Photoelectrochemistry of ZnO thin film electrode sensitized by an oxouranium (VI) complex in an acetonitrile photocell

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Abstract. The photosensitizing ability of tetraethylammonium *bis*-(isomaleonitrilo) dioxouranate(VI), $(Et_4N)_2[UO_2(i\text{-}MNT)_2]$, studied at the n-ZnO/acetonitrile interface, is shown by the enhancement observed in photocurrent with $(Et_4N)_2[UO_2(i\text{-}MNT)_2]$ in comparison to that obtained without the sensitizer. The flat-band potential is -0.40 V vs SSCE. $(Et_4N)_2[UO_2(i\text{-}MNT)_2]$ acts as an acceptor-type sensitizer as concluded from the energy-level diagram constructed using its redox potential coupled with its excitation energy and the flat-band potential of ZnO electrode. Long-term stability of the photocurrent under continuous illumination of the electrode is also studied.

Keywords. Thin film; n-ZnO semiconductor; PEC cell; photosensitization.

1. Introduction

Transition metal complexes have been tested as sensitizers by earlier investigators (Connolly 1981; Kalyanasundaram 1981; Alonso-Vante *et al* 1983; Grätzel 1983), with particular emphasis on ruthenium complexes (Gerischer 1972; Dabestani *et al* 1988; Amadelli *et al* 1990; O'Regan and Grätzel 1991), to extend the spectral response of high band-gap semiconductors to the visible region (abundant part) of solar radiation, for its application in photo-electrochemical cells for conversion of solar energy to electrical energy. Continued efforts in this direction are quite desirable to explore the possibility of using other metal complexes as photosensitizers. With this in view, we selected two new oxouranium complexes of dithioligands and they have been tested for their sensitizing ability. The results obtained with one of these complexes have already been published (Lal Bahadur and Pandey 1993).

Now, in this paper, we report the results of our investigations with the second oxouranium complex, namely. tetraethylammonium *bis* (isomaleonitrilo) dioxouranate (VI), $(Et_4N)_2[UO_2(i\text{-}MNT)_2]$, for spectral sensitization of the n-ZnO electrode in an acetonitrile medium. The purpose of selecting acetonitrile for the investigation is described elsewhere (Lal Bahadur and Rao 1992).

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2. Experimental

Thin films of ZnO prepared on microscopic glass substrates by spray pyrolysis method were subsequently annealed in controlled hydrogen atmosphere at 400°C to get the semiconducting n-ZnO films to be used as photoelectrodes. Further details regarding the preparation and mounting of electrodes are described in our earlier publication (Lal Bahadur and Pandey 1990).

For the preparation of $(Et_4N)_2[UO_2(i\text{-}MNT)_2]$, used as sensitizer, and purification of acetonitrile (E Merck, India), we refer to our earlier publication (Lal Bahadur and Pandey 1990). Anhydrous sodium perchlorate (Aldrich Chemicals) and hydroquinone (BDH, India) were used as received.

Photoelectrochemical studies were performed in a single compartment cell having a three-electrode system. The cell was equipped with an optically flat quartz window for electrode illumination. A spiral Pt-wire served as the counter electrode and a sodium-chloride-saturated calomel electrode SSCE, $[E^0 = -0.008\ V\ vs\ SCE\ (KCl)]$ (Headridge 1969), separated from the test solution by Luggin capillary agar salt (NaCl) bridge was used as the reference electrode.

For photoelectrochemical measurements, a 150 W xenon arc lamp was used as the light source along with fused silica condensing lenses, a monochromator (Model 77250 with a model 7798 grating), and neutral density filters (Model No. 50490–50570) (all from Oriel Corporation, USA). The light intensity was measured with a digital photometer (Tektronix Model J 16 with J 6502 sensor). Instruments used for current-potential measurements, absorption spectra, action spectra and long-term stability experiments were described earlier (Lal Bahadur and Pandey 1992, 1993).

