

# Interparticle Charge Transfer in Dye-Sensitized Films Composed of Two Kinds of Semiconductor Crystallites

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**Interparticle charge transfer between different types of semiconductor crystallites in contact on band gap excitation or dye-sensitization is documented. The general consensus had been that electrons always transfer from particles of higher conduction band position to those with lower conduction band position. Observation on dye-sensitized photoelectrochemical cells made from SnO<sub>2</sub>/ZnO films sensitized with different dyes suggests that the electron transfer could occur in either direction, that is from semiconductor of high band position to the semiconductor of the low band position or vice versa, depending on which surface adsorbs the dye more strongly.**

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**Key Words:** dye-sensitization; PVC cells; tin(IV) oxide; zinc oxide.

## 1. INTRODUCTION

Electron transfer between semiconductor microparticles have been recognized and adopted as a means of enhancing the photoinduced charge separation in photocatalysis (1–6). The general consensus is that the electrons are transferred from the semiconductor of higher conduction band (CB) position to that of the lower CB position. The same effect occurs in dye-sensitized (DS) composite semiconductor particulate systems (6, 7). Here again the assumption had been that electron transfer takes place only if the semiconductor with the relatively higher CB position is sensitized (6, 7), when injected electrons are transferred to the semiconductor having the lower CB position and in contact with the first (Fig. 1a, i). One of the authors of this paper (K.T.) and his coworkers have pointed out that the impressively high efficiency of a DS photoelectrochemical cell made from a composite SnO<sub>2</sub>/ZnO film sensitized with the ruthenium bipyridyl dye results from tunneling of electrons across SnO<sub>2</sub> to ZnO which has a higher CB position compared to SnO<sub>2</sub> (8, 9). In this note we present our observations on sensitization of nanocrystalline films of SnO<sub>2</sub>, ZnO, and SnO<sub>2</sub>/ZnO with different dyes to show that in composite DS semiconductor particles, electron transfer would occur in either direction, if the excited level of the dye molecule is greater than the CBs of both of the semiconductors and depending on which surface adsorbs the dye more strongly.

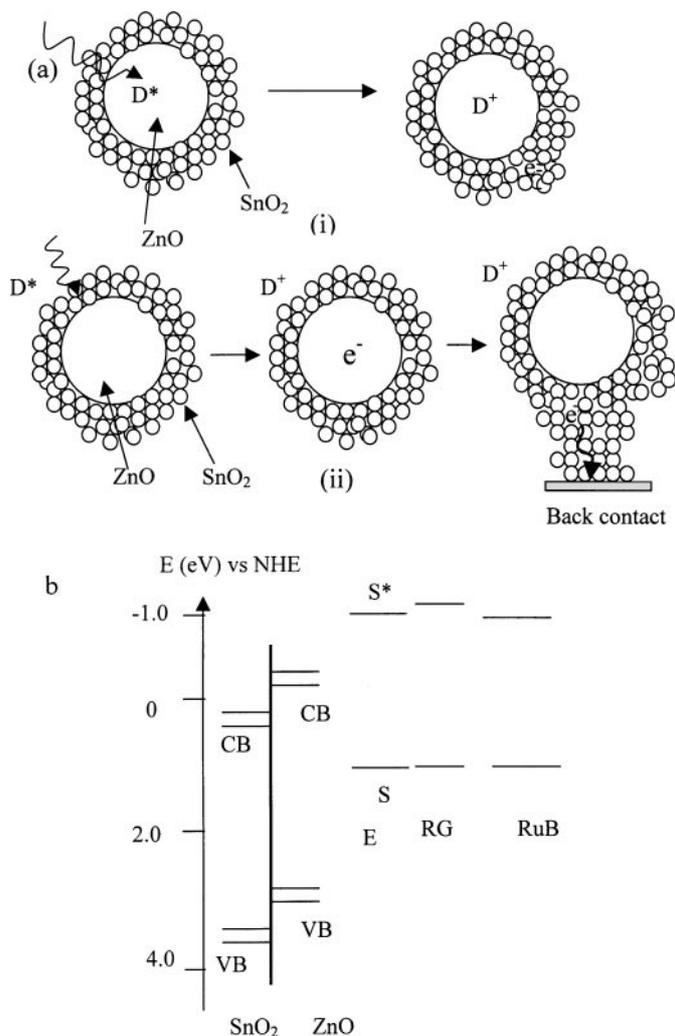
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Electron transfer from low- to high-band-position semiconductor (e.g., from SnO<sub>2</sub> to ZnO) is more advantageous, because in this case wider charge separation could be achieved by tunneling of the electron injected by the excited dye to the CB of the semiconductor with the higher CB position and subsequent relaxation to the CB of another lower band position semiconductor particle in contact with the high-band-gap semiconductor (Fig. 1a, ii)

