The suppression of the recombination of photogenerated carriers in a dye-sensitized nano-porous solid-state photovoltaic cell

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Abstract. The p–n junction p-CuI/nano-porous n-TiO$_2$ made by coating CuI on a nano-porous film of n-TiO$_2$ does not show a photocurrent action spectrum corresponding to the bandgap excitation of TiO$_2$. However, if the surface is lightly coated with the dye cyanidin the peak corresponding to bandgap excitation of TiO$_2$ is clearly manifested in addition to the sensitization peak. The effect is explained as originating from the relay action of the dye molecules adsorbed at the surface of TiO$_2$ mediating hole transfer from the valence band of TiO$_2$ to the valence band of p-CuI.

1. Introduction

Devices based on dye-sensitized semiconductor surfaces are receiving much attention as solar energy conversion systems [1–4]. Most studies on this subject deal with dye-sensitized photoelectrochemical cells of low efficiency [5–7]. An exception is the nano-porous dye-sensitized solar cell developed by Gratzel *et al*, with an efficiency exceeding 10%. The main disadvantage of the Gratzel cell is its dependence on a liquid electrolyte, which gives rise to several technological difficulties. One of the authors (KT) of this paper and his group have developed a cell based on dye-sensitized nano-porous TiO$_2$, where the liquid is replaced by the p-type semiconductor CuI [3]. Further improvements of this novel device depend on understanding the light-induced charge transfer mechanisms at the heterojunction n-TiO$_2$/dye/p-CuI.

This paper reports the following interesting effect we have observed. The p–n junction p-CuI/nano-porous n-TiO$_2$ shows no photoresponse at the bandgap wavelength of either n-TiO$_2$ or p-CuI. However, the photocurrent action spectrum of the heterojuction n-TiO$_2$/cyanidin/p-CuI shows a conspicuous peak corresponding to the bandgap wavelength of TiO$_2$, when the TiO$_2$ surface is lightly covered with the dye (cyanidin). The above observation is explained as originating from the relay action of dye molecules adsorbed at the surface of TiO$_2$ mediating hole transfer from n-TiO$_2$ to p-CuI.

2. Experiment

Nano-porous layers of TiO$_2$ were coated on fluorine-doped conducting tin oxide glass (CTO) by the method given below [3]. Titanium isopropoxide (1 ml) and glacial acetic acid (5 ml) were added to isopropanol (15 ml) and 5 ml water was added drop by drop to the mixture, which was kept stirred. Hydrolysis of titanium ispropoxide produces fine crystallites of TiO$_2$ and the above procedure prevents their agglomeration. The CTO glass plate was placed on the surface of a hot plate (surface temperature about 125 °C) and the solution was evenly spread using a glass rod and allowed to dry. The plate was then sintered at 450 °C for 4 min and the process repeated until a fully covered semitransparent film had been deposited. TiO$_2$ film (kept in an electrolytic medium) showed a characteristic blue-shifted band edge at about 368 nm corresponding to a crystallite dimension of about 15 nm [3].

