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Semiconductor Electrodes. 43. The Effect of Light Intensity and Iodine Doping on the Stabilization of n-Silicon by Phthalocyanine Films

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The stability of n-Si vacuum-coated with metal-free phthalocyanine (H₂Pc) and copper phthalocyanine (CuPc) was studied as a function of the light intensity and redox couple in aqueous solutions. Although the photocurrent at an n-Si coated with H₂Pc or CuPc decayed slowly at low light intensities (1 mW/cm²), photopassivation was rapid at higher light intensities (100 mW/cm²). The magnitude of photocurrent and the inhibition of photocorrosion depended upon the solution conditions. Addition of iodine, which is a dopant for the Pc layer, led to larger photoeffects and a lower rate of photopassivation, although the electrode was still unstable after longer irradiation times. Further improvement in stability was observed in the presence of the highly concentrated electrolyte, 11 M LiCl.

Introduction

Although n-type silicon is an attractive semiconductor with respect to band-gap energy and cost for photoelectrochemical (PEC) cells, it rapidly forms an insulating oxide film under irradiation in aqueous solution and passivates. Several techniques have been suggested to improve the stability of this semiconductor; these include derivatization of the electrode surface,¹ coverage by thin metal layers,² semiconductor,³ electroinactive polymers,⁴ or conductive polymers, sometimes undercoated with very thin metal layers.⁵⁻⁷ To stabilize the n-Si electrode, one must rapidly remove the photogenerated holes from the semiconductor surface and prevent water from reaching the Si where the photooxidation can occur. For this purpose phthalocyanine (Pc) films are potentially useful because of their hydrophobicity and semiconducting properties.⁸⁻¹⁰

The recent report that n-Si can be stabilized by coating with Pc films¹¹ has prompted us to report our independent findings with several phthalocyanine systems under different light-intensity conditions and with various redox electrolytes. We have found that, while some stabilization can be achieved under very low irradiation intensities, no conditions could be found where long-term stability of n-Si occurred with Pc layers under light fluxes characteristic of solar radiation (~135 mW/cm²).

Experimental Section

The electrodes were fabricated and treated as previously described⁸ by using n-Si (0.4-0.6 Ω cm) obtained from Texas Instruments (Dallas, TX). Chemical etching was

performed with HNO₃/HF/CH₃COOH (5:3:3 by volume) or with HNO₃/HF/CH₃COOH (3:1:1) with bromine (one drop per 70 mL) for 10-20 s followed by a 1-min treatment with concentrated HF. The electrodes were thoroughly rinsed with deionized water and methanol before the deposition of the phthalocyanine films. These organic films were formed by vacuum sublimation (at 10⁻⁵-10⁻⁶ torr) as reported previously;¹⁰ the thicknesses of the films ranged from 500 to 2000 Å (with coating times of 5-7 min). The coated silicon electrodes were kept under vacuum before use.

The light source was a 450-W xenon lamp (Oriel Corp, Stamford, CT) filtered through a 10-cm water filter combined with a 600-nm cutoff red filter (i.e., passing wavelengths >600 nm) or an 800-nm cutoff infrared filter to prevent light absorption and reflection by the iodine layer formed during the photoprocess¹² or by the phthalocyanine layer. The photocurrents generated by light absorption and photoeffects in the phthalocyanine layers are much smaller than those in the Si,^{11,13} so that this contribution can generally be neglected. All chemicals were reagent grade and were used without further purification. CuPc and H₂Pc were purchased from Kodak. Water was triply distilled from an alkaline potassium permanganate solution. All solutions were deaerated with nitrogen, and the electrodes were immersed for 10-20 min in the medium before the measurements.

A PAR Model 173 potentiostat and a Model 175 programmer (Princeton Applied Research Corp, Princeton, NJ) and a Model 2000 X-Y recorder (Houston Instruments, Austin, TX) were used for the electrochemical experiments.

