adsorb CO and NH_3 irreversibly) of WC and β-W_2C adsorb NH_3 quite strongly and other molecules might also adsorb on them strongly.

Chemisorption of most O and NH_3 is very strong on fresh carbide samples. This is an interesting result, especially because our data suggest that the surface is equilibrated with bulk stoichiometric carbide. The addition of carbon to tungsten should decrease the binding energy of adsorbed molecules. In fact, CO chemisorbs at room temperature associatively on WC(100)-(5×1)C but dissociatively on tungsten.[27,28] Carbon clearly changes the properties of our carbide samples because the removal of some chemisorbed oxygen with H_2 occurs at room temperature, a process that occurs only at much higher temperatures on W metal sites (cf. Figures 7a and 8). The reactivity of less strongly bound species may account for the unique rate and selectivity of tungsten carbide in many catalytic hydrocarbon reactions.[7,8]

Summary

A new procedure to prepare WC with high specific surface area was developed. The surface of WC does not have appreciable amounts of polymeric carbon and seems equilibrated with bulk stoichiometric carbide. Following chemisorption of H_2 and CO, and NH_3 TPD, the surface number density was the same for H, CO, and N. Thus the active sites on the surface of a fresh sample can be counted by irreversible chemisorption of CO. The amount of oxygen on the surface of a fresh sample is less than 10% of a monolayer of oxygen. Most of the carbide surface still binds oxygen and NH_3 strongly. After oxygen is adsorbed on WC at room temperature, only 10% of the surface oxygen can be removed by H_2 at room temperature. The TPR in H_2–He of tungsten carbides exposed to O_2 showed that 50% of the oxygen could be desorbed only at 1150 K, so that it is difficult to rid a tungsten carbide surface of oxygen once it is exposed to O_2.

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Registry No. W_2C, 12070-13-2; WC, 12070-12-1; O_2, 7782-44-7; NH_3, 7664-41-7; CO, 630-08-0; H, 1333-74-0.

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Electrochemical and Photoelectrochemical Processes on Thin Films of Perylenetetracarboxylic Dianhydride

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Thin films of perylene derivative perylenetetracarboxylic dianhydride (PTCDA) have been examined as electrodes and photoelectrodes on both metal and metal oxide substrates. These thin films gave only anodic photocurrents (reverse bias condition) in contact with various aqueous electrolytes and facile dark currents negative of ca. −0.1 V vs. Ag/AgCl (forward bias condition). The origin of this photoeffect appears to be due to differential rates of charge injection at the PTCDA/solution interface and/or an asymmetric distribution of traps at that same interface. Electron microscopy of the PTCDA films indicated that they were deposited as elongated crystallites, with spaces between individual crystallites that strongly affected their dark and photoelectrochemical behavior, especially on Au substrates. Electrochemical polymerization with α-naphthol was carried out to passivate sites that were electrochemically active in the dark, a treatment that greatly enhanced the overall photoelectrochemical activity of the PTCDA thin films. Cathodic polarization of the PTCDA thin films caused surface bound electrochemically active redox couples to be produced at the film's surface, and this polarization step further enhanced the photoelectrochemical activity. These experiments suggest that the PTCDA photoelectrochemical activity is strongly dependent upon near-surface composition and morphology and that, because of the highly porous nature of these thin films, the photoactive interfaces extend throughout most of the bulk of the PTCDA film.

Introduction

Cyclic conjugated molecules such as perylenes (Pe) and phthalocyanines (Pc), primarily in thin-film form, continue to be of interest as molecular electronic materials. Their electronic properties (dark and photoconductivity) can be adjusted over a wide range through additions of electron acceptors or donors.[1-4] In addition to the influence of other molecular additives, chemical reactions at interfaces with metals and inorganic semiconductors have been implicated as controlling the electronic properties of certain Pc's and Pe's.[5-7] The importance of these reactions are

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demonstrated for the perylene derivative perylenetetracarboxcylic dianhydride (PTCDA), in this paper. The following paper in this journal describes bilayers and multilayers of PTCDA and various phthalocyanines, where interfacial processes control much of the photochemical behavior of those assemblies.[8] The electrochemical and photoelectrochemical experiments described here give insight into the types of photoactivity expected of perylenes such as PTCDA and provides useful comparisons with phthalocyanine thin films that gave similar photoanodic behavior Pc's, that behave more like highly doped p-type semiconductors and yield only photocathodic behavior.[5a,b]

PTCDA and related perylenes are vacuum-compatible molecules of electronic interest, which have been extensively studied in organic–inorganic–contact barrier diodes with Si and InP and GaAs.[9a–j] PTCDA and related compounds can form high potential barriers with the inorganic semiconductor surfaces, allowing the application of a large reverse bias and, therefore, the depletion of carriers deep within the bulk of the inorganic material. This behavior facilitates the nondestructive measurement of several semiconductor properties such as free carrier concentration, deep-level densities, and band energies across a wafer's surface.[9] Apart from being usied for semiconductor wafer diagnostics, PTCDA (on p-Si) has recently produced high-efficiency, high-bandwidth, organic-on-inorganic heterojunction photodetectors.[9a–j] Perylenetetracarboxcylic derivatives have also been used in two-layer photovoltaic cells with phthalocyanines.[10,11] The best power conversion efficiencies (approximately 1% under simulated AM2 illumination) have been obtained with bilayers of benzimidazolylperylenetetracarboxylic acid dianhydride (BPT) and copper phthalocyanine.[10] Their applications have been recently extended to multilayers with other related dianhydrides that produce interesting nonlinear optical properties.[9k,l]

The photoconducting properties of perylene pigments have also been exploited in electrophotography.[12,13] For some perylene derivatives, the carrier generation efficiencies under an applied electric field can be nearly as large as for the x-polymorph of metal-free phthalocyanine.[14] Recently, the xerographic evaluation of a series of dual-layer photoreceptors incorporating thin evaporated films of perylene pigments (N,N′-disubstituted diimide and bisarylimidazole derivatives of PTCDA) demonstrated a correlation between molecular planarity and photosensitivity, with the best response observed for the planar bisbenzimidazolylperylene. Furthermore, it was found that the spectral sensitivity could be extended to the near-IR region by adding chloroindium phthalocyanine in a bilayer assembly as a second photogenerator.[15]

We report here the photoelectrochemical properties of vacuum-deposited thin films of perylenetetracarboxcylic dianhydride. The subsequent paper in this journal will discuss the photoelectrochemical characterization of PTCDA in heterojunction structures with vanadylphthalocyanine (VOPc). In this paper it will be shown that PTCDA in contact with redox systems such as benzoquinone/hydroquinone, or iodine/iodide, yields photoelectrochemical behavior resembling that of an n-type semiconductor where photocurrent activity is seen only under positive bias. This response is likely due to differential kinetics of charge injection at the PTCDA/solution interface (preferential hole injection into solution) and/or to an asymmetric distribution of traps in the film. In some instances, it is possible, by electrochemical "activation" of the PTCDA, to enhance the anodic photocurrent generated by the organic film.