The nano-porous n-TiO$_2$/p-CuI junction was made by deposition of a polycrystalline layer of p-CuI on porous TiO$_2$ using a solution of p-CuI in acetonitrile [3]. Nano-porous TiO$_2$ surfaces were coated with the dye cyanidin by warming the plate in an aqueous solution of cyanidin [8, 9] for 2 min [3]. The surface concentration (SC) was adjusted by varying the concentration of the cyanidin solution. The heterojunction n-TiO$_2$/cyanidin/p-CuI was fabricated by deposition of a layer of p-CuI on dye-coated nano-porous TiO$_2$ from a solution of CuI in acetonitrile. The back contact to the cells was made by depositing gold on the CuI surface by vacuum evaporation. The construction of the cells is illustrated in figure 1. The photocurrent action
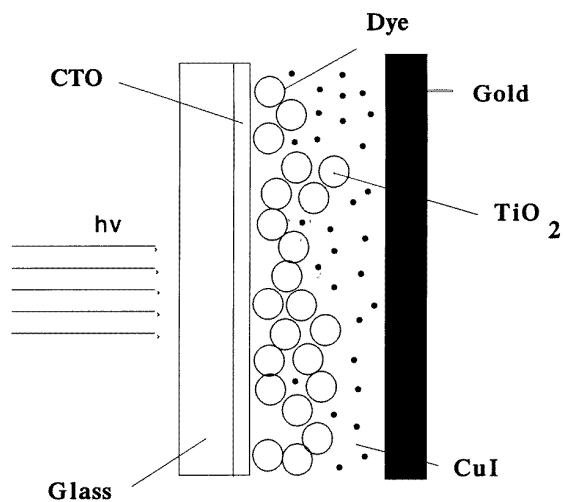
Figure 1. Construction of the n-TiO₂/p-CuI cell. In the n-TiO₂/dye/p-CuI cell, TiO₂ crystallites marked as large circles are coated with the dye (cyanidin).
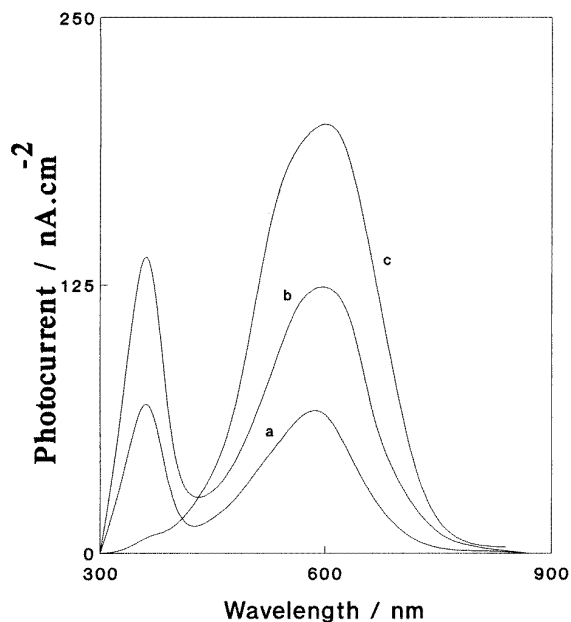

Figure 3. A plot of the peak height of the TiO₂ bandgap photocurrent against the peak height of the dye-sensitized photocurrent.

Figure 2. Photocurrent action spectrum of the cell n-TiO₂/cyanidin/p-CuI (front wall illumination) for three different surface concentrations SC_a, SC_b and SC_c of the dye ($SC_a < SC_b < SC_c$).

spectrum was recorded using a monochromator (Nikon Monochromator Auto-Scanner AS-C 101) coupled to a light chopper and a lock-in-amplifier.

3. Results and discussion

The cell n-TiO₂/p-CuI did not show a detectable photoresponse in the bandgap region of n-TiO₂ or p-CuI. However, when the nano-porous TiO₂ film was lightly coated with cyanidin (the cell n-TiO₂/cyanidin/p-CuI) and illuminated in the front wall mode (light incident on
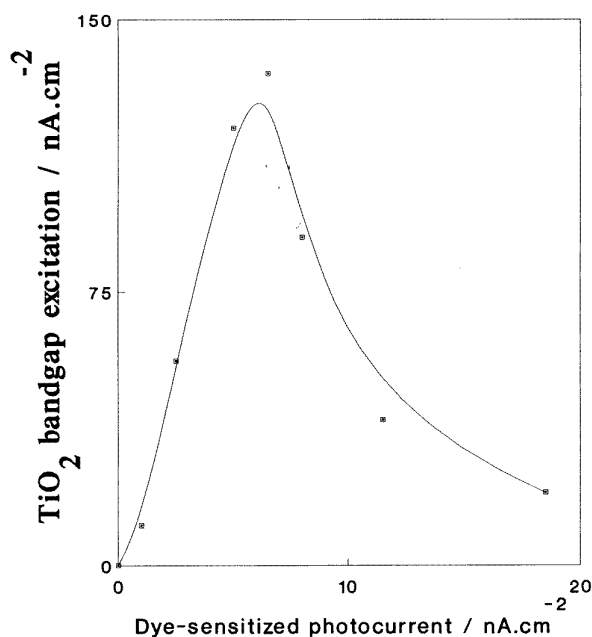
the TiO₂ film), the photocurrent action spectrum clearly showed the TiO₂ bandgap excitation peaked at 360 nm. Figure 2 compares the photocurrent action spectrum at three different selected surface concentrations, SC_a, SC_b and SC_c of cyanidin, where $SC_a < SC_b < SC_c$. It is seen that the peak height of the sensitized spectrum has increased with increasing SC of the dye. However, the peak at 360 nm originating from bandgap absorption in TiO₂ (which begins to appear only in the presence of cyanidin) initially increases with the increase of SC and then begins to decrease, and this becomes maximum for a certain critical SC of the dye. Figure 3 shows a plot of the peak height of the TiO₂ bandgap spectrum versus the peak height of the sensitized spectrum, which gives an indication of the variation of the peak height of the TiO₂ bandgap excitation with SC of the dye.

