ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 91 (1995) 233–240

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

# Photoelectrochemical investigations on particulate ZnO thin film electrodes in non-aqueous solvents

Lal Bahadur [a], Tata N. Rao [b]

[a] *Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221 005, India*
[b] *Materials Science Research Center, Indian Institute of Technology, Madras 600 036, India*

Received 8 November 1994; accepted 25 April 1995

## Abstract

Thin particulate films of ZnO prepared from its ultrafine colloidal particles obtained by the sol–gel technique were studied as photoelectrodes in non-aqueous photoelectrochemical cells. With the use of non-aqueous (acetonitrile and propylene carbonate) electrolytes, higher photovoltage and photocurrent were observed as compared with those obtained with aqueous electrolyte. In propylene carbonate medium the particulate ZnO thin film electrode exhibited an almost ideal current–potential characteristic. By measuring the open-circuit photovoltage ($V_{oc}$) and short-circuit photocurrent ($i_{sc}$) as a function of monochromatic light ($\lambda = 360$ nm) intensity, the diode quality factor ($n$) and reverse saturation current ($i_o$) were evaluated as $n = 1.5$ and $i_o = 0.75$ nA in propylene carbonate medium and $n = 1.6$ and $i_o = 2.6$ nA in acetonitrile electrolyte. The Mott–Schottky plots for particulate ZnO thin film electrodes were found to be non-linear, so the flat-band potentials in various solvents were determined using the approximated Gartner equation (i.e. from the $i_{photo}^2$ vs. $V$ curve). Transient photocurrent–time profiles were also determined in various solvents using white light as well as monochromatic light for irradiation of the working electrode. The incident photon-to-current conversion efficiency (IPCE) at the peak wavelength ($\lambda = 360$ nm) was found to be 27%, 24% and 14% in propylene carbonate, acetonitrile and aqueous electrolytes respectively, indicating clearly the advantage of non-aqueous solvents. The power conversion efficiency of the cell was found to vary with a change in counterelectrode and electrolyte medium. A high power conversion efficiency of about 1.8% was found in the case of propylene carbonate medium and carbon counterelectrode for monochromatic incident light ($\lambda = 360$ nm). The fill factor in this case was 0.49.

*Keywords:* Particulate films; ZnO electrode; PEC cell; Non-aqueous solvent

## 1. Introduction

Thin particulate films of semiconductors prepared from their ultrafine colloidal particles are attractive particularly because of their size quantization effect [1] and high surface area [2]. The enhanced effective surface area is essentially required for greater adsorption of dye molecules to sensitize wide band gap semiconductors. Recently O'Regan and Grätzel [2] have reported as high as 12% solar-to-electrical energy conversion efficiency with dye-sensitized colloidal $TiO_2$ film and this has generated new hope in the field of photoelectrochemical (PEC) cells. However, a literature survey reveals that most of the investigations conducted with particulate films have been confined mainly to $TiO_2$ [2,3] and some chalcogenide semiconductors [4]. Particulate films of ZnO colloidal semiconductor have scarcely been studied in this connection [5,6].

With particulate ZnO thin film electrodes, Hotchandani and Kamat [5] obtained a power conversion efficiency $\eta = 0.05\%$ at an excitation wavelength of 350 nm and an incident photon-to-current conversion efficiency (IPCE) of 15% for light of 320 nm wavelength. These authors used in their investigations an aqueous electrolyte, which in our opinion is not a suitable medium for ZnO semiconductor owing to its amphoteric nature. This might be the reason for the low values of $\eta$ and IPCE obtained by these authors. Thus we thought of using non-aqueous media (acetonitrile (ACN) and propylene carbonate (PC)) for such investigations and in accordance with our expectations a significant improvement was observed in the photoelectrochemical behaviour of particulate ZnO thin film electrodes in these solvents. Further, the use of a carbon counter electrode instead of the traditional platinum electrode was found to lead to better performance of the PEC cells. The detailed results of these investigations are described below.

1010-6030/95/$09.50
*SSDI* 1010-6030(95)04104-4

## 2. Experimental details

In the present work, acetonitrile and propylene carbonate have been used as non-aqueous solvents for preparing the electrolytes. Acetonitrile (E. Merck, India) was purified as described previously [7], while propylene carbonate (E. Merck, Germany) of purity greater than 99% was used without any further purification. Dehydrated alcohol (Bengal Chemicals, India) was dried by activating magnesium in the alcohol with iodine following the method of Lund and Bjerrum [8]. This dry alcohol was used for preparing ZnO colloids by the sol–gel method. Anhydrous $NaClO_4$ (EGA-Chemie, Germany) was used as supporting electrolyte and 0.1 M $NaClO_4$ and 0.01 M hydroquinone (AR grade, BDH, India) solution was used for all electrochemical and photoelectrochemical experiments. Zinc acetate ($ZnC_4H_6O_4 \cdot 2H_2O$; CDH, India) and $LiOH \cdot H_2O$ (Riedel) were used as received in the preparation of ZnO sol.

The ZnO colloids were prepared by the procedure of Spanhel and Anderson [9]. A 0.1 M solution of zinc acetate in dry ethanol was refluxed for 3 h at 80 °C. Then, keeping the precursor in an ice-cold bath, equimolar $LiOH \cdot H_2O$ was added to it and hydrolysis was allowed to continue for 30 min with the reaction vessel in an ultrasonic bath. These colloidal particles, typically of 7.5 nm size, were coated on a conducting glass ($F{:}SnO_2$) substrate by dipping it in the suspension and subsequently drying it for 1 min in an oven maintained at 80 °C. This dipping and drying process was repeated five times and finally the films were fired at 400 °C for 1 h, since any organic byproducts decompose above 350 °C [10]. The films prepared in this manner were usually of 0.8 $\mu$m thickness. The ohmic contact on the film was made using silver paste (Eltek Corporation, India) and was covered with Araldite and air dried before use.

