JOURNAL OF APPLIED ELECTROCHEMISTRY **29** (1999) 109–116

A binary mixture of dyes (2-imidazolin-5-one and Rose Bengal) for photosensitization of *n*-ZnO thin film electrodes in aqueous and acetonitrile media

L. BAHADUR, L. ROY

Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India

Received 22 April 1997; accepted in revised form 7 July 1998

Two well characterized photosensitizers, namely, 4-*m*-methoxy-*p*-hydroxy benzylidene-2-*m*-methoxy-*p*-hydroxystyryl-1-phenyl-2-imidazolin-5-one (subsequently referred to as 2-imidazolin-5-one) and Rose Bengal, have been used together to sensitize sprayed ZnO thin film electrodes in aqueous and acetonitrile media. Through current–potential curves and action spectra (i_{photo}/λ), it has been confirmed that both dyes, when present together, contribute additively to the sensitized photocurrent. The quantum efficiencies of the dye-sensitized photocurrent at 480 and 555 nm wavelengths ($\lambda_{\max}$ of 2-imidazolin-5-one and Rose Bengal, respectively) were found to be 3.5 and 4.4%, respectively, in aqueous solution, while in acetonitrile medium the corresponding values were 4 and 6.5%.

Keywords: *photoelectrochemical cell*, *binary mixture*, *dyes*, *2-imidazolin-5-one*, *Rose Bengal*, *sprayed ZnO thin film*, *acetonitrile*

1. Introduction

During the last two decades, there have been extensive studies of dye-sensitized photoelectrochemical cells and a variety of photosensitizers has been tested [1–11]. However, in most investigations, the dyes were used individually and very little attention has been directed towards the use of binary mixture of dyes [12–15] for sensitizing the semiconductor electrodes. An effort has been made in the present work to sensitize sprayed ZnO semiconductor electrodes using a binary mixture of 2-imidazolin-5-one (a synthetic compound [16]) and Rose Bengal, which have absorption peaks at wavelengths of 480 and 555 nm, respectively, with the objective of utilizing the larger fraction of the solar radiation for conversion to electrical energy.

2. Experimental details

2.1. *Materials*

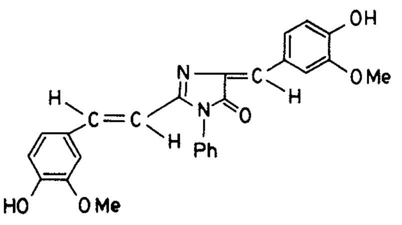
Thin films of ZnO were prepared by spraying 0.1 M aqueous solution of $Zn(NO_3)_2$ (A.R. grade, E. Merck, India) on ultrasonically cleaned nonconducting glass substrate maintained at 400 °C using a thermostatically controlled vertical furnace. These films ($\sim$5 μm thick) were subsequently annealed in hydrogen atmosphere for about 1 h at 400 °C.

To make electrical contact to the films the exposed tip of an insulated copper wire was attached to the surface of the film using silver paste (Elteck Corporation, India). The occluded solvent in the silver paste was removed by drying in air. The silver was covered with an insulating resin (Araldite) and finally dried in air.

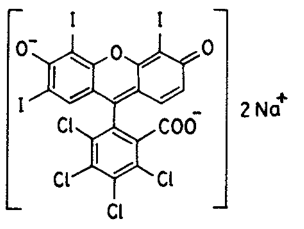
Double distilled water was used as solvent for studies carried out in aqueous medium. Acetonitrile (Qualigens, HPLC grade) was purified as described earlier [17]. Anhydrous sodium perchlorate (Purum Fluka), as-received, was used as supporting electrolyte. One of the dyes, 2-imidazolin-5-one (Fig. 1), was synthesized in house [18]. The other test sensitizer, Rose Bengal (Romali, USA), was used as received. Hydroquinone (H_2Q) obtained from BDH (India) was used as supersensitizer.

2-Imidazolin-5-one is insoluble in water. Thus, when a ZnO electrode was to be sensitized using this dye and studied in aqueous solution, the dye was adsorbed from a 10^{-5} M solution in acetonitrile. The ZnO electrode was kept immersed in the dye solution for 1 h. The dye coated ZnO electrode was then used in aqueous electrolyte solution containing hydroquinone (0.01 M) and $NaClO_4$ (0.1 M). The pH of this aqueous electrolyte solution was found to be 6.1.

