ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 92 (1995) 207–212

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

Characterization of $[Fe(o\text{-}phen)_3][Ni(CS_3)_2]$ as a photosensitizer for wide-band gap semiconductor (ZnO) electrodes in acetonitrile media

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Received 16 February 1995; accepted 14 June 1995

Abstract

A newly synthesized transition metal complex tris-1,10-ortho-phenanthroline iron (II) bis-thiocarbonato nickelate (II), $[Fe(o\text{-}phen)_3][Ni(CS_3)_2]$, has been studied for its photosensitizing properties at *n*-ZnO semiconductor electrodes prepared by spray pyrolysis and sol–gel techniques. The absorption spectrum of this inorganic complex in acetonitrile solution exhibits a strong peak at 462 nm and a shoulder at 510 nm wavelength of light. From cyclic voltammetric studies it has been found that this compound can undergo reversible, one-electron transfer oxidation with formal redox potential $E^0 = 0.985$ V vs. SSCE in acetonitrile medium. The sensitization of the photocurrent at the ZnO electrode by the test dye was confirmed by determining current-potential curves and action spectrum. As compared with sprayed ZnO thin films, particulate films prepared by sol–gel technique were found to give better performance.

Keywords: Photosensitizer; ZnO electrode; Hydroquinone; Acetonitrile

1. Introduction

For photosensitization of wide band-gap semiconductor electrodes, a variety of compounds (photosensitizers) have been tested in the past by several groups of investigators [1–14]. In pursuance of similar investigations, a series of synthetic compounds (organic and inorganic complexes) have been studied in our laboratory on ZnO thin film electrodes [15–19]. This work is in continuation of this series of investigations in which a newly synthesized transition metal complex, $[Fe(o\text{-}phen)_3][Ni(CS_3)_2]$ [20], has been characterized for its photosensitizing properties at *n*-ZnO thin film electrodes prepared by spray pyrolysis and sol–gel methods. The results of this investigation are reported here.

2. Experimental

Thin films of ZnO were prepared on glass substrate (2×1×0.1 cm) by spraying 0.1 M aqueous solution of $Zn(NO_3)_2$ (A.R. grade, E. Merk, India) on ultrasonically-cleaned hot substrate maintained at 400 °C with the help of a thermostatically-controlled vertical furnace. These films (~5 μm thick) were subsequently annealed for 1 h in a hydrogen atmosphere at 400 °C.

The films of nanometer sized colloidal ZnO were prepared following the method of Spanhel and Anderson [21]. The organometallic precursor was prepared by refluxing 0.1 M $Zn(CH_3COO)_2$ (CDH, India) solution in absolute ethanol (dehydrated) for about 3 h avoiding its exposure to moisture. The precursor solution was stored in a desiccator. Later it was hydrolysed by adding to it an equimolar amount of lithium hydroxide powder, $LiOH \cdot H_2O$ (Alfa product), keeping the container in an ultrasonicator. The ZnO colloid prepared was quite stable and no precipitate was observed even after 25 days at 25 °C. To prepare the particulate films from this colloidal ZnO, SnO_2-coated glass plates were dipped in the sol and dried in air. This process was repeated 6–7 times to get the films of the required thickness (~0.5 μm). These films were finally annealed in air at 400 °C for 1 h.

For ohmic contact, a copper wire was attached on the surface of these films with the help of silver paste (Elteck Corporation, India). The occluded solvent in the silver paste was removed by drying it in air. Finally, silver was covered with the araldite which was air dried before use.

Acetonitrile of HPLC grade (Qualigens, India) was purified as described earlier [22]. The transition metal complex $[Fe(o\text{-}phen)_3][Ni(CS_3)_2]$, studied as a sensitizer, was obtained by the courtesy of Dr. N. Singh of our Department and its preparation method has been described elsewhere [20]. In all experiments, 0.1 M solution of anhydrous $NaClO_4$ (Fluka) was used as the supporting electrolyte and in all photoelectrochemical experiments 0.01 M hydro-

SSDI 1010-6030(95)04138-9

quinone (BDH, India) was used as the dye reducing agent (supersensitizer).