Experimental Section

PTCDA. 3,4,9,10-Perylenetetracarboxylic dianhydride was purchased from Aldrich. The powder was subsequently purified by sublimation under vacuum at ca. 10^{-7} Torr. Care was taken to maintain a sublimation temperature less than 400 °C to avoid decomposing the red PTCDA into a brown solid that contains 3,4-perylene dicarboxcylic anhydride, the decomposition product resulting from the loss of the anhydride from one end of the molecule. The loss of CO_2 and CO by PTCDA is well documented, since it is the first step in the production of carbon fibers composed of poly(perinaphthalene) derived from PTCDA.[16–19] Thermal gravimetry curves of PTCDA reported by Murakami[19] indicate that a small weight loss seems to already occur at 400 °C, even if the important drop in weight starts at 490 °C.

Film Preparation. PTCDA films were obtained by sublimation under vacuum (ca. 10^{-6} Torr) of the purified powder. The thin-film deposition chamber is similar to previously described chambers[5] and will be described in detail in the following paper.[8] The deposition rate was maintained at 15 ± 3 Å min^{-1} by controlling the temperature of the PTCDA source from 370 to 395 °C. Five types of electrode substrates were used: Au–MPOTE (a gold-metallized plastic optically transparent electrode composed of a thin Au film ($\approx$300 Å thick on a polyester substrate $\approx$ 0.25 mm thick, from Sierracin, Sylmar, CA), Au vacuum deposited on mica, Au foil, doped SnO_2 on glass ($\rho_s \approx$ 25–30 Ω/square), and polished Pt foils. The substrates were maintained at a temperature of 95 °C during the sublimation. PTCDA film thicknesses were approximated during depositions by quartz crystal microgravimetry, and they were then quantitated from the UV–visible

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thin-film absorbance measurements, after calibration of several films with a stylus profilometer (Dektak Model 3030). There was no variation in the shape of the absorption spectrum with the PTCDA layer thickness. At the maximum at 470 nm, the absorptivity, β, is 4.3×10^4 cm^{-1}.

Photoelectrochemical and Electrochemical Measurements. The configuration for electrochemical and photoelectrochemical experiments, along with the photocurrent action spectra measurements, has been described elesewhere.[20,21] Voltammetric data were obtained at a sweep rate of 10 mV s^{-1} in a one-compartment, three-electrode cell with Ag/AgCl as a reference electrode. All chemicals used in the electrochemical studies were research grade. All electrolyte solutions were preparaed with triply distilled water and degassed with high-purity nitrogen for at least 15 min. All electrolyte solutions were used at room temperature. The area of the PTCDA films in contact with the solution was 0.64 cm^2. At its maximum, the average white-light power density from the high-pressure Xenon lamp was approximately 225 mW/cm^2. Lower intensities were obtained through the use of neutral density filters.

Results and Discussion

I. Structure of PTCDA Thin Films. Vacuum-deposited PTCDA thin films have a somewhat different appearance compared to phthalocyanine thin films reported earlier from this group.[5,6,21] Figure 1 shows some typical electron micrographs of PTCDA films (ca. 600 Å thick) on both Au-MPOTE and SnO_2 substances, along with the micrographs of the substrates themselves. The Au-MPOTE substrate (Figure 1a) is quite smooth, with defects averaging less than 10-20 nm in size.[22] The PTCDA films on this substrate (Figure 1c) are quite regular in appearance and appear to consist of long, thin crystallites, oriented upright on the substrate, with cross sections of 50-80 nm and with spaces between these vertically oriented crystallites of 10-30 nm. The apparent overall porosity of these PTCDA thin films is in sharp contrast to most of the phthalocyanine thin films we have grown under similar deposition conditions in the past,[5,6,21] and this porosity is confirmed in many of the electrochemical studies described below. PTCDA films on Au-MPOTE after contact with electrolyte solutions (Figure 1d) appear to have undergone small microstructural changes as a result of that exposure. In these electrolyte-treated films, there appears to be more space between the crystallites (an average of 30-60 nm versus 10-30 nm for the untreated films), and the average crystallite diameters appear larger (80-100 nm versus 50-80 nm, respectively).

The SnO_2 surface consists of a tightly packed array of oxide microcrystallites with an average feature size of ca. 200-300 nm (Figure 1b). The PTCDA film, deposited on the SnO_2 substrate at the same time as for those films on the Au-MPOTE (Figure 1e), tended to mimic the rougher contours of the SnO_2 substrate, with occasional long, thin crystallites that were similar in appearance to those on the Au-MPOTE substrate. PTCDA films on SnO_2 show no apparent difference in structure after contact with the electrolyte solution (Figure 1f). This is probably due to the rough structure of the SnO_2 substrate, which would likely mask any small structural changes. However, as described below, the PTCDA thin films grown on the SnO_2 substrates showed the least tendency toward large changes in photoelectrochemical behavior after contact with the electrolyte, while those grown on the Au-MPOTE surfaces showed the greatest tendency for such changes.

X-ray diffraction spectra (Cu Kα, λ = 1.5418 Å) of 2000-Å-thick films of PTCDA vacuum deposited on either an amorphous glass substrate or on Au foil show a single prominent peak at $2\theta \approx 27.8°$. This reflection corresponds to the (102) molecular orientation of PTCDA as reported in previous studies of the X-ray powder diffraction patterns and for vacuum-deposited films on glass and (100)-oriented Si,[9,23] and it corresponds to an interplanar spacing of $d_{102} \approx 3.2$ Å. These films, which are similar to those previously studied and used in the electrochemical studies described below are apparently composed of PTCDA molecules oriented in stacks aligned close to parallel with respect to their substrates, with an inclination angles of 10-15° to the horizontal.[23] Other studies have suggested that perfection of PTCDA orientation was enhanced with faster deposition rates (2-50 Å/s) than used in this investigation. However, we have observed a higher order of crystallinity with those films grown at much slower deposition rates (ca. 0.25 Å/s).

