# Phthalocyanization of Cadmium Sulfide and Zinc Oxide. Effects on the Photochemistry in Aqueous Dispersion

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A novel method for the synthesis of metal phthalocyanines on inorganic semiconductive powders is described. Coverage roughly equivalent to a monolayer is achieved for cadmium phthalocyanine on CdS and zinc phthalocyanine on ZnO. This surface modification increases the quantum efficiency, $\Phi$, for $H_2O_2$ generation in CdPC/CdS up to a factor of 3 while reducing $\Phi$ by a factor of 2 in the ZnPC/ZnO. These results are discussed in relation to surface states and $O_2$ adsorption. In the donor-free cases, photodissolution is still observed with the phthalocyanized powders. Although the phthalocyanines do not sensitize $H_2O_2$ formation, ESR results reveal that charge transfer does occur between ZnPC and ZnO.

## Introduction

One of the major problems encountered upon illumination of n-type semiconductors in contact with solution is the oxidation of the semiconductor itself.[1-4] This photocorrosion causes the dissolution of the pigment and/or the creation of an insulating layer on the surface. Therefore, in most applications the problem of photooxidation must be overcome. Secondly, it is usually of benefit to maximize the overall quantum efficiency which combines the inherent hole/electron separation ability and the subsequent interfacial electron-transfer efficiency. Finally, many n-type semiconductors do not absorb in the desired spectral region and therefore sensitization to wavelengths greater than the band-gap wavelength is desired. One method of dealing with these issues is through surface modification or derivatization of the semiconductor itself.[5-8] We have employed the technique of surface modification in a study of the photochemistry of pigment powders dispersed in liquid media. Adsorption of charged surfactants was found to have a profound effect on $H_2O_2$ photoformation using metal-free phthalocyanines.[9,10] Platinization of CdS increased the rate of $O_2$ uptake by 1 order of magnitude in aqueous dispersion[11] in addition to giving rise to an independent hydrogen-production reaction.[11-13] This work details our efforts at the synthetic deposition of metal phthalocyanine layers on inorganic semiconductor powders and the effect that this modification produces in the photochemistry.

Uchida et al.[14] in 1977 coated ZnO powder through evaporation of tetrahydrofuran solutions of various phthalocyanines (PC). Their results, which were based on the photooxidation of 2-propanol, suggested that the oxidation potential of the adsorbed PC determines the rate of oxidation. McGregor et al.[15] in 1978 reported that deposition of a monolayer of ZnPC on a sintered polycrystalline ZnO electrode essentially precludes photodissolution. Fan and Bard[16] deposited $H_2Pc$ on $TiO_2$ powder and demonstrated that sensitization of the oxidation of hydroquinone could be accomplished with this system. These studies were extended[17] to photoelectrochemical cells using a variety of semiconductors coated with relatively thick layers of $H_2Pc$. Anodic photocurrents were consistent with sensitization of the n-type semiconductors.

There has been considerable interest in the utilization of powders for solar energy utilization.[7,18-22] Our efforts have been directed toward a basic understanding of pigment photochemistry in dispersion and the changes which occur with surface modification. This present work describes a novel method of coating powders of inorganic semiconductors with phthalocyanine and the characterization of the resultant coated pigments.[23] The role that phthalocyanization plays in quantum efficiency, photodissolution, and sensitization will be discussed.

## Experimental Section

CdS (Fisher) and ZnO (Alpha Products) were used as received. The water used in these experiments was purified and deionized by passage through a series of Millipore filters. A BET surface area determination by Robert Nash (Webster Research Center, New York) revealed that CdS has a surface area of $\sim 5$ m$^2$/g whereas the ZnO surface area was $\sim 2$ m$^2$/g.

