

# Dye-Sensitized Photoelectrochemical Cells Based on Porous SnO<sub>2</sub>/ZnO Composite and TiO<sub>2</sub> Films with a Polymer Electrolyte

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Polyacrylonitrile polymer electrolyte based photoelectrochemical cells have been fabricated with ruthenium bipyridyl complex as the sensitizer using porous films of SnO<sub>2</sub>/ZnO composite and also TiO<sub>2</sub> films. The redox component of the electrolyte is XI + I<sub>2</sub>, where X<sup>+</sup> = Cs<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>, or tetrabutylammonium ion. For both types of cells (SnO<sub>2</sub>/ZnO and TiO<sub>2</sub>) highest short-circuit photocurrents and efficiencies are obtained when X = Cs and in all cases these parameters were higher for the cells made from SnO<sub>2</sub>/ZnO. Results are explained as originating from the dependence of the mobility of I<sup>-</sup> in the polymer electrolyte on nature of the cation X<sup>+</sup> and the necessity of wide separation of photogenerated electron and the resulting dye cation to overcome the diffusion-controlled kinetics of I<sup>-</sup> transport.

## Introduction

In recent years, considerable effort has been diverted to development of dye-sensitized (DS) photoelectrochemical cells (PECs) based on nanoporous films of high band gap semiconductors.<sup>1–4</sup> Although these devices are cheap and the energy conversion efficiencies are reasonable, the practical application requires resolution of fabrication problems and improvement of the long-term stability. The main problem is encapsulation of the cell with a liquid electrolyte. Completely foolproof sealing is difficult, and the loss of volatile components in the electrolyte cannot be ensured. The problem is aggravated by a build up of pressure inside the cell due to gaseous degradation products of the electrolyte. The ideal solution to this problem would be the replacement of the liquid electrolyte by a high band-gap (BG) solid hole conductor.<sup>5–8</sup> However, the choice of the hole conductor is highly restrictive and fully solid-state DS solar cells present different type of fabrication problems that are been investigated.<sup>9,10</sup> Suggestion has been made to use solid electrolytes<sup>11</sup> instead of a liquid to avoid

the difficulties of sealing. Obviously as ionic transport is diffusion limited, high short-circuit (SC) photocurrent (and therefore reasonable efficiency) cannot be expected from a cell utilizing a solid electrolyte, because the mobilities of ions in solid electrolytes are generally lower than that of liquids. In dye sensitization, the photoexcited dye molecule injects an electron into the conduction band (CB) leaving the dye cation (D<sup>+</sup>) on the surface. The efficient removal of the positive charge on the D<sup>+</sup> is an essential condition for obtaining high quantum efficiencies. Otherwise recombination of photogenerated electron and the D<sup>+</sup> becomes more probable. Thus slow diffusion-limited transport of the ionic species that scavenge the positive charge on D<sup>+</sup>, increases the recombinations, reducing the SC photocurrent.

Recently it has been found that DS PECs made from porous films containing a mixture of tin(IV) and zinc oxides generates high photocurrents because of the efficient separation of the injected electron and the D<sup>+</sup> in the composite system.<sup>4</sup> In this work we compare the performance of DS PECs made from TiO<sub>2</sub> and SnO<sub>2</sub>/ZnO films that use the quasi-solid polymer electrolyte based on polyacrylonitrile (PAN). As expected, cells based on SnO<sub>2</sub>/ZnO films deliver conspicuously higher photocurrents with this electrolyte than those made from TiO<sub>2</sub> films.