Results

Stability of Phthalocyanine-Covered n-Si Electrodes. Stable operation and photooxidation of Fe(CN)₆⁴⁻ was recently reported for photoelectrochemical cells with n-Si/CuPc and n-Si/H₂Pc¹¹ at low light intensities. The effect of light intensity on the stability of a Pc-coated n-Si electrode is demonstrated by the experiments in Figures 1-3. When irradiated at low intensities (<1 mW/cm²) in I₃⁻/I⁻, Fe³⁺/Fe²⁺, or Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ solution, the n-Si/CuPc photoanode is obviously more stable than bare silicon. The very slow decay of photocurrent can be ascribed to the partial protection of the electrode surface by

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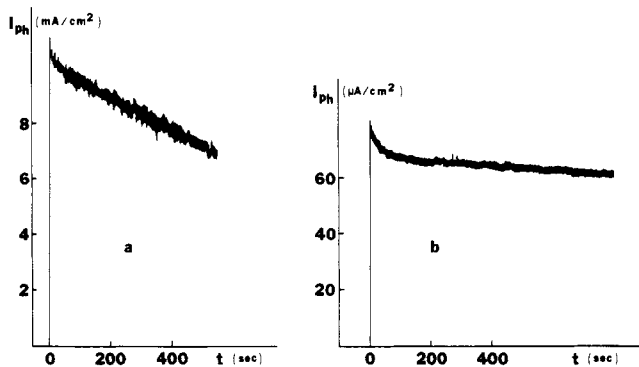


Figure 1. Photocurrent-time behavior for n-Si/CuPc (800 Å) in 1 M NaI/10⁻³ M I₂ under stirred conditions. (a) Light intensity, 72.5 mW/cm²; bias potential, 0.2 V vs. SCE. (b) Light intensity, 0.3 mW/cm²; bias potential, 0.1 V vs. SCE.

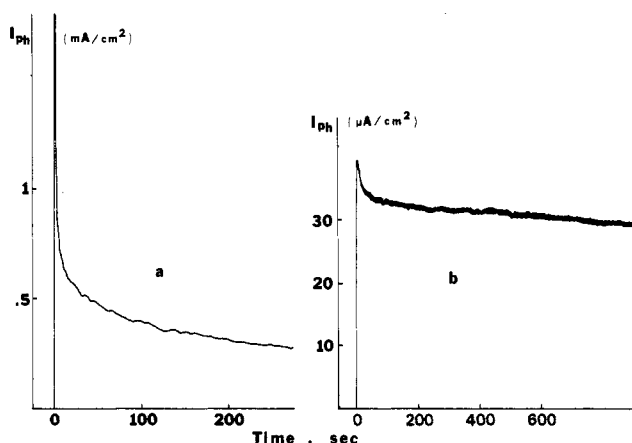


Figure 2. Photocurrent-time behavior for n-Si/CuPc (800 Å) in 0.7 M K₄Fe(CN)₆/0.05 M K₃Fe(CN)₆ under stirred conditions at 0.4 V vs. SCE. (a) Light intensity, 114 mW/cm². (b) Light intensity, 0.72 mW/cm².

the organic layer. Similar behavior is found for all three redox solutions.

For a light intensity close to 100 mW/cm², where bare n-Si passivates completely in a few seconds, the photo-corrosion process is remarkably decreased with the Pc coating, but the rate of formation of the insulating layer is very much dependent upon the nature of the redox couple. As compared with other redox couples, slower passivation occurred in iodide solutions where the decay of the photocurrent was only 35% in 10 min. The photocurrent-time behavior shown in Figures 1a and 2a represents some of the best results that we have obtained with such systems in the absence of highly concentrated electrolyte. The rate of passivation of Pc-coated n-Si in a given solution depended upon film thickness, stirring rate, and previous history of the electrode.

Iodine Doping of Phthalocyanine Films. A problem with the thicker Pc films used as coating is their high resistance which generally decreases the maximum photocurrents (i_{ph}) at a given light intensity compared to that initially observed on bare n-Si. For example, photo-oxidation of a 0.7 M solution of Fe(CN)₆⁴⁻ at bare n-Si yields 11.5 mA/cm² while a n-Si/CuPc (800 Å) electrode under the same conditions produces only 0.6–1 mA/cm². However, much larger currents are found with Pc-coated electrodes in I₃⁻/I⁻ solutions. Thus, the n-Si/CuPc (800 Å) electrode in 1 M I⁻/10⁻³ M I₃⁻ shows $i_{ph} = 12$ –13 mA/cm².

