Photoelectrochemical Cells Made from SnO_2/ZnO Films Sensitized with Eosin Dyes

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Photoelectrochemical cells have been constructed with SnO_2/ZnO, SnO_2, ZnO and TiO_2 films sensitized with eosin Y (sodium salt and triethyl ammonium salt). SnO_2/ZnO composite system gives a significantly high short-circuit photocurrent and an efficiency compared to the cells made from SnO_2, ZnO or TiO_2. It is suggested that the recombination is better suppressed in the composite system and a possible mechanism involved is discussed.

The use of dye-sensitized (DS) photoelectrochemical cells (PECs) for solar energy conversion initiated in 1970s,[1,2] now receive much attention as a promising method suitable for practical application. The low energy and photon-to-photocurrent conversion efficiencies (η and Φ) of earlier DS PECs, ruled out their use as practical devices. A major breakthrough that changed this situation was the observation that dyed nano-porous TiO_2 films of high surface area, efficiently transfer the photo-injected carriers to the conducting substrate where the film is deposited.[3] Attempts have also been made to adopt nano-porous films of other semiconducting materials (e.g. ZnO, SnO_2, Nb_2O_5)[4–6] for construction of DS PECs. However PECs constructed from these oxides yield significantly lower values of η and Φ compared to those based on TiO_2. Recently two of the authors of the present paper (KT and GRAK) and their collaborators demonstrated a highly efficient DS PEC made from a composite film consisting of SnO_2 and ZnO.[7,8] Notable differences between SnO_2/ZnO and TiO_2 cells sensitized with the Ru-dye (ruthenium (II) *cis*-bis (thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) complex) and using the redox couple I_3^-/I^- (0.5 mol dm^{-3} of tetrapropylammonium iodide, 0.05 mol dm^{-3} of iodine in mixed solvent of ethylene carbonate and acetonitrile (60:40% by volume)) are as follows; 1. SnO_2/ZnO system generates a short-circuit photocurrent (I_{SC}) comparable to or higher than the optimized TiO_2 cell sensitized with the same Ru-dye. 2. The dye concentration per unit film area (S) for SnO_2/ZnO and TiO_2 cells are of the same order of magnitude, but the film thickness (t) that yields highest I_{SC} is greater in the case of SnO_2/ZnO. 3. The values of η and the fill factor (FF) of the SnO_2/ZnO cells as at present are slightly less than the best reported values for the TiO_2 cell. In order to confirm and understand the mechanism of operation of the SnO_2/ZnO cell, it is important to study the behavior of the system, when other dyes are used as sensitizers. Here we report the characteristics of the SnO_2/ZnO cells sensitized with eosin-Y sodium salt (EYNa) and eosin-Y triethylammonium salt (EYTEA). We chose eosin dyes as sensitizers for the SnO_2/ZnO cells because PECs sensitized by eosin dyes have been well known and Arakawa et. al. have recently reported fairly good performance of eosin Y-sensitized solar cell using porous TiO_2 electrode.[9]

SnO_2/ZnO films were prepared by the described method[7] using SnO_2 colloidal dispersion (crystallite size 10–15 nm, Alfa Aesar Chemicals) and ZnO powder (crystallite size 250 nm, Aldrich). The mixing ratio giving the highest I_{SC} and the open-circuit voltage (V_{OC}) was found to be 53% of ZnO by weight, for all the dyes tested. TiO_2 films were prepared by the literature method[10] using TiO_2 colloid supplied by Solaronix. Film thickness and particle sizes were estimated by SEM. Films were coated with the dyes EYNa (Wako Chemical) and EYTEA (gift from Mitsubishi Chemical Co.) from alcoholic solution (3×10^{-4} mol dm^{-3}). The amounts of dye adsorbed were estimated by extraction of the dye into alkaline alcoholic solution and spectrophotometric estimation. I–V characteristics and photocurrent action spectra were recorded with a Calibrated Solar Cell Evaluation System (JASCO, CEP-25BX).

Table 1 summarizes the results of the measurements and representative I–V curves and photocurrent action spectra are shown in the Figures 1 and 2. Cells based on SnO_2/ZnO give higher V_{OC}, I_{SC} and η compared to those made from single oxides SnO_2, ZnO or TiO_2, when sensitized with eosin dyes (Table 1). The film thickness corresponding to the optimum values for the above parameters is seen to be higher for the composite system (Table 1). Difference between EYTEA and EYNa sensitized SnO_2/ZnO cells (i.e. higher values of I_{SC} and η for EYTEA compared to EYNa) results from stronger adsorption of

Table 1. Characteristic parameters of the SnO_2/ZnO, SnO_2, ZnO and TiO_2 cells sensitized with eosin dyes

Film	t/μm	Dye	$S/10^{-8}$ mol cm^{-2}	V_{OC}/mV	I_{SC}/mA cm^{-2}	η/%
SnO_2/ZnO	14.0	EYTEA	7.1	609	8.0	3.2
SnO_2	7.0	EYTEA	2.4	293	4.9	0.6
ZnO	6.5	EYTEA	0.46	561	4.7	1.3
TiO_2	8.0	EYTEA	2.7	491	4.3	1.3
SnO_2/ZnO	14.0	EYNa	3.0	590	5.6	2.2
SnO_2	7.0	EYNa	1.2	398	3.8	0.9
ZnO	6.5	EYNa	0.46	550	4.6	1.2
TiO_2	8.0	EYNa	3.1	539	4.6	1.7

Film thickness (t) given is the value that gives the highest I_{SC}. S: the dye concentration per unit film area, V_{OC}: open-circuit voltage, I_{SC}: short-circuit photocurrent, η: light to electric energy conversion efficiency.

