Photosensitized Oxidation of SO_2 at an Optically Transparent Electrode coated with Poly(vinylpyridine) Co-ordinated Zinc(II) Tetraphenylporphine

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Large sensitized photocurrents in acidic media are observed for the title system; these display the action spectrum of zinc(II) tetraphenylporphine and a power efficiency of up to 2% based on absorbed light.

The observation that π-acid ligands axially co-ordinated to metalloporphyrins improve photovoltaic properties[1,2] led us to consider electrode films of zinc(II) tetraphenylporphine (ZnTPP) bound to the pyridine sites of poly(vinylpyridine) (PVP) (10% co-styrene). Our objective was to improve the photoelectrochemical response of a stable large band gap semiconductor with a dye sensitizer using considerably more than a monolayer (*e.g.* refs. 3, 4, and 5) thickness so that the optical absorbance is notably large. A key requirement is adequate electrical conductivity in the film.

An optically transparent electrode (O.T.E.) on n-doped SnO_2 coated glass (O. H. Johns Co., Industrial Glass Division) was used. One drop of a freshly prepared chloroform solution containing ZnTPP (1—30 mg/ml) and PVP (13—80 mg/ml) was placed on the plate, spread evenly with a glass cover, and dried in air. Film thicknesses were determined approximately to be 0.40—4.0 μm from optical absorbance measurements, assuming that the film density is 0.7 and that the solution extinction coefficient of the ZnTPP–pyridine(py) complex is appropriate. The absorption maxima from the films (565 and 605 nm; intensity ratio 1.8) were very similar to those in $CHCl_3$ solution in the presence of a large excess of PVP (562 nm, $\epsilon = 2.1 \times 10^4$ dm^3 mol^{-1} cm^{-1} and 602 nm, 1.1×10^4 dm^3 mol^{-1} cm^{-1}; intensity ratio 1.9). This shows that ZnTPP in the film is co-ordinated by the pyridine moiety in PVP.

The O.T.E. was mounted as a window (available area for photoelectrolysis 0.3 cm^2) of an electrochemical cell, with a platinum wire counter electrode and an Ag–AgCl reference electrode. Aqueous electrolyte solution (10 ml) ($[SO_2] \simeq 1$ M, $[H_2SO_4] = 0 \rightarrow 0.1$ M, $[KI] = 0 \rightarrow 0.01$ M) was placed in the cell. Current–voltage curves were obtained using a Metrohm EA412 potentiostat. The O.T.E.'s were irradiated with a focussed 200 W tungsten lamp through water and an L-47

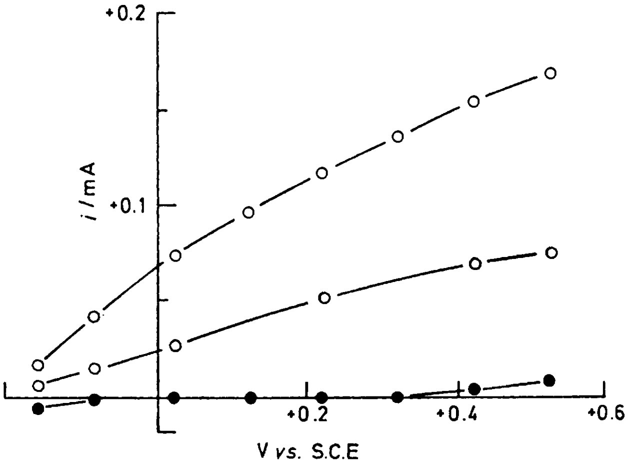

Figure 1. Representative steady-state current–voltage curves for 0.3 cm^2 ZnTPP–PVP/SnO_2 electrodes irradiated with a 200 W tungsten lamp (> 470 nm, 75 mW/cm^2). Open circles: photocurrent; closed circles: dark current. Conditions for the two films are given in Table 1 as runs 7 and 8.

Table 1. Photoelectrochemical data for the oxidation of SO_2 at ZnTPP–PVP coated n-SnO_2 electrodes.[a]

Run	[Zn]:[py][b]	d[c] /μm	A[d]	j_{ph}[e] /mA cm^{-2}	ϕ^{app},[f] %
1	1:24	0.35	0.08	0.13	2.2
2	1:24	1.0[i]	0.23	0.40	2.9
3	1:24	1.7	0.38	0.37	1.9
4	1:24	3	0.7	0.37	0.9
5	1:24	3.9	0.89	<0.2	<0.7
6	1:72	3.3	0.25	<0.1	<0.7
7	1:8	0.33	0.23	0.19	1.4
8	1:24[g]	0.49	0.11	0.45	6.0
9	1:24[h]	0.49	0.11	0.50	6.5

[a] The solution contains *ca.* 1 M SO_2, 3 mM H_2SO_4, and 5 mM KI. Input power is from a tungsten lamp (> 470 nm, 75 mW/cm^2). Irradiated area is 0.3 cm^2. [b] Molar ratio of ZnTPP to the pyridine moiety in the PVP in the film. [c] Thickness of the film. [d] Absorbance of the film at 605 nm. [e] Photocurrent density at +0.2 V *vs.* S.C.E. [f] Apparent intrinsic current quantum efficiency at +0.2 V *vs.* S.C.E. based on the corresponding value for A. [g] I_2-charged film (see text). [h] Br_2-charged film (see text). [i] ZnTPP 1.5×10^{-8} mol/cm^2.