The absorption spectra of ZnO colloidal particles and of the thin film coated on a quartz plate were recorded on a Cary 2390 spectrophotometer (Varian). The X-ray diffraction pattern of the film was recorded with a Philips PW-1710 diffractometer. A 150 W xenon arc lamp (Oriel Corp., USA) was used as light source and its IR part was filtered by inserting a water column 6 inches long in the light path. An Oriel Model 77250 monochromator along with a Model 7798 grating was used to obtain monochromatic light. The light intensity was varied when required with the use of neutral density filters (Models 50490–50570, Oriel Corp., USA) and was measured with a Scientech 362 Power and Energy Meter (Boulder Corporation, USA).

Electrochemical and photoelectrochemical measurements were carried out using a three-electrode system in a single-compartment cell equipped with a flat quartz window. The reference electrode was an aqueous sodium chloride saturated calomel electrode (SSCE) which was separated from the cell electrolyte by a Luggin capillary containing an aqueous agar salt (NaCl) bridge. All potentials are reported with respect to this electrode without any correction for the liquid junction potential existing at the aqueous salt bridge–non-aqueous solution interface [11]. Solutions were degassed by bubbling purified nitrogen through them before each experiment.

Current–potential measurements were made with a bipotentiostat (Model AFRDE4E, Pine Instrument Corp., USA) and a Houston Model 2000 X-Y1-Y2 recorder. To obtain the space charge capacitances for the Mott–Schottky plots, impedance measurements were made using an electrochemical impedance system (EG&G, PARC Model 378/3) consisting of a PAR Model 5208 lock-in amplifier, a PAR Model 273 potentiogalvanostat and a PS/2 (Model 30) IBM computer.

## 3. Results and discussion

### 3.1. Structural characterization of particulate ZnO film

For structural analysis the ZnO colloids were coated on a glass substrate by dipping it in freshly prepared ZnO sol. The film was air dried and used for X-ray diffraction studies. The diffraction pattern shown in Fig. 1 confirms the formation of the hexagonal wurtzite ZnO phase. The particle size calculated from the Scherrer formula [12] was found to be around 7.5 nm.

### 3.2. Optical properties

The absorption spectra of ZnO colloidal particles in ethanol and of the ZnO thin film prepared on a quartz substrate from these colloidal particles and sintered at 400 °C are shown in Fig. 2. The colloidal ZnO in ethanol shows an absorption peak at 320 nm (curve a), indicating that the size of ZnO particles is in the nanometre range [9]. However, the absorption spectrum of the particulate ZnO film (curve b) shows a red shift. This observation suggests that the particle size is increased owing to forced aggregation during film formation and subsequent sintering. It also indicates that the film material attains almost the same band gap as that of bulk ZnO (curve c).

### 3.3. Photoelectrochemical properties

#### 3.3.1. Open-circuit photovoltage

The photoresponse of the particulate ZnO thin film electrode was tested first by measuring the photovoltage under open-circuit conditions. The photovoltage–time ($V_{oc}$–$t$) plots

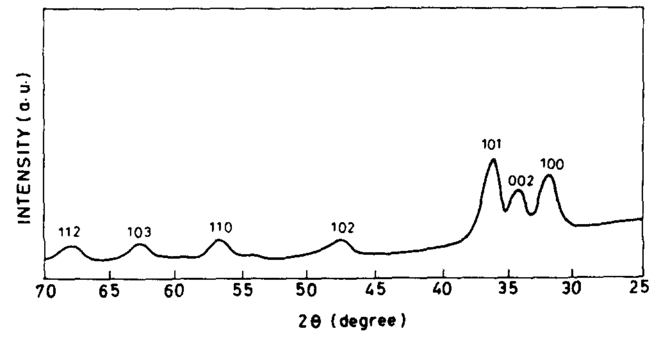

Fig. 1. X-ray powder pattern of fresh ZnO colloidal film.

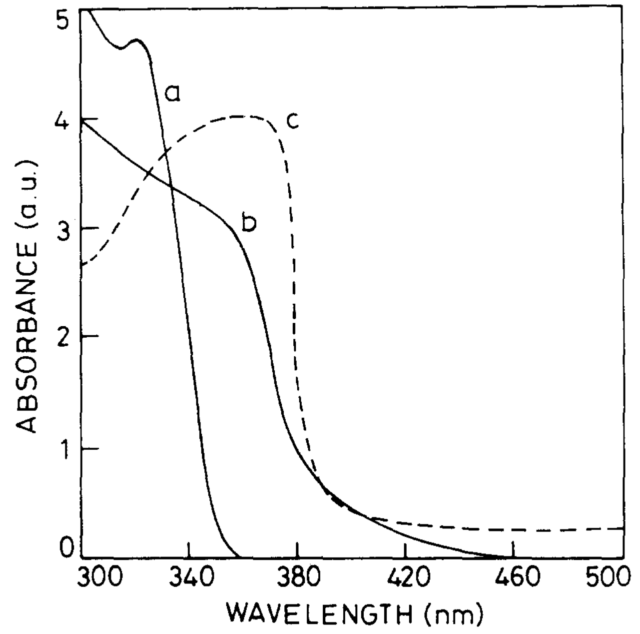

Fig. 2. Absorption spectra of ZnO colloids in ethanol (a), particulate ZnO film coated on quartz substrate (b) and bulk ZnO (c).