3. Results and discussion

Keeping in mind its final application as a photosensitizer in a PEC cell, preliminary investigations were made on the redox behaviour of $(Et_4N)_2[UO_2(i\text{-}MNT)_2]$ at Pt and n-ZnO electrodes in an acetonitrile medium using cyclic voltammetry (Lal Bahadur and Pandey 1990). In pursuance of the set objective, further studies have been made on the photoelectrochemical behaviour of the n-ZnO electrode sensitized by this oxouranium (IV) complex in the PEC cell configuration. The results obtained constitute the content of the present paper.

3.1 *Photovoltage determination*

When a semiconductor electrode, in equilibrium with the electrolyte solution, is illuminated, photovoltage is generated providing part of the potential required for the occurrence of a reaction at a semiconductor electrode. To determine the magnitude of this photovoltage (V_{photo}), the open circuit potential at the ZnO electrode was measured in the dark and under illuminated conditions; the results are shown in figure 1. As can be seen in the figure, photovoltage increases slowly, preceded by a fast change in the beginning, before attaining a steady value. This may be due to the following reasons. As the concentration of photo-induced majority carriers changes at a faster rate in the beginning and the recombination of photo-generated carriers is lower, initially the major part of the photovoltage is built up in a short time. But
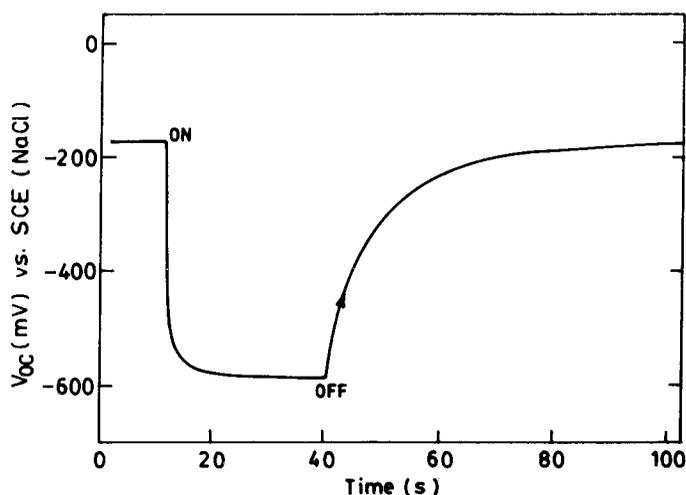
Figure 1. Open circuit potential at ZnO electrode in acetonitrile solution of 0·1 mM $(Et_4N)_2$ $[UO_2(i\text{-MNT})_2] + 0\cdot01$ M hydroquinone $+ 0\cdot1$ M $NaClO_4$. Intensity of light $= 477$ mW/cm^2.

as time passes, carrier concentration also increases, resulting in more recombination, thereby taking more time to acquire the remaining part of the photovoltage before reaching a steady value. Further, when light is put off, the photovoltage vanishes slowly and takes a much longer time to attain the steady state dark potential. With this system, photovoltage was found to be $-0\cdot41$ V, with the light intensity being 477 mW/cm^2.

3.2 *Current–potential curve*

Current–potential $(J - V)$ plots of n-ZnO thin film electrodes were obtained in the dark and under illumination with white light, figure 2 shows such plots with a ZnO electrode in a deaerated solution of $0\cdot1$ mM $(Et_4N)_2[UO_2(i\text{-MNT})_2]$, $0\cdot01$ M hydroquinone and $0\cdot1$ M $NaClO_4$ in acetonitrile. The dark current $(< 1\,\mu A)$ was practically negligible in the voltage range studied. The effect of momentary manual interruption of illumination is also shown in figure 2. The curve obtained with the illuminated electrode indicates that photocurrent initiates at $-0\cdot40$ V. Hence, this onset potential can be taken as the flat-band potential of ZnO in the present test solution. Though the flat band potential is also determined by impedance measurements (through a Mott–Schottky plot), due to the dispersion effect, i.e. frequency dependence of the Mott–Schottky plot, this is not always the preferred technique to be used for this purpose (Dutoit *et al* 1976; Bard *et al* 1980; Morrison 1980). In the light of this fact, the flat band potential determined from the potential of photocurrent onset was preferred in the present case also. Further, with increasing applied potential, there was quite a slow increase in photocurrent initially, followed by sharp increase at higher anodic potential, without showing any tendency to saturation.

