Photoelectrochemical Effects in the Electrolyte–Pigment–Metal System

II. Metal-Free Phthalocyanine Film Action Spectra of Short-Circuit Photocurrents with Increase of the Film Thickness

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Abstract

The electrolyte–pigment–metal system can be described as analogous to a photosensitive junction region. When the thickness of the pigment film is increased, the action spectra of the maximum short-circuit photocurrent under continuous illumination differ from the absorption spectra both in direct illumination (pigment–electrolyte) and in back illumination (metal–pigment). One is led to believe that there exist two photoactive regions in the system for the production of the short-circuit photocurrent; these two active regions are associated respectively with each interface. When the metallic semitransparent electrode is made of aluminum the two interfaces have opposite sign contributions to the photocurrent; this allows the determination of conditions in which one can observe specifically the contribution of the pigment–electrolyte interface, that is the interactions between excited pigment molecules and the redox system in the electrolyte.

Introduction

The electrolyte–pigment–metal system has a real interest as a model system for the primary light energy conversion in the photosynthetic

apparatus as far as the description of processes between excited pigment molecules and the redox system in the electrolyte is possible in this system. Some authors [1–4] consider that under these experimental conditions it is impossible to correlate directly measured electrical transients and kinetic processes for excited pigment molecules. Others [5] conclude that the production of electrical phototransients has its origin only in a photovoltaic process specific of the pigment–metal interface.

The description we have given [6], for thin films of pigment, of the short-circuit photocurrents suggests the analogy of functioning with a photosensitive rectifying system. One looks here for the region of the system where the charge separation takes place being the origin of the production of photocurrents.

Results

As previously described [6], we measure the maximum short-circuit photocurrent under continuous illumination.

1. On direct illumination (pigment–electrolyte interface) a weakly absorbed wavelength (470 nm) gives a maximum photocurrent i_M continuously increasing when film thickness is increased in the range studied. With the use of a strongly absorbed wavelength (620 nm), however, i_M decreases after passing through a maximum value (Fig. 1).

This corresponds to a "main absorption distance" effect for the illuminating wavelength: That is, the strongly absorbed wavelength is mainly absorbed near the illuminating plane, while the weakly absorbed wavelength is more uniformly absorbed through the whole thickness of the film in the thickness studied here ($1\ \mu$).

2. The action spectrum is drawn with the value of (di_M/dI) for $I = 0$. In a first approximation we have used for the function $i_M = f(I)$ the expression $I_M = I/(a + bI)$, b being independent of wavelength and a dependent on wavelength; thus the action spectrum is drawn with a^{-1} obtained in the linear representation $1/I = a/I + b$ (I: light intensity).