## 2. EXPERIMENTAL

SnO<sub>2</sub> nanocrystallites were coated on conducting tin oxide (CTO) glass plates (1 × 2 cm<sup>2</sup>, sheet resistance ~10Ω□<sup>-1</sup>) as follows: 5 ml colloidal tin oxide aqueous dispersion (Alpha Chemicals, 15% SnO<sub>2</sub>, average crystallite size ~15 nm) mixed with 15 ml of methanol and few drops of acetic acid is ultrasonically agitated. The solution is then sprayed onto CTO glass plates heated to 150°C and sintered in air at 450°C for 30 min. ZnO was coated on CTO glass by the same procedure using a dispersion of 0.50 g ZnO (Aldrich, average particle size ~600 nm) in 15 ml methanol to which few drops of acetic acid are added. Composite films comprising of SnO<sub>2</sub> and ZnO were prepared by the method described below. Colloidal SnO<sub>2</sub> (1.5 ml), acetic acid (0.1 ml), and ZnO (0.30 g) are ground in an agate mortar, mixed with 20 ml methanol, and ultrasonically agitated. The dispersion was sprayed onto CTO glass plates and sintered as in the previous cases. Films used in all experiments had a thickness and area of ~10 μm and 1 cm<sup>2</sup>, respectively. Film densities were determined gravimetrically. Films were coated with the dyes Eosin Y (E) (BDH), Rose Bengal (RB) (Aldrich), Rhodamine 6G (RG) (Aldrich), Hematoxylin (H) (BDH) and Ru bipyridyl dye (RuB) (Solaronix) by immersing them in a solution (~1.5 × 10<sup>-4</sup> M) of the dye for a sufficient amount of time. The surface concentration of the adsorbed dye was determined by observing the decrease in dye concentration of the coating solution. This was also confirmed by extraction of the dye into an alkaline alcoholic solution and spectrophotometric estimation after adjustment of the pH to neutral. Absorption and fluorescence spectra of the dye adsorbed films were also recorded (Shimadzu UV-1601 spectrophotometer and Shimadzu Spectrofluorophotometer RF-5000).

Photoelectrochemical cells were constructed by placing a lightly platinized CTO glass (as the counter electrode) in



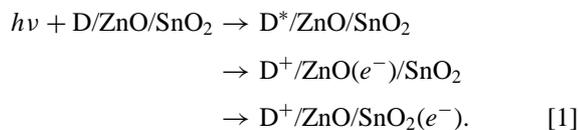
**FIG. 1.** (a) A schematic diagram illustrating (i) electron transfer from an excited dye molecule on a ZnO particle to a SnO<sub>2</sub> particle in contact with the ZnO particle. (ii) Electron transfer from an excited dye molecule on a surface of a SnO<sub>2</sub> crystallite to a ZnO particle in its vicinity and subsequently to a SnO<sub>2</sub> crystallite in contact with ZnO particle. The movement of this electron to the back contact via the interconnected SnO<sub>2</sub> crystallites is also illustrated. (b) An energy level diagram indicating the bands positions of ZnO, SnO<sub>2</sub>, ground (S) and excited (S\*) levels of the dyes.

contact with the dyed film and the electrolyte (0.5 M KI + 0.05 M I<sub>2</sub> in acetonitrile) introduced into the capillary space between the two electrodes. The open-circuit voltage ( $V_{oc}$ ) and the short-circuit photocurrent ( $I_{sc}$ ) of PECs were measured at an illumination intensity of 1000 Wm<sup>-2</sup> (tungsten filament lamp). Photocurrent spectra were obtained using a Nikon Autoscaner AS D102 monochromator and Stanford Research System lock-in-amplifier, connecting the cell output to an X-Y recorder.