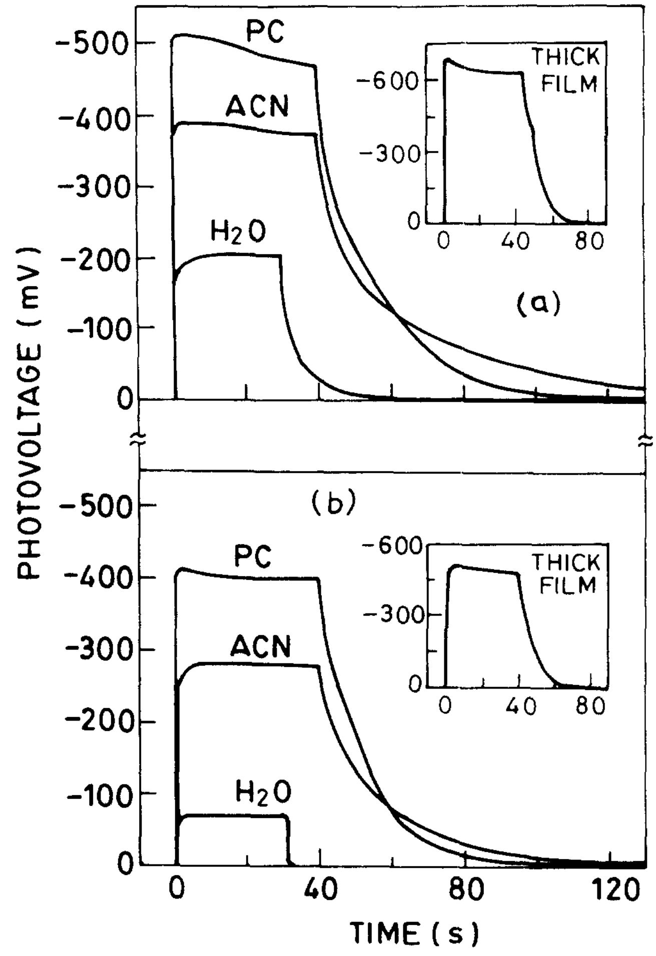

Fig. 3. Open-circuit photovoltage of particulate ZnO thin film electrode in propylene carbonate (PC), acetonitrile (ACN) and aqueous media containing 0.1 M $NaClO_4$ and 0.01 hydroquinone (a) under white light illumination (450 mW $cm^{-2}$) and (b) under monochromatic light ($\lambda = 360$ nm) illumination (400 $\mu$W $cm^{-2}$). Insets in both figures are for thick particulate film (1.5 $\mu$m) in PC medium.

obtained under white light as well as monochromatic light illumination are shown in Fig. 3 for three different solvent media. Under white light illumination (Fig. 3(a)) the photovoltage was found to vary with the solvent in the order $V_{oc}(PC) > V_{oc}(ACN) > V_{oc}(H_2O)$. From these curves it is also evident that upon illumination of the electrode the photovoltage rises sharply to its highest value in non-aqueous media while the rise time is comparatively longer in aqueous medium. On the other hand, the photovoltage decay upon interruption of the light is comparatively faster in aqueous medium than in non-aqueous solvents. Since the rise time of the photovoltage under illumination is determined by the reaction of photogenerated minority carriers (holes) with redox species in the electrolyte, which competes with electron injection into the conductive band, from the results it can be inferred that the former reaction is faster in non-aqueous media than in water. On the other hand, the relaxation of the photovoltage depends on the mechanism of the reverse reaction of photoinjected electrons with oxidized species in the electrolyte and hence the fast decay of the photovoltage in aqueous electrolyte indicates that this reverse reaction is more facile in this case than in non-aqueous electrolytes. The inset of Fig. 3(a) shows a similar ($V_{oc}$–$t$) plot obtained with a comparatively thicker film (1.5 $\mu$m) in propylene carbonate. In this case the observed photovoltage is greater (about 600 mV) than that obtained with the thinner film under identical conditions. However, such films exhibited drastically reduced photocurrent as discussed later.

The results of similar experiments conducted under monochromatic light ($\lambda = 360$ nm) illumination are presented in Fig. 3(b). On comparison with Fig. 3(a) these results suggest that the major part of the photovoltages obtained with white light could still be achieved with monochromatic light of band gap energy, even though the intensity of monochromatic light (0.4 mW $cm^{-2}$) was nearly three orders of magnitude less than the intensity of white light (450 mW $cm^{-2}$). Further, it is worth noticing that upon interruption of illumination there is a sharp decrease in the photovoltage in aqueous medium (Fig. 3(b)) unlike that observed in the previous case (Fig. 3(a)) in the same solvent. In the two non-aqueous media (PC and ACN) the decay rates are almost the same irrespective of the light used for illumination. Under monochromatic light illumination a thicker film again shows (see inset of Fig. 3(b)) a higher photovoltage (about 500 mV) than that observed with the thinner film (about 400 mV). On the basis of these observations it can be concluded that with the use of non-aqueous solvents a higher photovoltage can be achieved.

### *3.3.2. Light intensity dependence of photovoltage*

Although nanocrystalline particles as such do not exhibit band bending owing to their inability to support a field in the bulk, the particulate ZnO films prepared from nanocrystalline particles do exhibit bulk semiconductor properties [5] as is

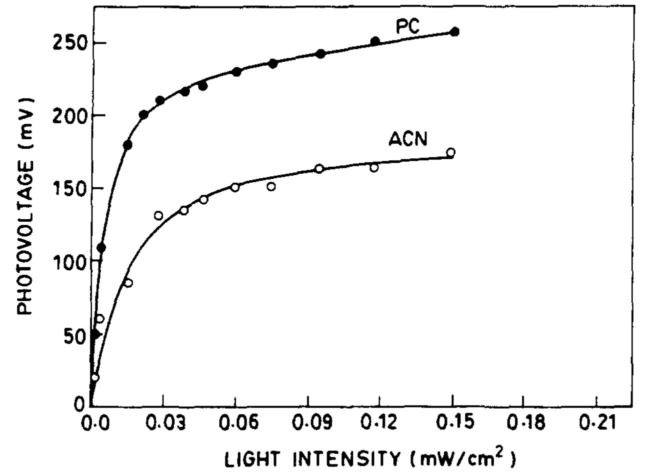

Fig. 4. Variation in open-circuit photovoltage ($V_{oc}$) at ZnO electrode in PC and ACN media with intensity of incident monochromatic light ($\lambda = 360$ nm). Electrolyte: same as for Fig. 3.

