Probing the tunneling of electrons from SnO_2 to ZnO in dye sensitization of composite SnO_2/ZnO by use of generated H_2O_2 *via* reduction of O_2

Jayasundera Bandara,†* Keerthi Tennakone and Prabath Binduhewa

Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka.
E-mail: jayasundera@yahoo.com, jayasund@ifs.ac.lk; Fax: +94 8 232131

Received (in Montpellier, France) 13th February 2001, Accepted 3rd May 2001
First published as an Advance Article on the web 5th September 2001

A composite system of SnO_2/ZnO semiconductors was found to generate a higher H_2O_2 yield than individual oxide semiconductors when they were sensitized with various dyes. The optimum quantum yields for H_2O_2 generation were found to be 6.00×10^{-2}, 4.05×10^{-2} and 3.33×10^{-2}, respectively, for Eosin Y, Rose Bengal and Rhodamine 6G. Under similar conditions, Eosin Y showed quantum yields of 2.03×10^{-2} and 2.34×10^{-3}, respectively, for ZnO and SnO_2 particles. With the higher yield of H_2O_2 for the composite system, the possibility of electron transfer from the low band position semiconductor to the high band position semiconductor is demonstrated and is attributed to the transfer of injected high-energy electrons from the excited dye molecules on SnO_2 to ZnO particles.

The dye-sensitization of semiconductor surfaces is a topic of intense research, mainly because of the potential applications in solar energy conversion.[1–3] The general consensus has been that electrons always transfer from the particles with the higher conduction band (CB) position to those with the lower conduction band position.[4,5] The same effect occurs in dye-sensitized (DS) composite semiconductor particulate suspension systems. Here again, the assumption has been that the interparticle electron transfer takes place only if the semiconductor with the relatively higher CB position is sensitized, when injected electrons are transferred to the semiconductor having a lower CB position and in contact with the first. Studies on dye-sensitized photoelectrochemical cells made from SnO_2/ZnO films sensitized with different dyes suggest that the electron transfer can occur in either direction, that is from the semiconductor with the higher band position to that with the lower band position, or in the opposite direction, depending on which surface adsorbs the dye more strongly.[6] It has been reported that DS photoelectrochemical cells made from composite SnO_2/TiO_2[5] and SnO_2/ZnO[7] films sensitized with ruthenium bipyridyl dye behave differently. Mixing of SnO_2 with TiO_2 decreases the V_{oc} and I_{sc} while mixing SnO_2 with ZnO increases both V_{oc} and I_{sc} dramatically. Taking into consideration the E_{ox} of the redox couple I_3/I^- and the reported values of E_{CB} for SnO_2, TiO_2 and ZnO, films made from SnO_2, TiO_2 and ZnO should deliver maximum photovoltages (V_{oc}) of 500, 1000 and 650 mV, respectively. However, the V_{oc} obtained for SnO_2, TiO_2 and ZnO are 350, 750 and 500 mV, respectively, at 1000 W m^{-2} irradiation. In the composite SnO_2/TiO_2 system, the V_{oc} obtained is 400 mV, which is close to the V_{oc} of SnO_2 as the electron transfer is from TiO_2 to SnO_2, the final electron acceptor being SnO_2. For the SnO_2/ZnO system the V_{oc} obtained is 750 mV, which is much higher than either ZnO or SnO_2 alone. The origin of this high V_{oc} has been attributed to tunneling of high-energy electrons across SnO_2 to ZnO, which has a higher CB position compared to SnO_2,[8] resulting in efficient spatial separation of the photogenerated charges (D^+ and e^-) and suppression of recombination.