To study the sensitization of a ZnO electrode by both dyes simultaneously in aqueous electrolyte, first 2-imidazolin-5-one was adsorbed on the ZnO electrode as described above, and the dye coated electrode was immersed in aqueous electrolyte solution containing Rose Bengal (10^{-5} M) (in addition to H_2Q (0.01 M) and $NaClO_4$ (0.1 M)) and left for an hour in order that Rose Bengal became adsorbed on the electrode. When acetonitrile was used as the medium



1



2

Fig. 1. The structural formulae of the dyes. **1**: 4-*m*-methoxy-*p*-hydroxybenzylidene-2-*m*-methoxy-*p*-hydroxystyryl-1-phenyl-2-imidazolin-5-one, and **2**: Rose Bengal.

of investigation and the ZnO electrode was sensitized by both dyes together, initially 2-imidazolin-5-one (10^{-5} M) was dissolved in the electrolyte (0.1 M $NaClO_4$ + 0.01 M H_2Q in ACN), the ZnO electrode was immersed in it and the adsorption of dye was allowed to take place for an hour. Then Rose Bengal (10^{-5} M) was added to the electrolyte and the electrode was kept immersed for a further hour for the adsorption of Rose Bengal before the experiments were performed. It must be emphasized that this particular sequence of adsorption of dyes is essential because 2-imidazolin-5-one is adsorbed slowly and to a lesser extent as compared to Rose Bengal. Thus, if these dyes are taken together in the electrolyte and simultaneous adsorption is allowed to take place, Rose Bengal is adsorbed preferentially and almost exclusively, leaving behind 2-imidazolin-5-one in the solution.

2.2. *Apparatus and instruments*

A three-electrode single compartment cell containing an optically flat quartz window was used for all the experiments. For the photoelectrochemical studies, *n*-ZnO thin film was used as the working electrode and a spiral platinum wire as the counter electrode. All potentials were measured with respect to a reference sodium chloride saturated calomel electrode (SSCE (aq.)), separated from the cell electrolyte by a Luggin capillary agar salt (NaCl) bridge. A carbon counter electrode, obtained from a Novino dry cell, was used to determine the power output efficiency of the cell.

A bipotentiostat (Pine Instruments Co., USA), along with a Houston model 2000 X–Y1–Y2 recorder, was used for the current–potential measurements. A 150 W Xenon arc lamp (Oriel, USA) served as the light source and for monochromatic light a grating monochromator (model 77250, Oriel, USA) was used. The i.r. part of the source light was filtered using a 6 in. long water column in its path and this i.r.-filtered light is referred to as 'white light'. The u.v. part of the white light was filtered, using a long pass filter (model 51280, Oriel, USA) and the resulting light (λ > 420 nm) is referred to as 'filtered visible light'. For the measurement of light intensities, a digital photometer (model J16 with model J6502 sensor, Tektronix) was used in combination with neutral density filters (model 50490–50570, Oriel, USA). The absorption spectra of these dyes were recorded on the Cary 2390 spectrophotometer (Varian).

3. Results and discussion

3.1. *Absorption spectra of the dyes*

Curves (a) and (b) shown in Fig. 2(A) represent the absorption spectra of 2-imidazolin-5-one (10^{-5} M) and Rose Bengal (10^{-5} M), respectively, dissolved in acetonitrile solvent while curve (c) is the same for the equimolar (0.5×10^{-5} M) mixture of both compounds dissolved in the same solvent. As 2-imidazolin-5-one is insoluble in water, the absorption spectrum of this dye alone or mixed with Rose Bengal could not be taken in aqueous solution. However, the absorption spectrum of Rose Bengal in aqueous solution (10^{-5} M) is shown in Fig. 2(B).

3.2. *Photovoltage under open circuit condition*

Open circuit potential–time (V_{oc}/t) curves for dyes sensitized ZnO electrodes in aqueous and ACN

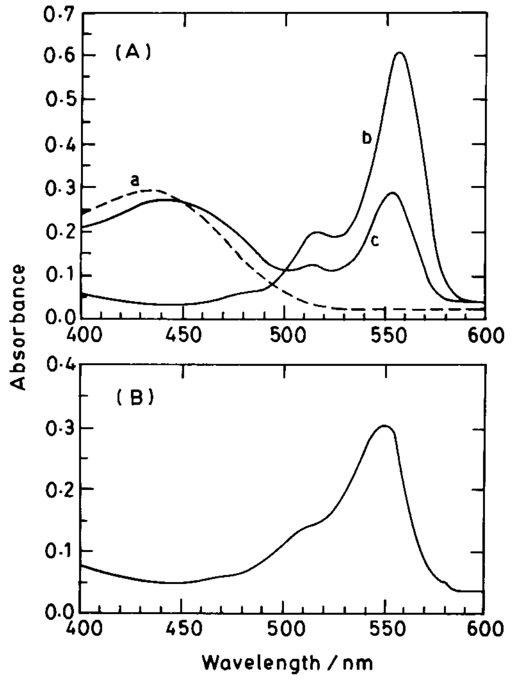


Fig. 2. (A) Absorption spectra of (a) 2-imidazolin-5-one (10^{-5} M), (b) Rose Bengal (10^{-5} M), and (c) equimolar mixture of both the dyes (0.5×10^{-5} M each in the solution) in acetonitrile medium. (B) Absorption spectrum of 10^{-5} M aqueous solution of Rose Bengal.

solutions were recorded under illumination of three different kinds of light. Starting with steady state open circuit potential in dark, when ZnO electrodes were illuminated with filtered visible light ($\lambda >$ 420 nm, $h\nu < E_g$), a substantial part of the steady photovoltage (−0.075 V in aqueous electrolyte and −0.160 V in ACN solution) was built up quickly (Fig. 3(A)). On excitation of the electrode with light of 480 nm wavelength (λ_{max} for 2-imidazolin-5-one), −0.018 and −0.014 V photovoltages were developed in aqueous and ACN solutions, respectively (Fig. 3(B)). When monochromatic light of wavelength 555 nm (λ_{max} of Rose Bengal) was used for illumination, the same electrode gave −0.007 and −0.014 V photovoltages in aqueous and ACN solutions, respectively (Fig. 3(C)). These photovoltages obtained on illumination by monochromatic light of subband gap energies can be ascribed fully to the electron injection into the conduction band of the semiconductor by the excited dye molecules.