## Experimental Section

Porous films consisting of SnO<sub>2</sub> and ZnO were prepared as described below. A colloidal 15% aqueous dispersion of SnO<sub>2</sub> (Alpha Chemicals) of crystallite size ~0.015 μm (1.5 mL), acetic acid (0.1 mL), and ZnO of crystallite size ~0.5 μm (0.3 g) were ground in an agate mortar, mixed with 20 mL of methanol and agitated ultrasonically for 30 min. The dispersion was then sprayed onto fluorine doped conducting tin oxide (CTO) glass plates (1.25 × 1.5 cm<sup>2</sup>, sheet resistance ~10 Ω □<sup>-1</sup>) heated to 150 °C, until a layer of thickness ~8–10 μm is deposited, and sintered at 500 °C in an air for 30 min. TiO<sub>2</sub> films were

(1) McEvoy, A. J. *Endeavour* **1993**, *17*, 17.

(2) Regan, B. O.; Gratzel, M. *Nature* **1991**, *353*, 737.

(3) Nazeerudin, M. K.; Kay, A.; Rodicio, I.; Baker, R. H.; Miller, E.; Liska, P.; Vlachopoulos, N.; Gratzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.

(4) Tennakone, K.; Kumara, G. R. R. A.; Kottegoda, I. R. M.; Perera, V. P. S. *Chem. Commun.* **1999**, 15.

(5) Tennakone, K.; Kumara, G. R. R. A.; Kumarasinghe, A. R.; Wijayantha, K. G. U.; Sirimanne, P. M. *Semicond. Sci. Technol.* **1995**, *10*, 1689.

(6) Tennakone, K.; Kumara, G. R. R. A.; Wijayantha, K. G. U.; Perera, V. P. S. *J. Phys. D.* **1998**, *31*, 1492.

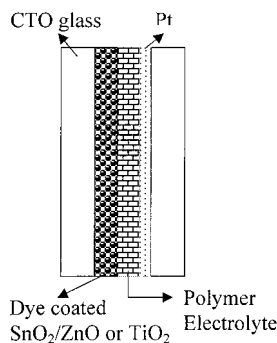
(7) Regan, B. O.; Schwartz, D. T. *Chem. Mater.* **1995**, *7*, 1349.

(8) Regan, B. O.; Schwartz, D. T. *Chem. Mater.* **1998**, *10*, 1501.

(9) Tennakone, K.; Kumara, G. R. R. A.; Kottegoda, I. R. M.; Perera, V. P. S.; Weerasundara, P. S. R. S. *J. Photochem. Photobiol.* **1998**, *117*, 137.

(10) Bach, W.; Lupo, D.; Comte, P.; Moser, J. E.; Weissortel, F.; Salbeck, J.; Spreitzer, H.; Gratzel, M. *Nature* **1998**, *395*, 583.

(11) Cao, F.; Oskam, G.; Searson, P. C. *J. Phys. Chem.* **1995**, *99*, 17071.



**Figure 1.** Schematic diagram illustrating the construction of the dye-sensitized photoelectrochemical cell with the polymer electrolyte.

prepared by the method described in the literature<sup>5</sup> using Degussa P25 titanium dioxide (surface area 50 m<sup>2</sup>/g). The sintered films were coated with the dye (*cis*-dithiocyanato-*[N*-bis(2,2'-bipyridyl-4,4-dicarboxylic acid)ruthenium(II)] by boiling the plate in the dye solution ( $2 \times 10^{-4}$  M in ethanol) for 2 min and allowing it to cool in the solution for 30 min.

PAN (MW 86200, Aldrich), LiI, NaI, KI, CsI (Aldrich), tetrabutylammonium iodide (Aldrich), propylene carbonate (PC, Fluka), ethylene carbonate (EC, Fluka), acetonitrile (ACN, Fluka), and iodine (BDH) were used as received. For preparation of the polymer electrolytes, 1.5 g of PAN, 5.6 g of PC, 10 g of EC, 3.7 g of ACN, and 0.1 g of I<sub>2</sub> were used. The amount of the iodide, XI, added was calculated so that the molar ratio [I<sub>2</sub>]/[X] is 0.1. Appropriate amounts of iodide salts were first added to the mixture PC, EC, and ACN with continuous stirring, and the mixture was heated to 140 °C for 20 min to initiate the polymerization. Iodine was added after the solution was cooled to room temperature to avoid loss due to evaporation. The viscous electrolyte was placed on the dye-coated films (SnO<sub>2</sub>/ZnO or TiO<sub>2</sub>) and pressed onto the platinized CTO glass counter electrode. When the polymerization is (in about 1 h), the cell is sealed with silicone gum to prevent the entry of moisture. The schematic diagram illustrating the construction of the cell is shown in Figure 1.