Photoelectrochemical experiments were performed in a three-electrode single compartment cell having an optically-flat quartz window for the illumination of the working semiconductor electrode. A spiral platinum wire was used as the counter electrode. The sodium chloride saturated calomel electrode [SSCE(aq.)], which served as a reference electrode, was separated from the working electrode by using a Luggin capillary agar salt (NaCl) bridge. In a selected experiment the carbon electrode, obtained from the Novino dry cell, was used as the counter electrode. Before each experiment, the electrolyte was deaerated by passing through it purified nitrogen for about 1 h.

For electrochemical measurements, a bipotentiostat (model AFRDE 4E, Pine Instrument Company, USA) together with a X-Y1-Y2 recorder (Houston Model 2000) was used. For photoelectrochemical experiments, a 150 W Xenon arc lamp was used as a light source and the semiconductor electrode was illuminated after passing the light beam through a six inch long water column (to filter IR) and condensing it with the help of fused silica lenses (all from Oriel, USA). light was monochromatized, when required, by using a grating monochromator (Oriel model 77250 fitted with model 7798 grating). To perform the experiments under visible light illumination, light was chopped off with the aid of a long-pass filter (Model No. 51280, Oriel, USA) and the intensity of light was measured with the aid of a digital photometer (Tektronix model J16 with J6502 sensor) and neutral density filters (Oriel, USA). The absorption spectrum of the test dye [Fe(o-phen)$_3$][Ni(CS$_3$)$_2$] was recorded on Cary 2390 (Varian) spectrophotometer.

3. Results and discussion

3.1. Redox behaviour of [Fe(o-phen)$_3$][Ni(CS$_3$)$_2$]

The cyclic voltammograms of [Fe(o-phen)$_3$][Ni(CS$_3$)$_2$] in acetonitrile solution obtained at different scan rates (0.020–0.100 V s^{-1}) at the platinum electrode are shown in Fig. 1. From these curves it is evident that this compound can undergo reversible oxidation with anodic peak potential $E_{pa}=1.015$ V and associated cathodic peak potential $E_{pc}=0.955$ V vs. SSCE. These peak potentials do not change with the scan rate and peak potentials separation is found to be $\Delta E_p=0.060$ V. Based on these observations it can be inferred that the test compound can undergo reversible one-electron transfer oxidation which can be assigned to Fe(II) → Fe(III) in the complex cation, [Fe(o-phen)$_3$]$^{2+/3+}$. The formal redox potential [$E^0=(E_{pa}+E_{pc})/2$] for this process is $E^0=0.985$ V vs. SSCE in acetonitrile medium. This value matches closely with that reported by Koepp et al. [23] (1.13 V vs. NHE) for the same cation, [Fe(o-phen)$_3$]$^{2+}$, in aqueous medium if the latter one is converted with respect to SSCE and liquid junction potential ($E_j=0.090$ V) [24] at SSCE (aq.)/acetonitrile junction is taken into account.