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The synthesis of phthalocyanine was accomplished by condensation of phthalonitrile.

phthalonitrile

metal phthalocyanine
M = Cd or Zn
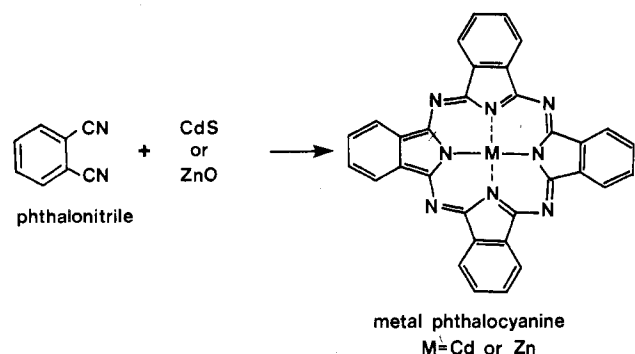
Three separate reactions were used to coat the inorganic semiconductor with PC. In the first case, the pigment was dispersed in a solution of phthalonitrile in 2-(dimethyl-amino)ethanol and the mixture was warmed to reflux at about 140 °C. While this resulted in a rapid coating of the pigment with phthalocyanine, it also resulted in the in-dependent formation of metal-free phthalocyanine, which was observed under a microscope as small needle crystals. The separation of the two powders is very difficult.

In a second method phthalonitrile (mp 140 °C) was heated to 220 °C in Soltrol 220 (bp 260 °C; a low na-phthanic hydrocarbon solvent available from Philips Pe-troleum Co.). Addition of pigment to the resultant emulsion gave coated material after 30–60 min.

A third method, which avoids the complication of sol-vent, simply involves dispersing the pigment in molten phthalonitrile at 220 °C. Under these conditions, the particles become colored after several minutes although the reaction was generally allowed to continue for up to 30 min. The particles used in this study were synthesized by this method.

In all cases the phthalocyanized pigment was isolated by filtration of the dispersions through a sintered glass funnel and thoroughly washed with acetone.

For the oxygen-uptake studies a YSI Model 53 oxygen monitor was used and has been previously described.[24] ESR experiments utilized a Varian E109E spectrometer interfaced with a Nicolet 1180 computer. The light source used for the ESR experiments was an Oriel Model 6107 Universal arc lamp source with an Oriel 150-W xenon lamp (Model 6253).

Ionic conductivity was measured with a Radiometer CDM3 conductivity meter. The dip cell was immersed in the dispersion contained in the solution holder of the YSI Model 53 $O_2$ monitor system. The ensured experimental conditions identical with those for the oxygen-uptake measurements. For the detection of $Cd^{2+}$ and $Zn^{2+}$ in solution, a spectrametrics, Inc. (SMI), plasma emission instrument was employed. The samples were illuminated again within the YSI Model 53 $O_2$ monitor for 60 min under $O_2$ purging. The dispersion was then centrifuged and the supernatant was evaluated for $Cd^{2+}$ or $Zn^{2+}$ by comparison to a standard set of solutions.

## Results and Discussion

*Characterization of the Phthalocyanized Powders.* CdPC powder exhibits an intense ESR signal with $\Delta H_{pp}$ of 2.7 G and a $g$ factor of 2.0025 ± 0.0003. The CdS powder which had been surface treated in the presence of phthalonitrile also exhibited an intense ESR signal with the same $g$ factor and only a slightly narrower $\Delta H_{pp}$ of 2.0
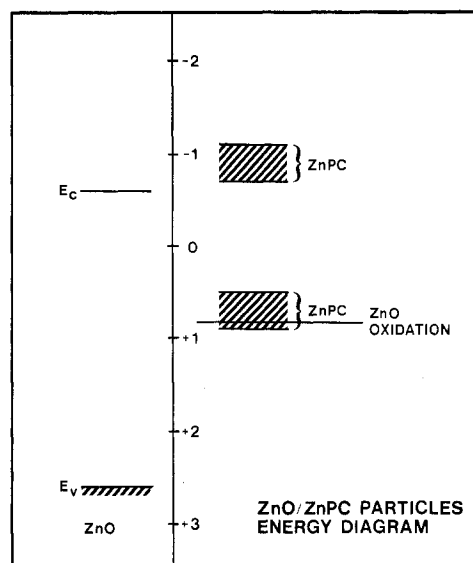


