Dye Photooxidation at Semiconductor Electrodes: A Corollary to Spectral Sensitization in Photography

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The silver halide grains used in photographic films are composed of selected mixtures of AgI, AgBr, and AgCl (1). These solids have band gaps which range from 2.7 to 3.2 eV and are, therefore, insensitive to light in the visible region of the spectrum. Alone, they cannot be used to produce a clear and useful photographic image. Consequently, they must be sensitized to radiation in this region through the use of dyes which are adsorbed to the silver halide crystals in the film. It is this layer of adsorbed dye which "sees" the light incident on the film in a camera.

When these dyes absorb light, they can inject an electron into the substrate silver halide, an event which eventually produces a latent image center on the surface of the grain. This center can be chemically reduced by developing agents to give us the picture we expect when we push the shutter release on a camera. The primary processes in the dye sensitization of silver halides through electron transfer are shown in Figure 1 by a simple energy level diagram. An electron in the excited state energy level $E^\circ_{D^*_{don}}$ of a dye is transferred to the conduction band of the silver halide which has a band edge at energy E_c. This electron is trapped at the surface or in the bulk by an Ag^+ ion which reacts further with other Ag^+ ions to yield the latent image center.

The basic processes involved in this spectral sensitization of silver halides can be investigated simply and directly using
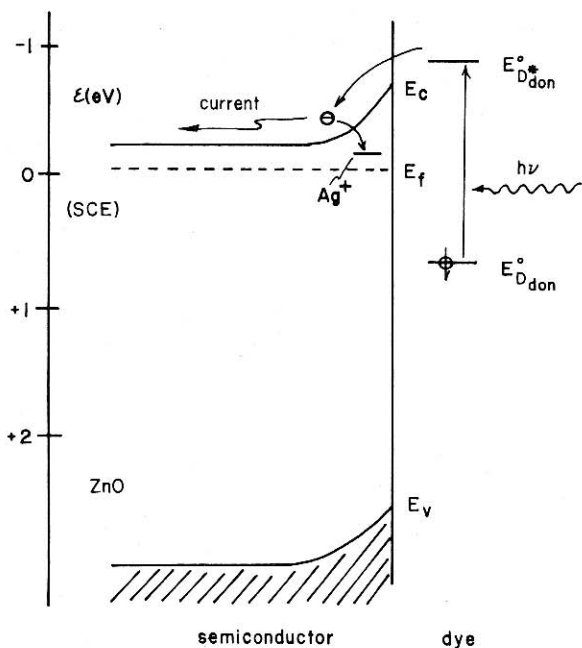

Figure 1. Electron transfer from an excited sensitizing dye to semiconducting silver halides is depicted here in an energy level diagram. An electron is promoted to an energy level $E^\circ_{D^*_{don}}$ through absorption of a photon by the dye. This electron can be transferred to the semiconductor where it is trapped by Ag^+ ions to initiate latent image formation. This same diagram can be used to describe dye sensitization in a photoelectrochemical system where an eletrochemical energy scale is used on the left. In this case a positive bias on the semiconductor draws electrons away from the surface to be measured as current.
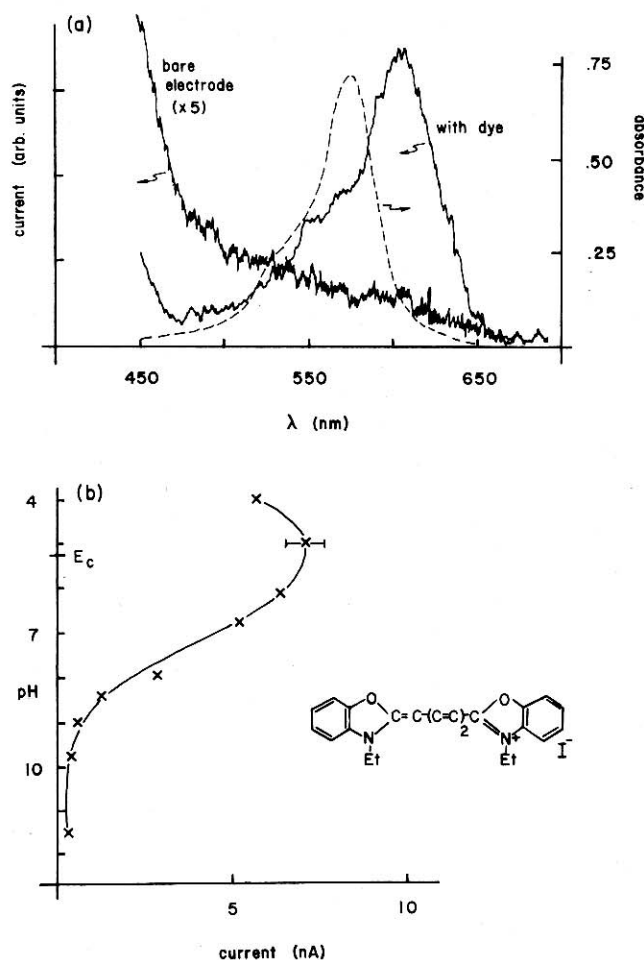
photoelectrochemical techniques. This can be seen through examination of the electrochemical research that has been done in the dye sensitization of wide band gap semiconductors such as ZnO, TiO₂, and SrTiO, (2–12). These investigations have employed single crystals of these compounds as anodes in electrochemical cells in which the sensitizing dye is present in the electrolyte. From solution the dye adsorbs onto the electrode surface. With a bias on the electrode that is sufficiently positive, the electron injected by an excited dye into the semiconductor can be drawn off as a current which is easily measured. This is also depicted in Figure 1.