In this paper, we present evidence for tunneling of injected electrons from the conduction band of SnO_2 to the conduction band of ZnO particles, which facilitates transport of electrons along the nanocrystalline aggregates, by means of H_2O_2 generation *via* O_2 reduction.[9,10] Electron transfer from low to high band position semiconductors is shown to be advantageous because of the wider charge separation achieved. It has been clearly demonstrated that a wider separation of the electron and the oxidized dye enhances the catalytic action by suppression of charge recombination.[11]

Experimental

Catalyst preparation

Composite ZnO/SnO_2 catalysts were prepared by the following method. Colloidal tin(IV) oxide aqueous dispersion (0.3 ml, crystallite size *ca.* 10–15 nm, Alfa Chemicals) was mixed with a few drops of glacial acetic acid and the mixture was thoroughly ground with 60 mg of ZnO (particle size *ca.* 600 nm, BDH). The mixture was diluted to 100 ml by addition of water, ultrasonically agitated and washed with water and ethanol by centrifuging. The ZnO content of the catalyst prepared in the above manner is *ca.* 54% by wt. when fully dried.

Irradiation procedure

A quantity of catalyst equivalent to 50 mg of (ZnO + SnO_2) was suspended in 20 ml of a known concentration (4.10×10^{-4} M) of sensitizer (Eosin Y, Fluka; Rose Bengal, Aldrich; Rhodamine 6G, Fluka). Photolysis experiments were carried out in a 50 ml pyrex flask illuminated with a Suntest lamp at 1000 W m^{-2} (with UV cut-off filter) under atmospheric conditions. In all cases, blank experiments were also conducted with the catalysts in the absence of light and

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† Present address: Department of Chemistry, Hunter Howard Chemistry Laboratory, Clemson University, Clemson, SC 29634-0973, USA.

DOI: 10.1039/b101411k

without the catalysts when the solution containing the dissolved dye was illuminated.

Analysis

The ZnO particle size was estimated by gradient centrifugation (Horiba CAPA-700 particle size analyzer) of an aqueous suspension in the presence of sodium hexametaphosphate (0.01 M), which disperses the particle aggregates. UV-vis absorption spectra were recorded with a Shimadzu UV-1601 spectrophotometer. Light intensities were measured using an Eko pyronometer (model MS-801). The adsorption isotherm of Eosin Y on ZnO/SnO_2 was ascertained by mixing a known amount of catalyst with various concentrations of the dye. The amount of adsorbed dye was determined either by desorbing the dye from the semiconductor surface into a solution of 0.1 M NaOH or by comparing the initial and final dye concentrations in the solution and measuring its UV-vis absorption spectrum. A triiodide method described by Klassen *et al.*[12] was used to measure the peroxide concentration. Samples were passed through an activated carbon column to remove the color, if any, before the peroxide test.

Results and discussion

Table 1 shows the H_2O_2 yields for the solutions containing Eosin Y (EY), Rose Bengal (RB) and Rhodamine 6G (R6G) in the presence of SnO_2/ZnO, ZnO or SnO_2 after irradiation (at 1000 $W\ m^{-2}$) for 2 h. Also given in Table 1 is the H_2O_2 yield when dye solutions alone are irradiated under O_2 saturated conditions in the absence of oxides. As shown in Table 1, H_2O_2 generation is observed under visible light irradiation for the composite SnO_2/ZnO, SnO_2 and ZnO with all the sensitizers used, as well as with the sensitizers alone.

Fig. 1(a) shows the quantum yield (ϕ) measurements for EY on SnO_2 (curve 2), ZnO (curve 3) and SnO_2/ZnO (curve 4), along with the dye solution only (curve 5) and SnO_2/ZnO in the absence of EY (curve 1) in the 400–600 nm spectral region. No H_2O_2 formation was observed when the irradiation was carried out with the composite SnO_2/ZnO in the absence of EY dye [Fig. 1(a), curve 1], indicating that H_2O_2 is generated only in the presence of EY *via* a sensitization process. The ϕ values given in Fig. 1(a), curves 2, 3, 4 and 5 for SnO_2, ZnO, SnO_2/ZnO and EY solution, respectively, show a maximum around 530 nm, which corresponds to the absorption maximum of EY shown in Fig. 1(b). The qualitative matching of the ϕ and absorption spectra of adsorbed EY suggests that the photosensitization mechanism is operative in the generation of H_2O_2. RB and R6G also show a similarity between the absorption spectra and the ϕ wavelength dependence, giving evidence that the photosensitization mechanism is also operative in both cases. The optimum quantum yields for H_2O generation were found to be 6.00×10^{-2}, 4.05×10^{-2} and 3.33×10^{-2}, respectively, for EY, RB and R6G.