**Figure 1.** Energy-level diagram for ZnO and ZnPC. The bands for ZnPC result from an uncertainty in their position.
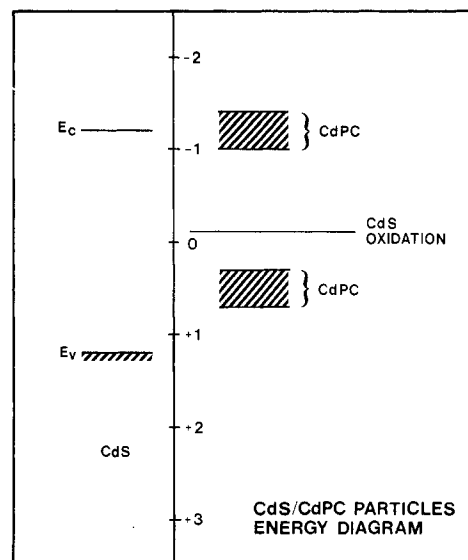


**Figure 2.** Energy-level diagram for CdS and CdPC. The bands for CdPC result from an uncertainty in their position.

G. This close correspondence strongly suggests that CdPC is present in this system with the minor difference in $\Delta H_{pp}$ attributable to a difference in a bulk vs. surface environ-ment.

A quantitative study revealed that approximately 1 out of every 25 CdPC surface molecules (see below) is giving rise to the observed paramagnetism. The origin of this signal is unknown but, from studies on metal-free sys-tems,[25] it is likely that it arises from either oxidized (radical cation) or reduced (radical anion) CdPC molecules or clusters of molecules. This suggests that charged sites are present for the adsorption of ionic solutes, an issue which will be addressed below. With the surface-treated ZnO, only a very small dark ESR signal is observed ($\Delta H_{pp}$ = 5.4 G and $g$ = 2.0025) which nevertheless is identical with that signal observed with ZnPC powder. Hence, ESR provides a surface characterization suggesting the presence of CdPC on CdS and ZnPC on ZnO.

It is interesting to consider why the CdPC on CdS (CdPC/CdS) should exhibit such an intense ESR signal

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(25) Harbour, J. R.; Loutfy, R. O. *J. Phys. Chem. Solids* **1982**, *43*, 513.
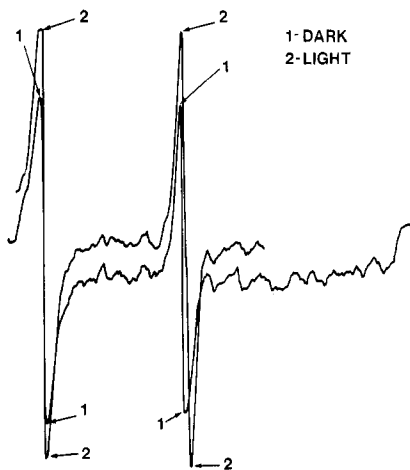
**Figure 3.** ESR spectra for ZnPC/ZnO powder both in the dark and after illumination.

relative to ZnPC on ZnO (ZnPC/ZnO). Comparisons of the band edges of the semiconductor with the redox levels of the corresponding metal PC's are shown in Figures 1 and 2. From these diagrams it can be observed that electron transfer from $E_c$ of CdS to CdPC appears feasible whereas the equivalent reaction in ZnPC/ZnO is not possible.[26,27] Hence, in CdS, a photon with $E \geq E_{BG}$ will create hole/electron pairs, the mobile electron of which can reduce a surface CdPC and the hole of which can oxidize a spatially separated CdPC surface molecule. This process would eventually saturate as the number of available sites fill up from the ambient light during or subsequent to the synthesis. Therefore, with CdPC/CdS both radical anions and cations are present at a concentration of ~4% of the total surface molecules. Finally, illumination of the CdPC/CdS powder did not result in any apparent change in the radical concentration. This can be contrasted with ZnPC/ZnO where illumination with red light resulted in an increase in both the ZnPC and ZnO ESR signals (Figure 3). Although this will be mentioned again during discussion of sensitization, this process demonstrates that the ZnPC is intimately associated with the ZnO and is consistent with a surface species. It is also consistent with the energy diagrams of Figures 1 and 2 in which a photon absorbed by the ZnPC can eventuate in the transfer of an electron to the $E_c$ of ZnO whereas this process is not allowed with CdPC/CdS.