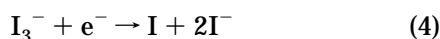
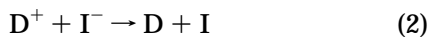
The I–V characteristics at 100 W m<sup>-2</sup> (diffuse day light) and 1000 W m<sup>-2</sup> (direct sunlight) for each type of cell (i.e., SnO<sub>2</sub>/ZnO and TiO<sub>2</sub> for different X) was determined several times and reproducible results were obtained. Light intensities were measured with a pyranometer (EKO Model MS 801) which could record total irradiance to an accuracy of ~7 W cm<sup>-2</sup>.

## Results and Discussion

DS PECs using the electrolyte XI + I<sub>2</sub> generate photocurrents via the following mechanism. The photoexcited dye molecule absorbed at the semiconductor surface injects an electron into the CB leaving a dye cation at the surface<sup>12,13</sup> i.e.



The positive charge on the D<sup>+</sup> is scavenged by I<sup>-</sup> and the redox cycle is completed by formation of I<sub>3</sub><sup>-</sup>, which accepts an electron from the counter electrode, i.e.



At a given intensity of illumination the rate determining steps for electron transfer are the forward reactions 2 and 3, which depends largely on the mobility of I<sup>-</sup>.

The I–V characteristics of the cells with different iodides XI (X = Li, Na, K, Cs) at 100 W m<sup>-2</sup> (diffuse day light) are presented in Figure 2a (SnO<sub>2</sub>/ZnO electrodes) and Figure 2b (TiO<sub>2</sub> electrodes). In both cases the SC photocurrent increases with X in the order Li, Na, K, Cs. This can be readily understood, because the mobility of the anion (I<sup>-</sup> in the present case) depends on the degree of interaction of X<sup>+</sup> with the polymer.<sup>14</sup> Naturally the larger cations of similar electronic configuration interacts more strongly with the polymer because of the viscous forces. The enhancement of anion mobilities in conducting polymers with the immobilization of cations is reported in the literature.<sup>14</sup> We have not attempted to verify this in context of the present investigation (i.e., measure the diffusivities of I<sup>-</sup> in PAN with various cations). The situation here is different from that of a liquid (e.g., water), where owing to hydration, Li<sup>+</sup> ion is less mobile. For the polymer, polarizable small molecules even if they are present in the medium, are largely immobile and will not get readily attached to cations in the polymer to interfere with their mobility. The increased mobility of I<sup>-</sup> resulting from stronger interaction of cation X<sup>+</sup> with the polymer facilitates its transport (i.e., increase the rate of the reactions 2 and 3) increasing the photocurrent.

The difference in the behavior of cells made from SnO<sub>2</sub> and TiO<sub>2</sub> films is more interesting. Figure 3 compares the I–V characteristics of cells with SnO<sub>2</sub>/ZnO and TiO<sub>2</sub> films. When the electrolyte is CsI + I<sub>2</sub> and the illumination is 1000 W m<sup>-2</sup> (direct sunlight), the former cell generates impressively higher SC photocurrents (11.5 mA cm<sup>-2</sup> compared to 5.7 mA cm<sup>-2</sup> for TiO<sub>2</sub>) and the energy conversion efficiency ( $\eta$ ) is also higher (Table 1). The same effect is noticeable when the electrolyte contains other iodides (Figure 2). The factor that severely limits the photocurrent quantum efficiency of a DS cell is the recombination of D<sup>+</sup> and e<sup>-</sup> or the back reaction:<sup>15,16</sup>