In the region where i_M is increasing with film thickness, under illumination with a wavelength that is strongly absorbed, the action spectrum remains identical to the absorption spectrum. For the film thickness range where i_M is decreasing under illumination with a strongly absorbed wavelength the action spectrum is first modified then completely reversed compared with the absorption spectrum. The intermediate forms present a lowering of the action spectra for wavelengths of maximal absorption; this leads to the appearance of "fictitious maxima" in the action spectrum on the sides of the absorption bands, for example at 420 and 530 nm (Fig. 2).
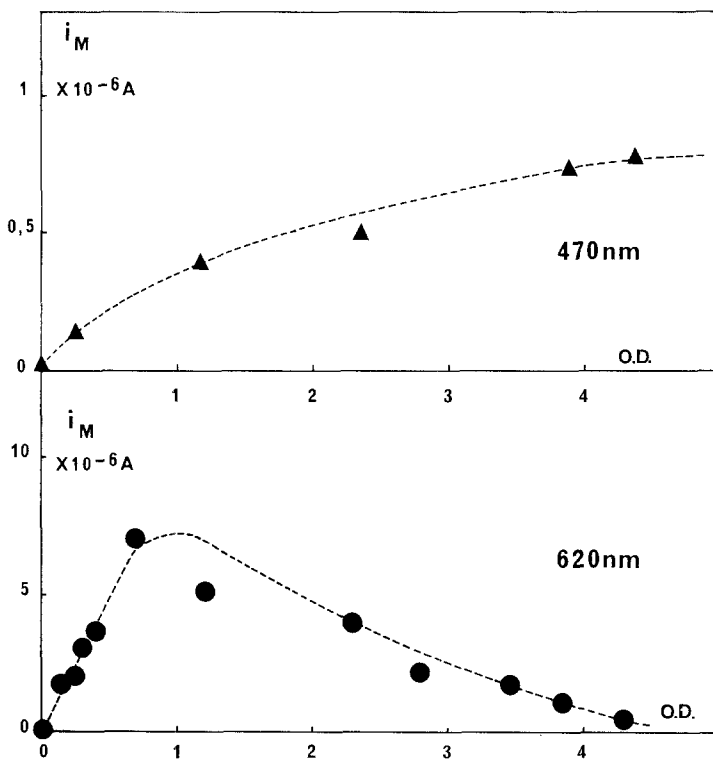
Figure 1. Variation of the maximum short-circuit photocurrent produced by a semitransparent platinum electrode covered with a metal-free phthalocyanine film when increasing film thickness (electrolyte 96%; glycerol 4% saturated KCl aqueous solution; reference electrode Ag/AgCl; active surface of electrodes 6.25 cm^2). (a) Direct illumination (pigment–electrolyte interface) with a weakly absorbed wavelength: 470 nm. (b) Direct illumination (pigment–electrolyte interface) with a strongly absorbed wavelength: 620 nm. Abcissa: optical density of the films at the maximum of absorption 620 nm. Ordinate: maximum short-circuit photocurrent.

This kind of evolution has already been observed both on some electrochemical systems and on dry systems used for photoconductivity measurements [7–10]. One interpretation leads to the assumption of an active region near the pigment–metal interface. Thus in our case only the photons absorbed in a thickness δ near the plane of the metallic electrode could contribute to the production of the short-circuit photocurrent; the remaining part of the film would play a screening role. As long as the thickness of the film l is less than δ, the number of "useful absorbed photons" increases with film thickness and similarly the photocurrent increases; also the action spectrum stays identical to the absorption spectrum. For thicknesses l greater than δ, the number of
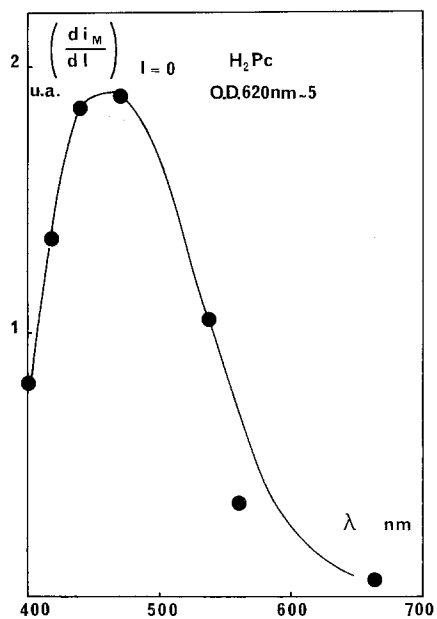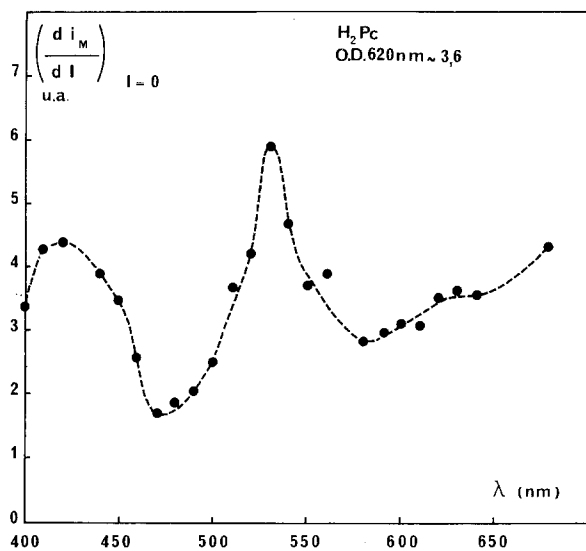
"useful absorbed photons" varies for a given wavelength λ as the function $z = 10^{-\epsilon_\lambda(l-\delta)}(1-10^{-\epsilon_\lambda\delta})$, where ϵ_λ is the extinction coefficient. Calculated along the absorption spectrum of the film this function z simulates, with increasing l, the evolution of the action spectrum registered here. But this interpretation cannot be fully satisfactory in our case as it implies that for values of thickness l greater than δ, the number of "useful" absorbed photons is simultaneously decreasing for all wavelengths; thus, if one assumes a direct correlation between the magnitude of the maximum photocurrent i_M and the number of "useful" absorbed photons in the thickness δ, i_M should decrease in the same way for strongly and weakly absorbed wavelengths.

