JOURNAL OF APPLIED ELECTROCHEMISTRY 22 (1992) 883–887

Spectral sensitization of sprayed thin film *n*-ZnO electrodes by 4-*p*-dimethylaminobenzylidene-1,2-diphenyl-2-imidazoline-5-one in acetonitrile solution

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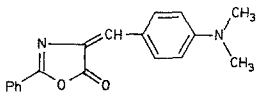
Received 28 October 1991; accepted 11 February 1992

A photoelectrochemical cell based on a thin film *n*-ZnO electrode sensitized by 4-*p*-dimethylaminobenzylidene-1,2-diphenyl-2-imidazoline-5-one (subsequently referred to as 5-imidazolone) has been studied in acetonitrile medium using hydroquinone as supersensitizer. The redox behaviour of 5-imidazolone at Pt and ZnO electrodes has been studied in the same medium through cyclic voltammetry. The redox potentials of 5-imidazolone coupled with the flat-band potential of the ZnO electrode (obtained from the potential for photocurrent onset) have been used to determine their respective energy levels. Transient open circuit photovoltage–time profile and transient photocurrent–time profiles at fixed biased potentials have been recorded to determine the obtainable photovoltage and photoresponse behaviour of the ZnO electrode in the presence of 5-imidazolone. The quantum efficiency of the sensitized photocurrent was found to be ~7% at 455 nm (λ_{max}), the wavelength of monochromatic light. The long-term stability of the ZnO electrode in the medium of investigation was tested in the presence of this compound and was found to give a quite stable photocurrent for 10 h of continuous operation at lower light intensity. The power efficiency of ZnO/5-imidazolone in a acetonitrile/Pt photocell was also determined without any external applied potential.

1. Introduction

Dye sensitization of semiconductor electrodes has been the subject of many investigations [1–23]. Such studies are important, particularly in the case of wide band-gap semiconductors ($E_g > 3$ eV), since they cannot absorb light in the visible region ($h\nu < E_g$) of the solar spectrum for conversion into useful energy and hence their spectral response needs to be extended. To achieve this objective, several dyes and organometallic complexes have been studied and found to sensitize the photocurrent at semiconductor electrodes in photoelectrochemical cells. To further such investigations, it is necessary to examine newer compounds for possible use as photosensitizers. With this objective 5-imidazolone (as shown below) was studied and the results are reported in this paper.



4-p-Dimethylaminobenzylidene-1,2-diphenyl -2-imidazoline-5-one: (5-imidazolone)

This compound has been studied with the particular aim of developing a new series of sensitizers by synthesizing tailor-made compounds taking 5-imidazolone as the basis.

In the present work, polycrystalline sprayed thin films of *n*-ZnO have been used as photoelectrode and acetonitrile as the medium of investigation. The purpose of selecting non-aqueous solvent was to see whether better stability of semiconductor electrodes can be achieved as suggested by Bard and coworkers [24–26].

2. Experimental details

2.1. *Materials*

Acetonitrile (E. Merck, India) was purified as described earlier [27]. Anhydrous sodium perchlorate (Ega Chemie, Germany, or Aldrich Chemical), as received, was used as supporting electrolyte. 5-imidazolone, used as sensitizer, was synthesized and purified by Mukerjee and coworkers [28]. Hydroquinone (BDH, India) was used as supersensitizer. Thin film *n*-ZnO electrodes were prepared as described earlier [27].