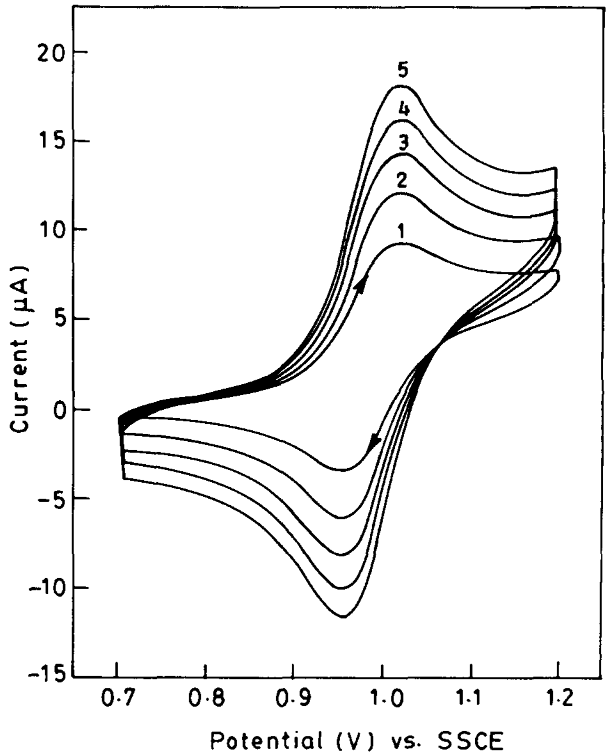

Fig. 1. Cyclic voltammograms of [Fe(o-phen)$_3$][Ni(CS$_3$)$_2$] at the platinum electrode. Solution: 10^{-3} M [Fe(o-phen)$_3$][Ni(CS$_3$)$_2$] + 0.1 M NaClO$_4$ supporting electrolyte in acetonitrile. Scan rates: 0.020, 0.040, 0.060, 0.080 and 0.100 V S^{-1} for curves 1, 2, 3, 4 and 5, respectively.

3.2. Optical properties of [Fe(o-phen)$_3$][Ni(CS$_3$)$_2$]

Since the optical property of a compound, to be used as a sensitizer, plays the decisive role in mediating the photoelectrochemical process at the semiconductor electrode (photosensitization) in a photoelectrochemical cell, the absorption spectrum of the test dye in an acetonitrile medium was determined and the same is shown in Fig. 2. This figure shows clearly that the onset of absorption occurs at a much longer wavelength (600 nm) and the spectrum exhibits a shoulder at 510 nm and a strong absorption peak at 462 nm. With this sensitizer it seems possible to extend the spectral response of the ZnO electrodes well into the visible region of the solar spectrum (up to 600 nm wavelength). After these preliminary characterizations of the test dye, photoelectrochemical investigations were performed in actual cell configuration in the presence of the test compound in the electrolyte.

3.3. Photo-electrochemical studies

Open-circuit photovoltage

In order to avoid the direct excitation of the ZnO electrode, only visible light of sub band-gap energy ($\lambda > 420$ nm) was used for illumination while determining the open-circuit potential-time (V_{oc}-t) profile of the dye-particulate ZnO elec-

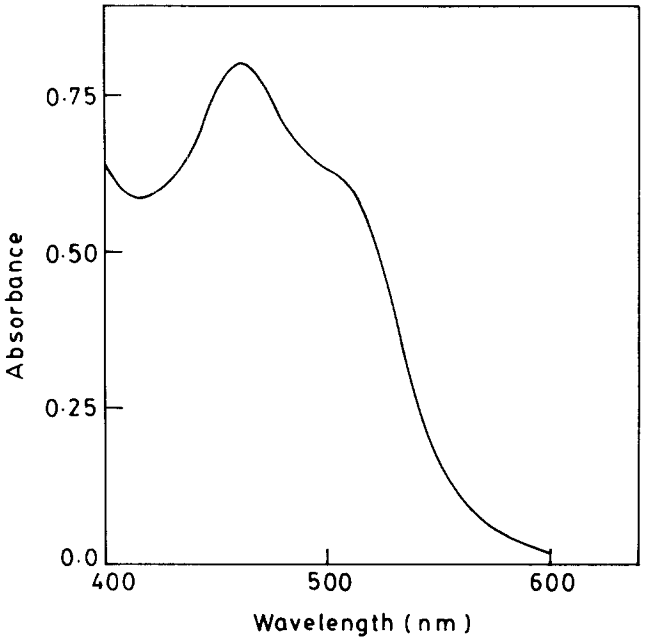

Fig. 2. Absorption spectrum of [Fe(o-phen)$_3$][Ni(CS$_3$)$_2$] taken in acetonitrile solution (10^{-5} M).

