Journal of ELECTRONIC MATERIALS, Vol. 30, No. 8, 2001 *Regular Issue Paper*

Dye-Sensitized Solid-State Photovoltaic Cells: Suppression of Electron-Hole Recombination by Deposition of the Dye on a Thin Insulating Film in Contact with a Semiconductor

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The heterojunction n-SnO_2/Ru-dye/p-CuI prepared by deposition of the ruthenium bipyridyl dye on a meso-porous film of SnO_2 followed by deposition of p-CuI was found to be inactive with respect to visible light photoresponse and dark current rectification. However, n-SnO_2/Al_2O_3/Ru-dye/p-CuI where the dye is coated on a thin film of Al_2O_3 first deposited on SnO_2, delivered a short-circuit current density of ~1.7 $mAcm^{-2}$ and an open-circuit voltage of ~350 mV, behaving as a dye-sensitized solid-state photovoltaic cell. This result is explained as a transfer of energetic electrons released by excitation of the dye molecules to the conduction band of SnO_2 via tunneling across the thin layer of Al_2O_3. The implications of the result on suppression of recombination in dye-sensitized photovoltaic cells are discussed.

Key words: Solar cells, nanostructures, tin oxide, aluminum oxide

INTRODUCTION

Photoelectrochemical cells (PECs) based on dye-sensitized (DS) nanocrystalline, semiconductor porous films seem to be low-cost devices with viable efficiencies.[1–5] Unfortunately, the liquid electrolyte and the chemistry of ionic transport present technical as well as fundamental problems.[6] These problems are circumvented if the liquid electrolyte is replaced by an optically transparent p-type semiconductor as the collector of holes.[4,7–9] In this n-type semiconductor/dye/p-type semiconductor (NDP) heterojunction, the photoexcited dye molecules sandwiched between two semiconductor surfaces inject electrons into the conduction band (CB) of the n-type material and holes into the valence band (VB) of the p-type material,[4] i.e.,

$$\begin{array}{ccccc} h\nu & + & D & \rightarrow & D^* \\ D^* & \rightarrow & e^- & + & h^+ \\ & & \downarrow & & \downarrow \\ & & \text{CB n – type} & & \text{VB p – type} \\ & & \text{material} & & \text{material} \end{array} \qquad (1)$$

Construction of fully solid-state DS solar cells of the above type also requires resolution of several challenging problems.[4] (1) A suitable p-type semiconductor needs to be found. It has to be transparent (therefore high band gap) and the band positions must match those of the n-type semiconductor and the energy levels of the dye. (2) A method has to be available for the deposition of the p-type material on the dye-coated n-type porous film without damaging the delicate monolayer of dye, while ensuring filling of the pores. (3) The contact between the dye and the p-type material should not deteriorate during operation or storage of the cell. (4) Charges injected into the semiconductors could migrate across the barrier of the dye layer and undergo recombinations. (5) Any contact between p-type material and the conducting surface would short-circuit the cell. Of the above requirements, (4) is the most crucial in obtaining a reasonably high photocurrent from a NDP device. Wet DS solar cells are able to deliver large short-circuit photocurrent densities (J_{sc}), as the recombinations at the semiconductor electrolyte interface happen less frequently in the ionic electron transfer.

One of the authors of this paper (K.T.) and his

(Received January 3, 2001; accepted May 15, 2001)

collaborators have found that with p-CuI as the hole conductor, a fully solid-state DS PEC can be fabricated, provided a nanocrystalline TiO_2 film is prepared in such a way as to minimize the contact between CuI and the conducting tin-oxide (CTO) glass surface on which the TiO_2 film is deposited.[4] However, we note that when attempts are made to construct DS PECs from SnO_2 films of similar morphology, they are completely inactive within detectable limits. As the dye used for sensitization is known to inject electrons efficiently to SnO_2, the absence of detectable photovoltaic effect in the junction SnO_2/D/CuI seems to be a result of rapid electron-hole recombinations. In this note we describe a method devised for suppression of recombinations in SnO_2 based DS solid-state cells. The cell n-SnO_2/Ru-dye/p-CuI does not yield a detectable J_{sc} or an open-circuit voltage (V_{oc}). However, it is found that when the SnO_2 crystallites are coated with a fine layer of Al_2O_3 and dyed (i.e., the heterostructure n-SnO_2/Al_2O_3 Ru-dye/p-CuI), the cell generates a J_{sc} and a V_{oc} of ~1.7 mA cm^{-2} and ~350 mV, respectively. The result is explained as originating from suppression of recombination of the separated carriers, by the Al_2O_3 layer where the dye is adsorbed. On excitation of dye molecules adsorbed on Al_2O_3, energetic electrons tunnel to SnO_2 across the Al_2O_3 barrier with concomitant release of holes to CuI. These electrons that quickly relax to the CB of SnO_2 are less likely to transfer back to the CuI, because of the Al_2O_3 barrier.