### 3. RESULTS AND DISCUSSION

Table 1 gives the  $I_{sc}$ s and  $V_{oc}$ s of the cells made from ZnO, SnO<sub>2</sub>, and SnO<sub>2</sub>/ZnO films sensitized with different dyes and the

quantities of dye adsorbed in each film. Location of the ground (S) and excited (S\*) levels of these dyes and band positions of SnO<sub>2</sub> and ZnO (based on literature data) are presented in Fig. 1b (10, 12). The anionic dye RB is very strongly adsorbed on ZnO and feebly on SnO<sub>2</sub>. Consequently the ZnO cell yields higher  $I_{sc}$  than the SnO<sub>2</sub> cell. As expected, the former cell has a higher  $V_{oc}$  because the CB position of ZnO is above that of SnO<sub>2</sub>. Again the faster rate of charge injection due higher coverage of dye on ZnO helps to build up the quasi-fermi level of electrons favoring an enhancement of the  $V_{oc}$  (the  $V_{oc}$  obtained from a cell is the difference between the quasi-fermi level and the potential of the redox couple). The cell constructed from a SnO<sub>2</sub>/ZnO film sensitized with RB shows a marked increase in both  $I_{sc}$  and  $V_{oc}$  compared to the cells made from the individual oxides. In this system, electrons injected into the CB of ZnO by the excited dye on the ZnO surface are transferred to lower lying CB of SnO<sub>2</sub>; i.e.,



The wide charge separation achieved as a result of transfer of electrons from ZnO to SnO<sub>2</sub> suppresses the recombinations of the electrons and the dye-cation (D<sup>+</sup>) enhancing the  $I_{sc}$  (Fig. 1b, i) Suppression of recombinations also raises the quasi-fermi level of electrons increasing the  $V_{oc}$ . When the photocurrent spectra of cells made from RB sensitized ZnO, SnO<sub>2</sub>, and

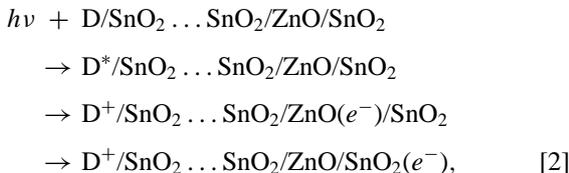
**TABLE 1**  
**Short-Circuit Photocurrent, Open Circuit Voltage, and Extent of Dye Adsorption in SnO<sub>2</sub>, ZnO, and SnO<sub>2</sub>/ZnO Films Sensitized with Different Dye**

Film	Dye	$I_{sc}$ (mA)	$V_{oc}$ (mV)	Adsorbed dye (mol/cm <sup>2</sup> ) × 10 <sup>-10</sup>
SnO <sub>2</sub>	E	0.050	175	149
ZnO	E	0.050	306	251
SnO <sub>2</sub> /ZnO	E	0.198	512	205
SnO <sub>2</sub>	RB	0.026	144	1.01
ZnO	RB	0.405	356	5.24
SnO <sub>2</sub> /ZnO	RB	1.32	574	2.54
SnO <sub>2</sub> /ZnO <sup>a</sup>	RB	0.920	596	3.22
SnO <sub>2</sub>	RG	0.166	293	548
ZnO	RG	0.035	321	148
SnO <sub>2</sub> /ZnO	RG	0.108	693	65
SnO <sub>2</sub> /ZnO <sup>a</sup>	RG	0.035	442	70
SnO <sub>2</sub>	H	0.152	174	79.2
ZnO	H	0.101	240	54.1
SnO <sub>2</sub> /ZnO	H	0.341	440	67.8
SnO <sub>2</sub>	RuB	2.50	335	145
ZnO	RuB	4.0	540	45.5
SnO <sub>2</sub> /ZnO	RuB	22.0	690	207.0
SnO <sub>2</sub> /ZnO <sup>a</sup>	RuB	14.5	635	187.0

<sup>a</sup> The particle size of ZnO is 50 nm; in all the other cases particle size of ZnO is 600 nm and that of SnO<sub>2</sub> is 15 nm.

SnO<sub>2</sub>/ZnO are examined, a higher photocurrent quantum efficiency for composite system is noticed.