More sophisticated treatments, taking into account diffusion of excitons produced by different wavelengths, have been proposed. Our purpose here is to discuss the fact that only a region near the metallic electrode is at the origin of the photocurrent production. It should be noted that other kinds of interpretation have been given, particularly by DeVore [11], Goodman [12], and Putseiko [7]. They admit a dependence of the action spectrum on the processes of recombination of the charge carriers at the surface of the pigment sample and in the bulk of the sample.

3. We have obtained further information by studying the system under back illumination (metal–pigment interface). For the small thickness range the situation is the same as for direct illumination, taking into account the reduction of light intensity by the semitransparent metallic electrode. We here present (Fig. 3) the action spectrum using back illumination for a 1-μ thick film: One can notice a lowering in the strong absorption regions and the presence of so called "fictitious" maxima at 550 and 420 nm; with direct illumination the action spectrum is completely reversed (Fig. 2).

We conclude that with an increase in thickness of the pigment film the evolution of the action spectrum for the maximum short circuit photocurrent is of the same kind for back and front illumination: The only difference seems to be that the same intermediate forms are observed on back illumination for thicker films, since a reversed form of the action spectrum on direct illumination corresponds to an intermediate form on back illumination.

Figure 2. Action spectrum of the maximum short-circuit photocurrent produced by a semitransparent platinum electrode covered with a film of metal-free phthalocyanine (electrolyte 96% glycerol 4% saturated KCl aqueous solution; reference electrode Ag/AgCl; active surface of electrode 6.25 cm^2). Abcissa: wavelength nm. Ordinate: $(di_M/dI)_{I=0}$, I light intensity, i_M maximum photocurrent; arbitrary unit. (Above) Direct illumination (pigment–electrolyte interface); intermediate form of the action spectrum; (film thickness $\simeq 0.7$ μ; optical density at the maximum of absorption 620 nm: $\simeq 3.6$). (Below) Direct illumination (pigment–electrolyte interface). Reversed form of the absorption spectrum (film thickness $\simeq 1$ μ; optical density at the maximum of absorption 620 nm: $\simeq 5$).
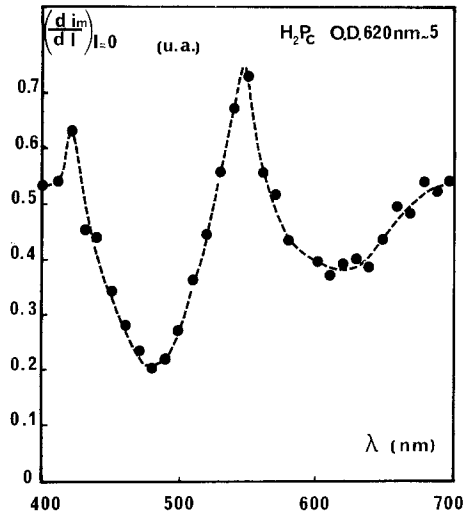
Figure 3. Action spectrum of the maximum short-circuit photocurrent produced by a semitransparent platinum electrode covered with a metal-free phthalocyanine film (electrolyte 96% glycerol 4% saturated KCl aqueous solution; reference electrode Ag/AgCl). Back side illumination (metal–pigment interface). Film thickness 1 μ, optical density at the maximum of absorption 620 nm $\simeq$ 5. Ordinate: $(di_M/dI)_{I=0}$, I light intensity, i_M maximum photocurrent: arbitrary units. Abcissa: wavelength: nm. length; nm.