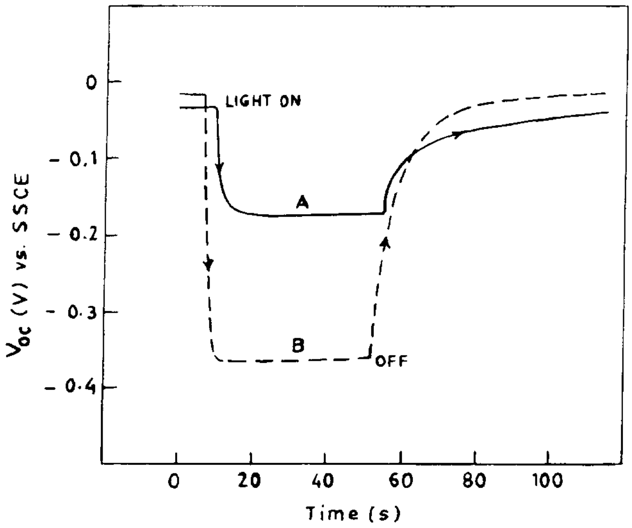

Fig. 3. Open circuit potential-time (V_{oc}-t) curves for ZnO electrodes ((a), sprayed film; (b), particulate film)), in acetonitrile solution containing 0.1 mM [Fe(o-phen)$_3$][Ni(CS$_3$)$_2$] + 10 mM hydroquinone + 0.1 M NaClO$_4$. Intensity of visible light ($\lambda > 420$ nm) = 480 mW cm^{-2}.

trode. These V_{oc}-t profiles for sprayed and particulate ZnO electrodes are shown in Fig. 3. Open-circuit photovoltage (V_{photo}) obtained from these curves are −0.145 V and −0.350 V for sprayed- and particulate-ZnO electrodes respectively. These photovoltages can be assumed to be owing to charge carriers injected mainly by the excited dye molecules as the light of only sub band-gap energy was used. From these curves it is further evident that the photoresponse of the sprayed ZnO electrode was slower (as it takes longer to attain the highest photovoltage) as compared with that of particulate electrode and charge carriers' recombination in the former situation is faster (as photovoltage is less) that the latter.

Transient photocurrent response

After evaluating the photoresponse in the open-circuit condition, the transient photocurrent-time (I-t) curves were determined under visible light ($\lambda > 420$ nm) and monochromatic light ($\lambda = 462$ nm, corresponding to the λ_{max} of the dye) illuminations keeping the working electrodes at 0.0 V vs. SSCE bias potential. In the case of illumination with visible light [Fig. 4(a)], the I-t curve for sprayed ZnO electrode exhibits a spike and the photocurrent decreases by about 40% from its initial value before it becomes stabilized. In the case of a particulate film electrode, no such spike is observed and the photocurrent remains at its highest initial value with time. This further confirms that the recombination of dye-injected electrons and the resultant oxidized dye occurs to a significant extent at sprayed ZnO electrode while the same is virtually absent for the particulate film electrode. Fig. 4(b) represents similar I-t curves obtained under illumination with monochromatic light with photons of 462 nm wavelength at which the test dye has a characteristic absorption peak. The observed photocurrent under this condition confirms the sensitization of the photocurrent by the test dye. Furthermore, although the photocurrents observed with both types of electrodes are almost of the same magnitude, the dark current was found to be more in the case of sprayed ZnO electrode