Photoelectrochemical data will be presented here to reveal how the use of sensitizing dyes extends the spectral range to which the substrate semiconductor is sensitive. They demonstrate that specific energetic requirements exist for a dye to be an effective sensitizer. By increasing the surface concentration of the dye it will also be seen how photooxidation can be increased, and how aggregate formation on the surface can change the spectral response and sensitizing efficiency of the adsorbed dye layer.

The Effects of Sensitizing Dyes

In an electrochemical cell the current produced by an adsorbed dye varies with the wavelength of the incident light and can be shown to extend the spectral sensitivity of the semiconductor into the visible region (7, 8). In Figure 2a the photocurrent produced by a cyanine dye adsorbed onto a SrTiO₃ electrode is contrasted with the electrode response without the dye. This photocurrent action spectrum is also compared with a solution spectrum of the dye. The presence of the dye increases the sensitivity of the SrTiO₃ system to light at 590 nm by a hundredfold, yet still retains the spectral characteristics of the monomeric form of the dye in solution. There is also a slight red shift of the action spectrum from the solution spectrum of the dye which is generally attributed to the higher polarizability of the semiconductor to which the dye is adsorbed (7, 8).

Extensive investigations in photographic research have demonstrated that an empirical correlation exists between the reduction potential of a dye and its ability to sensitize silver halides (1). There is a threshold for reduction potentials: a dye with a reduction potential more positive than the cut-off is not able to sensitize.

A threshold for sensitization of photocurrent can also be demonstrated electrochemically. From Figure 1 it is evident that there is an energetic requirement for the electron-transfer process. $E^\circ_{D^*_{don}}$ must be more negative than E_c for oxidation to occur. The energy level E_c of SrTiO₃ can be moved with respect to $E^\circ_{D^*_{don}}$ through a change in pH of the electrolyte (4). As the pH increases, the electrode adsorbs OH⁻ ions and becomes a less attractive acceptor for electrons as E_c shifts negative of $E^\circ_{D^*_{don}}$. The resultant tenfold change in current is shown in Figure 2b as this threshold is crossed.

To improve the sensitivity of a film to visible light it is possible to increase the amount of dye on the semiconductor surface. In an electrochemical system this can be accomplished through an increase in the concentration of dye in the electrolyte.

Figure 2. (a) The photocurrent produced by the dye 3,3'-diethyloxadicarbocyanine adsorbed on $SrTiO_3$ single crystal electrodes is many times greater than the bare electrode. The spectrum of the dye as monomer in the electrolyte is represented by the dashed curve. The concentration shown here is 3.4×10^{-6} M. (b) The maximum photocurrent of this dye at 610 nm is plotted as a function of pH; a change in pH shifts the relative energies of E_c and $E^{\circ}_{D^*_{don}}$ by 60 mV per pH unit. If E_c of $SrTiO_3$ is perceived as being fixed at the energy represented by pH 5.2, the photocurrent produced by the dye falls dramatically as $E^{\circ}_{D^*_{don}}$ drops below E_c.