The sensitized photocurrent is generated by the following mechanism. A dye molecule (D) adsorbed at the surface of TiO₂, gets excited (D*) from the ground singlet state S_0 to the excited state S* and injects electrons into the conduction band of n-TiO₂. The resulting dye cations now transfer holes to the valence of band of p-CuI, i.e.

$$D + h\nu \longrightarrow D^* \tag{1}$$

$$D^* \longrightarrow D^+ + e^- \tag{2}$$

$$\downarrow$$

conduction band of TiO₂

$$D^+ \longrightarrow D + h^+ \tag{3}$$
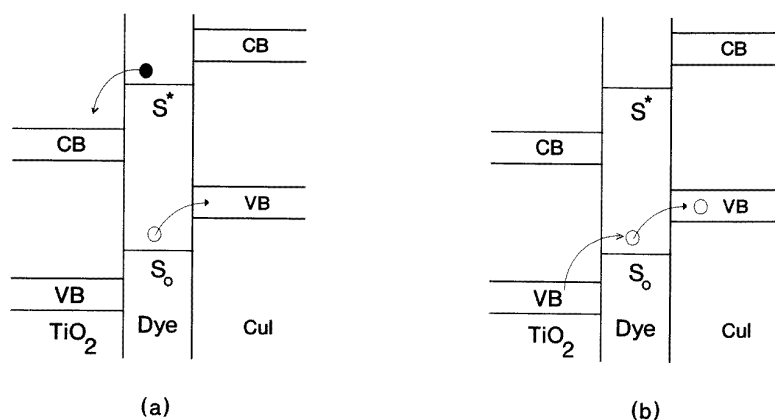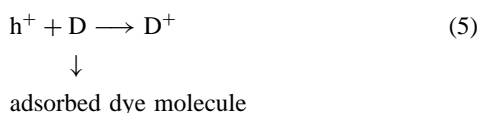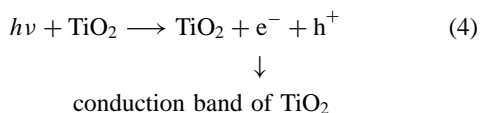
$$\downarrow$$

valence band of CuI

Figure 4. Schematic diagram showing the band positions of TiO$_2$ and CuI and energy levels of the dye: (a) charge transfer process generating the sensitized photocurrent; (b) charge transfer processes generating the bandgap current.

The location of bands of n-TiO$_2$, p-CuI and ground and excited states (S$_0$ and S*) of the dye, as in figure 4, favours the above charge transfer energetically.

In the nano-porous n-TiO$_2$/p-CuI junction, irradiation of n-TiO$_2$ with bandgap radiation generates electron–hole pairs in TiO$_2$. Unless the minority carriers tending to tunnel across the crystallite boundaries of n-TiO$_2$ are rapidly removed, recombination predominates, suppressing the generation of a photocurrent. A dye molecule adsorbed at the surface of n-TiO$_2$ acts as a relay in accepting electrons from TiO$_2$ and transferring them to p-CuI (figure 4). The steps involved in the process are:

$$h\nu + TiO_2 \longrightarrow TiO_2 + e^- + h^+ \qquad (4)$$
$$\downarrow$$
conduction band of TiO$_2$

$$h^+ + D \longrightarrow D^+ \qquad (5)$$
$$\downarrow$$
adsorbed dye molecule

$$D^+ \longrightarrow h^+ + D \qquad (6)$$
$$\downarrow$$
valence band of CuI

The location of the conduction band of n-TiO$_2$, the S$_0$ level of the dye and the valence band of p-CuI as in figure 4 permits the above charge transfer energetically.

The existence of a critical surface concentration of dye, at which the bandgap excitation of TiO$_2$ is optimum, can be easily understood. The rate of the process (5) increases with increasing SC of the dye molecules. However, cyanidin

also absorbs light in the wavelength region of the bandgap excitation of TiO$_2$ [8], decreasing the photon flux available for electron–hole pair creation in TiO$_2$.

4. Conclusion

Recombination of photogenerated carriers is a major factor that limits the efficiency of solar cells based on polycrystalline materials. In a nano-porous semiconductor film, minority carriers can tunnel to the surface of the crystallites rapidly and their efficient scavenging suppresses recombinations. The above investigation shows that molecules strongly adsorbed at the surface of the crystallites are effective as relays that mediate charge transfer and reduce recombinations.

References

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