Table 1 H_2O_2 yield for SnO_2, ZnO and SnO_2/ZnO oxides (50 mg of oxide and 20 ml of dye solution) sensitized with different dyes after irradiation at 1000 $W\ m^{-2}$ for 2 h. The dye concentrations were kept constant at 4.10×10^{-4} M

	H_2O_2 concentration/10^{-4} mol l^{-1}		
Oxide	EY	RB	R6G
SnO_2/ZnO	2.91(±0.10)	2.00(±0.20)	1.46(±0.20)
ZnO	1.00(±0.10)	0.96(±0.08)	0.28(±0.09)
SnO_2	0.12(±0.05)	0.08(±0.04)	0.05(±0.02)
None	0.011	0.005	0.008

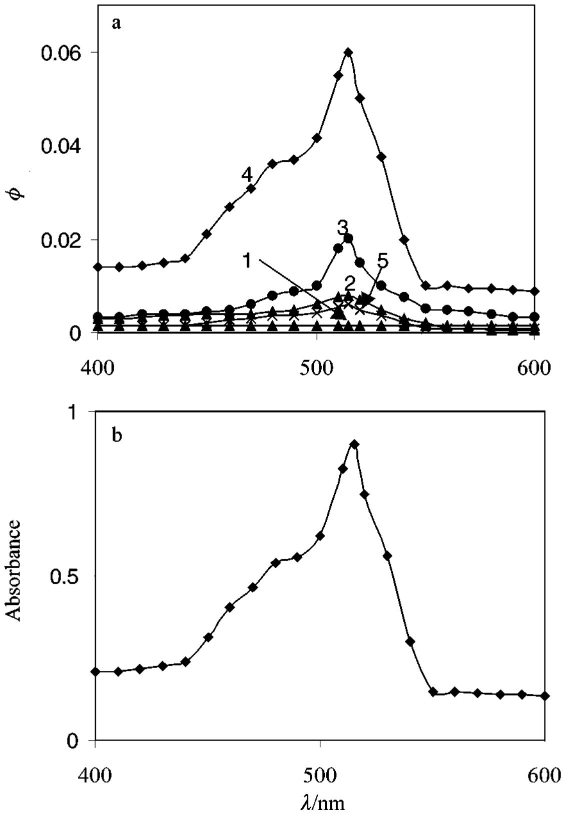

Fig. 1 (a) Quantum yields for the EY sensitized solutions on (1) SnO_2/ZnO in the absence of EY, (2) SnO_2, (3) ZnO, (4) SnO_2/SnO and (5) EY solution only. (b) Absorption spectrum of the EY solution.

The formation of H_2O_2 in O_2-saturated dye solutions upon visible light irradiation takes place *via* the following reactions:[9]

$$\text{dye} \xrightarrow{h\nu} \text{dye}^* \tag{1}$$

$$\text{dye}^* + O_2 \longrightarrow \text{dye}^{\cdot +} + O_2^{\cdot -} \tag{2}$$

$$O_2^{\cdot -} + e^- + 2H^+ \longrightarrow H_2O_2 \tag{3a}$$

$$2O_2^{\cdot -} + 2H^+ \longrightarrow 2HO_2^{\cdot -} \longrightarrow H_2O_2 + O_2 \tag{3b}$$

The excited dye transfers an electron to the dissolved O_2 to form the superoxide radical anion $O_2^{\cdot -}$ [E° ($O_2/O_2^{\cdot -}$) = −0.16 V *vs.* NHE in aqueous solution at pH ⩾ 7[13]], which under acidic conditions leads to formation of H_2O_2 *via* either eqn. (3a) or (3b). As the redox level of the excited dye is well above the O_2 reduction potential (Fig. 2) excited dye is capable of reducing molecular O_2 to form $O_2^{\cdot -}$ and H_2O_2, as explained above. The amount of H_2O_2 generated when dye solution alone was irradiated was quite low, due to rapid self-quenching of excited dye molecules by ground state dye molecules.