Figure 3. (a) The photocurrent action spectrum for the dye 3,3'-diethylthiacarbocyanine at TiO_2 is shown as its concentration in the electrolyte is increased from (1) 3.6×10^{-7} M to (11) 2.9×10^{-6} M to (111) 7.4×10^{-6} M. Note the appearance of a blue shifted peak attributed to an H band aggregate. An absorption spectrum of the monomer dye is given as a dashed curve. (b) The photocurrent action spectrum for the dye 1,1' diethyl-2,2' cyanine at ZnO is shown at concentrations of (1) 4.0×10^{-5} M, 0.1 M KCl (11) 5.8×10^{-4} M, 0.1 M KCl (111) 2.85×10^{-5} M, 1.0 M KCl. Note the appearance of a red shifted peak attributed to a J band aggregate. An absorption spectrum of the monomer dye is given as a dashed curve.

An equilibrium exists between the dye in solution and the dye adsorbed on the surface; it has been shown that adsorption isotherms can be established for these electrochemical systems (7, 8). For dyes which adsorb as monomers, such as rhodamine B or rose bengal, a Langmuir-type isotherm is observed with single crystal electrodes. The heats of adsorption are low, about 7–8 kcal mol^{-1} so that dimerization and aggregation of the adsorbed dye can become significant if the free energy of formation approaches 5–7 kcal mol^{-1}.

The result of such an increase in solution concentration is shown in Figure 3a and 3b for two different cyanine dyes as their concentration in the electrolyte is increased from 1×10^{-6} M to 5×10^{-5} M. Both dyes are planar; so at low concentrations they adsorb flat on the surface of the electrode. However, as more dye adsorbs, the molecules tend to stand on edge and form aggregates with neighboring molecules. The photocurrent response of these dyes differs greatly as they pass from monomeric photocurrent production at low concentration to aggregate sensitized current at higher dye concentration.

Initially, the photocurrent increases as more dye adsorbs although more sophisticated experiments using internal reflection techniques (10, 12) have shown that this increase is not necessarily in direct proportion to the amount of adsorbed dye. At high dye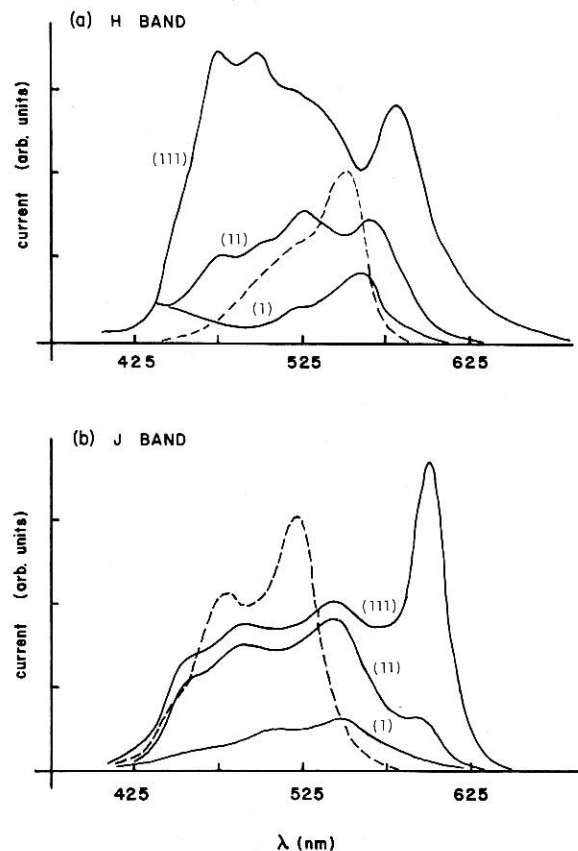 concentrations, however, the action spectra reveal formation of aggregates on the surface. In Figure 3a, photocurrent is produced by a broad band which is blue-shifted from the monomer absorption of the dye. This current can be attributed to an H band aggregate. In Figure 3b, a narrower, red-shifted photocurrent peak is observed which is induced by a J band aggregate. These distinct and different spectral responses result from the different structure of the aggregates formed by these dyes. Dyes forming H band aggregates are thought to adsorb on the surface like a deck of playing cards on its side, whereas J band aggregates are composed of a brickwork or herringbone arrangement of the monomer units (1). The aggregate which is formed by a dye depends on its structure; if steric hindrance precludes an ordered stacking of the adsorbed dye, then a staggered J band structure is assumed. In this way the highest surface concentration of a dye can be attained with retention of distinct and well-defined spectral characteristics.