Vibrational spectroscopies have been shown to be sensitive to phase changes and other morphology differences in crystalline phthalocyanine thin films, which arise from different stacking geometries of the adjacent conjugated systems.[6] Using the ATR-FTIR of PTCDA/Au thin films, only relatively small shifts in the vibrational band positions and band shapes in the region near 1025 cm^{-1} have been observed, which has recently been assigned to a γ_{C-H}-like band for PTCDA in a vibrational spectroscopic study of this molecule and other related perylenes.[24] Annealing the PTCDA films under conditions that normally produce some phase transformation of certain Pc's and that alter the photoelectrochemical behavior of such Pc films did little to produce changes observable with either SEM or FT-IR spectroscopy in our studies. It should be noted that the temperature of the substrate was maintained at a reasonably high level during the deposition process for all photoelectrodes (ca. 95 °C), so that some annealing of these films may have occurred during that time.

II. Electrochemistry and Photoelectrochemistry of PTCDA Films. Current-Voltage Characteristics. Parts a and b of Figure 2 show the current-voltage curves observed for the polarization of PTCDA thin films on SnO_2 and Au-MPOTE substrates, respectively (thickness ca. 900 Å). The PTCDA films on Au foil, Au on mica, and Pt substrates all behaved in a manner similar to that observed for the PTCDA on Au-MPOTE, except for small differences in the onset for dark electrochemistry, although the photopotentials and photocurrent yields for these substrates were rarely as large as those observed by using SnO_2 as a substrate. For all films studied, regardless of thickness or pretreatment (passivation) conditions, electrochemistry of redox couples with formal potentials negative of ca. -0.1 V versus Ag/AgCl was facile; i.e., the apparent electron-transfer rates for reduction of a redox couple such as anthraquinone or methylviologen were ca. 10^{-3} cm/s. At potentials positive of -0.1 V, there was generally no reaction observed in the dark for redox couples with formal potentials positive of that point, up to ca. +0.3 to +0.4 V. As discussed below, this onset for the oxidation current in the dark was quite dependent upon the porosity of the PTCDA film. The porosity of the PTCDA film led to

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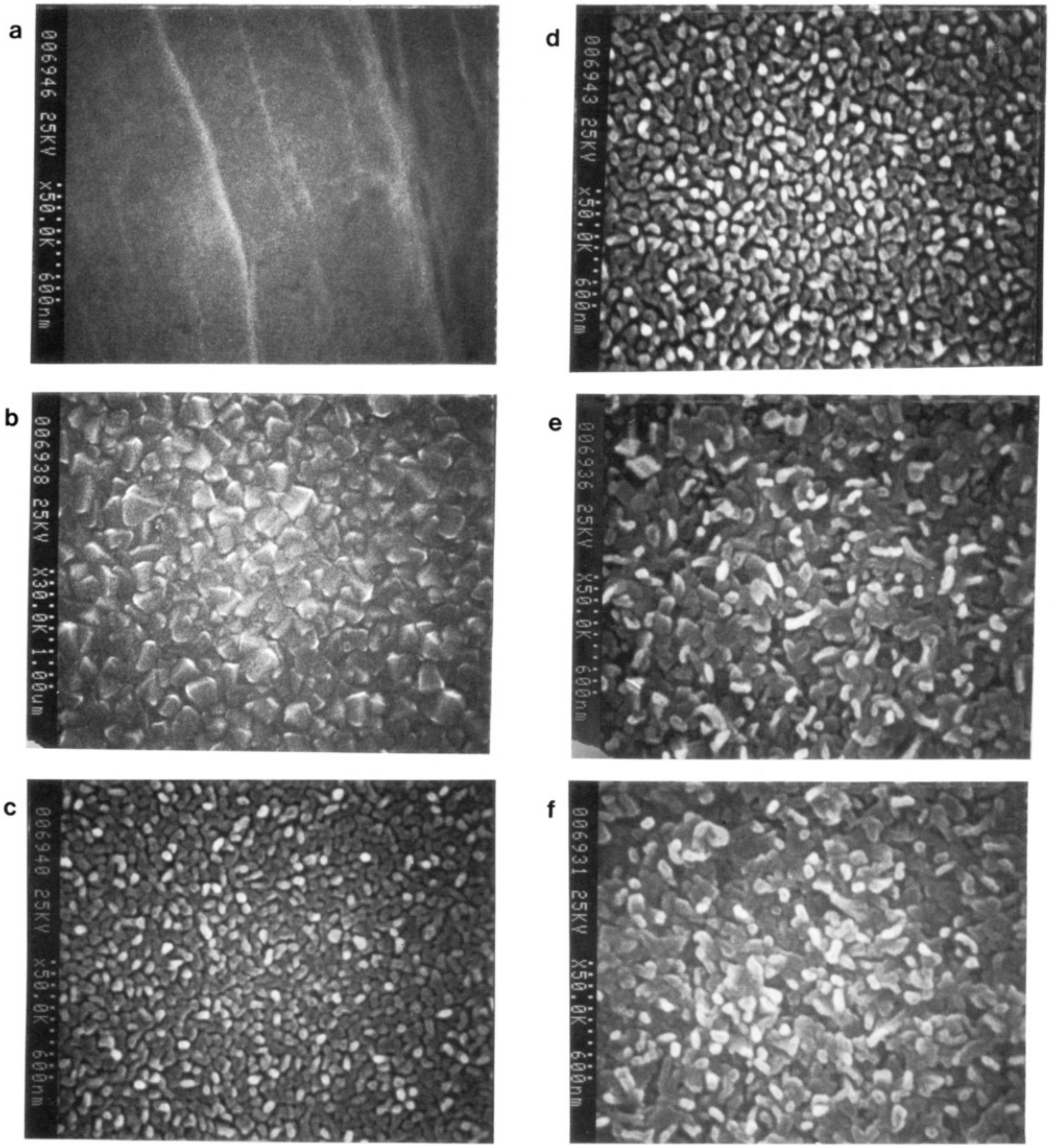

Figure 1. Scanning electron micrographs of the substrate materials and of the PTCDA thin films on these substrates. All magnifications are 50 000, unless specified. (a) Au–MPOTE substrate; small structures and poorly resolved lines are typical of the defects seen in this very smooth material. (b) SnO_2 substrate (magnification 30 000, structures present in this micrograph will appear larger in subsequent pictures); (c) 630-Å-thick PTCDA film/Au–MPOTE electrode, before contact with electrolyte; (d) 630-Å-thick PTCDA film/Au-MPOTE electrode after contact with 0.2 M KHP, 0.2 M H_2Q, pH = 4 electrolyte for 17 h, removed and rinsed before SEM; (e) 620-Å-thick PTCDA/SnO_2 electrode before contact with electrolyte; (f) 620-Å-thick PTCDA/SnO_2 electrode, after contact with the electrolyte in (d).

contact of redox solutions with the underlying substrate, and this could be controlled to some extent by other electrochemical passivation reactions.

