Spectral sensitization of sprayed \( n \)-ZnO electrode by rose bengal in non-aqueous photoelectrochemical cell

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Photosensitising ability of rose bengal was studied at semiconducting \( n \)-ZnO electrode in acetonitrile medium using hydroquinone as supersensitizer. In order to ascertain the exclusive effect of dye sensitization on photocurrent at ZnO electrode, studies have been conducted under filtered light (\( \lambda > 420 \) nm) illumination also. Energy level diagram was constructed using redox potentials of rose bengal determined from cyclic voltammetric studies (reduction potential = \(-0.77 \) V and oxidation potential = + 0.93 V vs SSCE), coupled with the flat-band potential of ZnO electrode (\( V_{fb} = -0.60 \pm 0.02 \) V vs SSCE) determined through \( i_{photo}/V \) curve and redox potential of quinone/hydroquinone (0.45 V). The results indicated that rose bengal can act as donor as well as acceptor type dye. The quantum efficiency of dye-sensitized photocurrent was found to be \( \sim 78\% \). Long-term stability experiments gave encouraging results.

Photoelectrochemical cells based on high band-gap semiconductors such as ZnO, TiO\(_2\), SnO\(_2\), etc., have attracted considerable attention of the workers for their possible use as solar energy conversion devices\(^{1,9}\). In order to harvest the larger fraction of the solar spectrum, the sensitivity of these high band-gap semiconductors needs to be extended to visible light and for this purpose they are generally sensitized by different kinds of dyes\(^{1,8,10-16}\).

Among commercial dyes, rose bengal (RB) is one which has been studied extensively for spectral sensitization of ZnO electrode\(^{17-26}\). However, most of these investigations have been confined to aqueous medium only and very limited studies are reported in non-aqueous\(^{25}\) or in mixed solvents\(^{26}\). Nakao et al.\(^{25}\) have reported the quantum efficiency of the dye (RB)-sensitized photocurrent at ZnO electrode in acetonitrile medium but the information is not adequate.

In the light of the above, it was planned for the present work to make detailed investigations on spectral sensitization of ZnO semiconductor electrode by rose bengal in acetonitrile medium and the findings are reported in this paper.

**Experimental Procedure**

For preparing thin films of ZnO, aqueous solution of 0.1 M Zn(NO\(_3\))\(_2\) was sprayed on ultrasonically cleaned glass substrate (2x1 cm) maintained at 400 ± 20°C. Thin films, thus prepared, were annealed for an hour in controlled hydrogen atmosphere at 400±20°C. Further details regarding the preparation and mounting of the electrodes is described earlier\(^\text{27}\).

Acetonitrile (E. Merk, India) was purified as described earlier\(^\text{27}\). Anhydrous sodium perchlorate (Aldrich) was used as supporting electrolyte without further purification. Rose bengal (Romali, USA) was used as sensitizer and hydroquinone (BDH, India) as redox reagent (supersensitizer).

Electrochemical and 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 platinum wire served as a counter electrode and a saturated sodium chloride calomel electrode, SSCE [\( E^0 = -0.008 \) V vs SCE (KCl)]\(^\text{28}\), separated from the test solution by a Luggin capillary agar salt (NaCl) bridge, was used as 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 Nos 50490-50570).
Redox potential of rose bengal—Since the knowledge of the ground state energy level of the dye is required to predict the thermodynamic feasibility of electron injection from photo-excited dye molecules into the conduction band of the semiconductor electrode, the cyclic voltammograms of rose bengal were recorded at Pt and ZnO electrodes in acetonitrile solution and are shown in Fig.1.