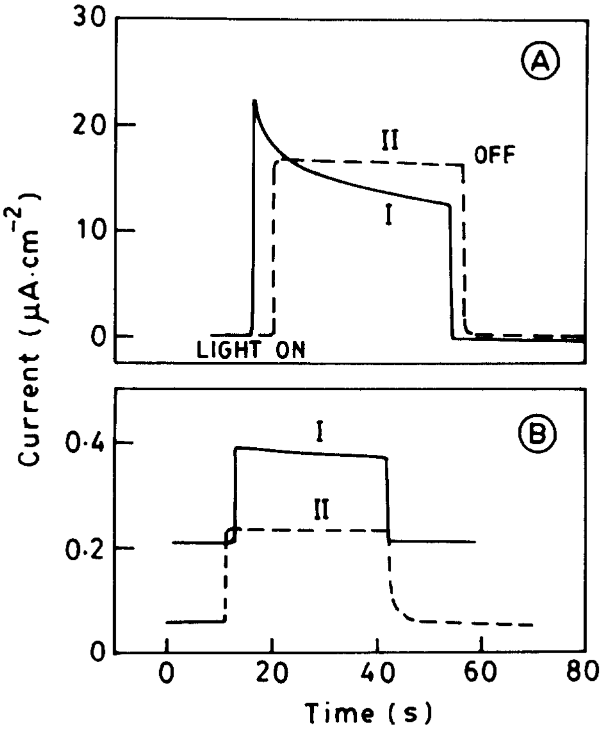

Fig. 4. Transient current-time (I-t) curves for ZnO electrodes at fixed bias potential, 0.0 V vs. SSCE; (a) under visible light ($\lambda > 420$ nm) and (b) under monochromatic light ($\lambda = 462$ nm) illumination. Curve I for sprayed film and II for particulate film ZnO electrodes. Visible light intensity = 480 mW cm^{-2}, monochromatic light intensity = 26.1 μW cm^{-2}.

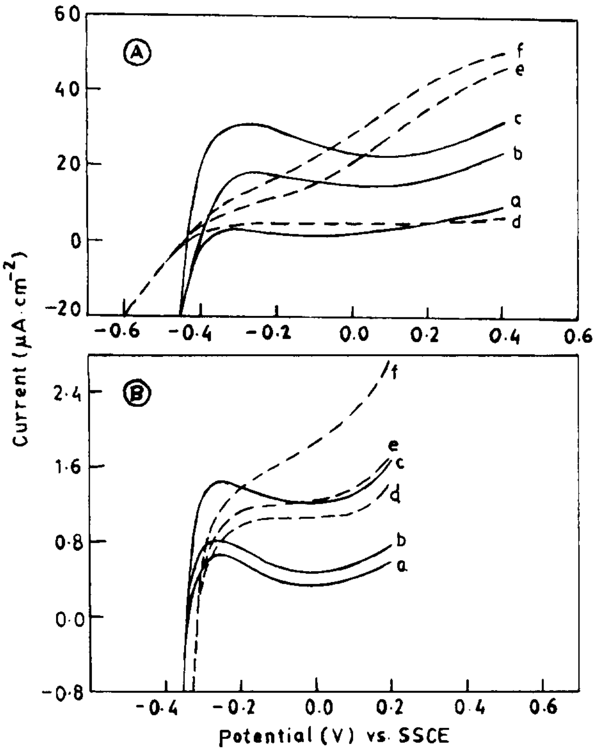

Fig. 5. Current-potential curves under illumination with (A) visible light ($\lambda > 420$ nm) and (B) monochromatic light ($\lambda = 462$ nm). Curves a, b, c with particulate-film, curves d, e, f with sprayed-film. Curves a, d in dark condition, curves b, e under illuminated condition without dye and curves c, f under illuminated condition with dye.

as compared with that observed with particulate film. Therefore the latter seems to be preferable.