When ZnO and SnO_2/ZnO were sensitized with EY, RB or R6G, an increase in H_2O_2 generation was observed, with SnO_2 the presence of a dye did not change the H_2O_2 yield. The formation of H_2O_2 on sensitized semiconductor dispersions irradiated with visible light involves the following reactions,[14] where MO represents SnO_2 or ZnO:

$$\text{MO/dye} \xrightarrow{h\nu} \text{MO/dye}^* \tag{4}$$

$$\text{MO/dye}^* \longrightarrow (e^-)\text{MO/dye}^{\cdot +} \tag{5}$$

$$\text{MO}(e^-) + O_2 \longrightarrow \text{MO} + O_2^{\cdot -} \tag{6}$$

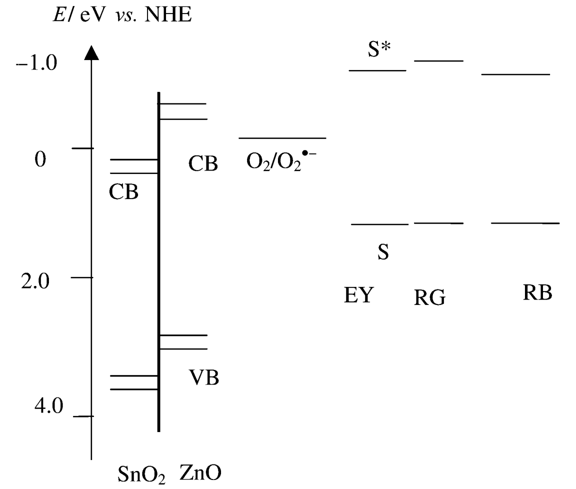

Fig. 2 Energy level diagram indicating the band positions of ZnO and SnO_2, and the ground (S) and excited (S*) states of the dyes.

$$O_2^{\bullet -} + e^- + 2H^+ \longrightarrow H_2O_2 \tag{7a}$$

$$2O_2^{\bullet -} + 2H^+ \longrightarrow 2HO_2^{\bullet -} \longrightarrow H_2O_2 + O_2 \tag{7b}$$

The adsorbed dye molecule on the oxide surface, upon excitation, injects an electron into the conduction band of the semiconductor. Preadsorbed O_2 on the semiconductor reacts with a conduction band electron to form a superoxide radical ion $O_2^{\bullet -}$ and under acidic conditions $O_2^{\bullet -}$ leads to the formation of H_2O_2.

Fig. 2 shows (based on literature data) the band positions of ZnO and SnO_2, and the ground and excited states of EY, RB and R6G, and the one-step O_2 reduction potential.[13–18] The band positions measured by a Mott–Schottoky plot for ZnO and SnO_2 in our laboratory are in good agreement with the reported literature values. As the excited levels of the dyes are well above the CBs of SnO_2 and ZnO, excited dye molecules can transfer electrons to the CBs of SnO_2 and ZnO. The amount of H_2O_2 formed on SnO_2 is not much different when no oxide was used (Table 1) because electrons transferred to the CB of SnO_2 *via* dye sensitization could not lead to superoxide radical formation as the O_2 reduction potential is higher than that of electrons in the CB of SnO_2. Therefore, it can be concluded that SnO_2 is inactive for H_2O_2 formation *via* eqn. (4)–(7). In the case of sensitization of ZnO and SnO_2/ZnO by EY, RB and R6G, a higher yield of H_2O_2 was observed than when solutions of EY, RB and R6G alone were irradiated. Higher yields of H_2O_2 on ZnO can be understood on the basis that the electron in the CB of ZnO is more reducing than the O_2 redox potential and the ability of ZnO to reduce molecular O_2 when subjected to direct band gap excitation is well known.[19]