2.2. *Apparatus and instruments*

For all electrochemical and photoelectrochemical experiments, a conventional three-electrode, single compartment cell having a quartz window was used. The counter electrode was a spiral platinum wire and an aqueous NaCl saturated calomel electrode, separated from the test solution by a Luggin capillary agar salt (NaCl) bridge, was used as the reference electrode. All the potentials are quoted with respect to

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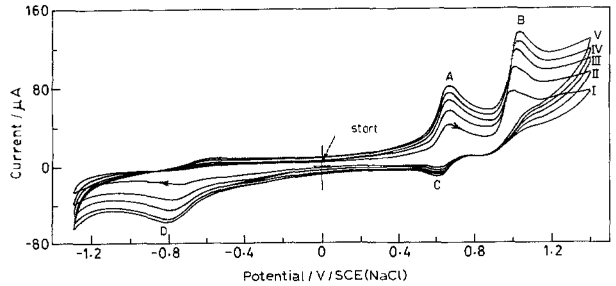

Fig. 1. Cyclic voltammograms of 5-imidazolone at Pt electrode (Solution: 10^{-3} M 5-imidazolone + 0.1 M $NaClO_4$ supporting electrolyte in CH_3CN) recorded at different scan rates starting from 20 mV s^{-1} (curve I) and increasing in steps of 20 mV s^{-1}.

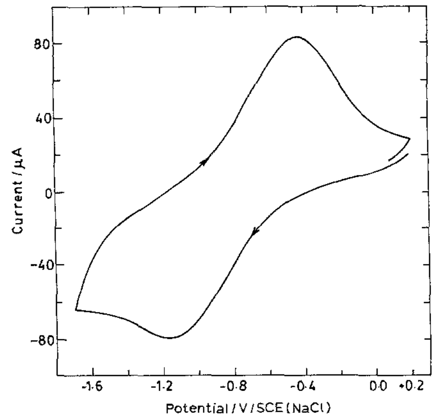

Fig. 2. Cyclic voltammogram of 5-imidazolone at ZnO electrode. Solution: 10^{-3} M 5-imidazolone + 0.1 M $NaClO_4$ supporting electrolyte in CH_3CN, scan rate = 20 mV s^{-1}.

this electrode. The experiments were performed after degassing the solution by bubbling purified nitrogen. For current-potential measurements, the same set of equipments described earlier [27] was used.

For photoelectrochemical measurements, a 150 W Xenon arc lamp was used as light source along with fused silica condensing lenses, a monochromator (Model 77250 with a model 7798 grating), neutral density filters (Model no. 50490–50570) and a long-pass filter (Model no. 51280, transmitting photons with $\lambda > 420$ nm) (all Orial Corp. USA). The light intensity was measured with a Digital Photometer (Tektronix Model J 16 with J 6502 sensor). The power output of the PEC cell (*n*-ZnO/electrolyte + sensitizer/Pt) was measured, under white light illumination, as a function of an external load resistance, without any external biased potential.

3. Results and discussion

3.1. *Redox behaviour of 5-imidazolone in acetonitrile medium*

In order to determine the electron donating/accepting energy levels of the sensitizer molecules in its ground as well as in the excited states, the knowledge of its ground state redox potential is essential [29]. For this purpose, the redox behaviour of 5-imidazolone in acetonitrile medium was studied at the platinum as well as at the ZnO electrode.

Cyclic voltammograms obtained at the platinum electrode at different scan rates are given in Fig. 1. These exhibit an irreversible cathodic peak (D), the peak potential varying from −0.75 to −0.80 V/SCE (NaCl) with change in the scan rate from 20 to 100 mV s^{-1}. In the anodic potential region, two peaks (A and B) are observed in the forwarded scan while during the reverse scan only one peak (C) is observed. The voltammograms obtained at different scan rates clearly indicate that the potentials corresponding to peak A ($E_{p,a}$ = 0.67 V) as well as peak C ($E_{p,c}$ = 0.61 V) are unchanged with change in the scan rate and the peak potential separation, ΔE_p, is ~60 mV, indicating the characteristic behaviour of a reversible one electron transfer process. However, since the peak current ratio ($i_{p,c}/i_{p,a}$) is not unity, it may be concluded that the first oxidation of 5-imidazolone, at lower anodic potential, is a one electron transfer process of a quasi-reversible nature. The formal redox potential for this oxidation process was found to be +0.64 V/SCE (NaCl). The second anodic peak (B), for which the peak potential varies from +0.98 V at 20 mV s^{-1} to 1.03 V at 100 mV s^{-1} exhibits irreversible behaviour.