Current–potential (I–V) characteristics

The curves shown in Fig. 5(A) represent the current-potential characteristics of the cell (ZnO/electrolyte/Pt) in the dark (with dye present in electrolyte) and under visible light illumination (in absence and presence of the dye) for both types of working electrode (sprayed- and particulate-ZnO films). Photocurrent enhancement observed in the presence of the dye confirms the sensitization of the photocurrent by dye molecules. However, this enhancement is greater with particulate ZnO electrode and the nature of curve shows that photocurrent attains saturation at a very low additional potential (0.150 V) above the onset. With the sprayed ZnO electrode, on the contrary, photocurrent saturation is observed at a much higher potential. It is also seen that even in the absence of dye, significant photocurrent is observed with both types of electrode (curves b and e), though the light of sub band-gap energy is used for illumination. This can be attributed to the presence of defect surface states at intermediate energy levels in both types of electrode, though their (defect states) density seems to be greater for the sprayed ZnO electrode. if the potential of the onset of photocurrent is taken as flat band potential, one gets $V_{fb} = -0.450$ V vs. SSCE.

Similar current-potential curves obtained under illumination with monochromatic light ($\lambda = 462$ nm) are shown in Fig. 5(B). Since in this case the monochromatic light of wavelength equal to λ_{max} of the dye is used, the enhancement in photocurrent in the presence of dye can be ascribed exclusively to dye-sensitization of the photocurrent.

Action spectrum

The spectral dependence of the photocurrent at bare (without dye) and dye-coated electrodes kept at 0.0 V vs. SSCE are shown in Fig. 6. The nature of the photocurrent spectra of dye coated electrodes (curves a and b) matches closely with the absorption spectrum of the dye in acetonitrile solution (Fig. 2) and in comparison to that observed with bare electrodes (curves c and d), the photocurrent is enhanced significantly in the cases of dye-coated electrodes. These observations provide conclusive evidence for the injection of electrons by excited dye molecules to the conduction band of the semiconductor electrode and hence for the dye sensitization of the photocurrent. Incident photon-to-current conversion efficiency [% IPCE = (no. of injected electrons/no. of incident photons) × 100], was found to be 4.3% and 3.7% for dye-coated sprayed- and particulate-ZnO electrodes, respectively, at the characteristic absorption wavelength (462 nm) of the dye.

Power conversion efficiency

The power outputs of the dye-sensitized photoelectrochemical cells [ZnO (sprayed- or particulate-films)/electrolyte containing 10^{-4} M dye/carbon counter electrode] were

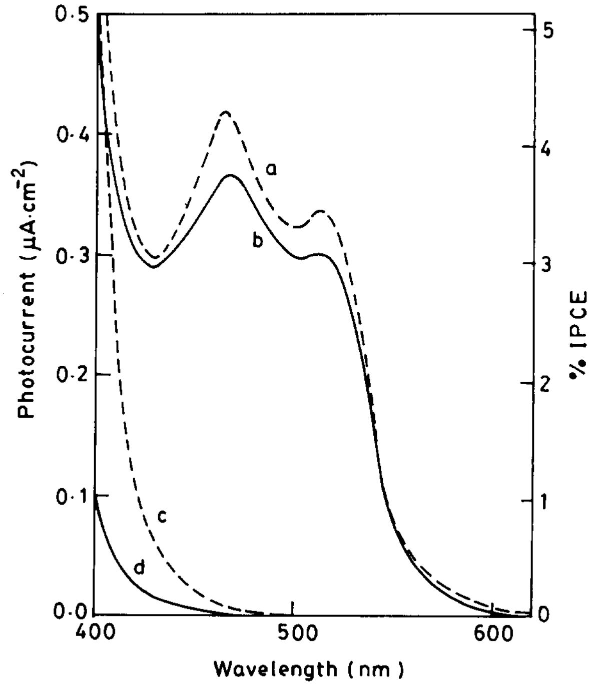

Fig. 6. Wavelength dependence of the photocurrent at (a) sprayed- and (b) particulate-ZnO electrodes sensitized by $[Fe(o\text{-}phen)_3][Ni(CS_3)_2]$ (10^{-4} M) in acetonitrile solution of 10^{-2} M hydroquinone and 0.1 M $NaClO_4$. Working electrode potential is 0.0 V vs. SSCE. Curves c and d are those determined for sprayed- and particulate-ZnO electrodes in absence of dye. Photocurrent was normalised for photon flux 6.1×10^{13} photons cm^{-2} s^{-1}. Right ordinate denotes incident photon-to-current conversion efficiency (IPCE).