Although the same trend is observed for electrodes with H₂Pc films, the limiting photocurrents are usually lower, e.g., 2.5 mA/cm² in I₃⁻/I⁻ vs. <0.2 mA/cm² in 0.5 M Fe²⁺/0.15 M Fe³⁺ at n-Si/H₂Pc (1000 Å). These low

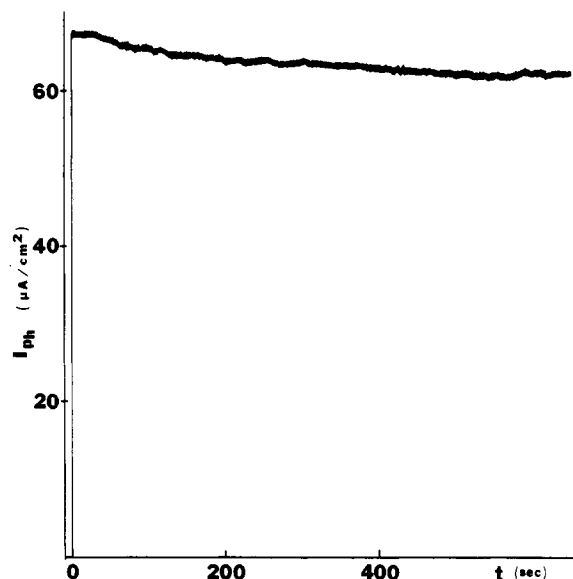


Figure 3. Photocurrent-time behavior for n-Si/CuPc (500 Å) in 0.05 M FeCl₂/0.05 M FeCl₃ under stirred conditions at 0.45 V vs. SCE for a light intensity of 0.44 mW/cm².

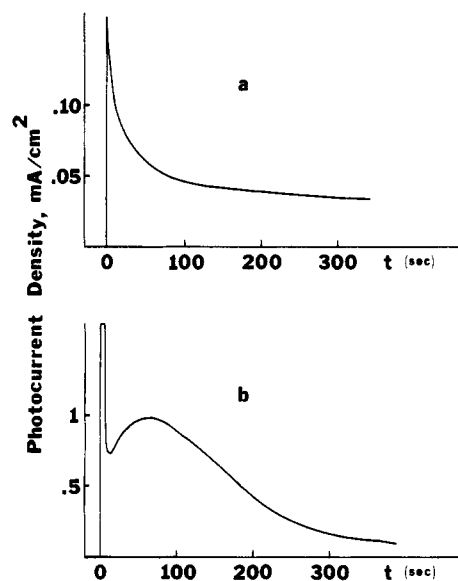


Figure 4. Photocurrent-time behavior for n-Si/H₂Pc (1000 Å) in 0.5 M FeCl₂/0.5 M FeCl₃/11 M LiCl at pH 0 and a bias potential of 0.4 V vs. SCE: (a) untreated electrode; (b) iodine-treated electrode.

photocurrents displayed by the n-Si/H₂Pc/Fe²⁺ system can be greatly enhanced by dipping the electrode for a few minutes in an I₃⁻/I⁻ medium. As shown in Figure 4, the photocurrent of an untreated electrode is low and decays rapidly while an I₃⁻ treated one shows significantly higher currents. The observed maximum might be caused by the oxidation of I₃⁻ (or I⁻ in the film, which in turn changes the conductivity of the film because of iodine doping.¹⁴ The effect of iodine is also reflected in the faster response of a n-Si/CuPc electrode to light in a solution containing I₃⁻/I⁻, as compared to a solution containing I⁻ alone (Figure 5).

Evidence for iodine penetration into the Pc layer was also obtained by the spectroscopic analysis of a CuPc layer treated for 17 h in an I₃⁻/I⁻ solution or with I₂ vapor. After treatment there was a general broadening of all absorption bands; the 617-nm peak was barely affected while the 695-nm band was slightly blue shifted by 5–10 nm. These