The question arises why the SnO_2/ZnO composite system generates more H_2O_2 than SnO_2 or ZnO alone when they are sensitized under similar conditions. A possible explanation is as follows: It was observed that the dye EY adsorbed well on both SnO_2 and ZnO while RB was better adsorbed on ZnO and R6G adsorbed best on SnO_2 particles. The maximum amounts of dye adsorbed on SnO_2, ZnO and SnO_2/ZnO are given in Table 2. As the dye EY strongly adsorbs on both ZnO and SnO_2, the generated H_2O_2 amount on SnO_2/ZnO is three times higher than that on ZnO alone. There are two possible routes for electron tunneling, illustrated schematically in Fig. 3 and 4. According to the elucidated[8] structural properties of the SnO_2/ZnO composite system, the large ZnO particles are surrounded by small interconnected SnO_2 crystallites. Since EY adsorbs on both SnO_2 and ZnO surfaces, it can be assumed that EY is present on the surfaces of both oxides. In the first case, shown in Fig. 3, there is a possibility that the electrons injected into the CB of ZnO by the excited

Table 2 Amount of adsorbed dye on SnO_2, ZnO and SnO_2/ZnO

	Adsorbed dye/10^{-10} mol cm^{-2}		
Oxide	EY	RB	R6G
SnO_2/ZnO	640	153	338
ZnO	550	387	186
SnO_2	410	9	1204

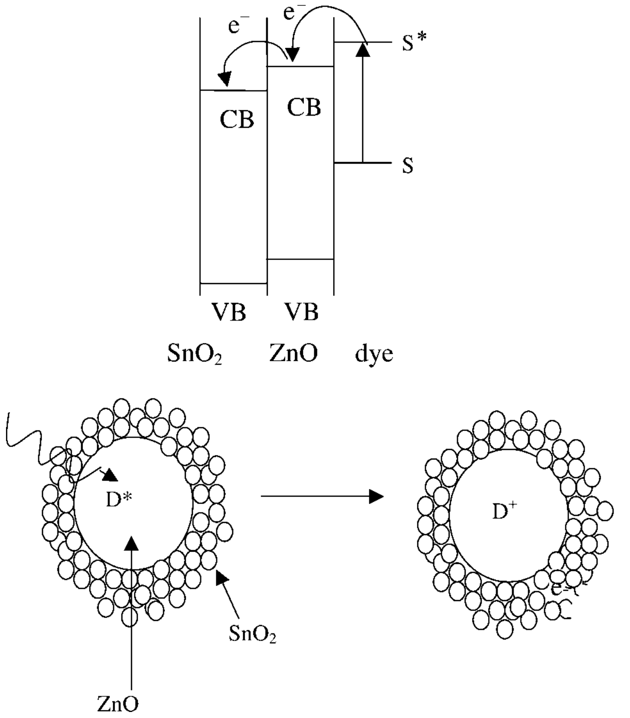

Fig. 3 Schematic diagram illustrating electron transfer from an excited dye molecule on a ZnO particle to a SnO_2 crystallite in contact with the ZnO particle.

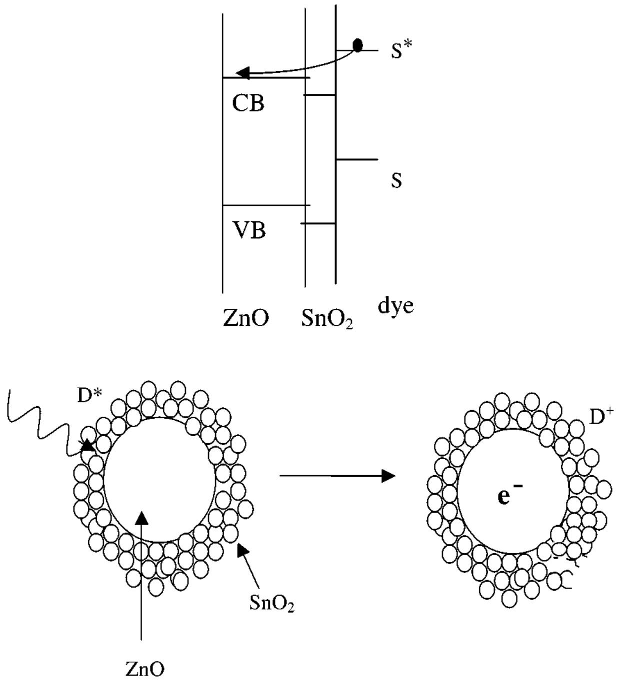

Fig. 4 Schematic diagram illustrating electron transfer from an excited dye molecule on the surface of a SnO_2 crystallite to a ZnO particle in its vicinity and, subsequently, to a SnO_2 crystallite in contact with a ZnO particle.