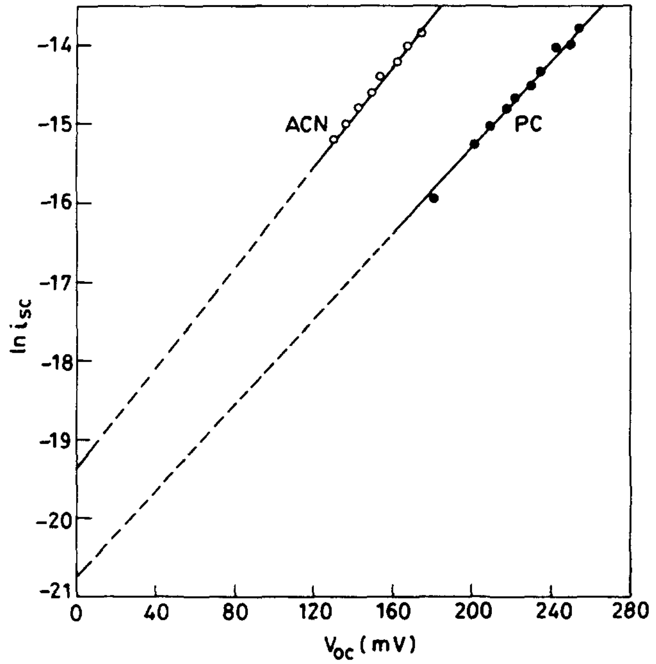

Fig. 5. Variation in short-circuit photocurrent ($i_{sc}$) with open-circuit photovoltage ($V_{oc}$) induced by various intensities of monochromatic light ($\lambda = 360$ nm). Electrolyte: same as for Fig. 3 in PC and ACN media.

evident from the results described below. To study the Schottky behaviour, the open-circuit photovoltage ($V_{oc}$) at the working electrode was measured as a function of the intensity ($I_{inc}$) of incident monochromatic light ($\lambda = 360$ nm) and the results obtained in PC and ACN media are shown in Fig. 4. From the figure it is evident that with increasing light intensity the photovoltage increases sharply at the beginning but then shows a tendency towards saturation in the higher range of intensity. Similarly, the short-circuit photocurrent ($i_{sc}$) was also measured at various intensities of monochromatic light, and when ln $i_{sc}$ was plotted against the corresponding $V_{oc}$ observed with the same intensity of light, linear curves were obtained for both solvents (Fig. 5). This shows that the particulate ZnO thin film PEC cell follows the Schottky barrier principle and obeys the familiar relation between $V_{oc}$ and $i_{sc}$ given by the equation

$$V_{oc} = \frac{nkT}{e_o} \ln\left(\frac{i_{sc}}{i_o} + 1\right) \qquad (1)$$

where $k$, $T$ and $e_o$ are the Boltzmann constant, absolute temperature and electronic charge respectively. Here $n$ is the diode quality factor and $i_o$ is the reverse saturation current. Such a logarithmic dependence of $V_{oc}$ on $i_{sc}$ has also been observed previously with particulate ZnO film in aqueous medium [5] and in other cases [13]. The values of $n$ and $i_o$ derived from ln $i_{sc}$ vs. $V_{oc}$ plots in Fig. 5 are 1.5 and 0.75 nA respectively in the case of PC medium while the corresponding values in ACN medium are 1.6 and 2.6 nA.

### 3.3.3. Dependence of short-circuit photocurrent on intensity of irradiation

The short-circuit photocurrent ($i_{ph}$) of the cell (particulate ZnO film/electrolyte/carbon counterelectrode) was measured as a function of the intensity ($I_{inc}$) of irradiation with monochromatic light ($\lambda = 360$ nm) and the results obtained in three different solvents (PC, ACN and $H_2O$) are presented in Fig. 6. These curves show slight deviations from linearity. However, ln $i_{ph}$ vs. ln $I_{inc}$ plots (inset of Fig. 6) are linear, following the relation $i_{ph} \propto I_{inc}^{\gamma}$, where the extent of deviation of the exponent $\gamma$ from unity is a measure of the amount of recombination of photogenerated charge carriers [13]. The values of $\gamma$ obtained from these curves are 0.75, 0.94 and 0.99 for PC, ACN and aqueous media respectively. These values indicate that the extent of recombination of photogenerated charge carriers varies in different solvents in the order PC > ACN > $H_2O$.

However, it is pertinent to mention here that in spite of the greater degree of recombination of charge carriers in PC and ACN media as compared with that in aqueous electrolyte, the overall obtainable photocurrent is greater in the former cases.

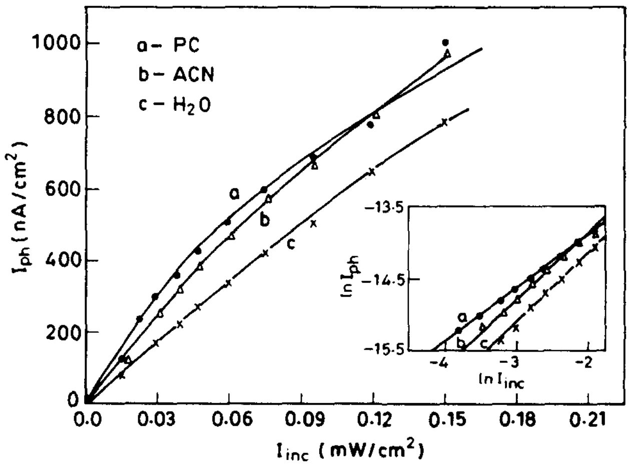

Fig. 6. Dependence of short-circuit photocurrent ($i_{ph}$) on intensity ($I_{inc}$) of incident monochromatic light ($\lambda = 360$ nm). Inset shows logarithmic plot. Electrolyte: same as for Fig. 3.