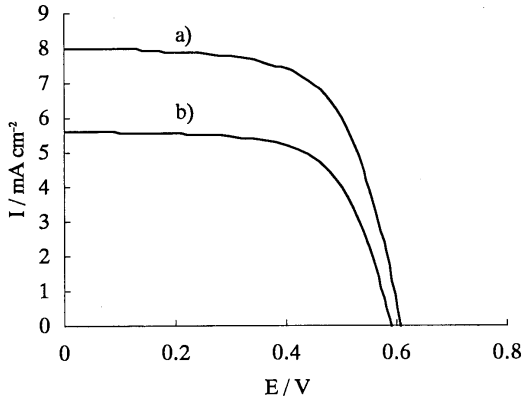

Figure 1. I-V curves for the SnO_2/ZnO cells sensitized with (a) EYTEA and (b) EYNa.

the former dye on SnO_2 and therefore on SnO_2/ZnO as well. Adsorption of EYTEA is the weakest on ZnO and we conclude that stronger dye adsorption on SnO_2 as an essential requirement for functioning of the SnO_2/ZnO cell. Furthermore in the composite film, the effective areas of SnO_2 and ZnO crystallites are respectively 1200 and 70 times larger than the geometrical area of the film (this estimation is based on average size of SnO_2 (15 nm), ZnO (250 nm) crystallite, respectively), making photocurrent resulting from ZnO almost insignificant. Again the main reason why we obtained higher efficiencies for eosin sensitized SnO_2/ZnO (compared to eosin sensitized TiO_2), seems to be the stronger adsorption of these dyes on SnO_2. It is also seen that SnO_2/ZnO cells sensitized with eosin dyes generate higher V_{OC} in comparison to the cells with single oxides SnO_2, ZnO or TiO_2. The difference between the quasi-fermi level (QFL) of electrons in the semiconductor and I_3^-/I^- redox level give the V_{OC} of a DS PEC. The level to which the QFL could be raised towards the conduction band depends on the probability of recombination (i.e. a lower rate of recombination of e^- with D^+ or I_3^- raises the QFL towards the conduction band).

Another distinct difference between PECs based on composite SnO_2/ZnO films and individual oxides SnO_2, ZnO or TiO_2 is the film thickness that gives the optimum I_{SC} as well as η. The optimum film thickness for the SnO_2/ZnO system is 13–14 μm, whereas the SnO_2, ZnO, TiO_2 cells gives highest I_{SC} and η at a smaller film thickness (Table 1). Here again the explanation seems to be the better suppression of recombination in the composite film. Under conditions of diffusion controlled ionic transport, the availability of I^- for scavenging positive charge on the dye cation D^+ (formed after electron injection to the semiconductor) is decreased by an increase of the film thickness, although an increase in the film thickness promotes light absorption. These two opposing factors determine the optimum thickness in relation to the extent of the recombination probability of the e^-/D^+ geminate pair, which depends on their separation. Thus effective charge separation or equivalently a slower recombination of the geminate pair in the composite system (possibly as a result of the transfer of the injected electron from SnO_2 crystallite to a ZnO crystallite via tunneling and subsequent movement to another SnO_2 crystallite in contact with the ZnO crystallite[7]) could compensate for the slow diffusion controlled supply of I^- ions in a thicker film.

Photocurrent action spectra of SnO_2/ZnO, SnO_2, ZnO cells

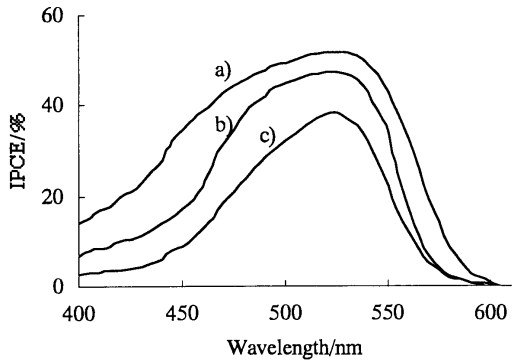

Figure 2. Photocurrent action spectra of the (a) SnO_2/ZnO, (b) SnO_2, and (c) ZnO cells sensitized with EYTEA.

illustrated in Figure 2 have another interesting feature. The spectrum of SnO_2/ZnO is conspicuously broader towards the left (shorter wavelength) of the peak position at 525 nm, compared to the spectra of SnO_2 and ZnO. This is quantitatively seen from the ratio of quantum efficiencies at the peak wavelength (525 nm) and shorter wavelengths with respect to the peak (e.g. Φ_{525}/Φ_{500} for SnO_2/ZnO, SnO_2, ZnO are respectively 1.02, 1.16, 1.19), indicating a higher sensitivity of the composite system to the blue-shifted light. A possible explanation is as follows: electrons injected from excited dye which absorbs blue-shifted light, have higher energy and become less susceptible to recombination, because these electrons could more readily reach to the conduction band of ZnO tunneling across SnO_2.

The present work on eosin dyes confirm that DS PECs based on the composite oxide system SnO_2/ZnO are indeed significantly more efficient than the cells made from the individual oxides and the reason seems to be the enhanced charge separation. Data obtained support mechanism of charge separation proposed earlier.[7] However, we emphasize that alternative explanations are not ruled out, as there is no direct experimental evidence for the mechanism suggested.

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