It is evident from Fig.1, when anodic scan alone was performed starting from 0.0 V vs SSCE, voltammogram exhibited two peaks in the forward direction indicated by A ($E_{p,a} = 0.34$ V) and B ($E_{p,a} = 0.65$ V), and one in the reverse scan, C ($E_{p,c} = 0.50$ V). These peaks were found to be reproducible on the subsequent scans provided the scan was restricted between 0.0 and +1.2 V only. However, when the anodic scan was performed after the cathodic limit of −1.2 V, peak A was not reproduced, instead a broad peak E (at ~ 0.67 V), closely corresponding to peak B, and a sharp peak F ($E_{p,a} = 0.93$ V) were observed. On repeated scan between +1.2 and −1.2 V, the voltammogram exhibited only peaks C,D,E and F, not A. On the other hand, the cathodic peak D ($E_{p,a} = −0.77$ V) was found to be reproducible and remained unchanged whether cyclic voltammograms were recorded starting from 0.0 V or from anodic potentials.

These observations clearly indicate that the reduced form of this dye (RB) has some influence on its oxidation behaviour. There is no report available in literature regarding the redox potentials of rose bengal in acetonitrile medium. However, the redox potentials of this dye in aqueous medium as reported by Simidzu et al.29 are as follows—Oxidation redox potential $E^\circ_{(S/S^+)} \approx 0.6$ V and reduction redox potential $E^\circ_{(S/S^-)} = −1.0$ V vs SCE. On the other hand, Chan and Bolton30 have reported the reduction redox potential of this dye as $E^\circ_{(S/S^-)} = −0.53$ V. When the peak potentials observed are corrected for the liquid junction potential (0.250 V) existing at the tip of aqueous agar salt bridge/acetonitrile solution interface, then the potential for peak D agrees well with the reduction redox potential of this dye reported by Chan and Bolton30, while the potential for peak F closely
corresponds to the oxidation redox potential reported by Shimidzu et al. 29.

Cyclic voltammograms of rose bengal at ZnO electrode recorded in the cathodic region at different scan rates are shown in Fig.2. With the change in the scan rate from 20 to 100 mV/s, reduction (cathodic) peak was shifted from -0.86 to -0.90 V while the reoxidation (anodic) peak was shifted from -0.47 to -0.43 V increasing the peak separation from 0.39 to 0.47 V. Formal (reduction) redox potential thus obtained was \( E^\circ = -0.665 \pm 0.020 \) V vs SSCE. In the anodic potential region, no peak was observed at ZnO electrode.

**Current-potential (i-V) curves**—Current-potential response of ZnO electrodes in dye containing acetonitrile solution was recorded both under dark and white light illumination (Fig.3). As can be seen from Fig.3, the dark current was practically negligible. The effect of momentary interruption of light is also shown in the same figure. The nature of the curve obtained with illuminated electrode exhibits quite a slow increase in photocurrent in the lower range of applied potentials (upto \( \pm 0.3 \) V) followed by a sharp increase in higher potential region showing no tendency for saturation in photocurrent. This behaviour shows that the nature of the curve is mainly controlled by the structural properties (bulk and surface both) of the electrode rather than the species present in the solution. The photocurrent observed in this case was found to be 2.4 mA/cm\(^2\) at 1.5 V vs SSCE. The onset of photocurrent occurred at \(-0.60 \pm 0.02\) V vs SSCE and the same was taken as flat band potential, \( V_{fb} \), of ZnO electrode in the test electrolyte. However, it should be noted that while recording i-V curve under irradiation (Fig.3), full spectrum of light (white light) obtained from the xenon arc lamp was used to illuminate ZnO electrode. Hence the observed photocurrent must have been contributed by photoexcited dye molecule and semiconductor electrode both.

To ascertain the exclusive effect of dye sensitization on photocurrent at ZnO electrode, i-V curves obtained under filtered light (\( \lambda > 420 \) nm) illumination is shown in Fig.4. Curve C in this figure recorded in the presence of rose bengal in the solution clearly shows the enhancement in photocurrent as compared to curve B obtained in the absence of the dye (RB). Further, the comparison of the nature of i-V curves given in the Figs 3 & 4 shows that i-V curves obtained under filtered light illumination, exhibit near saturation behaviour with the increasing potential unlike that observed with white light irradiation. From this, it can be concluded that surface states act as recombination centres and are mainly responsible for lack of saturation in photocurrent, when white light \((h\nu > E_g)\) is used for irradiation of the semiconductor electrode. Under filtered light \((h\nu < E_g)\) illumination, recombination of injected electrons and the oxidized dye molecules seems to be absent or reduced substantially.