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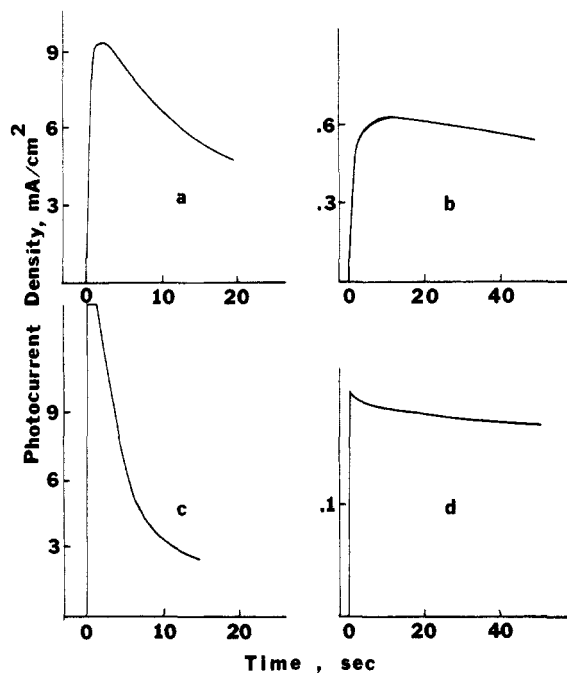


Figure 5. Photocurrent-time behavior for n-Si/CuPc (1500 Å) in 0.2 M NaI/0.5 M Na₂SO₄ at 0.2 V vs. SCE: (a) new electrode; (b) passivated electrode; (c) new electrode; (d) passivated electrode in 0.2 M NaI/4 × 10⁻³ M I₂/0.5 M Na₂SO₄ at 0.2 V vs. SCE.

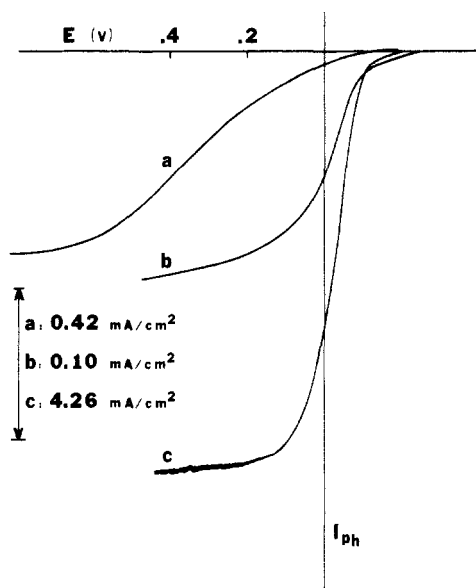


Figure 6. Photovoltaammograms for n-Si/CuPc under stirred conditions, with a scan rate of 50 mV/s: (a) n-Si/CuPc (800 Å) in 0.7 M K₄Fe(CN)₆/0.05 M K₃Fe(CN)₆ at 72.5 mW/cm²; (b) n-Si/CuPc (800 Å) in 1 M NaI/10⁻³ M I₂ at 0.73 mW/cm²; (c) n-Si/CuPc (800 Å) in 1 M NaI/10⁻³ M I₂ at 72.5 mW/cm².

spectral features reverted to those of the untreated film upon exposure to air or vacuum expected for iodine penetration into the film. Iodine is known to be a dopant for Pc films¹⁴⁻¹⁷ and improves their conductivity considerably.

The nature of the redox electrolyte influenced not only the magnitude of the photocurrent but also the shape of the i_{ph} -V curve (Figure 6). For a Fe(CN)₆^{3-/4-} solution (Figure 6a), the increase of i_{ph} with V was relatively flat

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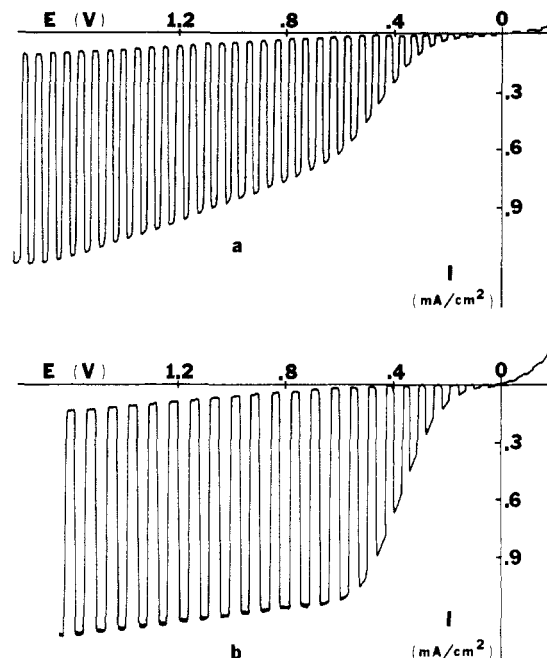