The ZnPC/ZnO powder is light blue whereas the CdPC/CdS pigment appears yellowish green. With these particles made from the neat phthalonitrile method, there appears to be no independent $H_2Pc$ particles created as deduced through settling experiments ($\rho_{ZnO} = 5.6$; $\rho_{PC} \simeq 1.6$). This also suggests that the PC formation occurs on the surface of the inorganic semiconductive particles. When these pigments were stirred in DMF, the solutions developed a blue color. The optical spectra of these solutions obtained after centrifugation proved to be identical with those for CdPC and ZnPC. The pigments revealed, after thorough extraction with hot DMF, the characteristic white of ZnO and yellow of CdS. This implies that essentially all of the PC which was created was in the form of the metal PC and that no $H_2PC$ was formed ($H_2PC$ is insoluble in DMF). The fact that the metal PC's are extractable with a solubilizing solvent suggests that the bonding is most likely one of relatively strong adsorption.

Since the metal PC's are not soluble in $H_2O$, the composite particles are stable in this medium.

Through exhaustive extraction of the PC in large volumes of DMF, it was determined optically that 0.4% of ZnPC/ZnO is ZnPC and that 2.4% of CdPC/CdS is due to CdPC. Using the measured surface areas of these pigments and assuming a planar PC molecule tangential to the surface and occupying 100 $\text{Å}^2$ per molecule, these values correspond to ~2 monolayers of ZnPC on ZnO and ~4 monolayers of CdPC on CdS. In spite of the fact that these are rather rough estimates, it can be concluded that these values support a surface modification at ~ the monolayer level.

**Effects on the Photochemistry**

As mentioned earlier, McGregor et al.[15] reported that a monolayer of ZnPC on a sintered polycrystalline ZnO electrode prevented photodissolution of the ZnO as the photoanode in a photoelectrochemical cell. Hence, it was one of the goals of this work to determine whether or not our surface-modified ZnO and CdS also exhibited protection against photodissolution. The oxidation of the semiconductors has been shown to occur as represented in eq 1 and 2.[27] Equation 1 occurs in photoelectrochemical

$$2ZnO + 2H_2O + 4h^+ \rightleftharpoons 2Zn(OH)_2 + O_2 + 4H^+ \quad (1)$$

$$CdS + 2H^+ \rightarrow Cd^{2+} + S \quad (2)$$
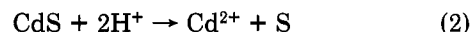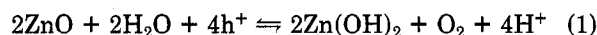
cells under anodic bias such that the electrons are driven through the circuit to the cathode. In dispersion, both the electrons and holes remain near the surface such that $O_2$, if produced by the photodissolution, would be rapidly reduced to $H_2O_2$. In fact, results from a previous study revealed the photoformation of ·OH radicals but no direct confirmation of $O_2$ production in dispersion. Also the reduction of $O_2$ to $H_2O_2$ is a two-electron process whereas the oxidation of ZnO to $O_2$ is a four-electron process. In the event that $O_2$ were produced in dispersion, the uptake would exceed evolution by a factor of 2. Hence, the $O_2$ monitoring experiments reported below always correspond to an uptake of $O_2$.

Illumination of the uncoated pigment dispersions in the absence of an added donor should therefore result in an increase in the ionic conductivity ($\rho$) of the solution as well as reveal the presence of either $Zn^{2+}$ or $Cd^{2+}$ ions in solution. We therefore monitored both the $\rho$ and the $M^{2+}$ concentration for the uncoated and coated pigments to determine whether or not photodissolution was prevented by phthalocyanization. For the unreacted pigments $\rho$ was found to remain essentially constant under illumination for $N_2$-purged dispersions of either CdS or ZnO. This is consistent with a rapid hole/electron recombination as the major process since there is no acceptor ($O_2$) to remove the electrons and thereby allow oxidation to occur. However, in $O_2$-purged samples, a marked increase in the conductivity was observed under illumination for both CdS and ZnO dispersions reflective of the photodissolution. When the phthalocyanized pigments were used, the $\sigma$ increased at rates faster than for their uncoated counterparts (Figures 4 and 5). This suggests that photodissolution has not been prevented by this particular surface modification of these powders.