Upon illumination with the polychromatic light source, the current–voltage curves showed sizeable photocurrents in the potential regions positive of –0.1 V, which was the onset voltage for photocurrent in the presence of high concentrations of an oxidizable molecule such as hydroquinone (H_2Q), with the maximum photoeffect observed at ca. 0.35 V. The initial photocurrent versus voltage responses immediately after contact of the film with the electrolyte (Figure 2a,b, curve 1) were usually less than those obtained after a stabilization period of contact between the film and the electrolyte for several minutes (Figure 2a,b, curve 2); i.e., it took several minutes for the photocurrent response at any positive potential to stabilize at the newer, larger values. For PTCDA on Au–MPOTE, the photocurrent amplitude following stabilization varied

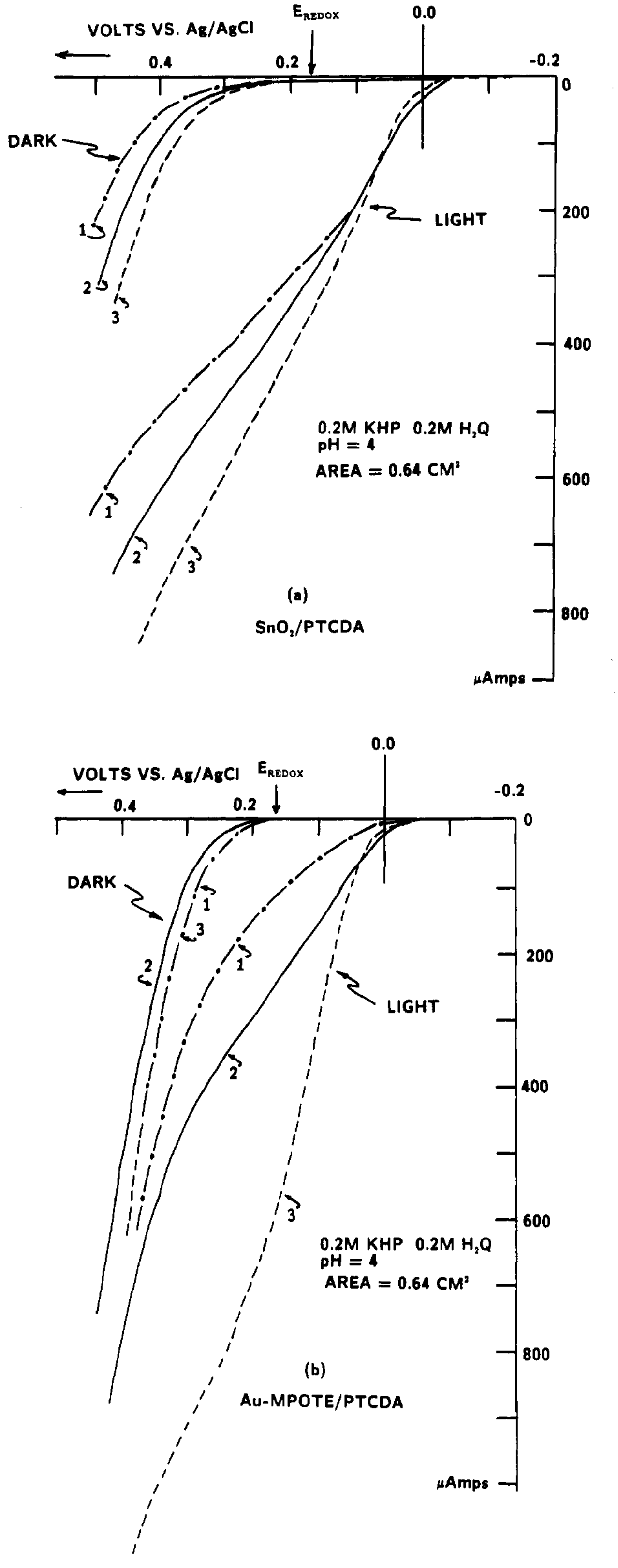

Figure 2. (a) Voltammetric response of a 825-Å-thick PTCDA/SnO_2 thin film electrode in the dark and under polychromatic illumination, in a pH = 4, 0.2 M H_2Q and 0.2 M KHP electrolyte. Curves labeled (1) indicate the response immediately after contacting the electrolyte, (2) indicates the response after the photocurrent had been allowed to stabilize for ca. 20–40 min, and (3) indicates the response after the cathodic polarization modification of the PTCDA films described below, in Figure 3. (b) Voltammetric response of a 900-Å-thick PTCDA/Au-MPOTE thin film electrode, as in (a) above.

by a factor of up to 2.5 versus the initial value, while for the SnO_2 substrate, the photocurrent varied by a factor as large as 1.2.

The dark current responses for H_2Q oxidation were always lower on the PTCDA films grown on SnO_2, which we attribute to the generally observed lower rates of H_2Q oxidation on these SnO_2 electrodes;[25] i.e., the dark electrochemistry is controlled by transport of the electrolyte through the pores in the PTCDA film to the substrate electrode. As a consequence, the contrast between dark and photocurrent activity was always greater for PTCDA films grown on SnO_2 in the potential region between 0.0 and 0.3 V. For PTCDA films grown on any of these substrates, the onset potential for oxidation of H_2Q is shifted ca. 0.2 V negative of the formal potential for this redox couple. Use of different redox couples consistently showed onset of the photocurrents at ca. −0.05 V.

The photocurrent yield at ca. +0.35 V, in this same H_2Q solution, was examined as a function of PTCDA film thickness (over the range 35–4500 Å) for both Au and SnO_2 substrates.[8b] It was observed that there was some variation in absolute photocurrent response over this thickness range, but that there was a general increase (a factor of 2–3×) in photocurrent yield from PTCDA thickness of 100 to ca. 1000 Å, followed by a general decline in photocurrent yield (a factor of 2–4×) for all subsequent increased thicknesses. The photocurrents were at nearly the same level for the 100-Å-thick films as the 4500-Å-thick films. As discussed further below, we expect that some of the photoelectrochemical activity of these PTCDA thin films arises because of different rates of hole and electron injection and charge trapping at the PTCDA/solution interface, where exciton dissociation likely occurs. The increase of photocurrent with PTCDA film thickness is likely to be due to the fact that excitons, created as a result of photon absorption, diffuse over distances as large as 1000 Å before dissociation into harvestable charge carriers or loss through recombination.[26]

Striking increases in photocurrent response could be obtained by first polarizing the PTCDA thin film electrode into a potential range negative of +0.1 V and then returning to the potential region where photocurrent generation was monitored. Figure 3 shows the voltammetric characterization of the electrochemical processes that lead to this increased photocurrent activity. These results could be obtained with no electroactive species in the solution (pH = 4, 0.2 M KHP) or with various redox agents present. Similar cathodic results (as seen in Figure 3) were observed whether the substrate was SnO_2 or Au, but the anodic photocurrent increases that resulted were limited to the Au substrate (or other Au or Pt substrates). Different pH electrolytes were also used, with comparable results, provided that the KHP was also present.