The cationic dye RG is strongly adsorbed by SnO<sub>2</sub> and very poorly by ZnO. When cells with ZnO, SnO<sub>2</sub>, and SnO<sub>2</sub>/ZnO are sensitized by Rhodamine 6G,  $I_{sc}$ s obtained are 0.035, 0.166, and 0.108 mA, respectively.  $I_{sc}$  of ZnO cell is insignificantly small owing to poor dye adsorption on ZnO. Cells made from SnO<sub>2</sub> and SnO<sub>2</sub>/ZnO films sensitized with the same dye generate comparable  $I_{sc}$ s and the slightly higher  $I_{sc}$  of the SnO<sub>2</sub> cell can be understood, as SnO<sub>2</sub> adsorbs more dye than SnO<sub>2</sub>/ZnO (Table 1). The cell made from SnO<sub>2</sub>/ZnO has an exceptionally high  $V_{oc}$  (~693 mV) compared to the cells made from the individual oxides (321 and 293 mV, respectively, for ZnO and SnO<sub>2</sub>) and we present the following explanation. An excited dye molecule on the surface of a SnO<sub>2</sub> crystallite could inject an electron to the CB of a ZnO particle in its vicinity tunneling across few SnO<sub>2</sub> crystallites. As the excited level of the dye is located well above the CB of ZnO, tunneling of the "hot carrier" (i.e., an electron not relaxed to the bottom of the CB of SnO<sub>2</sub>) to the CB of ZnO is permitted. Subsequently, this electron relaxes to the CB of another SnO<sub>2</sub> particle in contact with a ZnO particle. The process can be schematically represented as



and the charge separation achieved here is wider than in [1] because of the larger ZnO particle size (Fig. 1a, ii). When the ZnO crystallite size is reduced to ~50 nm, the maximum  $V_{oc}$  achievable on varying the mixing ratio was 442 mV, compared to 693 mV for particles of larger size (~600 nm) used earlier (Table 1). It is interesting to note that when smaller crystallite size ZnO is used, the  $V_{oc}$  of the RB-sensitized cell is increased (Table 1), because of size quantization effect (this manifests readily in ZnO as the effective mass of electrons in ZnO is small). The mechanism [2] seems to be occurring in the case reported earlier (8, 9) on sensitization of SnO<sub>2</sub>/ZnO films with RuB. Both  $I_{sc}$  and  $V_{oc}$  are very much higher in the composite system and the effect of the ZnO crystallite size becomes evident (Table 1).

The dye E is strongly adsorbed on both SnO<sub>2</sub> and ZnO and the cells made from both these films generate nearly same  $I_{sc}$ s. As expected, ZnO cell gave a higher  $V_{oc}$  because of higher CB position of ZnO. SnO<sub>2</sub>/ZnO films sensitized with E yield much higher  $I_{sc}$  and  $V_{oc}$ . In this case, the electron transfer could be in both directions (i.e., from ZnO to SnO<sub>2</sub> or SnO<sub>2</sub> to ZnO) via mechanisms [1] and [2], both of which assists suppression of recombinations.

Sensitization of ZnO, SnO<sub>2</sub>, and SnO<sub>2</sub>/ZnO films with H presents another interesting example. In this case ZnO and SnO<sub>2</sub> and therefore SnO<sub>2</sub>/ZnO adsorb this dye strongly. However, because of surface complexation, the peak positions in the absorp-

tion spectra of H-coated ZnO and SnO<sub>2</sub> films are different (i.e., 610 and 540 nm, respectively). When photocurrent spectra of cells made from SnO<sub>2</sub>, ZnO, and SnO<sub>2</sub>/ZnO sensitized with H are examined, it is found that in the cell with the film SnO<sub>2</sub>/ZnO, the peak corresponding to light adsorption in SnO<sub>2</sub> is more pronounced than that seen in the cell with a SnO<sub>2</sub> film sensitized with the same dye. Thus it becomes clear that the photocurrent originating from sensitization of SnO<sub>2</sub> gets enhanced when there are ZnO crystallites on the neighborhood, suggesting that electrons are transferred from SnO<sub>2</sub> to ZnO.