This contention is supported by the results obtained by plasma emission which reveal that $Cd^{2+}$ ions[28] are produced to essentially the same extent (Table I) for both CdS and CdPC/CdS (after 1 h of illumination). With ZnPC/ZnO

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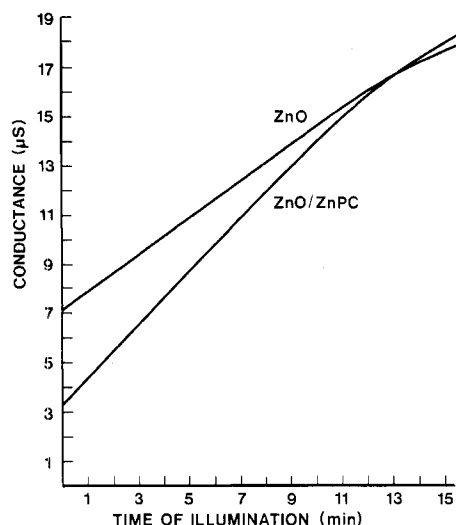(28) Frank, A. J.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 1933.

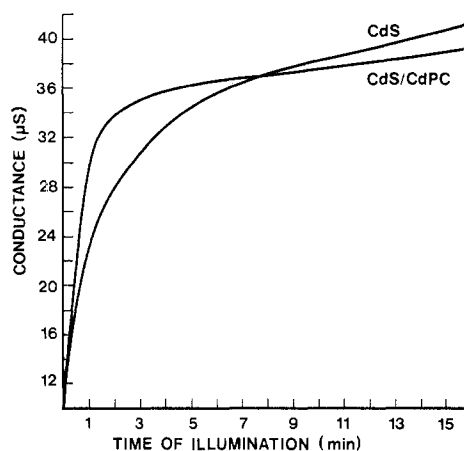**Figure 4.** Ionic conductivity of ZnO and ZnPC/ZnO dispersions as a function of time of illumination.



**Figure 5.** Ionic conductivity of CdS and CdPC/CdS dispersions as a function of time of illumination.

TABLE I:  Plasma Emission[a] and $SO_4^{2-}$ Analysis Results

| pigment system | [ion],[c] % | $[SO_4^{2-}]$, % |
|---|---|---|
| CdS | 4.5 ($Cd^{2+}$) | 0.6 |
| CdS/formate[b] | 0.02 ($Cd^{2+}$) | |
| CdPC/CdS | 6.0 ($Cd^{2+}$) | 0.6 |
| CdPC/CdS/formate[b] | 0.03 ($Cd^{2+}$) | |
| ZnO | 0.1 ($Zn^{2+}$) | |
| ZnO/formate[b] | 0.03 ($Zn^{2+}$) | |
| ZnPC/ZnO | 0.6 ($Zn^{2+}$) | |
| ZnPC/ZnO/formate[b] | 0.04 ($Zn^{2+}$) | |

[a] Results obtained after 0.1 g of pigment in 10 mL of $H_2O$ was illuminated for 60 min with $O_2$ purging. [b] Formate concentration was 0.1 M.  [c] Ion concentration in solution.

the amount of $Zn^{2+}$ ions produced is greater than for ZnO alone. This will be discussed below. Finally, a chemical determination of $SO_4^{2-}$ (ref 29) demonstrates that this species is also formed in both CdS and CdPC/CdS to roughly the same extent but to a concentration only 12% that of $Cd^{2+}$. The remaining 88% can be accounted for in the production of elemental sulfur (eq 2).