Scan 1 in Figure 3 shows two large reduction peaks that are observed on the first negative sweep, one positioned at ca. 0.0 V (reduction of benzoquinone formed during anodic scans back to H_2Q) and the other at ca. −0.6 V. Upon scan reversal at −0.6 V and sweeping positive from that point, the scans 2 and 3 were observed, indicating the formation of a chemically reversible redox species, with a reduction peak potential at ca. −0.40 V and an oxidative peak potential at ca. −0.35 V. The symmetric appearance of these peaks, coupled with the linear dependence of peak current with voltammetric sweep rate (10–100 mV/s), in-

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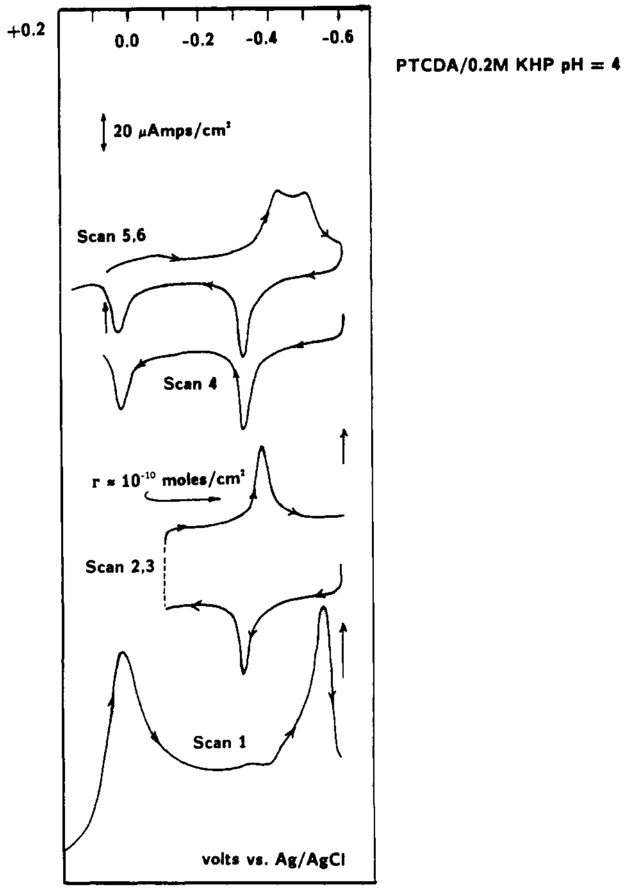

Figure 3. Cathodic polarization/activation of the PTCDA thin films. Scan 1: first cathodic sweep after immersion into the 0.2 M KHP electrolyte. Scans 2 and 3: evidence for reversible, surface-bound redox couple created after the first voltammetric sweep. Scan 4: voltammetric response realized after sweeping positive of −0.1 V. Scans 5 and 6: voltammetric response realized after scan 4, returning sweep negative to −0.6 V.

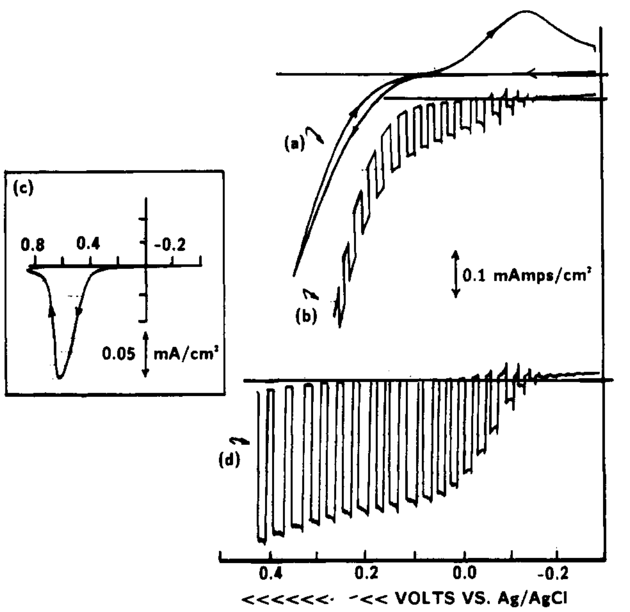

Figure 4. Effects of electropolymerized α-naphthol on the PTCDA photoelectrochemical response. (a) Polarization curve for a bare Au electrode in the 0.2 M H_2Q solution. (b) Polarization curve for a 450-Å-thick PTCDA/Au-MPOTE electrode in the same solution; both dark and photocurrents are shown by virtue of the slow modulation of the light source. (c) Voltammetric response of the PTCDA/Au-MPOTE electrode, in the presence of a 2 mM, pH = 4 solution of α-naphthol; the first voltammetric scan is shown, corresponding to the accumulation of the polymer surface coverage of $\Gamma = 10^{-8}$ mol/cm², assuming $n = 1$ and the active electrode area equals the geometric area; subsequent voltammetric scans yielded barely detectable dark currents. (d) Voltammetric response of the α-naphthol-modified electrode after returning to the H_2Q solution in (a) and (b). Potential sweep rates for all experiments were 10 mV/s.

dicates that this is a PTCDA surface-confined species. Integration of the charge under either the reduction or oxidation peaks, and assuming $n = 1$ for the charge-transfer process, leads to an estimate of surface coverage: $\Gamma = Q_{\text{ads}}/nFA = 1 \times 10^{-10}$ mol/cm². If the potential of the PTCDA electrode was maintained in the potential region between −0.1 and −0.6 V, the intensity of these voltammetric peaks did not diminish over several potential scans. Interestingly, this surface-confined species did not change in its concentration, regardless of the PTCDA film thickness (100–1000 Å), suggesting that only the outer, electroactive portion of the PTCDA crystallites are involved in this process, regardless of the size of these crystallites in various thickness films. Sweeping the potential positive of −0.1 V gave the results of scan 4, which included the formation of an oxidation peak, centered at +0.05 V. Reversal of the voltammetric scan at this point resulted in scans 5 and 6, which showed the formation of an additional reduction wave at ca. −0.5 V, which lasted only for this one scan. Subsequent cycling of the potential in the range −0.6 to −0.1 V repeated the behavior observed in scans 2 and 3.