To summarize these data, we propose to admit the existence in the electrolyte–pigment–metal system of two photoactive regions: One has a thickness δ_1 near the electrolyte–pigment interface, the other has a thickness δ_2 near the pigment–metal interface.

For small film thickness, where $l < \delta_1 + \delta_2$, the functioning of the system is symmetrical for direct and back illumination. For thicker films the product of the numbers of "useful" absorbed photons in the two regions is $y_1 = (1-10^{-\epsilon_\lambda \delta_1}) (1-10^{-\epsilon_\lambda \delta_2}) 10^{-\epsilon_\lambda (l-\delta_2)}$ on direct illumina-tion, $y_2 = (1-10^{-\epsilon_\lambda \delta_1}) (1-10^{-\epsilon_\lambda \delta_2}) 10^{-\epsilon_\lambda (l-\delta_1)}$ on back illumination. If one assumes $\delta_1 > \delta_2$ it is well understood that the deformation of the action spectrum takes place on back illumination for thicker films than on direct illumination.

In the electrical analogy frame already employed [6] one can use a scheme composed of two photosensible junctions in series, one associated with the pigment–electrolyte region, the other with the pigment–metal region. In darkness this scheme gives the same current–tension characteristic as a unique junction, the region of negative applied potentials corresponding to the reverse functioning, the region of positive applied potentials to the direct functioning, as for each

junction alone. With a strongly absorbed wavelength, one gets the photocurrent contribution of the junction associated with the illuminated interface; the other one staying in darkness, its functioning is in reversed side. On the contrary, with a weakly absorbed wavelength, one can get a contribution of the two junctions, absorption being more uniform through the whole thickness of the film.

4. We confirm the usefulness of this global description by data obtained using aluminum as the metal for the semitransparent metallic electrode; these data concern a film thick enough for the effect of "main absorption distance" of wavelengths to exist.

On direct illumination with a strongly absorbed wavelength the photocurrent transient is positive (electrons moving in the direction metal $\rightarrow$ pigment $\rightarrow$ electrolyte). This transient is negative when illuminating with a weakly absorbed wavelength. On back illumination, the transient is negative for all wavelengths. Thus it is evident that photons absorbed near the pigment–electrolyte interface give a positive contribution to the photocurrent and that is the reverse of photons absorbed near the pigment–metal surface. When the two interfaces can capture photons, that is with illumination by a weakly absorbed wavelength, one concludes a greater efficiency in conversion for the pigment–metal interface, as-the transient is negative.