The redox behaviour of 5-imidazolone was also studied at the ZnO electrode. In this case, no peak was observed in the anodic region up to +2.0 V. In the cathodic region, the voltammogram obtained at 20 mV s^{-1} is shown in Fig. 2. This figure indicates that 5-imidazolone is reduced at around −1.15 V and is reoxidized almost completely, but at a much different potential ($E_{p,a}$ = − 0.43 V). Although the peak current ratio ($i_{p,a}/i_{p,c}$) is unity, the peak potential separation (ΔE_p = 0.73 V) is too large for any definite conclusion to be drawn regarding the nature of the process. The average of the peak potentials is −0.79 V/SCE (NaCl) which is close to the reduction potential at the platinum electrode. The use of these redox potentials to determine the electron energy terms of the sensitizer will be discussed later.

3.2. *Photoelectrochemical studies*

3.2.1. Photoresponse of the ZnO electrode at open circuit. The photoresponse of the ZnO electrode under open circuit condition, with 5-imidazolone and hydroquinone present in the solution, is shown in Fig. 3. This figure clearly indicates that, on illumination of the photoelectrode, the open circuit potential shifts

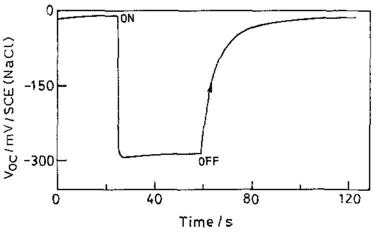

Fig. 3. Open circuit potential at ZnO electrode in acetonitrile solution containing 0.1 mM 5-imidazolone + 10 mM hydroquinone + 0.1 M $NaClO_4$. Intensity of light = 564 mW cm^{-2}.

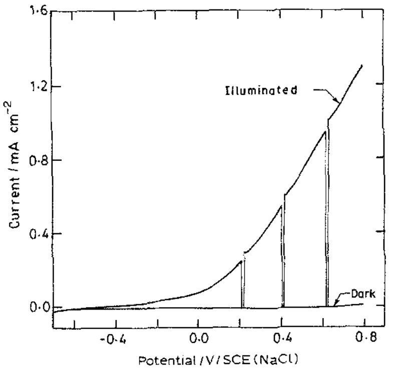

Fig. 4. Current-potential curves for ZnO electrode in dark and under full light illumination in acetonitrile solution containing 10^{-4}M 5-imidazolone + 10^{-2}M hydroquinone + 0.1 M $NaClO_4$. Light intensity 564 mW cm^{-2}, scan rate 20 mV s^{-1}.

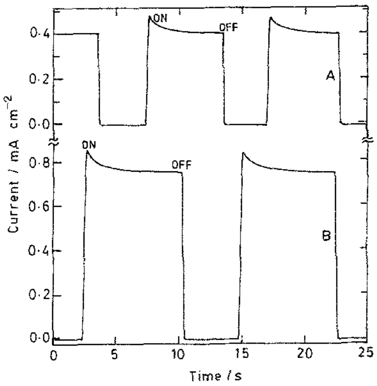

Fig. 5. Transient *i–t* curves for ZnO electrode at fixed biased potentials, A: +0.40 V B: +0.60 V/SCE (NaCl). Solution composition and intensity being the same as in Fig. 4.

negatively, a characteristic feature of an n-type semiconductor. The photovoltage develops quickly, with little overshoot in the initial stage, followed by a slight decrease with time. However, when illumination is interrupted, it takes comparatively a much longer time to attain the steady state potential corresponding to the initial value in dark. The photovoltage obtained in this case was around −0.28 V.