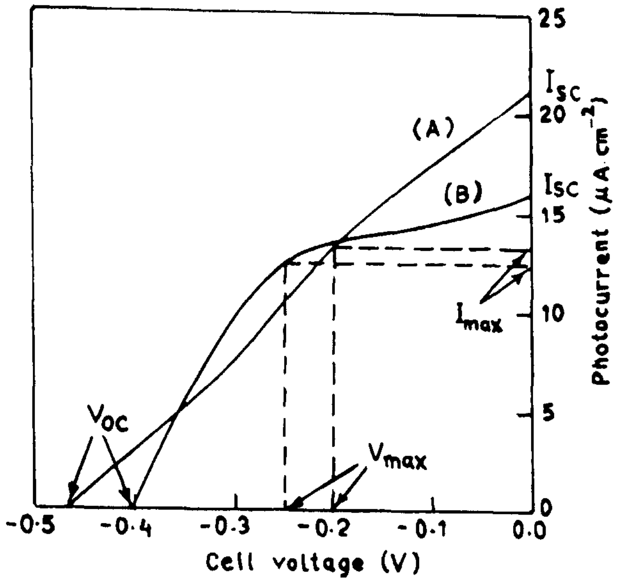

Fig. 7. Photocurrent-cell voltage curves for the dye sensitized cell with (a) sprayed- and (b) particulate-ZnO thin film electrodes illuminated with visible light ($\lambda > 420$ nm, intensity = 480 mW cm^{-2}). Solution composition: 10^{-4} M [Fe(o-phen)$_3$][Ni(CS$_3$)$_2$] + 0.1 M NaClO$_4$ + 10^{-2} M hydroquinone.

determined under visible and white light illumination and the results are shown in Figs. 7 and 8. Although the maximum power conversion efficiency [$\eta = (I_{max}V_{max}/\text{incident light intensity}) \times 100$], was found to be low with both types of the working electrode ($\eta = 5.5 \times 10^{-4}\%$ and $6.5 \times 10^{-4}\%$ under visible light illumination and 1.15×10^{-3} and 1.67×10^{-3} under white light illumination with sprayed- and particulate-ZnO electrodes, respectively), the fill factor ($FF = I_{max}V_{max}/I_{sc}V_{oc}$) was significantly higher for the cell with particulate ZnO electrode than with sprayed thin film electrode, the values for the former one being 0.49 under visible light illumination and 0.44 under white light illumination while in the latter case the respective values are 0.27 and 0.25.

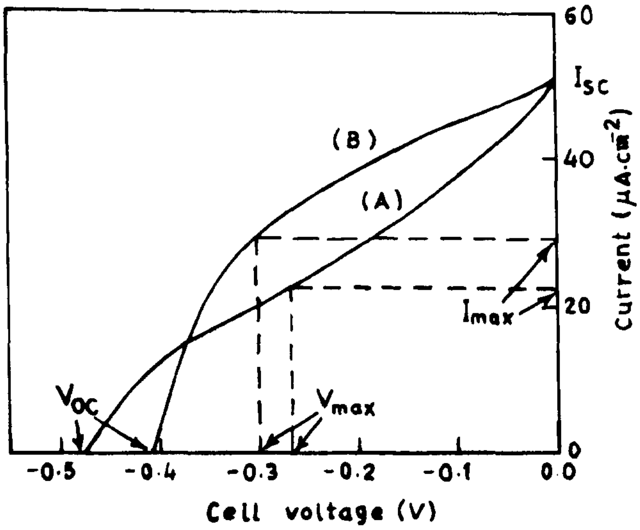

Fig. 8. Photocurrent-cell voltage curves for the dye sensitized cell with (a) sprayed- and (b) particulate-ZnO thin film electrodes illuminated with white light (intensity = 540 mW cm^{-2}). Solution composition being the same as in Fig. 7.