If the rate constant of this reaction ( $k_{D^+e^-}$ ) is reduced, a significant portion of the D<sup>+</sup> remains unrecombined to participate in [2] to generate a useful photocurrent. The rate constant ( $k_{D^+e^-}$ ) depends on the distance of separation of e<sup>-</sup> and D<sup>+</sup> and a wider separation increases the photocurrent. The higher photocurrent quantum efficiency of SnO<sub>2</sub>/ZnO originates from wider separation of these charges in the composite oxide films. The mechanism involved is as follows.

In SnO<sub>2</sub>/ZnO films dye sensitization occurs almost entirely at the SnO<sub>2</sub> surface. Because the total surface area of smaller SnO<sub>2</sub> crystallites in the film is nearly 2

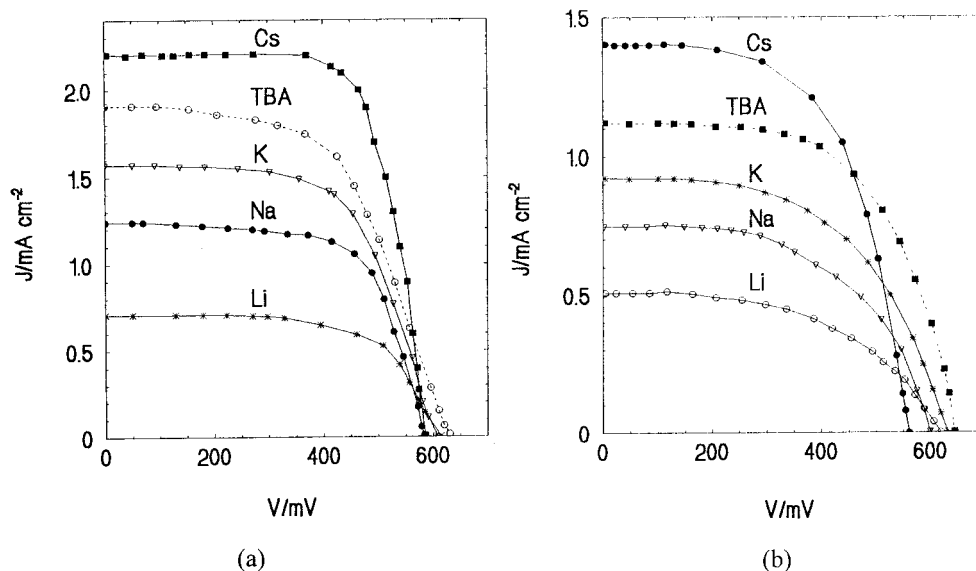
(14) Bruce, P. G.; Gray, P. M. *in Polymer Electrolytes II: Physical principles in Solid State Electrochemistry*; Cambridge: Cambridge, 1995.

(15) Kamat, P. V.; Patrick, B. *Electrochemistry in Colloids and Dispersions*; VCH Publishers: New York, 1992.