3.2.2. Current potential curve. Current–potential curves, in dark and with white light illumination, for the ZnO electrode immersed in deaerated acetonitrile solution are shown in Fig. 4. The dark current was comparatively negligible ($< 1\,\mu$A) over the entire potential range. The effect of momentary interruption of illumination is also indicated in the figure. Although the photocurrent was found to rise at about 0.0–0.5 V, there was no appreciable increase in photocurrent even up to +0.1 V biased potential. Beyond this, however, the photocurrent was found to increase sharply, but without showing any tendency of saturation. The sluggish onset of the photocurrent and also some variations observed in the onset potential with light intensity and different electrode samples make the precise determination of the flat band potential rather difficult. However, such variations were found to be within ±50 mV. Hence, the value of the flat-band potential of ZnO in the test solution can be taken as $V_{fb} = -0.50 \pm 0.05$ V/SCE (NaCl). A slow increase in photocurrent at lower anodic potential and its unsaturation seem to be due to structural and chemical imperfections (such as grain boundaries and steps) of the electrode surface enhancing the surface recombination [30] of photogenerated electrons with holes.

3.2.3. Transient i–t curve. The transient response to light of the *n*-ZnO electrode kept at a fixed potential was measured in terms of current output and the results are shown in Fig. 5. The curves recorded at two different biased potentials, which are similar, indicate that when the electrode kept in dark is illuminated, the photocurrent rises to a high value almost instantaneously and then decays, before attaining a steady state value. Since the net photocurrent flowing in the external circuit is contributed to by photo-induced charge carriers generated in the semiconductor and injected electrons from the excited sensitizer molecules, the decay in photocurrent is indicative of recombination of injected electrons and the resulting oxidized species of the sensitizer molecules, and partial recombination of photogenerated charge carriers through surface states. The probability of recombination of charge carriers is expected to be less at higher positive potentials since, in such cases, due to high band bending charge carrier separation will be more efficient. So at comparatively higher positive potential the decay in photocurrent is expected to occur to a lesser extent and this has been observed in the present case. The decrease in photocurrent from its highest to its steady state value is less (~12%) at higher potential (Fig. 5, curve B) than that obtained (~16%) at lower biased potential (Fig. 5, curve A). Very recently, Kucernak and coworkers [31] have made a successful attempt to provide the theoretical basis to interpret the transient photocurrent response to chopped light and the present results are in good agreement with those predictions.

3.2.4. Energy level of 5-imidazolone and ZnO semiconductor. For the energy level diagram shown in Fig. 6, the redox potential for the oxidation of 5-imidazolone [$E^0(S/S^+) = +0.64$ V/SCE (NaCl)] obtained from

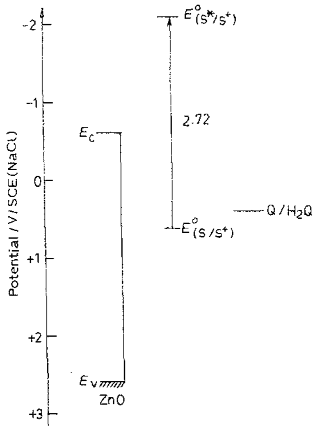

Fig. 6. Energy level diagrams of ZnO, 5-imidazolone (as donor) in the ground state(s) and excited state (S*), and hydroquinone supersensitizer.

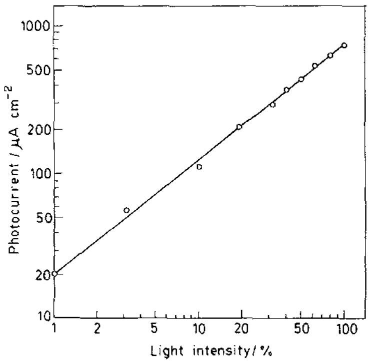

Fig. 7. Photocurrent dependence on light intensity for ZnO electrode in acetonitrile solution containing 10^{-4} M 5-imidazolone + 10^{-2} M hydroquinone + 0.1 M $NaClO_4$. Electrode potential +0.4 V.

cyclic voltammetry at the platinum electrode (*cf.* Section 3.1) was used for the ground state energy level of the sensitizer molecules and for the excited state, the excitation energy of 5-imidazolone (λ_{max} = 456 nm) equal to 2.72 eV was used. The band edges of the semiconductor (ZnO) were determined using the flat band potential V_{fb} = − 0.50 V/SCE (NaCl) (*cf.* Section 3.2.2). This energy diagram clearly demonstrates that the excited molecules of 5-imidazolone can inject electrons into the conduction band of the ZnO electrode.