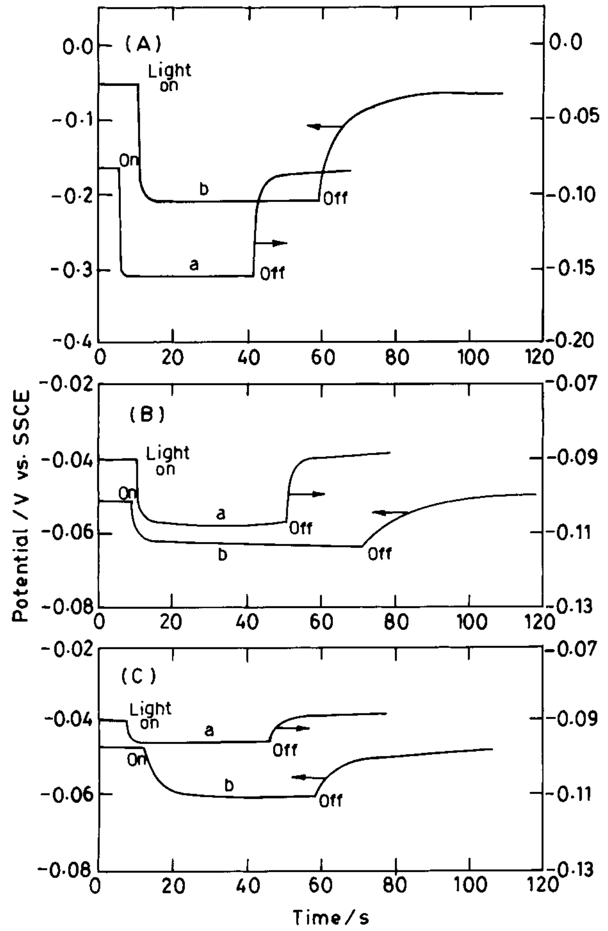


Fig. 3. Open circuit potential–time curves for sprayed *n*-ZnO thin film electrode in aqueous (curve (a)) and acetonitrile (curve (b)) solutions under illumination with (A) visible light ($\lambda >$ 420 nm), and (B, C) monochromatic lights. λ = 480 nm and 555 nm for (B) and (C), respectively. *Solutions*: (i) in H_2O (curve (a)) : 0.1 M $NaClO_4$ + 0.01 M H_2Q + 10^{-5} M Rose Bengal. (2-imidazolin-5-one being insoluble in H_2O, was not taken in the solution though it was adsorbed on ZnO electrode from acetonitrile solution); (ii) in ACN (curve (b)): same as above + 10^{-5} M 2-imidazolin-5-one. Light intensities: (A) 4630 W m^{-2} in both H_2O and ACN media; (B) 1.21 W m^{-2} in H_2O and 0.68 W m^{-2} in ACN; (C) 0.28 W m^{-2} in both H_2O and ACN.

Further it is noticed that the rise of photopotential on illumination and its decay on switching off the light, occurs at a faster rate in aqueous solution than in ACN. Although the fast rise in photovoltage is desirable, its faster decay in aqueous solution indicates faster recombination of dye molecules in this medium.

3.3. *Current–Potential (i/V) characteristics*

Current–potential curves for the ZnO electrode exposed to visible light in aqueous and ACN solutions are shown in Fig. 4. The photocurrent–potential curves were obtained first in the absence of dyes (curve (b)), then in the presence of only 2-imidazolin-5-one (curve (c)), or Rose Bengal (curve (d)), and finally in the presence of both dyes (curve (e)). Curve (a) represents the current–potential characteristic of the ZnO electrode in the dark condition.

In the aqueous solution (Fig. 4(A)) the magnitude of the dark current was found to be large (about 0.9 A m^{-2} at 0.4 V) and increased further with applied potential without showing any tendency to saturation, while in the ACN solution (curve (a) in Fig. 4(B)), it was negligible (0.04 A m^{-2} maximum) and remained almost constant over the whole range