Analysis of such modified PTCDA thin films by X-ray photoelectron spectroscopy did not show sufficient chemical shifts in either the C(1s) or O(1s) peaks to determine the chemical identity of these surface species. FT-IR spectroscopy analysis of these films by ATR methods likewise did not show significant shifts in the major bands on PTCDA films thick enough to produce a discernible IR absorption spectrum. Comparable increases in photocurrent behavior in the positive potential regions could be obtained by moving the potential into that region immediaely after scan 1 or could be obtained after the repeated voltammetric scans (1–6 in Figure 3) described above. It should be noted that these increases in photocurrent yield were transient in nature—if one poised the photoelectrode at ca. +0.6 V and observed the photocurrent after the cathodic modification step, there was a steady decline in response over a period of ca. 6–8 h, until the original photocurrent response was approached. The increased level of photocurrent activity could be recovered by following the cathodic activation procedure outlined above, and this cycle could be repeated several times, following which there was a general decline in the photoelectrochemical activity of the PTCDA thin film. As discussed below, we believe these effects to be due to modification of the near-surface regions of the individual PTCDA microcrystallites, which is the region where the bulk of the photoelectrochemical activity originates and where differential charge injection may occur.

In addition to this cathodic activation process, the photoactivity of these PTCDA films was strongly dependent on their porosity, which is controlled by the microstructure of the crystallites shown in Figure 1. The effect of porosity on the photocurrent response is shown in Figure 4. In Figure 4a, the dark current response of the Au-MPOTE substrate in the H_2Q solution is shown with the onset of appreciable dark current due to the oxidation process at ca. 0.1–0.2 V. The photocurrent response of the PTCDA film (ca. 450 Å thick) on a Au-MPOTE substrate is shown in Figure 4b, where both the light and dark responses are observed by slowly modulating the light source. On this film, there is clear evidence for the onset of dark electrochemical activity at the same potential as on the bare Au–MPOTE substrate, which can be interpreted as an indication of the porosity of the films.

The efficacy of passivating the potoelectrode surfaces with electrochemically grown, insulating polymer thin films has been previously shown.[26,27] If the polymer can be grown in the dark, then only those sites with dark electrochemical activity (i.e., the Au sites accessible through the porous PTCDA film) will be covered with the passivating polymer, and hence the photoactivity of the organic film may be enhanced. Polymerizable phenols are suitable for such modification, since their oxidative polymerization occurs at potentials where the PTCDA is electrochemically inactive in the dark.[27] Figure 4c shows the voltammetric response of the PTCDA/Au–MPOTE electrode in a solution of 2 mM α-naphthol, a molecule that has been demonstrated to undergo electrochemically induced, oxidative polymerization, to give an insulating polyphenoxide film.[27] Integration of the voltammetric scan in Figure 4c, assuming $n = 1$ in the electrooxidation process, gives a surface coverage of polyphenoxide of $\Gamma \approx 1.1 \times 10^{-8}$ mol/cm^2. By scanning the potential region from 0.0 to +0.8 V (vs. Ag/AgCl) three to four times, it is possible to deposit a surface layer corresponding to an approximate coverage of 1.3×10^{-8} mol/cm^2, or ca. 100 equivalent monolayers of polymer. Other phenols can be similarly deposited, including *m*-aminophenol, in or near this same potential range, with similar results.[27,28] Following this polymerization step, rinsing with pure H_2O, and reimmersion of the PTCDA/Au–MPOTE film into the H_2Q solution, the photocurrent yield at all positive potentials was greatly improved, and the dark current response was significantly diminished, so that no appreciable H_2Q oxidation occurred out to potentials to excess of +0.4 V, and only a small amount of H_2Q oxidation was seen at potentials in excess of 1.0 V. To achieve the photocurrent levels shown in Figure 4d, the cathodic modification process described above was carried out, but the dark current and qualitative features of the photocurrent–voltage curves are the same as seen immediately following the polymeric modification process.

As a direct comparison with previous studies of certain GaPc–Cl thin films, dark and illuminated voltammetric responses were determined in dilute (10^{-3} M) H_2Q solutions.[26,29,30] Figure 5 shows the voltammetric response for a bare Au–MPOTE electrode (a), a PTCDA (800 Å)/Au–MPOTE electrode in the dark (a) and illuminated (b), and the same electrode after passivation with α-naphthol, both dark and illuminated (c). Because of the porosity of the PTCDA thin film, the voltammetric response toward 10^{-3} M H_2Q in the dark is indistinguishable from that for the bare Au electrode at the voltammetric sweep rates (e.g., 10 mV/s) used here. Upon illumination, the porous PTCDA/Au electrode shows a strikingly improved rate of electrolysis of H_2Q, and an onset potential for the oxidation process that is negative (ca. 0.3 V) of the apparent $E^{\circ\prime}$ for this redox couple. Following passivation with α-naphthol, the dark current is greatly suppressed and the photocurrent response shows the lack of a well-defined peak, with the current reaching its plateau value at near the same potential as the peak current in (b).

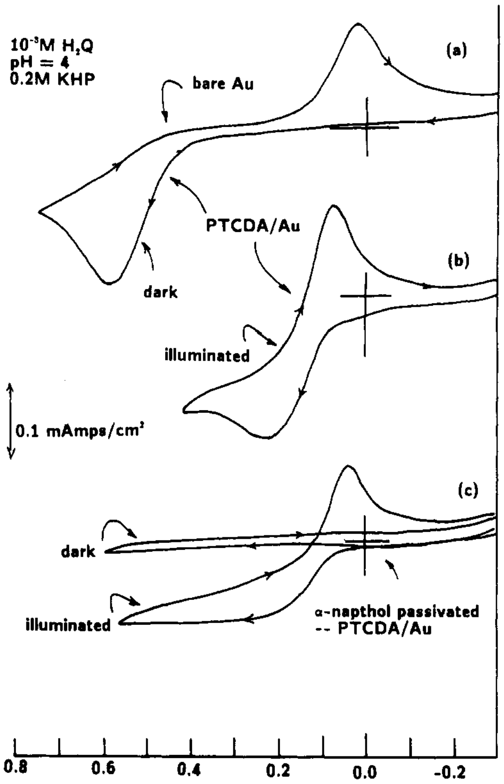

Figure 5. Voltammetric response toward the 10^{-3} M H_2Q solution at a sweep rate of 10 mV/s for a (a) bare Au-MPOTE electrode and an 800-Å-thick PTCDA/Au-MPOTE electrode in the dark (because of the porosity of the PTCDA thin film, the voltammetric response in the dark is indistinguishable from that for the bare Au electrode), (b) 800-Å-thick PTCDA/Au-MPOTE electrode illuminated, (c) and the same electrode after passivation with α-naphthol, both dark and illuminated.