The precise determination of the flat-band potential becomes rather difficult due to variations observed in onset potential with light intensity and different electrode samples and also the sluggish nature of the onset of photocurrent. However, such variations were found to be within ± 50 mV. Hence, the value of flat-band potential
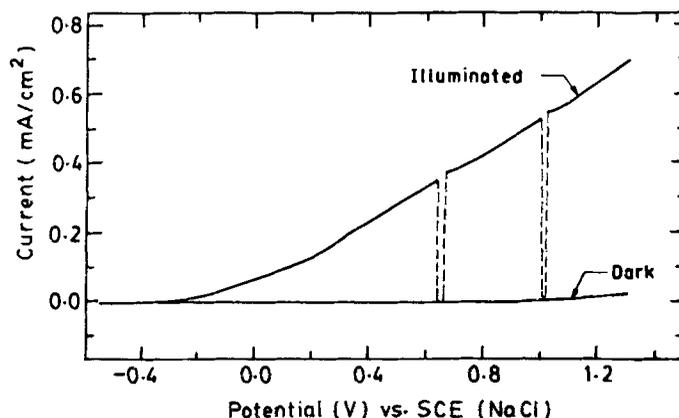
Figure 2. Current potential curves for ZnO electrodes in the dark and under white light illumination. Solution: 0.1 mM $(Et_4N)_2[UO_2(i\text{-}MNT)_2] + 0.01$ M hydroquinone $+0.1$ M $NaClO_4$ in acetonitrile. Light intensity $= 477$ mW/cm^2.

of ZnO in the test solution can be taken as $V_{fb} = -0.40 \pm 50$ mV. The slow increase in photocurrent in the lower potential region is an indication of inefficient removal of electrons injected by the excited sensitizer molecules or those produced by photo-excitation of the ZnO electrode, from the surface of the electrode towards its bulk at lower applied potential. Hence, the oxidized sensitizer molecules (resulting from the electron transfer) or holes recombine with the injected photoexcited electrons through surface states (Gerischer 1983).