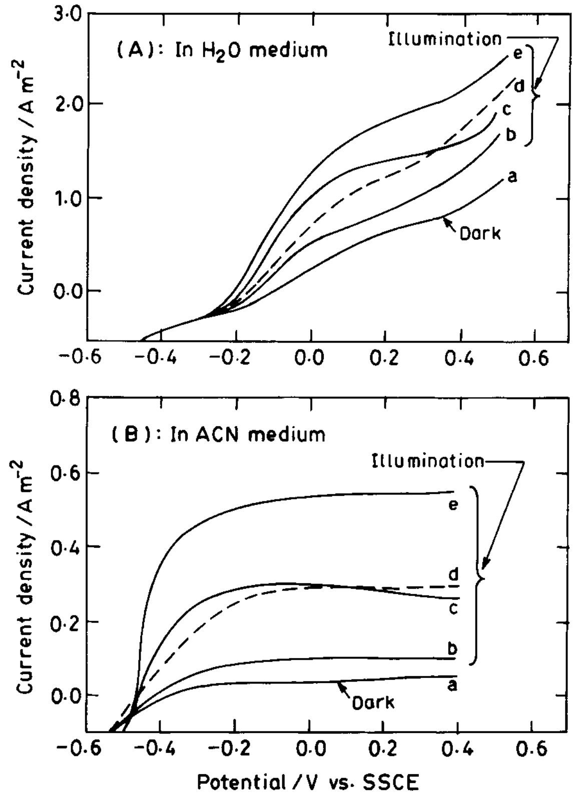


Fig. 4. Current–potential curves for sprayed ZnO thin film electrode determined in aqueous (A) and acetonitrile (B) solutions in dark (curve (a)) and under illumination by visible light ($\lambda >$ 420 nm; curves (b), (c), (d), (e)). These curves were obtained when ZnO electrode was sensitized by none of the dyes (b), by 2-imidazolin-5-one only (c), by Rose Bengal only (d), and by both these dyes together (e). Electrolyte: 0.1 M $NaClO_4$ + 0.01 M H_2Q in all solutions (for dye concentration, refer to the text). Light intensity 4900 W m^{-2} in all cases.

of applied potential. The appearance of photocurrent on illumination of the ZnO electrode (curve (b)) with light of subband gap energy ($h\nu < E_g$) in the absence of dye molecules, is indicative of the presence of surface states at intermediate energy levels within the band gap of the semiconductor electrode. The enhancement in photocurrent observed in the presence of both dyes (curve (e)) as compared to that observed with the use of a single dye (curve (c) and (d)) shows the additive effect of these dyes on the sensitized photocurrent. It is also noticed that i/V curves obtained in aqueous solution (Fig. 4(A)) do not show a tendency to saturation in photocurrent with the applied potential. In contrast, the photocurrent attains saturation beyond −0.2 V vs SSCE (only at 0.3 V above the onset potential) in ACN solution and hence it (ACN) is the preferable medium over the aqueous one.

The flat band potential (V_{fb}) of the semiconductor electrode (ZnO) obtained from the onset of photocurrent, is $V_{fb} = -0.30 + 0.01$ V vs SSCE in aqueous solution, and −0.50 + 0.01 V in ACN solution.

3.4. *Photocurrent transients*

Photocurrent transients measured for the ZnO electrode in electrolyte containing $NaClO_4$ (0.1 M) and H_2Q (0.01 M) were recorded under different conditions keeping the electrode biased at 0.0 V vs SSCE (Fig. 5).

In aqueous solutions under filtered visible light ($\lambda > 420$ nm) illumination (Fig. 5(A)), curves were recorded (i) in the absence of dyes (curve (a)), (ii) in the presence of 2-imidazolin-5-one on the electrode (curve (b)), and (iii) in the presence of both the dyes (2-imidazolin-5-one and Rose Bengal) on the electrode (curve (c)). On sudden illumination of the electrode the photocurrent initially overshoots then decreases and takes about 10–15 s to attain a steady value. The decrease in photocurrent after the initial spike is probably due to the recombination of dye-injected electrons and oxidized dye molecules or surface states acting as electron traps. The decrease in photocurrent with time may also be the result of slow regeneration of dye molecules after electron injection. On interruption of light the current was found to diminish quickly, but instead of attaining the dark current, an initial overshooting in the opposite direction was observed before the attainment of the steady dark current. Such reverse current indicates the back tunneling of the dye-injected electrons toward the surface of the electrodes and their recombination with the oxidized dye molecules. Similar behaviour has also been observed with different systems [19]. Further, when Rose Bengal was used along with 2-imidazolin-5-one, the photocurrent was