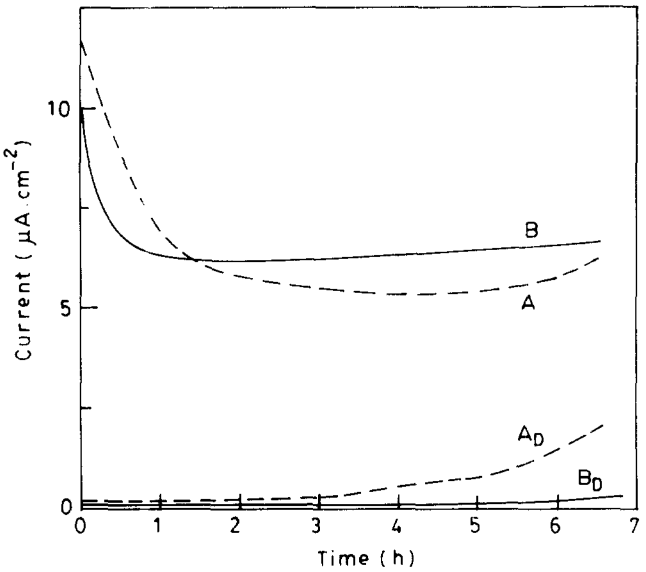

Fig. 9. Stability of the photocurrent with time at a fixed bias potential (0.0 V vs. SSCE) for (A), sprayed-film and (B), particulate-film ZnO electrode in acetonitrile solution under visible light ($\lambda > 420$ nm) illumination (480 mW cm^{-2}). A_D and B_D are the respective curves in dark. Solution composition is the same as in the case of Fig. 7.

Long-term stability of photocurrent

The stability of the photocurrent of dye-sensitized cell(s) was monitored continuously with the passage of time (~7 h), the light was chopped off momentarily at the interval of 1 h to measure the dark current. The results obtained are represented in Fig. 9 for the cells with particulate- and sprayed-ZnO thin film electrodes. In the former case, the photocurrent was found to decrease continuously up to about 1 h and thereafter it was almost stabilized. The dark current remains at a very low value throughout the experiment. With the sprayed ZnO electrode, however, the photocurrent drops to ~50% of the initial value in 1 h and then it decreases slowly up to 4 h. Beyond this the photocurrent was found to increase. The dark current in this case remains at a low value for about 3 h but increases afterwards (probably owing to some side reaction resultant from photocorrosion of the test electrode). So, under illuminated conditions, the increase in current after 4 h is owing to increase in the dark current, as such photocurrent component is not increased. The observed decay in photocurrent during the first hour can be attributed partly to increase in defect surface states providing more recombination centres for dye injected electrons and oxidized dye species and partly to slow regeneration of dye molecules ($D^+ \rightarrow D$) by reducing agent (hydroquinone). The visual inspection (by eye) of the working electrodes at the end of the experiment, however, did not show any apparent damage.

4. Conclusion

Based on the findings of this investigations it can be concluded that [Fe(o-phen)$_3$][Ni(CS$_3$)$_2$] can extend the spectral response of high band-gap semiconductor electrodes to visible light (up to about 600 nm wavelength) and hence can sensitize the photocurrent. Further, the test dye gives higher photovoltages and power output and photocurrent is found to be more stable when it is used at particulate ZnO thin film electrode in comparison with the sprayed ZnO electrode.

Acknowledgement

The financial assistance for this work provided by the Department of Non-conventional Energy Sources (DNES), Ministry of Energy, Government of India, is gratefully acknowledged. Authors are thankful to Dr. N. Singh, Department of Chemistry, B.H.U., for supplying the sample of complex studied.

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