Figure 7. Photovoltaammograms for n-Si/CuPc (800 Å), with a chopped light intensity of 70 mW/cm² and a scan rate of 50 mV/s: (a) in 0.7 M K₄Fe(CN)₆/0.05 M K₃Fe(CN)₆; (b) in 0.7 M K₄Fe(CN)₆/0.05 M K₃Fe(CN)₆/1 M NaI. Electrode is partially passivated because of previous measurements in ferrocyanide solution.

and the limiting i_{ph} was only reached at fairly positive potentials (0.8 V vs. SCE). The i_{ph} -V wave was significantly steeper in an I₃⁻/I⁻ solution (Figure 6, b and c). This behavior can also be attributed to doping by I₂ decreasing the film resistance. Similar behavior was observed for n-Si/H₂Pc electrodes.

The effect of iodine doping on the i_{ph} -V behavior is also illustrated in Figure 7. In a Fe(CN)₆^{3-/4-} solution, under chopped illumination, the photocurrent at the n-Si/CuPc electrode rises rather slowly. Its limiting value is reached at large positive potentials (Figure 7a). When NaI is added to the medium, the curve becomes much steeper (Figure 7b). The magnitude of the limiting i_{ph} is only slightly affected, however, and is much smaller than that observed in the solution containing NaI alone (Figure 6c).

For all of the electrodes and solutions, i_{ph} was linearly related to the light intensity, at least up to 75 mW/cm² (Figure 8).

We also briefly investigated the effect of adding highly concentrated inert electrolyte (e.g., 11 M LiCl) to the solution. Under these conditions, the water activity is lowered significantly, and this has been shown to improve the stability of semiconductor electrodes.^{6,18} In such a solution (11 M LiCl/0.5 M LiI, pH 0), a stable photocurrent of 1 mA/cm² at n-Si/H₂Pc was observed for more than 1.3 h. However, slow photopassivation still occurred under these conditions, as shown by a slight shift of the i_{ph} -V wave toward more positive potentials.

Discussion

Charge Transport in (n-Si/Pc) System. Photoelectrochemistry for the n-Si/Pc/solution system involves a number of different processes: charge transport in n-Si, charge transfer at the n-Si/Pc interface, electron transfer reactions on any exposed silicon surface, charge transport through the Pc phase, charge transfer at the Pc/solution interface, and mass transport in the electrolyte solution.

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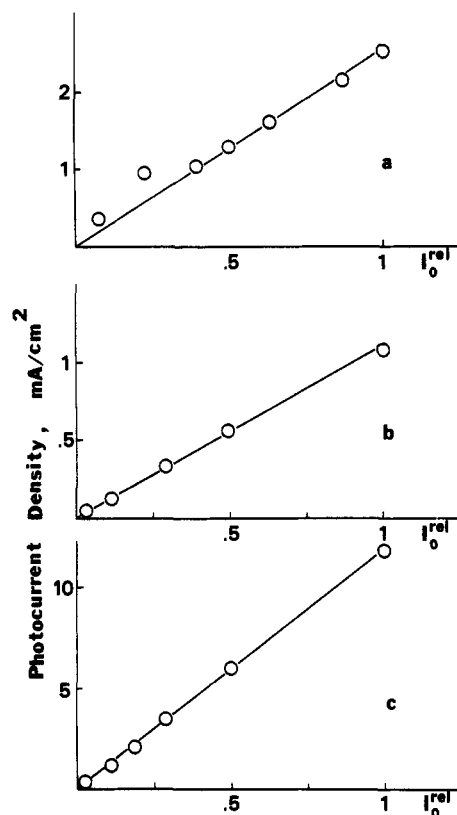


Figure 8. Light-intensity dependence of limiting photocurrents, with $I_0 \sim 70 \text{ mW/cm}^2$; (a) n-Si/H₂Pc (1000 Å) in 0.5 M I⁻/10⁻³ M I₂/11 M LiCl, pH 0; (b) n-Si/CuPc (800 Å) in 0.7 M K₄Fe(CN)₆/0.05 M K₃Fe(CN)₆; (c) n-Si/CuPc (800 Å) in 1 M NaI/10⁻³ I₂. Stirred conditions.