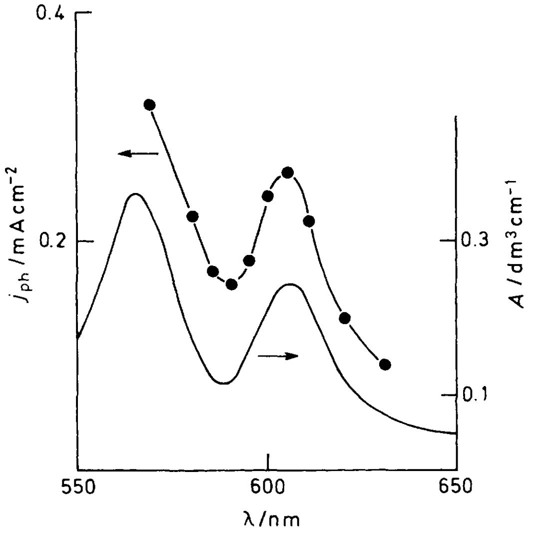

Figure 2. Optical absorption and action spectra. A = absorption of a ZnTPP–PVP film; j_{ph} = photocurrent density observed under irradiation with a dye-laser (90 mW/cm^2). Electrolyte = [SO_2] *ca.* 1 M, [H_2SO_4] = 0.1 M, [KI] = 5 mM.

470 nm cut-off filter (20 → 200 mW/cm^2 at the front face of the O.T.E.). A Coherent Model 590 Dye Laser using Rhodamine 6G was also employed (100 mW/cm^2).

In typical runs, anodic photocurrent increased with time during the initial 10 to 30 min of the illumination, and reached plateau values, which were almost constant (or *ca.* 5% reduced) throughout a period of prolonged illumination (12 h). Figure 1 shows representative steady-state current–voltage curves. They are very similar to those observed by Calebrese and Wrighton[6] for the photoelectrochemical oxidation of SO_2 in strong acidic solution at an n-MoS_2 semiconductor electrode where the SO_2 oxidation was mediated by an I_2/I^- couple.

In our system, SO_2 was essential for photocurrent flow, but KI and H_2SO_4 were not. The action spectrum shown in Figure 2 clearly indicates that ZnTPP sensitizes the photooxidation.

The observed photoelectrochemical data in the steady-state are collected in Table 1. The values of the photocurrent density (j_{ph}) at +0.2 V *vs.* standard calomel electrode (S.C.E.) are high compared with those reported for earlier dye sensitization systems. The high j_{ph} in the present system is attributable to the effective absorption of photons by the multimolecular layer. In fact, the increase in the absorbance of the film (A), due to the increase in the thickness of the film (d) and also an increase in the molar ratio of the complex to pyridine moiety in PVP ([ZnTPP]: [PVP]), caused higher j_{ph} values (runs 1, 2, and 7). However, when d exceeded 1 μm, j_{ph} did not increase further and ϕ^{app} decreased with increase in d. This is probably due to the decrease in the conductivity of the film (runs 3—6). ϕ^{app} denotes 'apparent' intrinsic current quantum efficiency at +0.2 V *vs.* S.C.E., defined for non-monochromatic illumination ($\lambda > 470$ nm) by reference to ϕ^0, the intrinsic current quantum efficiency at 605 nm as evaluated with the laser (*i.e.* the apparent yield is low since the 605 nm light is more completely absorbed).

A notable and sustained increase in ϕ^{app} was found with I_2- and Br_2-charged films. These were prepared either by exposure of the film to I_2 vapour for 30 min or the addition of Br_2 to the original ZnTPP–PVP–$CHCl_3$ solution at the molar ratio of Br_2 : ZnTPP = 0.5 : 1 (runs 8 and 9). The increase in the conductivity of the film caused by the halogens might be attributed to the formation of a charge transfer complex with an unco-ordinated pyridine moiety[7] and/or to the formation of the cationic radical complex, $ZnTPP^{+\bullet}$, which is known to be formed from ZnTPP and Br_2 in CCl_4.[8] In the present system, the absorption spectrum of the film immediately after irradiation suggests the formation of $ZnTPP^{+\bullet}$. The spectrum showed a decrease (>10%) in absorption intensity at the maxima (435, 565, and 605 nm) and the emergence of a new peak at 420 nm. This compares well with the maximum at 410 nm reported for $ZnTPP^{+\bullet}$ in CH_2Cl_2 without co-ordinated pyridine.

The film used for run 2 is estimated to have 1.5×10^{-8} mol of ZnTPP per cm^2, and ZnTPP is separated by about 20 Å and *ca.* 650 layers of the complex. The j_{ph} and ϕ^{app} values are too high to be attributed only to the first layer in contact with the n-SnO_2 semiconductor surface and therefore the absorption of photons from inner layers must also play a part. The inter-complex distance is short enough to suppose energy and/or electron transfer in the film in the direction of the semiconductor surface with the aid of the cationic radical complex.

The power efficiency for the conversion of light into current for run 9 is evaluated to be 0.1 and 2%, respectively for the irradiated and absorbed power of the light.

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References

1 C. H. Langford, B. R. Hollebone, and D. Nadezhdin, *Can. J. Chem.*, 1981, **59**, 652.
2 S. Seto, C. H. Langford, and B. R. Hollebone, *Can. J. Chem.*, submitted for publication.
3 M. T. Spitler and M. Calvin, *J. Chem. Phys.*, 1977, **66**, 4294.
4 T. Yamase, H. Gerischer, M. Lubke, and B. Pettinger, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 1041.
5 T. Iwasaki, T. Swada, H. Kamada, A. Fujishima, and K. Honda, *J. Phys. Chem.*, 1979, **83**, 2142.
6 G. S. Calebrese and M. S. Wrighton, *J. Am. Chem. Soc.*, 1981, **103**, 6273.
7 E. P. Goodings, *Chem. Soc. Rev.*, 1976, **5**, 95.
8 W. R. Browett and M. J. Stillman, *Inorg. Chim. Acta*, 1981, **49**, 69.