) on Pt electrode (b); PcAlOH film (200Å) on a TPP-AlOH/Pt electrode (c); TPP-AlOH film (500Å) on Pt electrode (d); and PcAlOH film (500Å) on Pt electrode (e).

effect is again possible. The SEM picture (Fig. 7B) of the thin film of Pc on top of the TPP layer also shows a very porous surface due to the needle-like structure of Pc. One may also suppose that the electrolyte can easily reach the two semiconductors and that each of them contributes independently to the cathodic current generation.

Although photocurrents given by TPPAlOH electrodes are lower than those given by ZnTPP or TPP electrodes, the combination TPPAlOH-η-PcAlOH as a photoelectrode with I_3^--I^- redox couple is one of the most efficient organic photoelectrochemical cell with peak quantum efficiency as high as 5.7% and solar conversion efficiency $\eta = 3 \cdot 10^{-2}\%$. The photoresponse then covers a large band between 400 and 900 nm in the visible and near infrared region, giving a good match with the solar emission spectrum.

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