This indicates that there are other factors besides recombination which determine the overall photocurrent output. One such factor may be the electron exchange energy level of the redox species, which is quite likely to change in different solvent media owing to the involvement of different solvent molecules in the solvation of the redox species.

### 3.3.4. *Current-voltage (i-V) characteristics*

The curves in Fig. 7 represent the dynamic current-potential characteristics (in the dark and under white light illumination) of the particulate ZnO thin film electrode in PC, ACN and aqueous media. In PC medium (Fig. 7(A), curve a) the photocurrent was found to increase sharply after its onset at about −0.5 V and attained saturation beyond −0.1 V (SSCE). Such photocurrent saturation was not observed with the sprayed ZnO thin film electrode (Fig. 7(A), curve b). In ACN medium (Fig. 7(B)) a comparatively slow rise in photocurrent was observed up to about 0.2 V, about 0.7 V above the onset potential, and only beyond this point was a saturation tendency exhibited. In the case of aqueous medium (Fig. 7(B)) the noticeable feature of the *i–V* curve is that it does not show any tendency towards photocurrent saturation with increasing applied potential. Further, in aqueous medium, high dark currents were observed even at lower anodic potentials, while in non-aqueous solvents the dark current remains negligibly small over the entire range of applied potential.

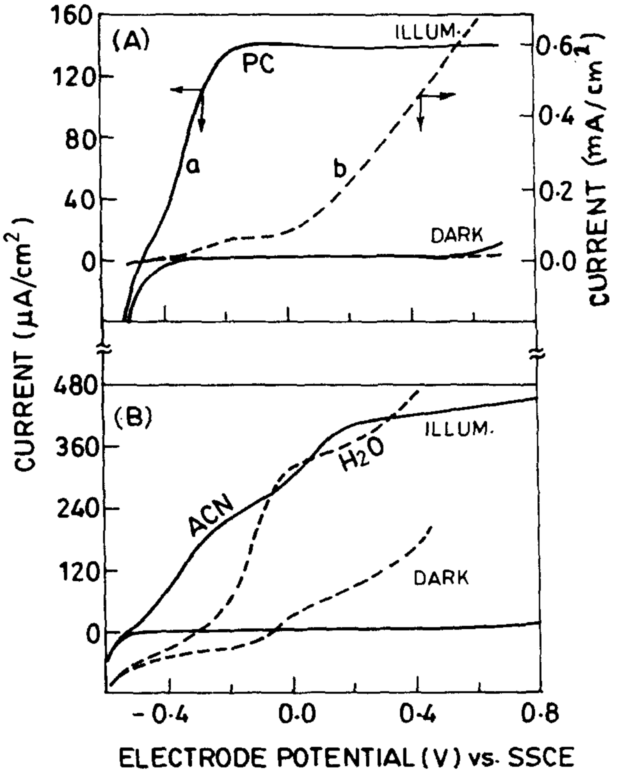

Fig. 7. (A) Current–potential curves determined in dark and under white light (300 mW cm$^{-2}$) illumination for particulate (a) and sprayed (b) ZnO thin film electrodes in PC medium. (B) Similar curves for particulate ZnO thin film electrode in ACN and aqueous media. Electrolyte: same as for Fig. 3 in both cases.

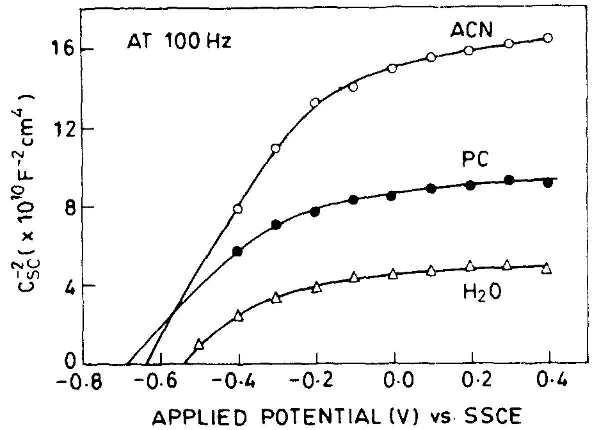

Fig. 8. Mott-Schottky plots for particulate ZnO electrode in ACN, PC and aqueous media containing 0.1 M $NaClO_4$ and 0.01 M hydroquinone.

These observations clearly indicate that for the particulate ZnO thin film electrode, non-aqueous solvents, PC and ACN in particular, are preferable over aqueous medium. In all three solvents used in the present investigation the photocurrent onset was observed at around −0.5 V (SSCE).

### 3.3.5. *Determination of flat-band potential ($V_{fb}$)*

The space charge capacitance ($C_{sc}$) of the particulate ZnO film electrode was determined as a function of bias potential using the electrochemical impedance spectroscopic technique. Such experiments were conducted in three different solvents (PC, ACN and $H_2O$) using an a.c. signal of fixed frequency (100 Hz). Experiments conducted at higher frequencies provided quite scattered data. Usually thin films with larger grain sizes and a uniform distribution of donor species obey the Mott–Schottky relationship and show a linear variation in $C_{sc}^{-2}$ with the applied potential *V*. However, in the case of particulate films with very small grain sizes the treatment may not be so straightforward. The Mott–Schottky plots shown in Fig. 8 for the particulate ZnO film electrode in three different solvents are not linear but curved. Similar behaviour was also observed by Blackwood and Peter [14] in the case of anodic film on $TiO_2$ and was attributed to defect states in the lattice which are not completely ionized since they occupy a broad energy distribution below the conduction band. Allard et al. [15], on the other hand, attributed such behaviour to a field dependence of the relative permittivity of the oxide. For nanocrystalline particulate film no earlier report is available in the literature for comparison with our results.