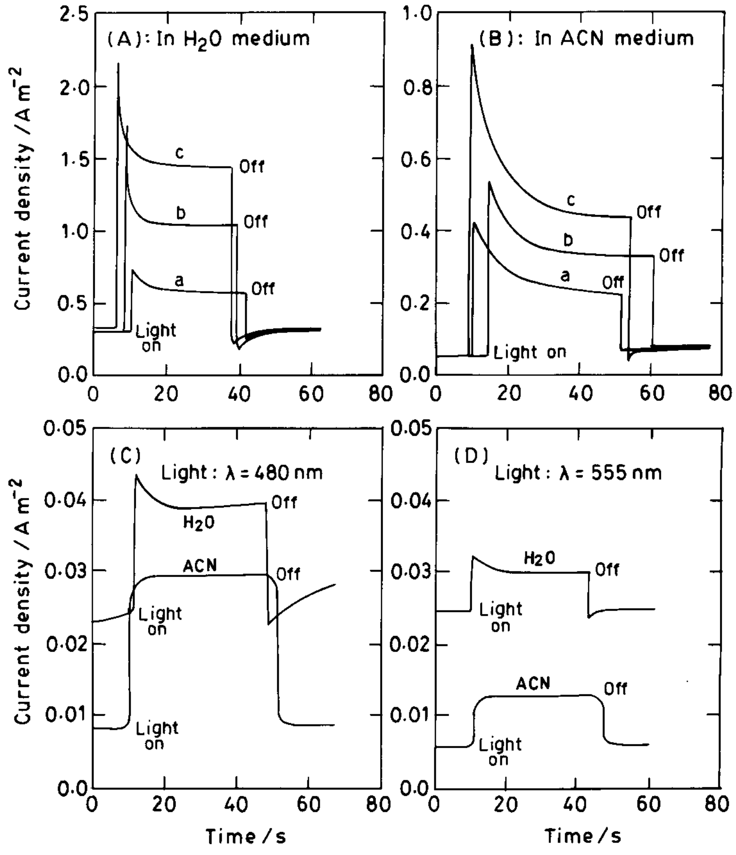


Fig. 5. Transient current–time curves for dye-sensitized ZnO electrode held at fixed bias potential (0.0 V vs SSCE) in aqueous and acetonitrile solution under illumination with visible light (A, B) and monochromatic light (C, D). In (A, B): (a) without dye, (b) sensitized by 2-imidazolin-5-one only, (c) sensitized by 2-imidazolin-5-one + Rose Bengal. In (C, D): sensitized by 2-imidazolin-5-one + Rose Bengal together. Electrolyte: 0.1 M $NaClO_4$ + 0.01 M H_2Q in all solutions (for dye concentration, refer to the text). Light intensities: (A, B) 4900 W m^{-2}; (C) 1.21 W m^{-2}; (D) 0.28 W m^{-2}.

enhanced (curve (c)) as compared to that observed with 2-imidazolin-5-one alone (curve (b)), which provides clear evidence for the additive effect of both dyes on the sensitized photocurrent. In ACN medium (Fig. 5(B)) the decrease in photocurrent from its initial to steady value is comparatively slow compared to that observed in aqueous medium. Further, when both the dyes are used, the photocurrent is reduced to about 40% of its initial value in ACN solution (curve (c) in Fig. 5(B)) whereas in aqueous solution (curve (c) in Fig. 5(A)) the photocurrent is reduced to only 55%.

Under monochromatic light irradiation (at $\lambda = 480$ nm, Fig. 5(C), and $\lambda = 555$ nm, Fig. 5(D)) *i*/*t* curves determined in ACN solution did not exhibit any overshoot in photocurrent and the curves were almost of rectangular shape. This contrasted with the observation under visible light illumination in the same solution (curve (c) in Fig. 5(B)). Although the reason for this difference is not clear, it may be due to enhanced recombination of injected charge carriers under high intensity of visible light. In the case of aqueous solution, however, the nature of the *i*/*t* curves, observed under monochromatic light illumination (Figs. 5(C) and (D)), was found to be similar to that observed under visible light (Fig. 5(A)).

3.5. *Action spectra (IPCE-λ)*

The spectral dependence of the photocurrent at the bare (without dye) and dye-coated electrodes (kept at a fixed potential of 0.0 V vs SSCE) was determined using aqueous and acetonitrile solutions, and from the observed photocurrent and corresponding intensity of monochromatic light (used for illumination of the semiconductor electrode), incident photon-to-current conversion efficiency (IPCE) was calculated. The variation of the IPCE as a function of the wavelength of monochromatic light (λ) is shown in Fig. 6, for a ZnO electrode sensitized by 2-imidazolin-5-one (curve (a)), Rose Bengal (curve (b)), and both dyes together (curve (c)). The curve (d) is the same for unsensitized ZnO electrode. The appearance of two photocurrent maxima at 480 and 555 nm in curve (**c**) provides clear evidence that if the dyes are used together, they can sensitize the photocurrent additively.

Here it needs to be pointed out that the absorption peak of 2-imidazolin-5-one observed at 435 nm wavelength in solution phase (curves (a) and (c) of Fig. 2) experiences a large (~50 nm) red shift and appears at 480 nm in the action spectra (curves (a) and (c) of Fig. 6). In addition a further peak is observed at 510 nm in the photocurrent spectrum. This shift in $\lambda_{\max}$ of 2-imidazolin-5-one results due to adsorption on the ZnO surface and the probable mechanism has already been discussed [16].

Further comparison of the action spectrum of the ZnO electrode coated with Rose Bengal alone (curve (b) of Fig. 6) with that of the ZnO coated with both the dyes (curve (c) of Fig. 6) shows that, in both cases, the photocurrent peaks due to Rose Bengal are observed at the same wavelength (555 nm). From this result it can be inferred that rose bengal adsorbs directly onto the semiconductor surface, not onto the first dye, when it is allowed to adsorb on a ZnO electrode already coated with 2-imidazolin-5-one.