The movement of large ions, e.g., I⁻, through the thin Pc film is probably very slow. However, penetration by iodine can occur. Thus, in the experiment in which Fe(CN)₆^{3-/4-} and I⁻ are present simultaneously in the solution, the maximum photocurrent is only slightly changed because of the addition of iodide, this ion being oxidized slower at the CuPc interface (*vide infra*) and iodine being trapped by ferrocyanide. In the presence of I⁻ alone, however, the photocurrent is dramatically enhanced probably because of the induced doping by the photogenerated iodine. (Compare Figures 6c and 7). Charge transport in n-Si and the mass transfer in the electrolyte solution at high concentration of redox species are not the processes limiting the photocurrent since the i_{ph} observed with the filmed electrode is near that of a bare n-Si electrode before it is passivated.

Facile electron transfer reactions on Pc-coated metal electrodes and photosensitized redox reactions on Pc-coated semiconductor electrodes have been recently demonstrated.^{8,19} Photoexcitation of H₂Pc on WO₃ and TiO₂ results in a rapid oxidation of hydroquinone, ferrocyanide, and iodide, although the quantum efficiencies for these processes are extremely low.¹⁹ Slower kinetics is observed for the photooxidation of I⁻ than for hydroquinone at SnO₂/CuPc.²⁰ All of these examples demonstrate that holes generated either by photoexcitation or by charge injection from the substrate into the phthalocyanine film are able to oxidize suitable redox species.

The flat-band potential, V_{fb} , of the n-Si electrodes used in this study at pH 0 is -0.2 V vs. SCE. (The onset potential of the photocurrent of bare n-Si electrodes at pH 0 is -0.15 V vs. SCE). The valence band edge of n-Si is

thus more positive than the uppermost occupied energy levels of Pc used in this study.^{21,22} The photogenerated holes in n-Si are thus energetically sufficient to oxidize (or inject into) Pc. Thus, the charge transport through the organic phase and the effect of the Pc layer on the generation and recombination mechanisms of photogenerated charge carriers in n-Si seem to be the two most important limiting processes in determining the photovoltaic behavior of a (n-Si/Pc) system.

Undoped Pc Films. Without doping, Pc films usually show high resistivity.^{23,24} When a potential is applied to a n-Si/Pc electrode, a large portion of the potential drop is absorbed across the Pc film. This reduces the band bending and the thickness of depletion layer of n-Si and thus decreases the photoeffect. In the low-biasing potential region, the charge transport through the n-Si/Pc system would be limited by the resistance of the Pc thin film. As the electrode potential is made more positive, the light-limiting process takes over. This photovoltaic behavior is observed in the photooxidation of Fe(CN)₆⁴⁻, as shown in Figure 6a. Note that the limiting photocurrent for the oxidation of ferrocyanide on n-Si/CuPc electrodes is at least 1 order of magnitude lower than that for the photooxidation of iodide on the same electrode at the same light intensity or that for the photooxidation of Fe(CN)₆⁴⁻ on bare n-Si electrodes. This lower photoeffect is attributed to the enhanced recombination in the n-Si at the interface due to the impedance to the transport of holes away from the interface and through the thin Pc film. However, it is difficult to account for the linear dependence of this reduced limiting photocurrent on the light intensity (Figure 8b). Whether first-order surface recombination²⁵ at the n-Si/Pc interface becomes predominant here is not clear and requires further investigation.

The influence of the resistance of the Pc film on the rate of passivation of n-Si is also accommodated by this model. (Compare Figures 1 and 2). With the high-resistance film on the surface, the holes photogenerated in n-Si will accumulate at the n-Si/Pc interface and will oxidize the surface if water is present close to it. A scanning electron microscope study of the Pc thin films on n-Si electrodes does not reveal the presence of large cracks or defect structures. The films are homogeneous and are made up of small grain with 50–100-Å diameters. This finding is consistent with that reported by Faulkner *et al.*⁹ Water penetration might occur through the grain boundaries.