In darkness (Fig. 4) the current–voltage characteristic is, in a first approximation, symmetrical in the -1 V, $+1$ V range of applied potential on each side of the short-circuit point without external applied potential. In an electrical analogy frame the system has a reversed functioning in the two regions of applied potentials. This allows the picture of two junctions in series and opposed: One, associated with the electrolyte–pigment interface, is reversed in the negative potential region, and direct in the positive potential region; the other, associated with the metal–pigment interface, is reversed in the positive potential region. With a weakly absorbed wavelength, the current–tension characteristic for maximum photocurrent is symmetrical in the regions $i > 0$, $V < 0$ and $i < 0$, $V > 0$. It has, roughly speaking, the same shape for direct and back illumination. With a strongly absorbed wavelength in direct illumination, the positive photocurrent increases in the region of negative potentials, decreases in the region of positive potentials. In back illumination the negative photocurrent increases in the region of positive potentials, decreases in the one of negative potentials. So in the case of a semitransparent aluminum electrode the situation is clearer than in the case of a platinum electrode: Photons absorbed specifically near each of the two interfaces lead to opposite signs for the contributions to the photocurrent. One can conclude that in direct illumination, for a pigment layer $0.5~\mu$ thick on a semitransparent aluminum electrode, the photocurrent transient, its first rapid phase particularly, is significant of the photoprocesses at the electrolyte–pigment interface.
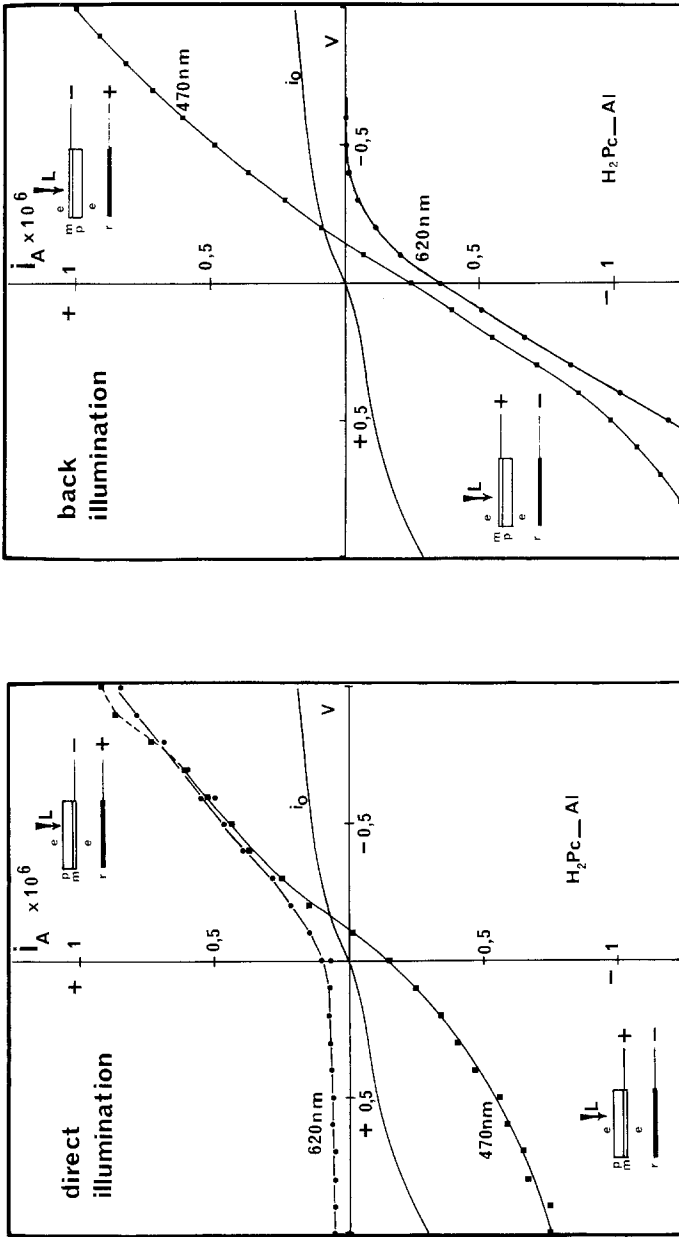
Figure 4. Current–tension characteristics of a semitransparent aluminum electrode covered with a film of metal-free phthalocyanine (electrolyte 96% glycerol 4% saturated aqueous solution; reference electrode Ag/AgCl). Abcissa: external applied potentials. Ordinate: short-current currents; i_0: dark short-circuit current; 620: maximum photocurrent on 620 nm illumination (strongly absorbed wavelength); 470: maximum photocurrent on 470 nm illumination (weakly absorbed wavelength). (Left) Direct illumination (pigment–electrolyte interface). (Right) Back illumination (pigment–metal interface (film thickness $\simeq$ 0.6 μ optical density at the maximum of absorption 620 nm $\simeq$ 3). Schematic picture of electrodes configuration. L: light; p: pigment; m: metal; r: Ag/AgCl electrode; e: electrolyte.