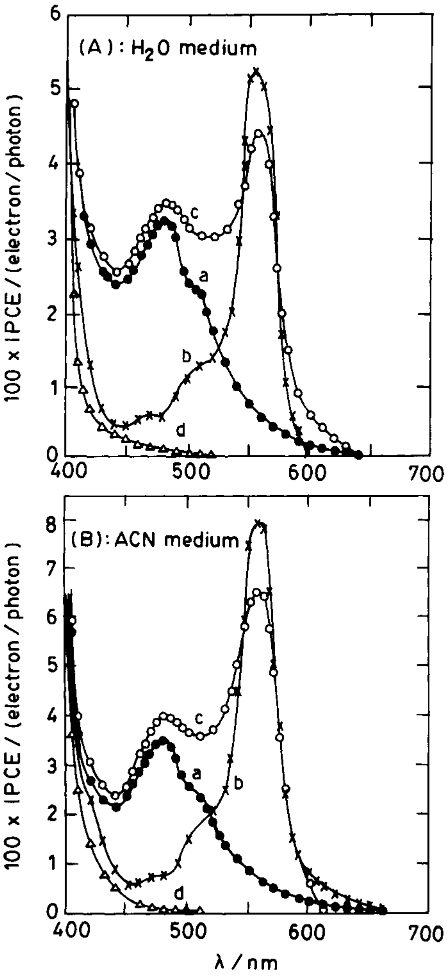


Fig. 6. Photocurrent action spectra (IPCE against λ) of sprayed ZnO thin film electrode (held at 0.0 V vs SSCE) in H_2O (A) and ACN (B) media sensitized by 2-imidazolin-5-one (curve (a)), Rose Bengal (curve (b)), and 2-imidazolin-5-one and Rose Bengal together (curve (c)). Curve (d) is for bare electrode (without any dye). (For solution composition, refer to the text.)

In general, the IPCE values were found to be higher in ACN solutions (Fig. 6(B)) than those observed in aqueous solutions (Fig. 6(A)). With the use of both dyes (curve (c) in both (A) and (B)), IPCE values for monochromatic lights of 480 and 555 nm wavelengths were found to be 3.5 and 4.4%, respectively, in aqueous solution, while in ACN medium the corresponding values were 4 and 6.5%.

3.6. *Energy level diagram*

To present a clear picture of the energetics of the sensitization of the photocurrent at the ZnO electrode by dye molecules and the dye regeneration process, a relative energy level diagram (on the electrochemical scale with respect to SSCE) of the cell components (ZnO | 2-imidazolin-5-one, Rose Bengal | redox

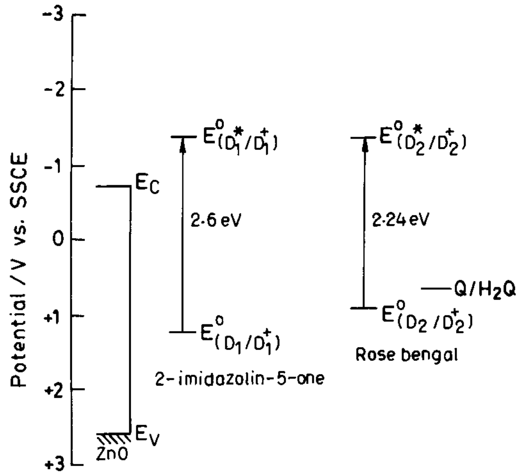


Fig. 7. Energy level diagram of ZnO, 2-imidazolin-5-one, Rose Bengal (both as donor) in ground state (D) and excited state (D*), and quinone/hydroquinone (Q/H_2Q) redox couple.

reagent) is shown in Fig. 7. Various energy levels of the cell components required to construct this diagram, such as the flat band potential of the ZnO electrode = −0.62 V vs SSCE and the formal redox potential of 2-imidazolin-5-one = 1.24 V vs SSCE are taken from earlier work [16]. The formal redox potential of Rose Bengal, that is, 0.93 V vs SSCE, is also taken from earlier work [20]. The excitation energies for 2-imidazolin-5-one and Rose Bengal were taken to be 2.6 and 2.4 eV, respectively, based on their λ_{max} values. The redox potential of the redox reagent hydroquinone is 0.70 V [21]. This diagram clearly indicates that the relative positions of various energy levels are such that the excited dye molecules (D*) can easily inject electrons into the conduction band of *n*-ZnO and the oxidized dye molecules (D^+), after returning to their ground states, can be reduced (regenerated to their original form) by hydroquinone present in the solution. Thus, the feasibility and sustainability of dye sensitization of photocurrent is clearly demonstrated.