3.3 *Energy-level diagram of the sensitizer and ZnO semiconductor*

The redox potential of $(Et_4N)_2[UO_2(i\text{-}MNT)_2]$, as obtained from the cyclic voltammetric measurements (Lal Bahadur and Pandey 1990), is -0.96 V at the Pt-electrode which gives the ground state energy level of the sensitizer acting as an electron acceptor (Gerischer and Willig 1976). The excited state of the sensitizer differs from its ground state energy term by the stored excitation energy (hv), which in this case can be taken as 2.7 eV, corresponding to photon energy of 460 nm wavelength as there is a shoulder around the same wavelength in the absorption spectrum of the sensitizer (Lal Bahadur and Pandey 1990). The position of the Fermi level of ZnO was taken to be equal to the flat-band potential (-0.40 V) obtained from the potential of the onset of photocurrent in the $J - V$ curve (figure 2). Since the donor density (N_D) of the identical ZnO electrode, as determined from the Mott–Schottky plot (Pandey 1991), has been found to be of the order of 10^{19} cm^{-3}, the position of the conduction band edge can be taken at 0.1 eV above the Fermi level, that is at -0.50 V. Using a band-gap of n-ZnO equal to 3.2 eV, the top of the valence band could be obtained. Various energy levels thus estimated are shown in figure 3, including those of the quinone/hydroquinone redox couple. All these values refer to the SSCE. The energy-level diagram indicates that the excited sensitizer molecules can be reduced by hydroquinone and its reduced form in the ground state can inject electrons into the conduction band of the semiconductor.
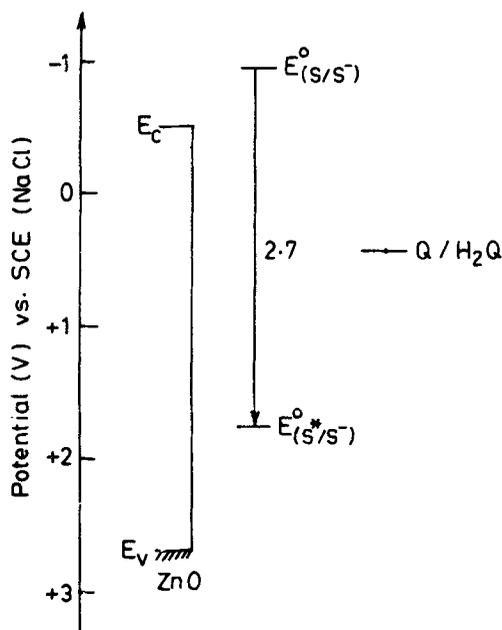
Figure 3. Energy level diagrams of ZnO, $(Et_4N)_2[UO_2(i\text{-MNT})_2]$ (as an acceptor) in ground state (s) and excited state (s^*), and quinone/hydroquinone (Q/H_2Q) supersensitizer $E_Q^0/H_2Q = 0\cdot45\,V$.

3.4 *Transient current–time curve*

To know the photoresponse behaviour of ZnO electrodes in the presence of $(Et_4N)_2$ $[UO_2(i\text{-MNT})_2]$, transient-photocurrent–time profiles at two fixed bias potentials have been recorded and the same are shown in figure 4. On illumination (indicated by 'ON') of the electrode, spikes are observed at both potentials and the extent of spikes (photocurrent in excess of the steady value) in the photocurrent was found to be almost the same in both the cases. After putting off the light, steady state dark current is achieved in comparatively much shorter time. Since, the photoinduced charge carriers generated in the semiconductor and the injected electrons from the sensitizer molecules contribute to the net photocurrent flowing in the external circuit, the decay in photocurrent, after the initial hike, is indicative of the recombination of the injected electrons and the resulting oxidized species of the sensitizer molecules. It is partially due to recombination of photogenerated charge carriers (electrons/hole) through surface states instead of all (holes) being captured in the redox process in the solution. These results are in accordance with the prediction of Kucernak *et al* (1991) who have proposed the theory of transient photocurrent response to chopped light.