Iodine-Doped Pc Films. Evidence for significant improvement of the conductivities of various Pc materials by doping with iodine has been reported in a number of studies.^{14–17} Iodine penetration into the films described in this report is supported by the spectroscopic analysis of the CuPc layer treated with an I₃⁻/I⁻ solution or with I₂ vapor. Induced iodine doping of the Pc matrix results in a Pc film of higher conductivity as manifested by the steepness of the photovoltaic waves and higher limiting photocurrents (Figure 6c). The photovoltaic behavior cannot be attributed to the penetration of I⁻ through the Pc film, as suggested by the results shown in Figure 7. The highly conductive iodine-doped Pc films can remove photogenerated holes more rapidly from the silicon surface, as compared with an undoped film, and thus better stabilizes the n-Si. Furthermore, only a small

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potential drop in the film occurs, and this increases the band bending in the n-Si and eliminates the recombination, as compared to highly resistive films. Higher photocurrents and fill factors and a linear dependence of the limiting photocurrent on light intensity similar to that found with the bare electrode before passivation are expected in such a system. The greater improvement in stability when a concentrated electrolyte is used can be attributed to a decrease in water activity¹⁸ and a concomitant decrease in the rate of water penetration through the film.

Conclusion

At low light intensities, n-Si coated with H₂Pc or CuPc

behaves as a fairly stable photoanode, as previously reported. Excitation at higher light intensities (typical solar levels) leads to a rapid passivation by the reaction of the photogenerated holes and the small amounts of water that penetrate the film, even in the presence of a substance such as iodine which decreases the resistance of the film.

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Spectroscopic Studies of Dicyanohemin in Cationic Micelles

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The incorporation of low-spin iron(III) dicyanoporphyrin IX (dicyanohemin) into micelles of hexadecyltrimethylammonium bromide (CTABr) was studied by visible absorption spectroscopy, fluorescence, and ¹H and ¹³C NMR spectroscopy. Dicyanohemin interacts strongly with CTABr, forming especially stable premicellar aggregates when the dicyanohemin and CTABr concentrations are roughly comparable, even if the CTABr concentration is 2 orders of magnitude more dilute than the critical micelle concentration. The spectroscopic properties of the premicellar aggregate indicate porphyrin-porphyrin interaction within the complex. A more conventional dicyanohemin-micelle aggregate is observed at higher CTABr-to-dicyanohemin ratios. The spectroscopic properties of both types of aggregates can be rationalized in terms of possible structures.

The high-field NMR spectroscopy of paramagnetic metalloporphyrins in membranes or lipid bilayers has not been investigated. This is surprising in light of the importance of membrane-bound metalloporphyrins in electron transport and photosynthesis and the clear success of the use of NMR with paramagnetic proteins.¹ As in the case of proteins, a study of a model system containing many of the features of a metalloporphyrin-membrane complex is a necessary first step. We report here a study of paramagnetic low-spin iron(III) porphyrin complexes in a model membrane system, micelles of hexadecyltrimethylammonium bromide (CTABr). The hydrophobic interior of a micelle has been often likened to that of a lipid bilayer,² and considerable work on the interactions between small aromatic molecules and CTABr micelles as models of interactions within membranes has been reported.³⁻⁵ Some older work on the spectroscopic and chemical properties of hemin incorporated into micelles,^{6,7} including

one 60-MHz ¹H NMR study,⁸ has also been reported, but these earlier studies were handicapped by an inability to define the local environment of the hemin except in quite general terms.

In paramagnetic heme complexes, the unpaired spin of the iron perturbs the ¹H and ¹³C resonances of groups near the iron permitting the resolution of many of these peaks outside the often poorly resolved diamagnetic spectral region.¹ These hyperfine shifted resonances are exceptionally sensitive to the heme microenvironment.¹ The direct interaction of the metalloporphyrin with surfactant molecules alters the balance of forces within a micelle, provoking changes in micelle structure and properties. Hence, changes in the chemical shifts and the line widths of both heme and surfactant resonances as a function of heme-to-surfactant concentration ratio can be interpreted in terms of changes in heme ligation, solvation, and orientation in the micelle. Electronic spectra taken over the same concentration range further characterize the system. A detailed understanding of how guest molecules alter surfactant aggregation is necessary to the design of micelles

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