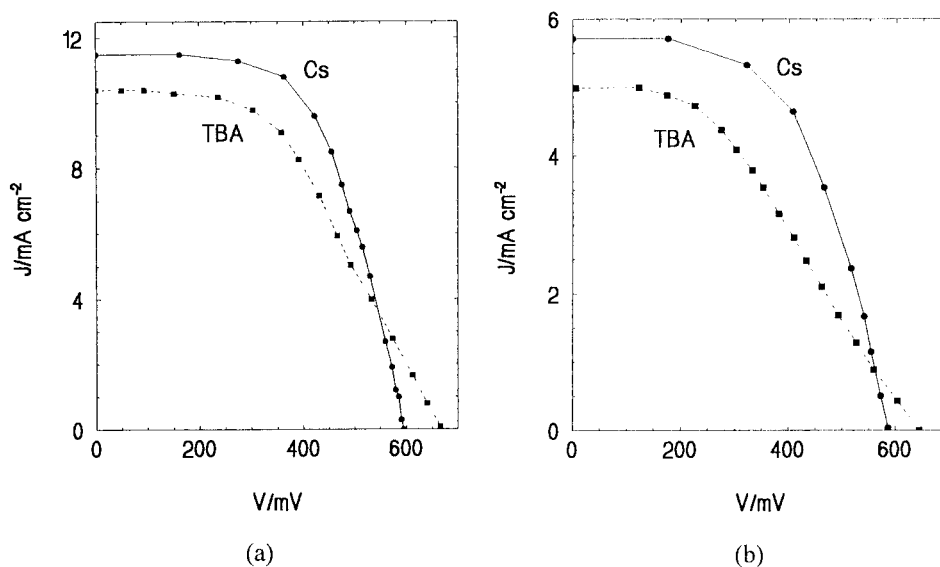
(16) Lu, H.; Prieskorn, J. N.; Hupp, J. T. *J. Am. Chem. Soc.* **1993**, *115*, 4927.

(12) Gerischer, H. *Photochem. Photobiol.* **1972**, *16*, 243.

(13) Memming, R. *Photochem. Photobiol.* **1972**, *16*, 325.



**Figure 2.** I–V characteristics of cells based on (a) SnO<sub>2</sub>/ZnO and (b) TiO<sub>2</sub> films at 100 W m<sup>-2</sup> (diffuse daylight) when the electrolyte contain the same molar concentration different alkali metal iodides and tetrabutylammonium iodide.



**Figure 3.** I–V characteristics of the cells (a) SnO<sub>2</sub>/ZnO and (b) TiO<sub>2</sub> at 1000 W m<sup>-2</sup> (direct sunlight) when the electrolyte contain same molar concentration of CsI and TBAI.

orders of magnitude larger than that of ZnO and furthermore dye is strongly adsorbed on SnO<sub>2</sub> and poorly adsorbed ZnO.<sup>4</sup> As the excited state of the dye is above CB of SnO<sub>2</sub> and ZnO and the CB edge of ZnO is higher than that of SnO<sub>2</sub> (Figure 4). The energetic “hot carrier” ballistically injected to the CB of a SnO<sub>2</sub> crystallite<sup>4,18</sup> could move to the CB of a ZnO crystallite tunneling across few SnO<sub>2</sub> crystallites (Figure 4). Subsequently the electron will “fall” into the CB of another SnO<sub>2</sub> crystallite in contact with the ZnO particle (Figure 4). This process widely separates the D<sup>+</sup> and the injected electron slowing down the recombination reaction. The larger size of the ZnO particle plays a crucial role in bringing about a wider separation of D<sup>+</sup> and e<sup>-</sup>. The SnO<sub>2</sub>/ZnO cells using liquid electrolytes (e.g., ACN)

generates higher photocurrents than those based on TiO<sub>2</sub> for the same reason.<sup>4</sup> However, when a polymer electrolyte is used, the difference in behavior of SnO<sub>2</sub>/ZnO and TiO<sub>2</sub> becomes more conspicuous, because even with lower mobilities of I<sup>-</sup> (compared that in a polar liquid), high photocurrents can be obtained only if the rate of recombination is slower. A slow recombination rate enables I<sup>-</sup> to scavenge the charge on D<sup>+</sup> even under conditions of relatively low mobility of I<sup>-</sup>. The same effect becomes again noticeable if the alkali ion X<sup>+</sup> is replaced by the tetrabutylammonium ion, which is highly immobile in the polymer matrix. The dotted curves in Figures 2 and 3 give the I–V characteristics of the cells in the presence of tetrabutylammonium iodide, when the light intensities are 100 W m<sup>-2</sup> and 1000 W m<sup>-2</sup>, respectively. Photocurrents and efficiencies obtained with TBAI are quite high and only next to cells with CsI. The reason CsI is superior to TBAI can also be explained. Although the TBA ion is less mobile than

(17) Nasr, C.; Kamat, P. V.; Hotchandani, S. *J. Phys. Chem. B* **1998**, *102*, 10047.