Since the Mott–Schottky plots were found to be non-linear, it was difficult to determine the flat-band potentials from these curves. Thus an alternative method was adopted to determine $V_{fb}$ via the Gartner equation [16–18]

$$i_{photo} = eI_0\left(\frac{\exp[-\alpha L(V-V_{fb})^{1/2}]}{1+\alpha l}\right) \qquad (2)$$

where $i_{photo}$ is the photocurrent measured under illumination with monochromatic light of flux $I_0$ and *e* is the electronic

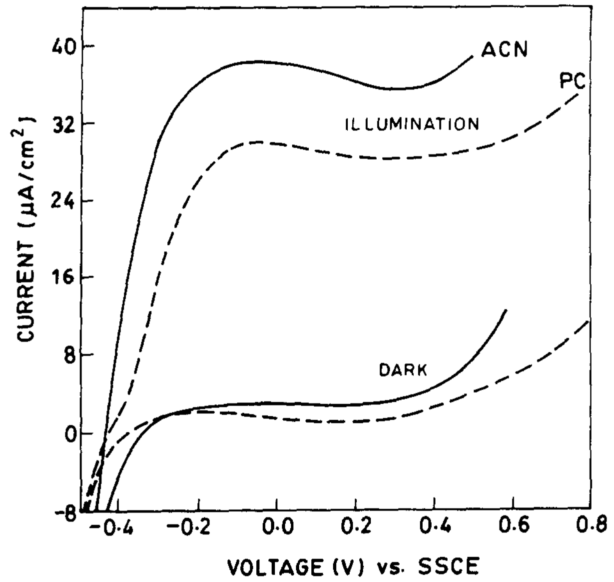

Fig. 9. Current–potential curves in dark and under monochromatic light ($\lambda = 360$ nm) illumination (400 $\mu$W cm$^{-2}$) for particulate ZnO electrode in PC and ACN media containing 0.1 M NaClO$_4$ and 0.01 M hydroquinone.

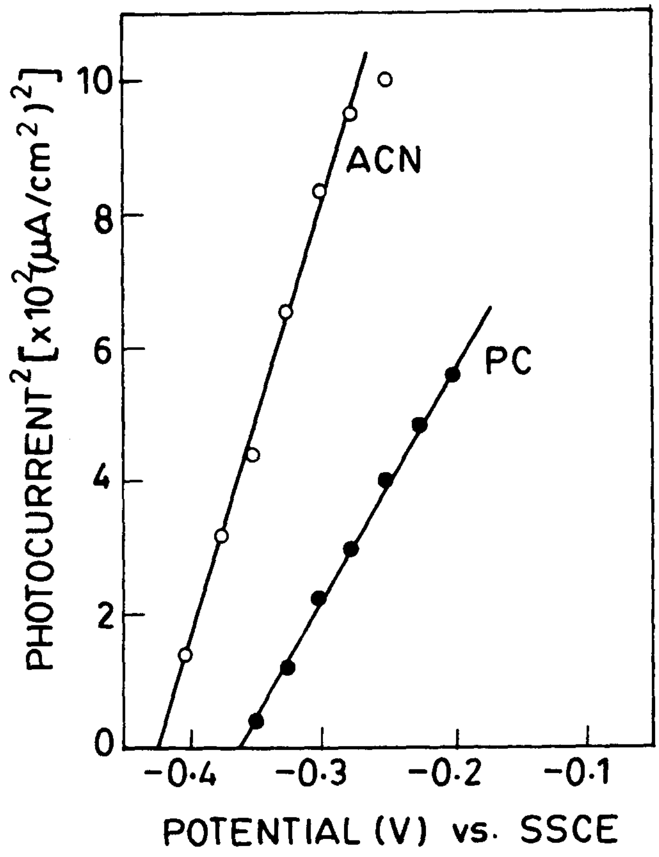

Fig. 10. Plots of $i_{\rm photo}^2$–$V$ in PC and ACN media derived from Fig. 9.

charge. Here $\alpha$ is the absorption coefficient of the semiconductor electrode, $L$ is the width of the depletion layer at a potential of 1 V across the semiconductor electrode and $l$ is the diffusion length of minority carriers (holes in the present case). Assuming $\alpha L \ll 1$ and expanding the exponential term for $\alpha L(V-V_{\rm fb})^{1/2} \ll 1$, Eq. (2) can be approximated [15,17,18] as

$$i_{\rm photo}^2 \approx A(V-V_{\rm fb}) \qquad (3)$$

where the constant $A$ includes $\alpha$, $I_0$, $L_D$ (Debye length), $T$ and universal constants $k$ and $e$. According to Eq. (3), an $i_{\rm photo}{}^2$ vs. $V$ plot will be linear and the potential corresponding to $i_{\rm photo}{}^2 \to 0$ will give $V_{\rm fb}$. To make use of this procedure for the determination of $V_{\rm fb}$, $i$–$V$ curves (Fig. 9) were obtained in the desired solvents (PC and ACN) using monochromatic light ($\lambda = 360$ nm) for illumination of the electrode. Considering the photocurrents in the lower potential region of these curves, $i_{\rm photo}{}^2$ vs. $V$ plots were drawn (Fig. 10), and by extrapolating the straight lines to the potential axis, the flat-band potentials were evaluated to be $-0.36$ and $-0.42$ V (SSCE) in PC and ACN media respectively.