These data bear a striking resemblance to our earlier studies of porous GaPc–Cl thin films, which had been grown on the Au–MPOTE substrate with a slow deposition procedure, which later proved to be essential to achieve this "n-type" semiconductor response, as observed for the PTCDA thin films (26a). Thicker nonporous GaPc–Cl films later showed an even more striking response, without the need for the α-naphthol passivation.[26b] Following those initial studies on the GaPc–Cl and InPc–Cl systems, it was determined that the apparent "n-type" photoelectrochemical response could be converted to a "p-type" semiconductor photoelectrode response, by annealing these films in O_2 at ca. 100 °C for several hours, and/or growth of the films in such a fashion as to insure higher oxygen content in the final film.[5] Reannealing in H_2 reversed this change in response, confirming that O_2 was acting to "dope" these films and thereby control their photoelectrochemical response. A similar series of gaseous doping experiments for these PTCDA films were attempted. When the PTCDA electrodes used in Figure 5c (or their equivalents) were annealed at ca. 100 °C for up to 8 h in the presence of O_2, no detectable changes occurred in *either* the dark or photoelectrochemical behavior of these films, suggesting that their photoelectrochemical properties are not as sensitive to interactions with O_2 as the trivalent metal Pc's.

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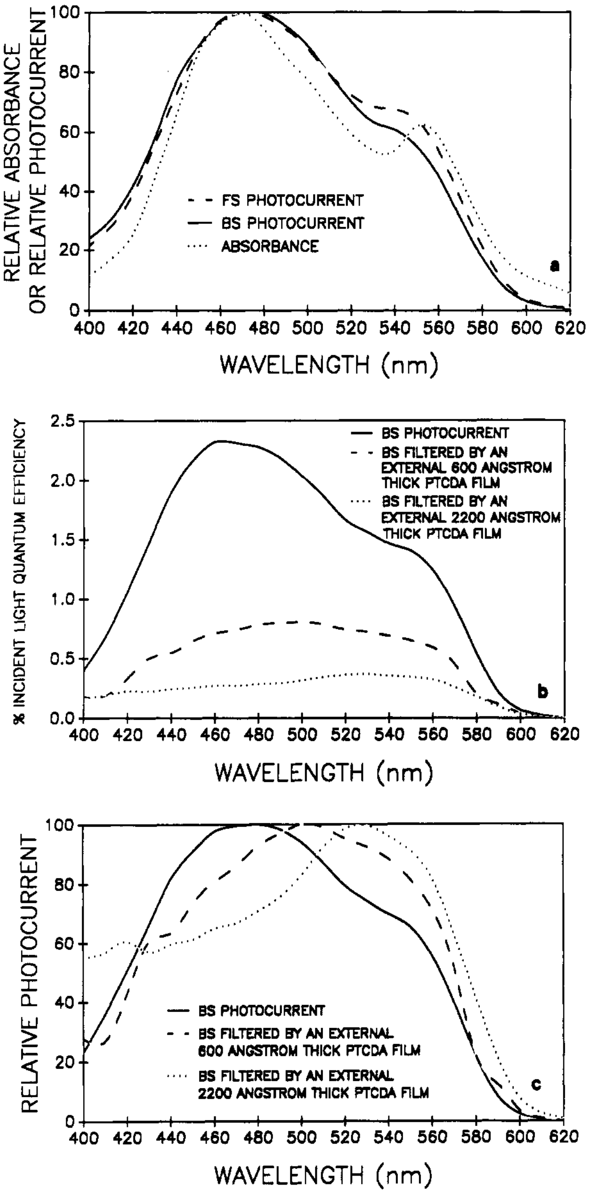

Figure 6. Photocurrent yield spectra and absorbance spectra for PTCDA thin films. (a) Relative photocurrent yield spectra and the absorbance spectum for a 2200-Å-thick PTCDA/SnO_2 thin film electrode in 0.2 M H_2Q and 0.2M KHP at pH = 4. FS indicates illumination of the PTCDA/solution interface first; BS indicates illumination of the SnO_2/PTCDA interface first. The absorbance spectrum and the two photocurrent yield spectra have been normalized to the peak value at 470 nm. (b) Photocurrent yield spectra represented as the number of electrons/incident photon at +0.2 V for the PTCDA thin film in (a) above for BS illumination, (—, BS photocurrent before filtering), (---, BS photocurrent with the light source filtered by a 600-Å-thick PTCDA thin film external to the electrochemical cell), (···, BS photocurrent with the light source filtered by a 2200-Å-thick PTCDA thin film external to the electrochemical cell). (c) Photocurrent yield spectra from (b) normalized with respect to their individual peak intensities.

Photocurrent Yield Spectra. Figure 6a shows the relative photocurrent yield measured under a +0.2 V polarization as a function of wavelength for a typical PTCDA thin film (ca. 2200-Å thickness on SnO_2, similar results were seen on Au-MPOTE substrates), along with the relative absorbance spectrum for this same film, with spectral intensities normalized to their respective maxima. There was a clear correspondence between the photocurrent yield spectrum and the absorbance spectrum for all PTCDA films, regardless of film thickness or deposition conditions. In addition, no modifications of the relative absorbance spectra or the relative photocurrent yield spectra were observed after the electrochemical manipulations, regardless of redox solution or substrate. This independence of the shape of the photocurrent yield spectrum with PTCDA film thickness is quite different from that observed for photoelectrochemically active phthalocyanine films of comparable thickness.[5,21] For those materials, there is a strong filtering effect observed if the direction of illumination does not strike the most photoactive interface first, and this effect is sufficient to cause complete inversion of the photocurrent versus the absorbance spectrum on the thicker Pc films, i.e., the photocurrent yield is minimized in regions of strong absorbance, and it is measurable in regions of weak absorption. The absorptivity (β) for these PTCDA thin films at 470 nm is ca. 4.3×10^4 cm^{-1}, based upon the measurement of the thin-film absorbance spectra of several samples whose thicknesses had been estimated from the thin-film thickness monitors used in the deposition chamber. If only one interface is photoactive and if the exciton diffusion length is less than the total thickness of the PTCDA film, a strong filtering effect would be expected.

To ensure that a filtering effect could be seen, if it were present, the photocurrent yield spectral measurements of Figure 6a were repeated, with an additional PTCDA thin-film external to the photoelectrochemical cell, but in the light path, so that some of the light flux would be captured by a PTCDA thin film that could not participate in photocurrent generation. The results of such an experiment are shown in Figure 6b, and they clearly show the attenuation of photocurrent in the regions of maximum absorbance due to the presence of the extra PTCDA film. Figure 6b also reveals that the decrease in the absolute photocurrent is substantial, even if the film external to the photoelectrochemical cell is only 600 Å thick. Figure 6c demonstrates that the shape of the relative photocurrent yield spectrum would be considerably affected if a non-photoactive region of only 600-Å thickness existed at one of the interfaces of the 2200-Å-thick PTCDA film. From this experiment, there is little doubt that there is a lack of a filtering effect in the PTCDA photoelectrodes.