(18) Tennakone, K. *Proceedings of the Workshop on Low Cost Electronic Materials and Solar cells*; University of Peradeniya: Sri Lanka, 1999.

**Table 1. Short-circuit Photocurrent ( $J_{sc}$ ), Efficiency ( $\eta$ ), and Fill Factor (FF) of Polymer Cells at Intensities ( $I$ ) When the Electrolyte Contains the Same Molar Amounts of Different Iodides XI<sup>a</sup>**

X	$I, W m^{-2}$	$J_{sc}, mA cm^{-2}$	$\eta$ %	FF
SnO <sub>2</sub> /ZnO				
Cs	1000	11.48	4.1 ± 0.03	0.59
K	1000	7.28	2.4 ± 0.02	0.50
Na	1000	5.65	1.7 ± 0.01	0.47
Li	1000	3.59	1.0 ± 0.01	0.43
TBAI	1000	10.43	3.3 ± 0.02	0.51
Cs	100	2.21	9.0 ± 0.6	0.72
K	100	1.58	6.0 ± 0.4	0.68
Na	100	1.24	5.0 ± 0.3	0.67
Li	100	0.71	3.0 ± 0.2	0.62
TBAI	100	1.91	7.0 ± 0.5	0.69
TBAI/PAN 19%	100	0.67	1.3 ± 0.01	0.30
TiO <sub>2</sub>				
Cs	1000	5.72	1.9 ± 0.01	0.57
K	1000	3.47	0.9 ± 0.01	0.38
Na	1000	2.67	0.6 ± 0.01	0.36
Li	1000	2.12	0.4 ± 0.01	0.29
TBAI	1000	4.99	1.2 ± 0.01	0.40
Cs	100	1.40	5.0 ± 0.3	0.59
K	100	0.92	3.0 ± 0.2	0.56
Na	100	0.75	2.0 ± 0.2	0.53
Li	100	0.52	2.0 ± 0.1	0.50
TBAI	100	1.11	4.0 ± 0.2	0.58
TBAI/PAN 19%	100	0.48	0.9 ± 0.06	0.25

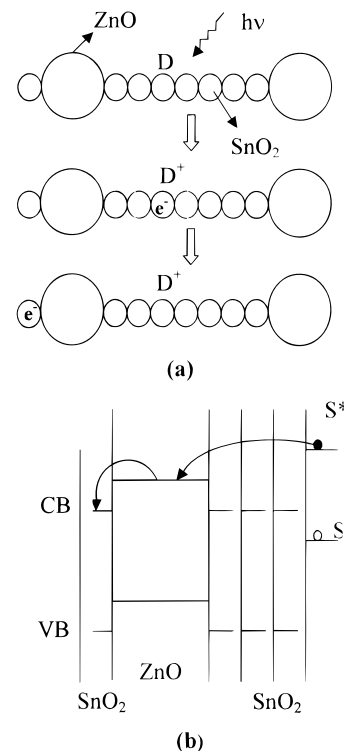
<sup>a</sup> The wt PAN /wt (EC + PC + CAN + I<sub>2</sub>) is the same in all cases except for the last row of the tables for SnO<sub>2</sub>/ZnO and TiO<sub>2</sub>.

CsI<sup>+</sup>, CsI is more readily ionizable than TBAI. Consequently the availability of I<sup>-</sup> is somewhat lesser when the electrolyte contain the same molar concentration of TBAI as CsI.