EXPERIMENTAL

Tin oxide was deposited on fluorine-doped CTO glass (1 × 1.5 cm^2, sheet resistance ~10 Ω/□, Nippon Glass) by the following method. Tin (IV) oxide powder (0.5 g, average particle size ~100 nm, Aldrich) and $SnCl_2$ (0.6 g, Aldrich) are ground thoroughly in an agate mortar adding 1-2 ml of propan-2-ol and a few drops of the non-ionic surfactant Triton X-100. The mixture is diluted to 15 ml with methanol, sonicated for 30 min and sprayed onto CTO glass plates laid on a hot surface (120–150°C). Plates are then sintered in air at 450°C for 30 min and the film is cleaned by boiling and washing in ethanol. Incorporation of $SnCl_2$ into the mixture improves the adherence of SnO_2 to the conducting glass surface. X-ray diffractometry indicated that the film is composed of SnO_2 crystallites.

SnO_2 films were coated with Al_2O_3 by the method described below. Plates are kept immersed in a solution of $AlCl_3$ (0.2 g of $AlCl_3.6H_2O$ in 5 ml of methanol containing 1% of water) for 8-10 hrs and sintered in air at 450°C for 45 min. The presence of Al_2O_3 in the film was confirmed by chemical analysis (atomic absorption spectrometry). Particle sizes were estimated by x-ray diffraction (XRD) (KINT 200, Rigaku) and gradient centrifuging (Horiba CAPA 7000 Particle Size Analyser). The average size of the SnO_2 particles is 75–100 nm and this was also confirmed by scanning electron microscopy (SEM) measurements (JSM-5600, JOEL). Al_2O_3 crystallites on SnO_2 are ultrafine and it is difficult to give an accurate estimate of their size from XRD or SEM. Transmission electron micrsoscopy (1299 EXII-JOEL) examination suggests that the Al_2O_3 crystallites have dimensions of the order 3–4 nm and are aggregated around the SnO_2 particles. Oxide films (SnO_2 and SnO_2/Al_2O_3) were coated with the dye (cis-dithiocyanato-bis(2,2'-bipyridyl-4, 4-dicarboxylate) ruthenium(II)) by boiling the plates in a solution of the dye in ethanol (2 × 10^{-4} M) and allowing them to cool in the same solution for 45 min. Dyed plates were rinsed with warm ethanol, dried and stored in the dark. Dye adsorbed into the film was determined by extracting the dye into an alkaline solution of ethanol and spectrophotometric estimation.

CuI was deposited on the dye-coated oxide film by the procedure described below. A solution of CuI was prepared by dissolving 0.6 g of CuI in 50 ml of moisture free acetonitrile. The plate was placed on hot surface (~110°C) with the glass surface in contact with it and the CuI solution was lightly spread over the dyed film using a dropper, allowing acetonitrile to

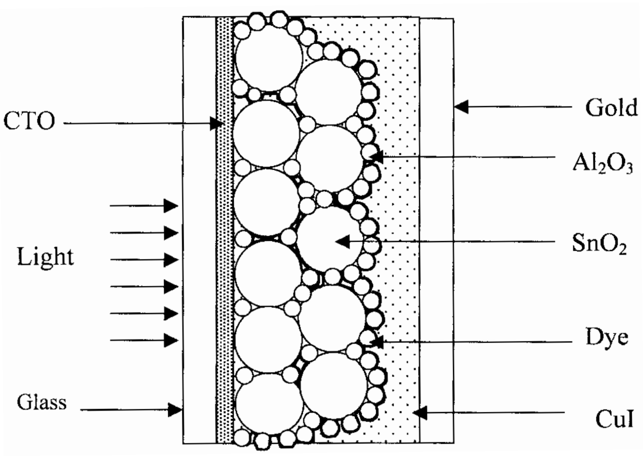

Fig. 1. Schematic diagrams illustrating the construction of the n-SnO_2/Al_2O_3/Ru-dye/p-CuI cell.