3.7. *Power conversion efficiency and fill factor*

The power outputs of the ZnO-based PEC cells sensitized by the dyes together were determined under illumination with filtered (λ > 420 nm) visible light (Fig. 8(A)) and white light (Fig. 8(B)) using aqueous (curve (a)) and ACN (curve (b)) media for electrolyte solutions (0.1 M $NaClO_4$ + 0.01 M H_2Q). These measurements were made with a two-electrode cell configuration using carbon as counter electrode. Under filtered visible light (λ > 420 nm) illumination, the power conversion efficiency (η) and the fill factor (*FF*) were found to be $\eta = 2.7 \times 10^{-3}\%$ and $FF = 0.28$ in the case of aqueous solution, and $\eta = 1.8 \times 10^{-3}\%$ and $FF = 0.45$ in ACN solution. When white light was used for the illumination, these parameters were found to be $\eta = 4.1 \times 10^{-3}\%$ and $FF = 0.18$ in aqueous solution, and $\eta = 2.1 \times 10^{-3}\%$ and $FF = 0.28$ in ACN solution. Thus, power

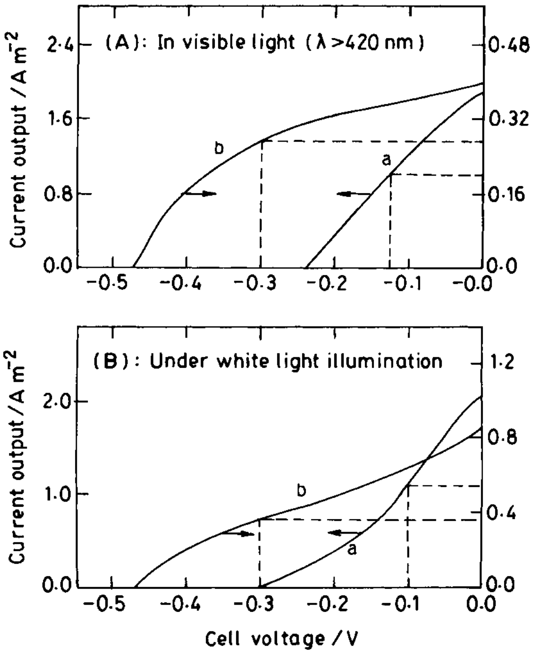


Fig. 8. Output current–potential curves for dye-sensitized aqueous (a) and nonaqueous (b) PEC cells (with carbon counter electrode) under illumination with visible light (A) and white light (B). Solution composition is the same as in case of Fig. 3. Light intensities: (A) 4620 W m^{-2} in H_2O (curve (a)) and 4650 W m^{-2} in ACN (curve (b)); (B) 5360 W m^{-2} in H_2O (curve (a)) and 5290 W m^{-2} in ACN (curve (b)).

conversion efficiencies were higher in aqueous solution, but fill factors were larger in ACN solutions.

3.8. *Long term photocurrent stability*

Keeping the dyes-coated ZnO electrode at a fixed potential and illuminating it continuously with either filtered visible light or white light, the photocurrent was monitored as a function of time and the results are represented in Fig. 9. In the aqueous medium (curve (a)), on illumination of the ZnO electrode with white light, the photocurrent decreased for half an hour and then remained steady for another half an hour, before decreasing continuously till the end of 7 h of the experiment. In ACN solution (curve (b)), on the other hand, the photocurrent increased for some time after its initial decrease for half an hour, but this increasing trend persisted hardly for 1 h and thereafter it decreased continuously before becoming stable beyond 5.5 h. The increase in photocurrent in the intermediate stage may be attributed to u.v. photoetching of the ZnO electrode, whereas the decrease in photocurrent might have been caused by various factors, such as photocorrosion of the ZnO electrode, the presence of surface states at intermediate energy levels providing recombination centres, and the regeneration of the dye molecules being unable to compete kinetically with the rate of electron injection by excited dye molecules to the conduction band of the semiconductor.

Under visible light illumination (Fig. 9(B)), the variation in photocurrent with time was found to be