3.2.5. Variation of photocurrent with light intensity. At a fixed applied potential the photocurrent at the ZnO electrode was measured as a function of light intensity (varied with the help of neutral density filters) and the result (Fig. 7) shows a linear variation in photocurrent with light intensity as observed by other investigators [32–34] for different systems. Although the photocurrent was found to vary linearly with light intensity, the slope of the curve ($\Delta \log i_{photo}/\Delta \log I_0$, I_0 being the intensity of light) is not unity, it is rather 0.79. This indicates the influence of other factors, besides the concentration of photogenerated charge carriers, in controlling the output photocurrent.

3.2.6. Action spectrum. The spectral dependence of the photocurrent at the ZnO electrode, kept at fixed biased potential (+0.40 V), was determined with and without 5-imidazolone present in the solution and the result is shown in Fig. 8 along with the absorption spectrum of the test compound in acetonitrile. The comparison of curve C (obtained with 5-imidazolone) with the base curve B (without 5-imidazolone) makes it clear that there is an enhancement in photocurrent due to the addition of 5-imidazolone. Furthermore, if the base line curve B is subtracted from the sensitized photocurrent spectrum (curve C), the nature of the resultant curve is almost identical to that of the absorption spectrum (curve A). Thus the sensitization of photocurrent by 5-imidazolone is evident. Since the photocurrents shown by curve C are normalized for the same flux of photons (1.23 × 10^{12} photons cm^{-2} s^{-1}) of each wavelength, the same curve also represents the variation in quantum efficiency (right side scale) as a function of the wavelength of the light. The quantum efficiency at the peak wavelength (λ_{max} = 455 nm) was found to be ~7%.

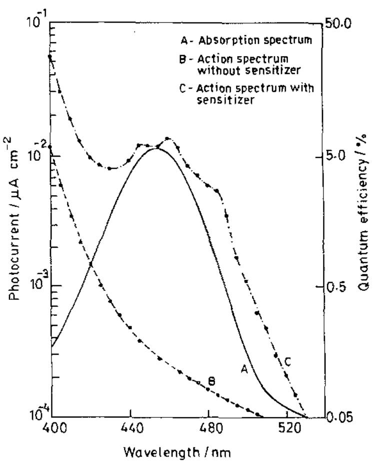

Fig. 8. Wavelength dependence of the photocurrent at ZnO electrode without and with 5-imidazolone (10^{-4} M) in acetonitrile solution of 10^{-2} M hydroquinone and 0.1 M $NaClO_4$ at electrode potential +0.40 V/SCE (NaCl). Photocurrent was normalized for photon flux 1.23 × 10^{12} photons cm^{-2} s^{-1}.

3.2.7. Output power characteristics. The power characteristics of a PEC cell, (ZnO/5-imidazolone + hydroquinone in CH_3CN/Pt), was determined by illuminating the ZnO electrode with white light (210 mV cm^{-2}) and measuring the photocurrent and the corresponding photovoltage across a variable resistance used as external load. The result is shown in Fig. 9 along with the power (i_{photo} × V_{photo}) curve. Maximum power (1.2 × 10^{-7} W) was obtained at 60 KΩ and the fill factor was estimated to be 0.16. The full light (xenon arc lamp) conversion efficiency was found to be 4 × 10^{-4}%. Thus, without any external biased potential, power output in this case was not encouraging. This unreasonably low output may be due to various factors. First, the major part of the white light, which was used for electrode illumination, is not absorbed either by 5-imidazolone (λ_{max} = 455 nm) or the ZnO electrode (E_g = 3.2 eV) corresponding to