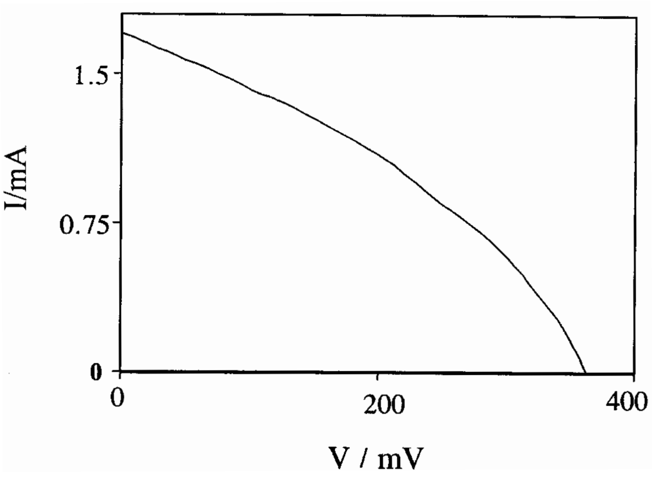

Fig. 2. I-V plot for the cell, n-SnO_2/ Al_2O_3/Ru-dye/p-CuI (Intensity of illumination is 1000 W m^{-2} from a tungsten filament lamp).

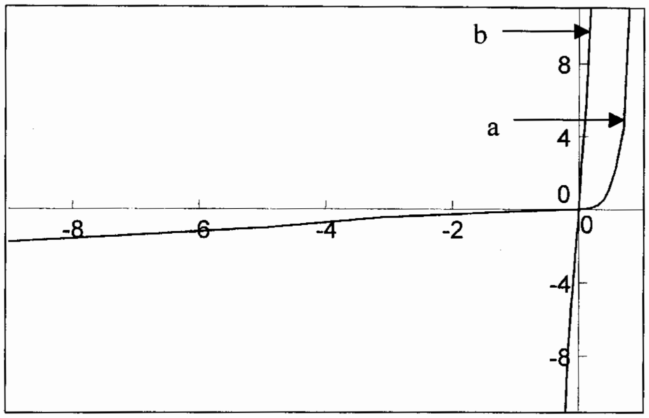

Fig. 3. Dark I-V characteristic for the cells (a) n-SnO_2/ Al_2O_3/Ru-dye/p-CuI, (b) n-SnO_2/Ru-dye/p-CuI.

evaporate. The process was repeated until all the pores were filled and CuI extended ~5 µm above the film (CuI film thickness was measured by SEM). The electrical contact to the CuI is made by pressing a gold or antimony coated CTO glass plate onto the CuI surface. A schematic diagram illustrating the construction of the cell is illustrated in Fig. 1. I-V characteristic under illumination (tungsten filament lamp at 1000 W m^{-2}) and rectification curves in the dark were recorded using cells with oxide films of area 1 cm^2 fabricated in the manner described above.

RESULTS AND DISCUSSION

The SnO_2/Ru-dye/CuI cell made from a film consisting of entirely SnO_2 did not give a measurable photoresponse (i.e., I_{sc} and V_{oc} to an accuracy of 10^{-3} mA and 10^{-3} mV, respectively) at an intensity of illumination 1,000 Wm^{-2}. The DS cell consisting of SnO_2/Al_2O_3/Ru-dye/CuI, where Al_2O_3 is coated on SnO_2 before dying, generated an I_{sc} of 1.7 mA cm^{-2} and a V_{oc} of 350 mV at the same intensity of illumination. The I-V characteristic for this cell (at ~1,000 W m^{-2} from a tungsten filament lamp) is presented in Fig. 2 and the maximum energy conversion efficiency and the fill factor derived from the curve are 0.25% and 32%, respectively. The rectification curves (I-V characteristics under forward and reverse biasing) in dark for the cells in the presence and absence of Al_2O_3 are shown in Fig. 3. In the absence of Al_2O_3 there is hardly any evidence for rectification, whereas a dramatic improvement in rectification is apparent when Al_2O_3 is coated on SnO_2 and Al_2O_3 is dyed. Presence of both dye and Al_2O_3 are found to be necessary for good rectifying action; the heterojunction SnO_2/Al_2O_3/CuI is only marginally better than SnO_2/CuI or SnO_2/Ru-dye/CuI. A SnO_2 film prepared by the method described in the experimental section can be impregnated with fine crystallites of SnO_2 by keeping it immersed in a solution of $SnCl_4$ in methanol containing 2% water, followed by sintering at 450°C for 30 min. By repetition of this process, we can prepare SnO_2 films where nearly all the pores are packed with crystallites of SnO_2. DS solid-state cells made from such films, that are highly fractal but non-porous, were also inactive with respect to photoresponse as well as dark rectification. This demonstrates that in the case of SnO_2 films, the blocking of the pores of the film to minimize the contact of CuI with CTO glass surface alone is ineffective. However, fractal and less porous films of TiO_2 are adaptable to solid-state cells, when CuI is used as the hole collector.[4] A conclusion from the above observation is that the dye barrier between SnO_2 and CuI is ineffective in preventing the migration of separated carriers in the opposite direction. The rectification action and the photoresponse seems to depend on the nature of the surface on which the dye is deposited.