dye on the ZnO surface are transferred to the lower lying CB of SnO_2.

$$D/ZnO/SnO_2 \xrightarrow{h\nu} D^*/ZnO/SnO_2 \longrightarrow D^+/ZnO(e^-)/SnO_2 \longrightarrow D^+/ZnO/SnO_2(e^-) \quad (8)$$

In such a case, a higher yield of H_2O_2 is not expected, as the reduction potential of the electron in the CB of SnO_2 is lower than the O_2 reduction potential, as explained earlier. The other possibility (Fig. 4) is that the high-energy electrons injected into SnO_2 by the excited dye on the SnO_2 surface are transferred to ZnO, where these electrons are engaged in the O_2 reduction reaction to form $O_2^{\bullet -}$ radical anions. Because of the larger size of the ZnO particles and the length of the SnO_2 chain, this process leads to a wider charge separation and recombination of charged species is largely suppressed, leading to a higher yield of H_2O_2.

Strong evidence for the involvement of high-energy electron tunneling in the SnO_2/ZnO system is obtained from the sensitization of SnO_2, ZnO and SnO_2/ZnO with R6G. The cationic dye R6G is strongly adsorbed by SnO_2 and very poorly by ZnO. As expected, due to poor adsorption of R6G on ZnO, the yield of H_2O_2 is low as poor overlapping of the wavefunctions of the excited dye and ZnO surface results in inefficient transfer of electrons to the CB of ZnO. H_2O_2 generation is five times higher on SnO_2/ZnO than on ZnO with R6G and we present the following explanation for the higher H_2O_2 yield of the system made from SnO_2/ZnO compared to ZnO alone.

An excited dye molecule on the surface of a SnO_2 particle could inject an electron into the CB of a ZnO particle in its vicinity, tunneling across the SnO_2 crystallite, as shown in eqn. (9). As the excited level of R6G is localized well above the CB of ZnO, tunneling of the hot carrier (electrons that are not relaxed to the CB of SnO_2) to the CB of ZnO is permitted. Furthermore, photoinjected electrons from SnO_2 particles can also tunnel to trap states below the CB of ZnO.

$$ZnO/SnO_2/D \xrightarrow{h\nu} ZnO/SnO_2/D^* \longrightarrow ZnO/SnO_2(e^-)/D^+ \longrightarrow ZnO(e^-)/SnO_2/D^+ \quad (9)$$

Subsequently, depending on kinetic factors, this electron in the CB of ZnO either reacts with adsorbed O_2 to generate $O_2^{\bullet -}$ radical anions [eqn. (6)] or relaxes into the CB of another SnO_2 particle in contact with the ZnO particle. Since electrons in the CB of SnO_2 cannot react with O_2, the electron tunneling path described above is a valid argument to explain the higher H_2O_2 yield observed for R6G on SnO_2/ZnO. Electrons which are left in the SnO_2 CB react with dye cations to regenerate dye molecules. However, it should be noted that, in the absence of a suitable electron donor, the dye molecules bleach away. As mentioned earlier, the aim of this investigation was to demonstrate the possibility of electron transfer from SnO_2 to ZnO particles rather than to create a regenerative system.

The anionic dye RB is strongly adsorbed on ZnO while poorly adsorbed on SnO_2. In this case also an increase in H_2O_2 yield was noticed in the composite SnO_2/ZnO compared to ZnO alone, due to participation of high-energy electrons, similarly to EY and R6G. However, the increase in H_2O_2 generation is not as dramatic as for EY and R6G, due to poor adsorption of RB on SnO_2.

Conclusion

This investigation clearly demonstrates that the higher yield of H_2O_2 observed for the dye-sensitized composite SnO_2/ZnO system originates from electron tunneling from the lower conduction band position to the higher conduction band position. The occurence of long-distance tunneling of electrons through chains of interconnected semiconductor nanocrystallites as a result of electron injection during dye sensitization has been shown.

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