On the basis of numerical data generally admitted for electronic extraction (Pt 6.3 eV; Al 4.36; phthalocyanine layer between 5.20 and 6) [13], it appears that platinum and aluminum have, respectively, higher and lower values than metal-free phthalocyanine in the state of an evaporated film; roughly speaking, one can admit that platinum injects positive charge carriers in the pigment layer, aluminum injecting negative charge carriers.

At this very qualitative level, it is possible to understand the fact that these two metal–pigment interfaces provide opposite sign contributions to the measured photocurrent.

One has to notice that the functioning of the aluminum–phthalo-cyanine contact has been studied on dry systems, that is, metal–pig-ment–metal systems, in which rectification and photovoltaic properties have been described [14, 15].

Conclusion

As a "model" system for primary light energy conversion in the photosynthetic apparatus, the electrolyte–pigment–metal system loses a part of its interest as it seems rather impossible to get a phthalocyanine-metal contact without specific contribution of this interface in the photocurrent production. However in this work it has been established that a judicious choice of the system parameters and experimental conditions allows measurements of the photocurrents directly correlated with light energy conversion in the electrolyte–pigment region; this conversion process implies evidently excited phthalocyanine molecules and the redox system (O_2, H_2O) present in the electrolyte. As was already noted, the description of the functioning of this system being more clear, now, it becomes possible to get valuable information on some aspects of photochemistry of pigment in such heterogeneous conditions.

Acknowledgments

References

1. H. Tributsch, 3rd International conference on photosensitization in solids, *Photochem. Photobiol.*, 16 (1972) 261.
2. H. Gerischer, 3rd International conference on photosensitization in solids, *Photochem. Photobiol.*, 16 (1972) 243.
3. H. Tributsch, *J. Bioenerg.*, 2 (1971) 249.

4. G.G. Kommissarov, Yu.S. Shumov, and O.L. Morozova, *Biofizika,* **15** (1970) 1120 [Engl. transl. *Biophysics,* **15** (1970) 1162].

5. G.K. Getov and S.T. Jordanova, *Biofizika,* **17** (1972) 782 [Engl. trans. *Biophysics,* **17** (1972) 818].

6. J.G. Villar, *C.R. Acad. Sci.,* **275** (1972) 595; J.G. Villar, *C.R. Acad. Sci.,* **275** (1972) 861; J.G. Villar, Thèse Doctorat es Sciences N°. 1374, Paris Centre d'Orsay (1974); J.G. Villar, this issue, *J. Bioenerg.,* **8** (1976) xxx.

7. E.K. Putseiko, *Dokl. Akad. Nauk SSSR,* **150** (1963) 343

8. J.P. Fillard, Thèse Doctorat es Sciences Montpellier (1967) 130.

9. I.S. Meilanov, V.A. Benderskii, and L.A. Blyumenfel'd, *Biofizika,* **15** (1970) 822 [Engl. transl. *Biophysics,* **15** (1970) 851].

10. G. Tollin, D. Kearns, and M. Calvin, *J. Chem. Phys.,* **32** (1960) 1013.

11. H.B. de Vore, *Phys. Rev.,* **102** (1956) 86.

12. A.M. Goodman, *J. Appl. Phys.,* **30** (1959) 144.

13. *Organic Semiconductors.* F. Gutmann and L.E. Lyons, eds., John Wiley and Sons, Inc., New York (1967), p. 372 and Table 6.7, p. 694.

14. N.N. Usov and V.A. Benderskii, *Fizika i tekhnika Poluprovodnokov,* **2** (1968) 699.

15. A.K. Ghosh, D.L. Morel, T. Feng, R.F. Shaw, and C.A. Rowe Jr., *J. Appl. Phys.,* **45** (1974) 230.