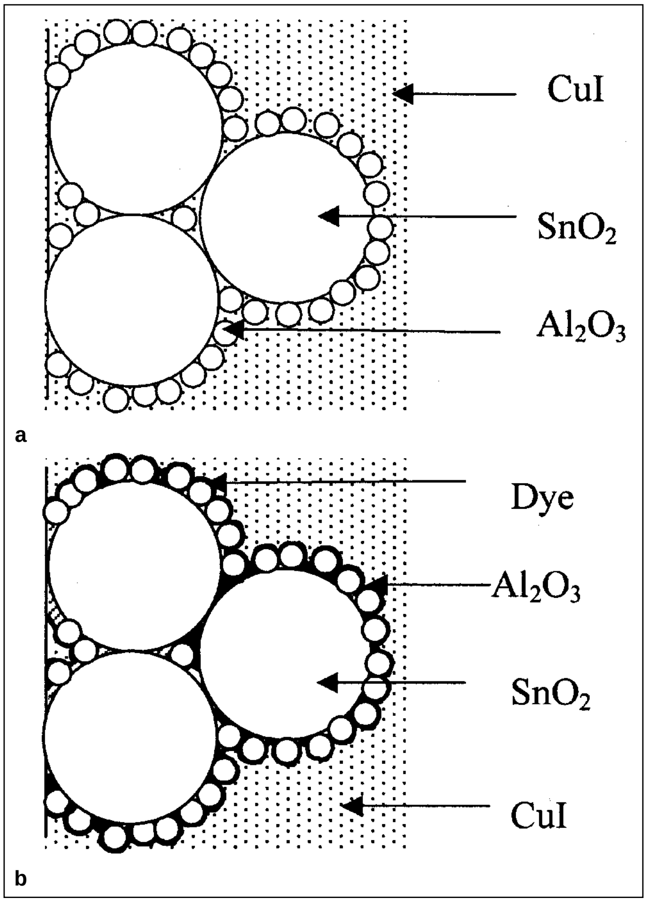

Fig. 4. Schematic diagram illustrating the structural morphology of the junctions (a) SnO_2/Al_2O_3/CuI (b) SnO_2/Al_2O_3/D/CuI.