### 3.3.6. Photocurrent action spectra

The short-circuit photocurrent $i_{\rm photo}$ was measured as a function of the wavelength of monochromatic light ($\lambda$) and from these values of $i_{\rm photo}$ and the corresponding intensity of incident monochromatic light, $I_{\rm inc}$, incident photon-to-current conversion efficiencies (IPCE) [5] were calculated using the equation

$$\text{IPCE} = \frac{\text{number of generated electrons}}{\text{number of incident photons}} \times 100\%$$

$$= \frac{1240 \times i_{\rm photo}\ (\text{A cm}^{-2})}{\lambda\ (\text{nm}) \times I_{\rm inc}\ (\text{W cm}^{-2})} \times 100\% \qquad (4)$$

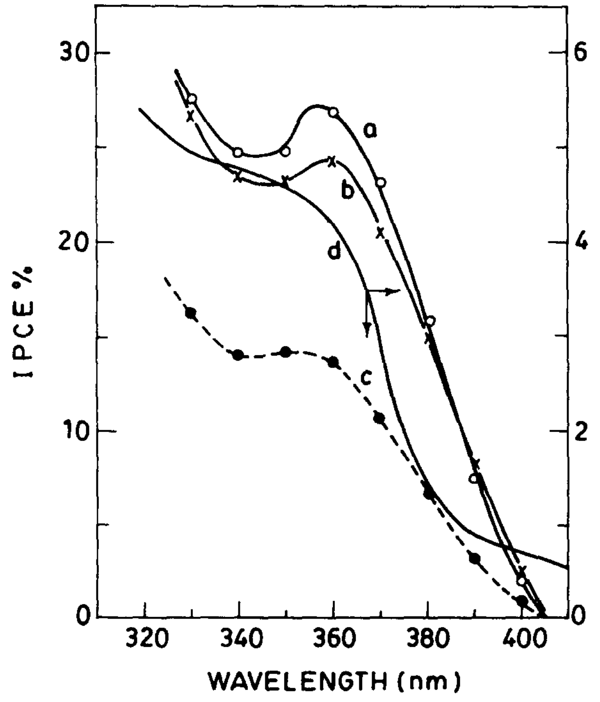

Fig. 11. Photocurrent action spectra (in terms of IPCE) of particulate ZnO thin film electrode in PC (a), ACN (b) and aqueous (c) media. Curve d is the absorption spectrum of particulate ZnO film (same as curve b in Fig. 2).

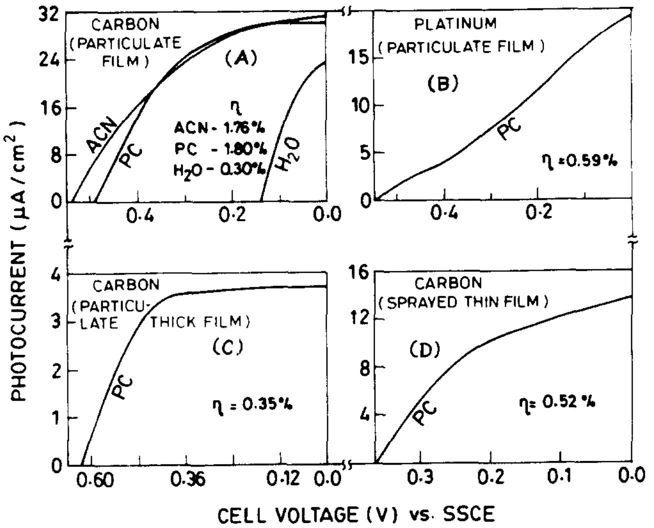

Fig. 12. Power output characteristics (cell photocurrent–cell voltage) of various PEC cells based on (A–C) particulate and (D) sprayed ZnO thin film electrodes and Pt or carbon counterelectrode. Monochromatic light ($\lambda = 360$ nm) of 400 $\mu$W cm$^{-2}$ intensity was used in all cases. Electrolyte: same as for Fig. 3.

The results thus obtained are presented in Fig. 11 (curves a–c) for three different solvents (PC, ACN and $H_2O$) along with the absorption spectrum (curve d) of the particulate ZnO film. The IPCE values corresponding to the peak wavelength ($\lambda = 360$ nm) were found to be about 27%, 24% and 14% in PC, ACN and aqueous media respectively. The IPCE of 14% obtained in aqueous medium in the present work is quite close to that reported by Hotchandani and Kamat [5] for a similar electrode in the same solvent. However, in the non-aqueous media used in the present work, significantly higher values of IPCE were obtained. Such improvement justifies the objective of using non-aqueous media in the present investigation. Further, the nature of all the action spectra resembles closely that of the absorption spectrum (curve d) of the semiconductor electrode, thus confirming the photoexcitation of the particulate ZnO thin film electrode.

### *3.3.7. Power characteristics*

The power conversion efficiency ($\eta$) and fill factor (FF) of various cells constructed with different electrolyte media and counterelectrodes have been determined from their cell voltage ($V$) vs. cell current ($i$) plots. Fig. 12(A) shows the $i$–$V$ curves obtained in three different solvents using a carbon counterelectrode and a particulate ZnO thin film as working electrode. From these curves the power conversion efficiency was evaluated using the equation

$$\eta = \frac{i_{\max} V_{\max}}{I_{\text{inc}}} \times 100\% \qquad (5)$$

where $i_{\max}$ (A cm$^{-2}$) and $V_{\max}$ (V) are the cell current and cell voltage respectively corresponding to maximum power and $I_{\text{inc}}$ (W cm$^{-2}$) is the intensity of incident light (optical input power). The values of $\eta$ were evaluated to be 1.8% (PC), 1.76% (ACN) and 0.3% ($H_2O$). The corresponding fill factors are 0.49 (PC), 0.42 (ACN) and 0.27 ($H_2O$). Thus the power conversion efficiency obtained in the case of the aqueous cell is about six times lower than that obtained with non-aqueous cells. However, $\eta = 0.3\%$ obtained in the former case is still higher than that reported (0.05%) by Hotchandani and Kamat [5] for a similar aqueous cell. This improvement is probably due to the carbon counterelectrode used in the present work.