For systems containing formate, photodissolution is, under these conditions, essentially precluded as there is no increase in either $Cd^{2+}$, $Zn^{2+}$, or $SO_4^{2-}$ species. These

TABLE II:  $O_2$ Uptake and Conversion Ratio[a] Results

| pigment system | $O_2$ uptake, % $O_2$/min | CR[a] |
|---|---|---|
| ZnO | 17 | 0.56 |
| ZnO/formate[b] | 55 | 0.91 |
| ZnPC/ZnO | 13 | 0.57 |
| ZnPC/ZnO/formate[b] | 26 | 0.89 |
| CdS | 49 | 0.35 |
| CdS/formate[b] | 72 | 0.82 |
| CdPC/CdS | 104 | 0.40 |
| CdPC/CdS/formate[b] | 198 | 0.90 |

[a] Conversion ratio (CR) is the percentage of $O_2$ converted to $H_2O_2$.  [b] Formate concentration was 0.1 M.
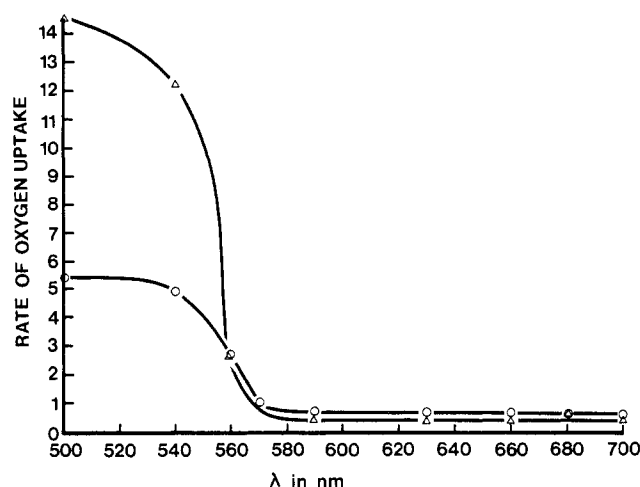


**Figure 6.** Action spectrum for the production of $H_2O_2$ using CdS (O) and CdPC/CdS (△) dispersions of 0.1 M formate.

results can be explained by the fact that the rate constant for formate oxidation is fast compared to the rate constant of self-oxidation.

The effect of phthalocyanization on the photoactivity of these pigments can be determined by monitoring the rate of $H_2O_2$ produced upon illumination of the dispersion. This was accomplished by using an $O_2$ electrode which continuously monitors the $O_2$ concentration of the dispersion. Results of these experiments are shown in Table II for both donor-free and formate conditions. In both cases similar results were obtained. For ZnPC/ZnO, the rate of $H_2O_2$ production is reduced 1.5–2 times compared to ZnO. However, for CdPC/CdS, the rate of $H_2O_2$ formation increased between 2 and 3 times over that of CdS alone. These results demonstrate that surface modification is playing a significant role in the $\Phi$ of $H_2O_2$ production ($\Phi(H_2O_2)$).

The decrease in $\Phi(H_2O_2)$ for ZnPC/ZnO seems in contradiction to the $\sigma$ data in Figure 4 and the $Zn^{2+}$ ion concentrations shown in Table I. However, it is known that $Zn^{2+}$ formed during photodissolution complex with $OH^-$ and establish an adsorption equilibrium on the ZnO surface.[30] Hence, even though $Zn^{2+}$ may be produced to a greater extent with ZnO, the adsorption of the complexes lowers the solution concentration. With ZnPC/ZnO the surface may not adsorb the complexes as readily and thereby give the impression of higher conductivity and $Zn^{2+}$ ion concentrations. Finally, the $Zn^{2+}$ concentration was determined at one point only (60 min) which is not directly comparable with either the $O_2$-uptake rate or the change in $\sigma$. It may also be pointed out that the conductivity and $Zn^{2+}$ or $Cd^{2+}$ concentration determinations

(29) Vogel, "Quantitative Inorganic Analysis", 3rd ed., Longman, New York, p 806.

(30) Dixon D. R.; Healy, T. W. *Aust. J. Chem.* 1971, *24*, 1193.

were useful mainly for the donor-free cases whereas the $O_2$-uptake data were consistent for both donor-free and formate cases.

This production of $H_2O_2$ from $O_2$ and sodium formate was not sensitized by either the ZnPC- nor the CdPC-coated pigments. The action spectra for the CdS and CdPC/CdS powders are shown in Figure 6. This may not be surprising given the low absorption by the PC. However, it has been shown[16,17] that phthalocyanized $TiO_2$ (which contains many layers of PC) does exhibit sensitization for the oxidation of the supersensitizer, hydroquinone ($H_2Q$) when $TiO_2$ is the photoanode in a PEC cell. This sensitization occurred with a $\Phi$ of only *0.1%* compared to the data in Figure 6, which represents a $\Phi(H_2O_2)$ approaching 0.5 for the CdPC/CdS system with formate. Hence, we would be unable to observe this level of sensitization using our system. Nevertheless, we attempted to observe sensitization with $H_2Q$, but these experiments demonstrated that $H_2Q$ was not an effective donor in these powder systems.