3.5 *Variation of photocurrent with light intensity*

A logarithmic plot of photocurrent (at a fixed applied potential, $0\cdot80\,V$) vs light intensity (varied with the help of neutral density filters) is shown in figure 5, and indicates a linear variation in photocurrent with light intensity as observed by other
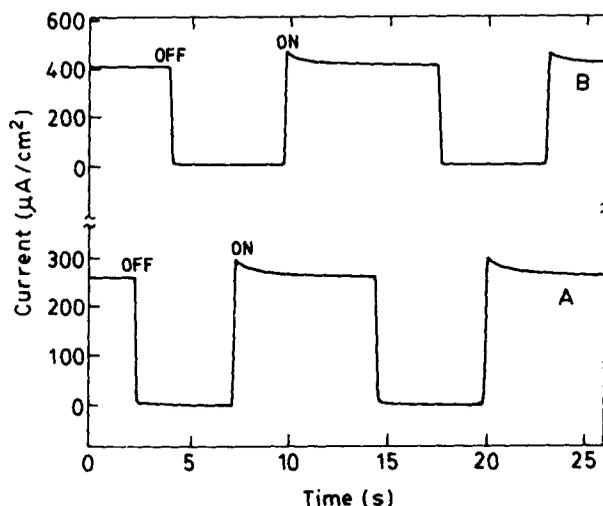
Figure 4. Transient current-time curves for ZnO electrodes at fixed bias potentials, A: + 0·50 V and B: + 0·80 V vs SSCE; solution composition being the same as in figure 2. Light intensity = 476 mW/cm².
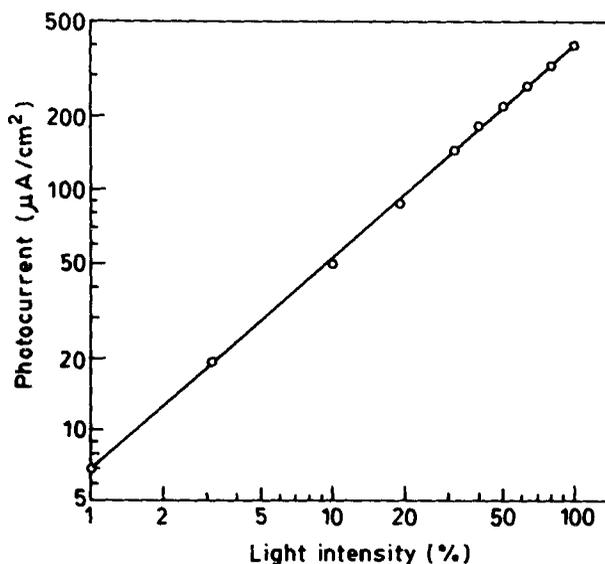

Figure 5. Photocurrent dependence on light intensity for ZnO electrode in acetonitrile solution containing 0·1 mM $(Et_4N)_2[UO_2(i-MNT)_2]$ + 0·01 M hydroquinone + 0·1 M $NaClO_4$. Electrode potential $E = 0·80$ V vs SSCE. Light intensity corresponding to 100% = 477 mW/cm².

investigators (Gerischer 1966; Dudkowski *et al* 1967; Matsumura *et al* 1977) for different systems. In spite of linear variation in photocurrent with light intensity, the slope of the curve $(\Delta \log J_{photo}/\Delta \log I_0$, I_0 being the intensity of light) is not unity, indicating thereby the role of some other factors in controlling the photocurrent, in addition to concentration of photogenerated charge carriers.
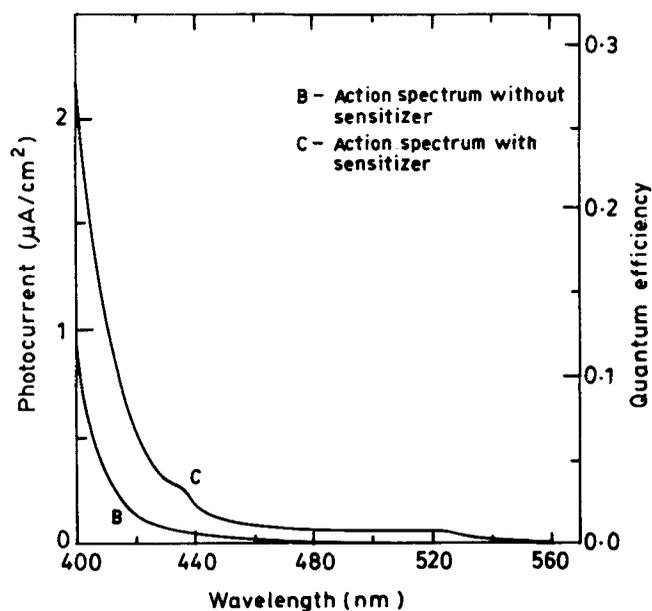
Figure 6. Wavelength dependence of photocurrent at ZnO electrode: curve B – without sensitizer, curve C – with sensitizer $(Et_4N)_2[UO_2(i\text{-MNT})_2]$, (0·1 mM). Electrolyte: 0·01 M hydroquinone + 0·1 M $NaClO_4$ in acetonitrile. Bias electrode potential = 0·80 V vs SSCE. Photocurrents have been normalized for photon-flux $3·52 \times 10^{13}$ photons $cm^{-2}s^{-1}$. Quantum efficiency refers to the curve C.