In SnO<sub>2</sub>/ZnO films the larger ZnO particles are embedded in a porous matrix of smaller tin oxide particles. If we assume that zinc oxide crystallites are spheres of radius  $R$  and density  $\rho_s$  (~5.6 g cm<sup>-3</sup>) surrounded by tin oxide matrix of gross density  $\rho_s$  (~2.0 g cm<sup>-3</sup>), the distance  $d$  between the centers of zinc oxide particles can be expressed as

$$d \cong \left[ \frac{4\pi}{3} \left( 1 + \frac{W_s \rho_z}{W_z \rho_s} \right) \right]^{\frac{1}{3}} R, \quad [3]$$

where  $W_s$ , and  $W_z$  are the weights of tin, zinc oxides in the film and value obtained for  $d$  from [3] is 240 nm. The mixing ratio ( $W_z/W_s = 1.33$ ) used in this investigation gives the optimum  $I_{sc}$  for several dyes (i.e., RuB, RG, E), suggesting that the distance between the zinc oxide particles is the crucial parameter. It seems that, even electrons injected to SnO<sub>2</sub> at a distance of ~120 nm are transferred to ZnO and then relax to SnO<sub>2</sub> crystallite in contact with the ZnO particle. Electrons should be finally transported to the back contact via the interconnection of SnO<sub>2</sub> crystallites (Fig. 1a,ii). Another important observation is the increase in the rate of quenching of the fluorescence of RG in the composite films compared to the films made from the individual oxides. Thus the rate of electron injection from the excited dye is also enhanced in the composite film. Presumably, the presence of ZnO particles increase the available phase space (i.e., the density of final states) for injected electrons increasing the transition probability. An alternative possibility is the existence of a local electric field around ZnO particles favorable for driving electrons toward ZnO particles.

#### 4. CONCLUSION

The above investigation clearly shows that PECs made from composite SnO<sub>2</sub>/ZnO films (at the optimum mixing ratio) yields higher  $I_{sc}$ s and  $V_{oc}$ s compared to the cells made from the individual oxides. This seems to hold irrespective of which surface (i.e., SnO<sub>2</sub> of lower CB position or ZnO of higher CB position) adsorbs the dye strongly. A more conspicuous enhancement  $I_{sc}$  and  $V_{oc}$  (notably  $V_{oc}$ ) is observed when the dye is strongly adsorbed on the semiconductor of lower CB position (i.e., SnO<sub>2</sub>). The effect of ZnO crystallite size becomes more clearly evident, when the dye is well adsorbed on SnO<sub>2</sub>. Larger size ZnO in the composite film gives higher  $I_{sc}$ s as well as  $V_{oc}$ s. The hypothesis we propose on the basis of above observations is that the electron

transfer could occur in both ways and the predominant process decided by which surface adsorbs the dye strongly. A wider charge separation (and therefore better suppression of recombination) is achieved in sensitization of the low band position semiconductor and the extent of charge separation depends size of the particle with the higher CB position. Again in the second mode of interparticle charge transfer, the "hot carrier" energy gets better utilized to achieve a wider charge separation and buildup the quasi-fermi level. Explanations we have given are qualitative and the exact mechanism of sensitization and charge transport in composite semiconductor films remains unclear.

## REFERENCES

1. Gerischer, H., and Lubke, M., *J. Electroanal. Chem.* **204**, 225 (1986).
2. Vogel, R., Pohl, K., and Weller, H., *Chem. Phys. Lett.* **174**, 241 (1990).
3. Vogel, R., Hoyer, P., and Weller, H., *J. Phys. Chem.* **98**, 3183 (1994).
4. Kohant, S., Kudo, A., and Sakata, T., *Chem. Phys. Lett.* **206**, 166 (1993).
5. Yoshimura, J., Kudo, A., Tanaka, A., Domen, K., Maruya, K., and Onishi, T., *Chem. Phys. Lett.* **147**, 401 (1988).
6. Vinodgopal, K., Bedja I., and Kamat, P. V., *Chem. Matters* **8**, 2180 (1996).
7. Nasr, C., Kamat P. V., and Hotchandani, S., *J. Phys. Chem. B* **102**, 10047 (1998).
8. Tennakone, K., Kumara, G. R. R. A., Kottegoda, I. R. M., and Perera, V. P. S., *Chem. Commun.* **1949**, 15 (1999).
9. Tennakone, K., Kottegoda, I. R. M., De Silva L. A. A., and Perera, V. P. S., *Semicond. Sci. Technol.* **14**, 975 (1999).
10. Ranby, B., and Rabek, J. F., "Photodegradation, Photooxidation and Photostabilization of Polymers." Wiley, London, 1975.
11. Gopidas, K. R., and Kamat, P. V., *J. Phys. Chem.* **93**, 33 (1989).
12. Zhang, F., Zhao, J., Shen, T., Hidaka, H., Pelizzetti, E., and Serpone, N., *Appl. Catal. B* **15**, 147 (1998).