The difference in behavior of the SnO<sub>2</sub>/ZnO and TiO<sub>2</sub> based cells on viscosity of the electrolyte was noted when PAN percentage in electrolyte was increased from 7.2% to 19% (with X = TAB) which makes polymer electrolyte more viscous and solid in appearance. Here the SC photocurrent and efficiency was higher for the SnO<sub>2</sub>/ZnO cells than TiO<sub>2</sub> cells (Table 1). Again the fill factor (FF) of cells made from SnO<sub>2</sub>/ZnO films is higher than those of TiO<sub>2</sub> films and the highest values of FF are obtained when X = Cs (Table 1).

## Conclusions

The above investigation clearly demonstrates that in DS PECs, a wider separation of the photogenerated electron and the D<sup>+</sup> assists overcoming of the diffusion-limited transport of I<sup>-</sup> significantly. The cell based on SnO<sub>2</sub>/ZnO is superior in this respect because the ballistically injected "hot carrier" is transported across the wide zinc oxide particle suppressing the recombination. The ZnO:SnO<sub>2</sub> mixing ratio we have used (~53% ZnO) gives the optimum SC photocurrent and at this mixing ratio, the average distance between centers of two ZnO particles (estimated from the knowledge of densities of ZnO and porous SnO<sub>2</sub>) is ~1.1 μm. Thus a chain of 6–7 tin oxide nanoparticles could link two ZnO particles



**Figure 4.** (a) Schematic diagram showing excitation of a dye molecule adsorbed on a SnO<sub>2</sub> particle and transfer of the electron into another SnO<sub>2</sub> particle, traversing across few SnO<sub>2</sub> particles to a ZnO particle. (b) Schematic energy level diagram depicting band positions of SnO<sub>2</sub> and ZnO particles as shown in a and the ground (S) and excited (S\*) energy levels of Ru dye.

(Figure 4) and electron injected by dye sensitization should travel across 3–4 tin oxide particles in reaching a ZnO particle. Pumping of electrons into the ZnO particles build up the quasi-fermi level that drives electron to the back contact via the interconnection of SnO<sub>2</sub> particles. Transfer of photogenerated electrons from the CB of a high to low BG semiconductor is well-known.<sup>19,20</sup> The SnO<sub>2</sub>/ZnO is unique as "hot electrons" are ballistically transported to a high BG material across few nanocrystallites of low BG material. Present work demonstrates that "hot carriers"<sup>21–23</sup> in photoelectrochemical devices could lead to novel effects of practical significance.

Preliminary experiments suggest that the SnO<sub>2</sub>/ZnO cell is more stable than the TiO<sub>2</sub> cell. When the cells were exposed to direct sunlight for 20 h. TiO<sub>2</sub>-based cells showed nearly 25% drop in the open-circuit voltage and 12% drops in the short SC photocurrent. Whereas in the case of SnO<sub>2</sub>/ZnO cell, the drop in the open circuit voltage and the SC photocurrent ~8% and 2% respectively. The difference is perhaps due to higher oxidative catalytic activity of TiO<sub>2</sub> compared to ZnO on absorption of BG radiation. Again dye photodegradation should be lesser in the SnO<sub>2</sub>/ZnO because dye is mostly adsorbed on SnO<sub>2</sub>, which is even a weaker oxidative photocatalyst than ZnO.

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(19) Liu, D.; Kamat, P. V. *J. Phys. Chem.* **1993**, *97*, 10769.  
 (20) Vogel, R.; Hoyer, P.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 3183.  
 (21) Nozik, A. J.; Cooper, G.; Turner, J. A.; Parkinson, B. A. *J. Appl. Phys.* **1983**, *54*, 6463.  
 (22) Turner, J. A.; Nozik, A. J. *J. Appl. Phys. Lett.* **1982**, *41*, 101.  
 (23) Sung, Y. E.; Gaillardot, F.; Bard, A. J. *J. Phys. Chem. B* **1998**, *102*, 9797.