**Electron exchange energy levels of rose bengal and n-ZnO electrode**—Relative positions of vari-
Energy level diagram of ZnO, RB (as donor and acceptor both) in the ground state (S) and excited singlet state (S*), and quinone/hydroquinone (Q/H2Q) supersensitizer E°Q/H2Q = 0.45 V.

Energy terms have been shown in Fig. 5. Redox potentials of Fig. 1, E°(S/S-) = -0.77 V and E°(S/S+) = +0.93 V vs SSCE, give the ground energy level of rose bengal acting as an electron acceptor and donor respectively. The excited state of RB sensitizer differs from its ground state energy term by the stored excitation energy (hν) which in this case is 2.24 eV corresponding to the energy of photons of 555 nm wavelength (λmax of the rose bengal). The position of the Fermi level of ZnO was taken to be equal to flat band potential (-0.60 V) obtained from the potential of onset of photocurrent in i-V curve (Fig.3). As per assumption in this case, the position of the conduction band edge can be taken at 0.1 eV above the Fermi level, that is at -0.70 V. Energy level of quinone/hydroquinone redox couple (supersensitiser in this case) was taken to be 0.45 V.

Fig. 5 clearly indicates that the excited dye molecules can inject electrons directly into the conduction band of ZnO electrode and the oxidized dye molecules can be converted back to its initial form by the reducing agent (hydroquinone) present in the solution, a necessary requirement for the sustainability of the process.

Variation in photocurrent with intensity of light—The variation in photocurrent with the intensity of light used for the illumination of ZnO electrode is shown in Fig. 6 for two different bias potentials. At lower bias (0.5 V), photocurrent was found to increase proportionally with the light intensity in the entire range studied as observed by other investigators 19,32,33 while at higher bias potential (0.80 V) there is slight departure from linearity in the higher range of light intensity. It seems at higher intensity of light, there is large carrier generation in the semiconductor and also higher electron injection by the excited dye molecules and the applied potential is not sufficient to remove them all from the surface of the electrode providing more chances of recombination resulting in less current than expected. At lower bias potential, no such departure was observed probably because the photocurrent observed in this case was already much less and also it changes with lesser rate with the intensity of light. So, the fraction of charge carriers which are manifested in current seems to be maintained due to its low value even at higher intensity of light.

Action spectra—Spectral dependence of the dye sensitised photocurrent at ZnO electrode is shown in Fig.7 along with the absorption spectrum of the
dye (RB) in acetonitrile solution. Action spectrum was normalized for photon flux $4.02 \times 10^{12} \text{photons cm}^{-2} \text{s}^{-1}$ corresponding to its value at 550 nm. Correction in the intensity of light for solution absorption was also made. Identical nature of the photocurrent spectrum and absorption spectrum of the dye confirms the sensitization of photocurrent by rose bengal. Wavelength dependent quantum efficiency of the sensitized photocurrent obtained in the present work is also shown in Fig.7. The highest quantum efficiency at the characteristic wavelength for rose bengal (555 nm) was found to be $\phi = 0.78$. In literature different values for the quantum efficiency of photocurrent at ZnO electrode sensitized by rose bengal have been reported by different group of investigators. Matsumura et al.\textsuperscript{19} have reported $\phi = 22\%$, while Tsubomura et al.\textsuperscript{18} obtained $\phi = 15\%$. In both these cases sintered disk of ZnO has been used as electrode in aqueous medium. On the other hand, Spitler et al.\textsuperscript{21} reported that the quantum efficiency of the photocurrent was decreased by the addition of hexacyanoferrate (II) in the solution and it was attributed to the quenching of the triplet state of the dye. Later on the same group of investigators while reporting the value of $\phi$ in the range\textsuperscript{22} of 0.9-2.4% showed that $\phi$ varied with the anions present in the solution. Matsumura et al.\textsuperscript{23} during their studies found that the efficiency of the photocurrent at ZnO sintered disk electrode sensitised by rose bengal, in addition to other dyes, was hardly affected by the presence of triplet quencher as reported by Spitler et al.\textsuperscript{21,22}. These authors have reported $\phi = 28\pm 5\%$. Nakao et al.\textsuperscript{25} have found probably the highest quantum efficiency ($\sim 55\%$) among those reported earlier for the photocurrent at thin film ZnO electrode sensitized by rose bengal in acetonitrile medium using hydroquinone as supersensitizer, the system being almost identical to that used in the present work with the only difference that previously\textsuperscript{25} indoped ZnO was used to control donor density while in the present work, no dopant was used. However, the quantum efficiency obtained in the present work ($\sim 78\%$) is still higher than that reported by Nakao et al.\textsuperscript{25} ($\sim 55\%$). Another point that needs to be mentioned here is that the photocurrent peak shifted by 3 nm towards the longer wavelength from that of the absorption spectrum of the dye (RB) in solution (Fig.7). Similar shift was observed by Matsumura et al.\textsuperscript{19} but the magnitude of shifting was more ($\sim 13$ nm) than observed in the present case. Such shift is attributed to the change in the absorption spectrum of the dye due to its adsorption on the surface of the semiconductor electrode\textsuperscript{34}. 