Although there was no evidence of sensitization for the $O_2$ reduction system, there is evidence for a photoinduced charge exchange in the ZnPC/ZnO powder (Figure 3). It has been known for some time that direct band-gap excitation of ZnO results in an increase in the ESR signal(s) at $g = 1.96$.[31-33] In the present system irradiation with light with $\lambda > 550$ nm also resulted in an increase in the $g = 1.96$ signal along with concomitant increase in the $g = 2.0025$ signal of ZnPC itself. Although the details of this work will form the basis of a separate report, this observation reveals that charge exchange between the surface-bound ZnPC and the bands of ZnO does occur. This is consistent with the band picture shown in Figure 2, in which an electron promoted to the excited state of ZnPC can transfer to the conduction band of ZnO. For the CdPC/CdS system this transfer is not allowed (Figure 3) and not experimentally observed.

The ability to control the $\Phi$ of semiconductive powders is fundamental to their usage in solar energy and electrophotographic systems.[34] In the present system there are two major factors which control the $\Phi$ once hole/electron separation has occurred. The first is the hole/electron recombination rate which is affected by the presence of surface states and which can be significantly enhanced by deep states (close to the midgap).[6,35] The other major factor which comes into play is the adsorption ability of the surface for both donors and acceptors. A donor molecule adsorbed on the surface can more effectively compete for the photogenerated holes before they recombine and similarly an adsorbed acceptor can react with generated electrons. The phthalocyanization of the surfaces of ZnO and CdS most likely affects both of these factors.

In ZnPC/ZnO we have reduced $\Phi(H_2O_2)$ for both the donor-free and formate cases by $\sim$1.5–2 times. The presence of a ZnPC band near the midgap may introduce a deep state which enhances hole/electron recombination. The fact that this reduction in $\Phi$ is observed for both the formate and donor-free cases suggests that donor adsorption is not playing a role here. However, this surface modification could alter $O_2$ adsorption and reduce the $\Phi(H_2O_2)$. The reduction of $O_2$ to $H_2O_2$ is a two-electron reduction which is thought to occur on the surface and therefore one must be concerned with adsorption of not only $O_2$ but also $O_2^-$ ($HO_2$), $HO_2^-$ ($H_2O_2$) and the kinetics of these adsorptions. For CdPC/CdS, the rates of $H_2O_2$ production are increased between 2 and 3 times for both the formate and donor-free cases. In this case the CdPC could either remove deep surface states and/or enhance the adsorption phenomena for reduction.

## Conclusions

It has been demonstrated that the inorganic semiconductor powders, CdS and ZnO, can be surface modified through the synthetic formation of metal PC's on the surface (phthalocyanization). CdPC is created on CdS while ZnPC is made on ZnO with approximately monolayer coverage. These PC's can be extracted with DMF, suggesting that the bonding is most likely one of strong adsorption. This phthalocyanization plays a significant role in the $\Phi(H_2O_2)$ with an increase of up to 3 times in the CdPC/CdS powder and a decrease by a factor of 2 in the ZnPC/ZnO powder. The changes can be accounted for in CdPC/CdS by the removal of deep traps and/or an enhancement in the adsorption process responsible for the reduction of $O_2$ to $H_2O_2$. In ZnPC/ZnO, the ZnPC can introduce deep traps and/or $O_2$ adsorption may be reduced. Although no sensitization of the reduction of $O_2$ to $H_2O_2$ by formate is observed, there is a photoinduced electron transfer between ZnPC and ZnO in that system. Surprisingly, the phthalocyanized pigments undergo photodissolution in the absence of formate. These results suggest that phthalocyanization can control certain properties of the semiconductive powders and that other novel methods of surface modification may provide for the control of the photoproperties of pigments.

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