3.6 *Photocurrent action spectrum* (J_{photo} *vs* λ)

In order to check the sensitization effect of the test compound on the photocurrent, the photoelectrode (n-ZnO) was kept at + 0·80 V bias potential and the photocurrent (J_{photo}) was determined as a function of the wavelength (λ) of monochromatic light used for the illumination of the n-ZnO electrode. In this way J_{photo} vs λ curves were determined, one without the test compound (figure 6, curve B) and another with the compound present in the electrolyte (curve C, figure 6). Both action spectra are normalized for equal photon flux ($3·52 \times 10^{13}$ photon $cm^{-2}s^{-1}$ corresponding to its value at 460 nm wavelength) at all wavelengths. A comparison of curve C with the base curve B shows that photocurrent is enhanced by the addition of $(Et_4N)_2$ $[UO_2(i\text{-MNT})_2]$ in the electrolyte and hence is sensitized. However, sensitization is more pronounced in the lower wavelength region. Quantum efficiency, ϕ, shown on the right ordinate of figure 6 which refers to curve C, was determined from the measured photocurrent density, J_{photo} (A/cm^2), at a particular wavelength of monochromatic light and photon flux, N_λ (photon $cm^{-2}s^{-1}$), at the same wavelength by using the following relation

$$\phi = (J_{photo}/e_0)/N\lambda,$$

where e_0 is the elementary charge on an electron.

3.7 *Long-term stability of ZnO semiconductor electrodes*

To assess the suitability of using a non-aqueous medium for better stabilization of the semiconductor electrode, the stability of the photocurrent at the ZnO electrode,
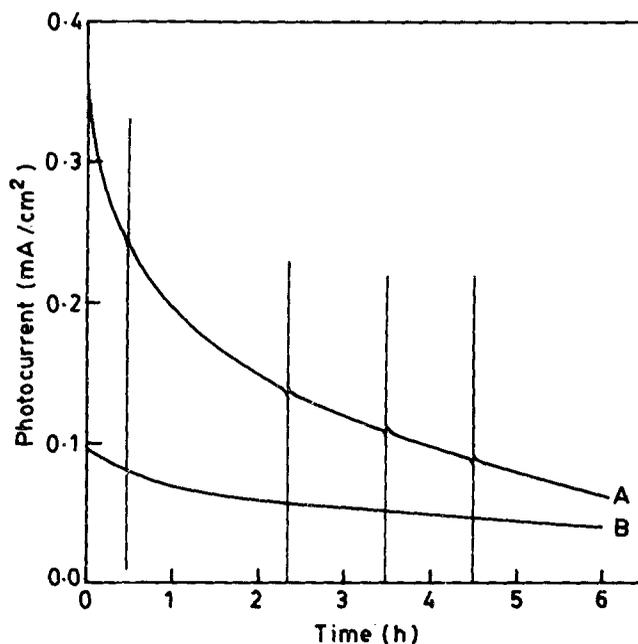
Figure 7. Stability of photocurrent with time at a fixed biased potential (+ 0·80 V) for ZnO electrode in an acetonitrile solution of 0·1 mM $(Et_4N)_2[UO_2(i\text{-MNT})_2]$ + 0·1 M $NaClO_4$ + 0·01 M hydroquinone. Curves A and B: electrode illuminated with white light of different intensities (A: 535 mW/cm², B: 66·5 mW/cm²).