Fig.7—Wavelength dependence of the photocurrent at ZnO electrode sensitized by RB (10$^{-3}$M) in acetonitrile solution containing 10$^{-3}$M hydroquinone and 10$^{-3}$M NaClO$_4$. Electrode potential $\pm 0.50$ V vs SSCE. Photocurrent was normalised for flux $4.02 \times 10^{12} \text{photons cm}^{-2} \text{s}^{-1}$.

Fig.8—Stability of the photocurrent with time at a fixed bias potential (+0.80 V) for ZnO electrode in acetonitrile solution (10$^{-3}$M RB+10$^{-3}$M NaClO$_4$+10$^{-3}$M hydroquinone). A: under white light illumination (intensity = 546 mW/cm$^2$) and B: under filtered light ($\lambda > 400$ nm) illumination (intensity = 456 mW/cm$^2$).
Long-term stability of the semiconductor electrode—To get the better stability of the semiconductor electrode, acetonitrile was selected as the medium of the cell electrolyte. To test this aspect, ZnO electrode was kept at a fixed bias potential (+0.8 V) and illuminating it continuously with the full spectrum of light (546 mW/cm²) the stability of the photocurrent was monitored with the passage of time and the result is represented in Fig.8 (curve A). Photocurrent was found to decrease initially upto about 1h and thereafter it started increasing slowly. This increasing trend continued for about 2h and then continuous decrease in photocurrent was observed. Here again the dark current, observed by interrupting light for a short while, was found to be negligible and unchanged throughout the measurement. After examining the curve carefully, one can find that upto 4h, the photocurrent varies within about 5% of the total current observed (indicated by dotted line) and thereafter the decrease is substantial. From the visual observation at the end of the experiment, the deterioration of the ZnO thin film was evident. Thus, one can conclude that photogenerated holes produced in the semiconductor are partly involved in the dissolution reaction with the reducing agent (hydroquinone) present in the solution. To avoid photoinduced generation of holes, another experiment was performed in which UV part of the light was cut off by using longpass filter (λ>420 nm) before illuminating the semiconductor electrode keeping all other conditions unchanged. Photocurrent time curve obtained under this condition is shown in Fig.8 (curve B). This curve clearly demonstrates that after a bit faster decrease in photocurrent in the very beginning, photocurrent decreases very slowly which can practically be taken as stable one. So, if direct excitation of ZnO electrode is avoided by using filtered light (λ>420 nm), better stability of the ZnO electrode can be achieved in acetonitrile medium.

Conclusion
Some of the main findings of the present investigations made with ZnO/RB in acetonitrile system are

(i) The quantum efficiency of the photocurrent, sensitized by rose bengal was found to be ~78%, probably the highest one ever reported.

(ii) Good stability of the semiconductor electrode can be achieved while using this system if direct excitation of ZnO electrode is avoided by using filtered light (λ>420 nm).

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References