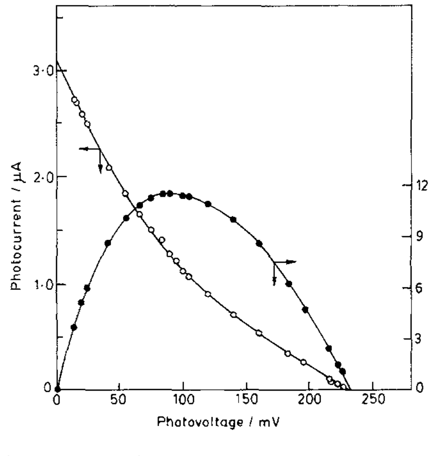

Fig. 9. Photocurrent–photovoltage curve for ZnO photocell sensitized by 5-imidazolone along with power (i_{photo} × V_{photo}) output. Solution composition: 10^{-4} M 5-imidazolone + 0.1 M $NaClO_4$ + 10^{-2} M hydroquinone. Light intensity 210 mW cm^{-2}, electrode area 0.14 cm^2.

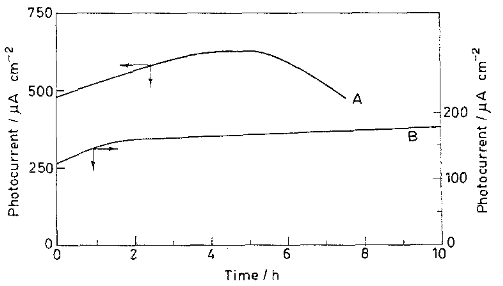

Fig. 10. Stability of photocurrent with time at a fixed biased potential (+0.40 V) for ZnO electrode in acetonitrile solution (composition being the same as in Fig. 9). A — illumination 411 mW cm^{-2}; B — illumination 93 mW cm^{-2}.

~380 nm wavelength of light thereby giving low values of photocurrent. Secondly, since power output was measured without any external biased potential, the separation of photogenerated charge carriers might not be efficient, and hence more surface recombination of charge carriers is likely to occur. Besides these factors, polarization of the counter electrode [35] during current flow may decrease the cell voltage leading to poor power output.

3.2.8. Long-term stability of the semiconductor electrode. The main objective of selecting a non-aqueous medium for the present investigation was to obtain better stability of the semiconductor electrode in PEC cell conditions. To test this aspect, the stability of the photocurrent at the ZnO electrode, kept at fixed biased potential (0.40 V), was monitored with time under continuous illumination of the photoelectrode. For the first experiment, the ZnO electrode was illuminated with white light from the Xenon arc lamp at its full intensity (411 mW cm^{-2}) and the result is shown in Fig. 10 (curve A). After continuous increase for about 4 h, the photocurrent remained steady for about 1 h and then decreased slowly. Every half hour the light was chopped off for a shortwhile to check the dark current and it was found to be almost negligible and unchanged throughout the experiment. The visual observation at the end of the experiment clearly indicated deterioration of the ZnO thin film electrode. From the observed decrease in photocurrent and the deterioration of the photoelectrode, it can be inferred that photocorrosion occurred. In the second experiment, white light with much lower intensity (93 mW cm^{-2}) was used and the result is represented by curve B in Fig. 10. From this curve it is evident that initially for about 2 h, the photocurrent increases at a comparatively faster rate and thereafter the increasing rate was much less. There was no indication of a decrease in photocurrent even up to 10 h of continuous operation. Thus it may be concluded that if a lesser amount of photocurrent is drawn by using lower intensity of light, better stability of the semiconductor electrode can be achieved in acetonitrile medium.

4. Conclusion

It can be concluded that 5-imidazolone acts as a donor sensitizer with a sensitized photocurrent efficiency (at a ZnO electrode) of around 7%. In the presence of this compound in solution, ZnO was found to give a stable photocurrent for 10 h of continuous operation at lower intensity (93 mW cm^{-2}) of light.

Acknowledgement

The Council of Scientific and Industrial Research, Government of India, is gratefully acknowledged for providing financial assistance. The authors also thank Dr A. K. Mukerjee, of this Department, for supplying the 5-imidazolone used as sensitizer.

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