Origin of Observed Photoeffects

The photoelectrochemical response of the PTCDA thin films represents an interesting difference from that behavior observed for most other crystalline organic thin-film systems. Most of the previously explored phthalocyanine thin-film systems have demonstrated p-type behavior with high concentrations of dopant (ca. 10^{18} cm^{-3}). Notable exceptions have been reported for certain trivalent metal Pc's such as GaPc–Cl and InPc–Cl, which, if deposited under the proper conditions and examined before extensive exposure to atmospheric pressure oxygen, can likewise demonstrate photoelectrochemical behavior like that seen for the PTCDA films studied here.[5] For GaPc–Cl and InPc–Cl thin films, the photoelectrochemical response in the presence of millimolar concentrations of hydroquinone, ferrocyanide, or other reducing agents consistently gave onsets for photocurrent activity (i.e., the apparent flat-band potentials) that were negative of the formal potentials for those redox couple by 0.2–0.3 V, as was observed for the PTCDA thin films. Annealing these Pc thin films in O_2 for several hours, however, converted their photoelectrochemical behavior to that of a p-type semiconductor photoelectrode. It is notable that for the PTCDA thin films we have studied, no such effects from annealing in O_2 are observed, which would indicate that the initial behavior is not due to a lack of O_2 in the thin film.

It is hard to rationalize n-type semiconductor behavior from such an organic material—it is generally expected that organic materials from extended conjugation systems will exhibit p-type electronic properties, since oxidative doping is the most likely process to occur in the presence of atmospheric constituents.[1] Highly purified single crystals of PTCDA, as well as vacuum-deposited thin films such as those studied here, have been reported to have exceptionally low charge densities and to behave as essentially undoped insulators (p = ca. 5×10^{14} cm^{-3}).[9] Previous studies have also inferred that this material in the dark may be susceptible to charge injection processes at interfaces, which determine its electrical properties.[9]

The origin of the photoaffect for these PTCDA thin films and for the Pc films with low oxygen content, reported earlier, can be due to either of two effects: (a) preferential injection of holes into the electrolyte, leaving the near-surface region with an excess of electrons or (b) buildup of electron concentration at the PTCDA/electrolyte interface due to trapping events, with the stable traps distributed in a nonuniform fashion over the thickness of the PTCDA thin film. Bonham and co-workers have argued in the past for nonuniform trap distributions as the origin of photopotentials in otherwise undoped organic thin films, with the magnitude of this effect resulting in 200–300 mV potential drops across the organic film, when the trap distribution was asymmetric by a factor of ca. 10^5 from one interface to the other.[32] The photopotentials observed in liquid-crystalline porphyrin thin films, which are also undoped materials, were rationalized as being due primarily to differential rates of charge injection at the illuminated interface.[33] Once again, photopotentials of a few hundred millivolts were obtainable.

The studies of PTCDA thin films reported here have been recently extended to other perylene derivatives, with comparable results—in contact with aqueous electrolytes these thin films invariably produced negative photopotentials (photoanodic activity).[34] It is likely that the "n-type" semiconductor behavior ascribed to perylene derivatives in solid-state cells (generally in contact with phthalocyanines) is also due to the same interfacial effects that produce the photoanodic behavior reported here.[10-12]

Our photovoltammetric results, at low concentrations of redox species, suggest that some trapping does take place for the electrons left behind after hole injection but that this effect does not account for the majority of the photoeffect. Referring to Figure 5 and back to the photovoltammetric results for GaPc–Cl in its low-O_2 state,[5b] at millimolar concentrations of a redox species such as H_2Q or ferrocyanide, the oxidation process is seen only upon illumination, but the reduction of the oxidized product, on the return voltammetric sweep, is facile, even though there should be few electrons available in this potential region, if the system is acting as a true "n-type" semiconductor. As the concentration of the redox species is increased, the onset potential for the photooxidation process changes by only ca. 50 mV, the photocurrent increases and becomes nearly potential independent at sufficiently positive bias, and the reduction activity diminishes in proportion to the photoanodic activity, until the photoactivity of Figure 2 or 4, is seen. As indicated above, this type of effect could be removed for the trivalent metal Pc's with annealing in O_2[5b] but remained constant in the PTCDA thin films. It would appear that sufficient trapped charge is created at the PTCDA/solution interface, during electrolysis of millimotor redox solutions, as to sustain reduction currents for the photogenerated products. At sufficiently high redox concentrations, these trap states are incapable of producing enough charge to sustain reduction of the oxidation products produced on the anodic sweep. Traps at that low a concentration (likely at a density of less than 10^{15} cm^{-2}) do not appear to effect the onset potential for the photoanodic effect by more than 50 millivolts, thus arguing for the role of preferential hole injection as the origin of the photopotential.

Proposed theories of charge generation in organic thin films, including the phthalocyanines and perylenes,[14,35] suggest that exciton dissociation (leading to hole injection into solution) at defects near the illuminated electrode gives rise to the observed photocurrents. Intrinsic and extrinsic exciton dissociation mechanisms have been proposed[35] and are explored further in the following paper.[8] It has been shown that mobile charges can be generated by dissociation of the (Frenkel) exciton at defect sites and at sites of fixed charge due to the presence of "impurities" introduced during the deposition of the thin film and/or by chemical modification following the deposition process.[4]

The observed porosity of the PTCDA films makes it possible to achieve charge injection along most of the length of the microcrystallite columns, giving rise to photocurrent yields that were independent of illumination direction. For previously studied GaPc–Cl thin films, with comparable thicknesses, their nonporous nature meant that charge injection was confined to the Pc/solution interface, and therefore strong filtering effects were seen. The columnar nature of the thin-film PTCDA deposits leads to special problems in the electrochemical and photoelectrochemical characterization of these materials, which can be partially rectified by the anodic passivation steps involving the polymerization of phenols and naphthols. Whether these PTCDA columns would promote short-circuit sites when the second contacting phase is another vapor-deposited metal and whether such an anodic passivation process is effective in preventing such shorting processes are currently under investigation.

The photoactivity of these PTCDA thin films appears confined to the solution interface. In the following publication[8] we show that, by interfacing PTCDA with a phthalocyanine (VOPc), photoactivity can be transferred mainly to an interfacial region between those two materials.

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