Dye Efficiencies

In some cases the J-band aggregate is found to be a much more efficient sensitizer than the H band aggregate or monomer dye (13). It has been reported to have an efficiency for photocurrent production of 50–100% in contrast to the 1–5% of the monomer; internal reflection measurements are also consistent with the conclusion that the mechanism for current production of aggregates may be different than that of the monomers (12).

In both photographic and electrochemical systems, these

efficiencies can be increased to almost 100% through adsorption of other molecules with the dye on the surface of the electrode (*1, 14–16*). This process is known as *supersensitization* and these special molecules are known as *supersensitizers*. These supersensitizing agents can heighten sensitization through several mechanisms, the most obvious of which is the reduction of the excited dye before it is quenched by reactions which compete with its oxidation. In photoelectrochemical systems, supersensitization can be seen through the addition of a reducing agent such as hydroquinone to the electrolyte. In most cases the photocurrent will show an immediate increase and remain at that level until the reductant is exhausted. It is not yet clear whether this effect can be attributed to the photoreduction of the adsorbed dye or to a simple reduction of the oxidized dye on the surface to regenerate the photoactive species on the surface (*17*).

Differences Between Photographic and Sensitized Photoelectrical Systems

There are many significant differences between photographic and sensitized photoelectrochemical systems. The dye-covered silver halides in films are multifaceted grains of micron size which are suspended in a colloidal matrix. The adsorbed dyes are surrounded by this semi-solid environment which differs greatly from the electrolytes used in electrochemical systems. Therefore, there are limitations to the carry-over of models from one system to the other. However, the data presented above demonstrate that the characteristics of many aspects of photographic sensitization can be explored using photoelectrochemical techniques.

Literature Cited

(1) James, T. H., "The Theory of the Photographic Process," 4th Ed., Macmillan, New York, 1977, and references therein. (This is the most informative single source of technical information about the photographic process that is in print.)
(2) Gerischer, H., and Willig, F., *in* "Topics in Current Chemistry," Davison, A., (*Editor*); Springer, New York, 1976, Vol. 61, p. 31.
(3) Gerischer, H., *Photochem. Photobio.*, 16, 243 (1972).
(4) Gerischer, H., *in* "Physical Chemistry, An Advanced Treatise," Vol. IXA, Eyring, H., (*Editor*), Academic Press, New York, 1970.
(5) Memming, R., *Photochem. Photobio.*, 16, 325 (1972).
(6) Arden, W., Fromherz, P., *J. Electrochem. Soc.*, 127, 370 (1980).
(7) Spitler, M. T., and Calvin, M., *J. Chem. Phys.*, 66, 4294 (1977).
(8) Spitler, M. T., and Calvin, M., *J. Chem. Phys.*, 67, 5193 (1977).
(9) Schumaker, R., Wilson, R. H., and Harris, L. A., *J. Electrochem. Soc.*, 127, 96 (1980).
(10) Spitler, M., Lubke, M., and Gerischer, H., *Ber. Bunsenges. Phys. Chem.*, 83, 663 (1979).
(11) Tributsch, H., and Calvin, M., *Photochem. Photobio.*, 14, 95 (1971).
(12) Spitler, M., *in* "Photoelectrochemistry: Fundamental Processes and Measurement Techniques," Wallace, W., Nozik, A., Deb, S., (*Editors*), Electrochemical Society, Princeton, 1982, p. 282.
(13) Hada, H., Yonezawa, Y., and Inaba, H., *Ber. Bunsenges. Phys. Chem.*, 85, 425 (1981).
(14) Bode, V., and Hauffe, K., *J. Electrochem. Soc.*, 125, 51 (1978).
(15) Fujishima, A., Iwase, T., and Honda, K., *J. Amer. Chem. Soc.*, 98, 1625 (1976).
(16) Watanabe, T., Nakao, M., Fujishima, A., and Honda, K., *Ber. Bunsenges. Phys. Chem.*, 84, 74 (1980).
(17) Nasielski, J., Kirsche-De Mesmaeker, A., and Leempoel, P., *Electrochim. Acta*, 23, 605 (1978).