To examine the effect of the counterelectrode on the power output characteristic of the cell, a similar $i$–$V$ curve was determined using a platinum counterelectrode in PC medium and the result is shown in Fig. 12(B). The $\eta$ and FF values in this case were evaluated to be 0.59% and 0.23 respectively. Both these values are significantly lower than those obtained with the carbon counterelectrode in the same PC medium ($\eta = 1.8\%$, FF = 0.49). The improvement in the power conversion efficiency and fill factor with the carbon counterelectrode seems to be due to the high porosity of this electrode, which provides a large effective surface area, thereby improving the collection and discharge of charge carriers at this electrode. This may avoid the undesired polarization of the counterelectrode during cell operation when current is drawn. A similar improvement was achieved by Murali et al. [19] in the case of a Cd (SeTe) septum cell by using a graphite counterelectrode.

Fig. 12(C) shows the $i$–$V$ curve obtained with a thicker particulate ZnO film (1.5 $\mu$m) in PC medium with carbon as counterelectrode. The power conversion efficiency in this case was found to be low ($\eta = 0.35\%$), though the fill factor was comparatively higher (FF = 0.61). The low value of $\eta$ in this case may be due to the increase in film resistance with its increase in thickness. Hodes et al. [4] proposed a model for the charge separation in nanocrystalline film. According to them, when the thickness of the film is greater than the light penetration length, the electron transfer to the substrate becomes difficult owing to the increase in distance (and hence the resistance in the direction of the current) from the substrate to the point of electron generation. Probably because of this, the photocurrent was drastically reduced in this case, giving a very low value of $\eta$. For the sake of comparison, the power conversion efficiency of a cell constructed with a sprayed ZnO thin film electrode in propylene carbonate medium was also determined (Fig. 12(D)) and $\eta = 0.52\%$ was obtained, which is much less than the value for the particulate film under similar conditions.

## 4. Conclusions

On the basis of the findings of the present investigation it can be concluded that the best performance of the photoelectrochemical cell was observed with the cell configuration (particulate ZnO electrode/electrolyte in propylene carbonate/carbon counterelectrode). Further, it should be emphasized here that the power conversion efficiency $\eta = 1.8\%$ obtained with the above-mentioned cell is the highest ever reported for pure ZnO film electrodes prepared by various techniques.

## Acknowledgements

Financial assistance for the present work provided by the Department of Non-conventional Energy Sources (DNES), Government of India is gratefully acknowledged. Our thanks are also due to Professor G.V. Subba Rao of the Indian Institute of Technology, Madras (presently Director, CECRI, Karaikudi) for providing some experimental facilities of his laboratory.

## References

[1] X.K. Zhao and J.H. Fendler, *J. Phys. Chem., 95* (1991) 3716.
[2] B. O'Regan and M. Grätzel, *Nature, 353* (1991) 737.
[3] A. Ennaoui, S. Fiechter, H. Tributsch, M. Giersig, R. Vogel and H. Weller, *J. Electrochem. Soc., 139* (1992) 2514.
[4] G. Hodes, I.D.J. Howell and L.M. Peter, *J. Electrochem. Soc., 139* (1992) 3136.
[5] S. Hotchandani and P.V. Kamat, *J. Electrochem. Soc., 139* (1992) 1630; *J. Phys. Chem., 96* (1992) 6834.
[6] P. Hoyer, Eichberger and H. Weller, *Ber. Bunsenges. Phys. Chem., 97* (1993) 630.
[7] L. Bahadur and T.N. Rao, *Solar Energy Mater. Solar Cells, 27* (1992) 347.
[8] A.I. Vogel, *Text Book of Practical Organic Chemistry*, ELBS, 4th edn., 1978, p. 269.
[9] L. Spanhel and M.A. Anderson, *J. Am. Chem. Soc., 113* (1991) 2826.
[10] S. Sakohara, L.D. Tickanen and M.A. Anderson, *J. Phys. Chem., 96* (1992) 11 086.
[11] L. Bahadur, T.N. Rao and J.P. Pandey, *Semicond. Sci. Technol., 9* (1994) 275.
[12] B.D. Cullity, *Elements of X-Ray Diffraction*, Addison-Wesley, Reading, MA, 1978, p. 102.
[13] J. Segui, S. Hotchandani, D. Baddou and R.M. Leblanc, *J. Phys. Chem., 95* (1991) 8807.
[14] D.J. Blackwood and L.M. Peter, *Electrochim. Acta, 34* (1989) 1505.
[15] K.D. Allard, M. Ahrens and K.E. Heuster, *Werkstoff Korrors, 26* (1975) 694.
[16] W. Gartner, *Phys. Rev., 116* (1953) 84.
[17] M.A. Butler, *J. Appl. Phys., 48* (1977) 1914.
[18] R. Memming, in B.E. Convey, J.O'M. Bockris, E. Yeager, S.U.M. Khan and R.E. White (eds.), *Comprehensive Treatise of Electrochemistry: Kinetics and Mechanism of Electrode Processes*, Vol. 7, p. 529.
[19] K.R. Murali, V. Subramanian, N. Rangarajan, A.S. Lakshmanan and S.K. Rangarajan, *J. Appl. Electrochem., 22* (1992) 87.