kept at a fixed bias potential (+ 0·80 V), was recorded with passage of time under continuous illumination of the photoelectrode. The result obtained, with white light used for illumination (535 mw/cm²), is shown in figure 7 (curve A). It is clear from the curve that photocurrent decreases continuously from the beginning, with the rate of decrease in photocurrent being higher initially. Occasionally light was chopped off for a short while and it was found that under dark conditions, the current became immediately very low. On illumination large spikes were observed, which decay within a very short time (figure 7, curve A). From this observation, it can be concluded that the kinetics of the reaction of hydroquinone with the excited sensitizer molecules or photogenerated holes in the valence band of the semiconductor is not able to keep up with the rate of electron injection from the sensitizer molecules or the rate of photoinduced generation of holes. The result of another experiment performed at much lower intensity of irradiance (66·5 mw/cm²) is shown by curve B in figure 7. In this case also, a decrease in photocurrent was observed but at a slower rate. The situation might improve with other redox reagents (supersensitizers) if they are kinetically more efficient than hydroquinone for this system. Studies in this direction are being carried out.

4. Conclusion

The present investigations made have shown that $(Et_4N)_2[UO_2(i\text{-MNT})_2]$ can act as an electron-acceptor type sensitizer having better sensitizing efficiency in the lower

wavelength region of the visible spectrum. Also, for getting lesser deterioration in photocurrent on prolonged operation of the cell using this sensitizer, low intensity of light should be used.

Acknowledgements

References

Alonso-Vante N, Ern V, Chartier P, Dietrich-Buchecker C O, McMillan D R, Marnot P A and Sauvage J P 1983 *Nauv. J. Chim.* **7** 3
Amadelli R, Aragazzi R, Bignozzi C A and Scandola F 1990 *J. Am. Chem. Soc.* **112** 7099
Bard A J, Nozik A J and Bockris J O'M 1980 *Faraday Discuss. Chem. Soc.* **70** 93
Connolly J S (ed.) 1981 *Photochemical conversion and storage of solar energy* (New York: Academic Press)
Dudkowski S J, Kepka A G and Grossweiner J 1967 *J. Phys. Chem. Solids* **28** 485
Dabestani R, Bard A J, Campion A, Fox M A, Mallouk T E, Webber S E and White J M 1988 *J. Phys. Chem.* **92** 1872
Dutoit E C, Cardon F and Gomes W P 1976 *Ber. Bunsen. Phys. Chem.* **80** 1285
Gerischer H 1966 *J. Electrochem. Soc.* **113** 1174
Gerischer H 1972 *Photochem. Photobiol.* **16** 243
Gerischer H 1983 *J. Electroanal. Chem.* **150** 553
Gerischer H and Willig F 1976 *Top. Curr. Chem.* **61** 31
Grätzel M (ed.) 1983 *Energy resources through photochemistry and catalysis* (New York: Academic Press)
Headridge J B 1969 *Electrochemical techniques for inorganic chemistry* (New York: Academic Press)
Kalyanasundaram K 1981 *Coord. Chem. Rev.* **46** 376
Kucernak A R, Peat R and Williams D E 1991 *J. Electrochem. Soc.* **138** 1645
Lal Bahadur and Pandey J P 1990 *J. Electrochem. Soc.* **137** 3755
Lal Bahadur and Pandey J P 1992 *J. Appl. Electrochem.* **22** 883
Lal Bahadur and Pandey J P 1993 *Indian J. Chem.* **A32** 283
Lal Bahadur and Rao T N 1992 *Sol. Energy Mater. Soc. Cells* **27** 347
Matsumura M, Nomura Y and Tsubomura H 1977 *Bull. Chem. Soc. Jpn.* **50** 2533
Morrison S R 1980 *Electrochemistry at semiconductor and oxidized metal electrodes* (New York: Plenum)
O'Regan B and Gratzel M 1991 *Nature (London)* **353** 737
Pandey J P 1991 *Photoelectrochemical studies of thin film n-ZnO/acetonitrile based solar cells using different sensitizers*, Ph D thesis, Banaras Hindu University, Varanasi