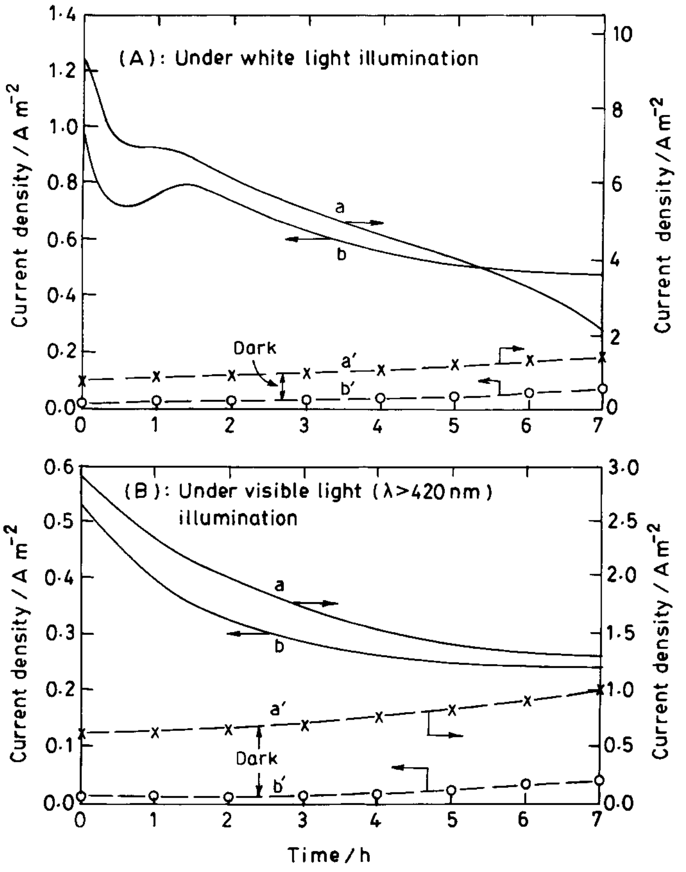


Fig. 9. Variation of photocurrent with time at fixed bias potential (0.3 V vs SSCE for H_2O medium and 0.0 V vs SSCE for ACN medium) in aqueous (curve (a)) and ACN (curve (b)) media on prolong operation of dye-sensitized ZnO cells under continuous illumination with (A) white light and (B) visible light ($\lambda > 420$ nm). Solution composition is the same as in case of Fig. 3. Light intensities: (A) 5560 W m^{-2} in H_2O and 5290 W m^{-2} in ACN; (B) 4640 W m^{-2} in both H_2O and ACN media.

similar in both aqueous and nonaqueous media. The photocurrent decreased continuously with time, though the decreasing rate was higher in the initial 4 h. In aqueous as well as ACN solutions, the total current was reduced to about 50% of its initial value after 7 h of continuous operation of the cells. In the case of aqueous solution, the dark current (curve (a′)), which was already high, was found to increase further (from 0.7 to 1.0 A m^{-2} in 7 h), so that its contribution toward the total current (obtained under illuminated condition, curve (a)) increased from 20% in the beginning to about 80% at the end of 7 h. In contrast, in ACN solution, the dark current (curve (b′)) remained low during the entire duration and its contribution toward the total current (curve (b)) was hardly 2.5% initially : this value increased at the end of 7 h, but only to 14%. Based on these experimental observations it can be concluded that acetonitrile is more suitable than water for preparing electrolyte solutions to be used in PEC cells.

4. Conclusions

It can be concluded that if 2-imidazolin-5-one is used along with Rose Bengal, both dyes sensitize the photocurrent at a ZnO electrode simultaneously and the observed photocurrent is almost the sum of their individual contributions. Acetonitrile was found to be a more suitable medium than water as electrolyte solution.

Acknowledgement

Financial assistance from the Ministry of Non-conventional Energy Sources, Government of India, is gratefully acknowledged. The authors also thank Dr A. K. Mukerjee of this Department for supplying 2-imidazolin-5-one.

References

[1] K. Rajeshwar, P. Singh and J. DuBow, *Electrochim. Acta* **23** (1978) 1117.
[2] R. Memming, *in* ‘Electroanalytical Chemistry’ Vol. II, edited by A. J. Bard (Marcel Dekker, New York, 1979), p. 1.
[3] S. R. Morrison, *in* ‘Electrochemistry at Semiconductor and Oxidized Metal Electrodes’ (Plenum Press, New York, 1980).
[4] K. Kalyansundaram, *Solar Cells* **15** (1985) 93.
[5] H. Gerischer and F. Willig, *Topics in Current Chemistry* **61** (1976) 31.
[6] K. Hauffe, H. Pusch, J. Range, and D. Rein, *in* ‘Current Problems in Electrography’, edited by K. Hauffe and W. Berg (De Gruyter, Berlin, 1972).
[7] K. Hauffe, *in* ‘Electrochemistry: The Past Thirty and Net Thirty Years’, edited by H. Bloom and F. Gutmann (Plenum Press, New York, 1977).
[8] K. Hauffe, *Phot. Sci. Eng.* **20** (1976) 124.
[9] M. D. Archer, *J. Appl. Electrochem.* **5** (1975) 17.

[10] H. Gerischer, *J. Electrochem. Soc.* **125** (1978) 218c.

[11] A. J. McEvoy and M. Grätzel, *Sol. Energy Mat. Sol. Cells.* **32** (1994) 221.

[12] K. Hauffe, H. Pusch and J. Range, *Z. Phys. Chem. (N.F.)* **64** (1969) 122.

[13] K. Hauffe and U. Bode, *Faraday Discuss.* **58** (1974) 281.

[14] H. J. Danzmann, K. Hauffe, and Z. G. Szabo, *Z. Phys. Chem. (N.F.)* **104** (1977) 95.

[15] N. Alonso-Vante, M. Belay, P. Chartier and V. Ern, *Revue Phys. Appl.* **16** (1981) 5.

[16] L. Bahadur and L. Roy, *Semicond. Sci. Technol.* **10** (1995) 358.

[17] L. Bahadur and T. N. Rao, *Sol. Energy Mater. Sol. Cells* **27** (1992) 347.

[18] A. Jain and A. K. Mukerjee, *J. Ind. Chem. Soc.* **67** (1990) 973.

[19] T. Yamase, H. Gerischer, M. Lubke and B. Pettinger, *Ber. Bunsenges. Phys. Chem.* **82** (1978) 1041: *ibid.* **83** (1979) 658.

[20] L. Bahadur and J. P. Pandey, *Indian J. Eng. Mater. Sci.* **4** (1997) 213.

[21] A. J. Bard and H. Lund, in 'Encyclopedia of Electrochemistry of Elements', Vol. **12** (Marcel Dekker, New York, 1973), p. 149.