Although a DS solid-state cell made from SnO_2 (with p-CuI as the hole collector) did not show any photoresponse, a wet cell made from the same film (with 0.5 M tetra-propyl ammonium iodide + 0.05 M I_2 in acetonitrile as the electrolyte and a platinized CTO glass plate as the counter electrode) generated a I_{sc} of ~5 mA cm^{-2} and V_{oc} of ~350 mV. A DS wet cell made from a SnO_2/Al_2O_3 film yielded much higher I_{sc} (~7.0 mA/cm^2) as well as a V_{oc} (~637 mV). The above observations show that the recombination of separated carriers is more critical in the case of solid-state cells. In a wet cell, the positive charge on the dye cation created from electron injection by the excited dye molecule is scavenged by an electron donor, which is regenerated at the counter electrode. Recombination could occur only by electron combining with the dye cation (before the positive charge is scavenged) or an acceptor in the electrolyte. Another important inference from our observations is the following. As SnO_2 crystallites are covered with a very thin film of Al_2O_3 (~2–3 nm) the dye coating is also mainly on Al_2O_3 (presumably Al_2O_3 crystallites are sintered to SnO_2 and the dye could touch SnO_2 only at points where there is no Al_2O_3 coating), which is an insulator, the very poor rectification at the junction SnO_2/Al_2O_3/CuI is an indication that there are contacts between CuI and SnO_2 across the voids in the Al_2O_3 film on SnO_2. When the film SnO_2/Al_2O_3 is dyed, these voids seem to get densely packed with dye molecules. As thick layers of dye are insulating the junction, SnO_2/Al_2O_3/D/CuI shows good rectification because the regions where the rectification is bad are now closed. These regions with a thick layer of dye on SnO_2 are unable to photo-inject electrons into the CB of SnO_2 owing to concentration quenching (mutual de-excitation of excited dye molecules). Hence, photocurrent generation in SnO_2/Al_2O_3/D/CuI should be entirely due to excitation of dye molecules adsorbed on Al_2O_3. The structural morphology of the films SnO_2/Al_2O_3/CuI and SnO_2/Al_2O_3/D/CuI are illustrated schematically in Fig. 4. Ru-dye is readily adsorbed on Al_2O_3/SnO_2 (when SnO_2 and SnO_2/Al_2O_3 films are kept immersed in the dye solution 30 min, the quantities of dye adsorbed are ~2 × 10^{-7} and 8 × 10^{-7} mole cm^{-2}, respectively). The higher dye coverage on SnO_2/Al_2O_3 films compared to SnO_2 films could also be due to the larger surface area of the former film. However, we did not succeed in devising a method determining the surface areas independent of estimates based on amount of dye coverage. As a thin layer of the dye is coated on the Al_2O_3 layer, the photocurrent generation could occur only via the mechanism described below. Photoexcited dye molecules at the Al_2O_3 surface injects an electron into the CB of SnO_2 traversing through the Al_2O_3 barrier and a hole is transferred to CuI. Tunneling of electrons across the barrier is facilitated as the excited level of the dye is well above the CB of SnO_2 (although the CB of Al_2O_3 is far above the excited level of the dye, the thin Al_2O_3 barrier permits quantum mechanical tunneling). When the energetic electron (i.e., the hot carrier) relaxes to the CB of SnO_2, the Al_2O_3 barrier prevents recombination of the electron with a hole in CuI. We summarize the above process as follows:

$$\begin{aligned} &SnO_2/Al_2O_3/D/CuI + h\nu \\ &\rightarrow SnO_2/Al_2O_3/D/CuI \\ &\rightarrow SnO_2(e^-)/Al_2O_3/D/CuI(h^+) \end{aligned} \tag{2}$$

An energy-level diagram indicating the relative positions of the bands of SnO_2, CuI and ground and excited levels of the dye (S_0 and S) is shown in Fig. 5.

The photocurrent spectra of the cell for front side (FS) (from oxide film to CuI) and back side (BS) (from CuI to oxide film) illumination presented in Fig. 6 show a distinct difference: The FS spectrum is broad with a peak at ~545 nm, whereas the BS spectrum has a sharper red-shifted peak at ~620 nm. Such a conspicuous difference between the FS and BS spectra are not seen in a DS wet cell made from an identical SnO_2/Al_2O_3 film. The difference between two types of spectra can be understood as originating from prefer-

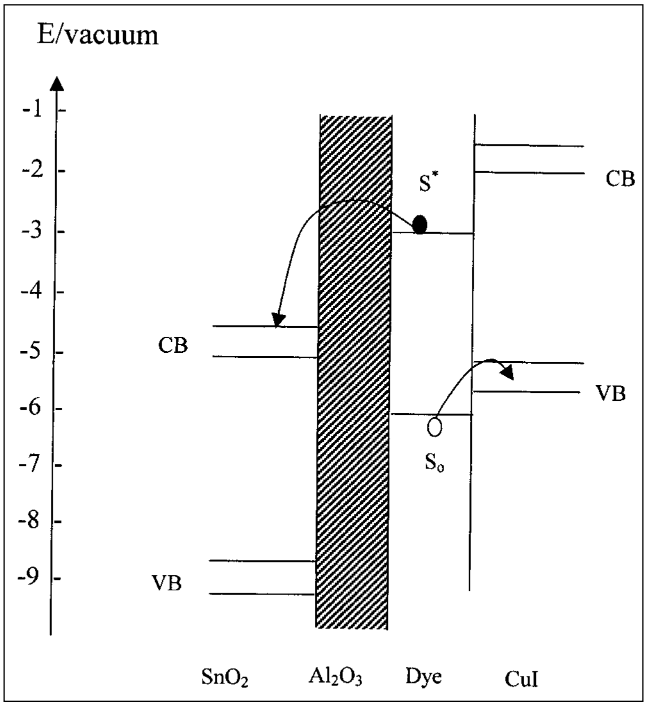

Fig. 5. An energy level diagram showing the relative positions of the bands of CuI, SnO_2 and ground and excited levels of the dye.

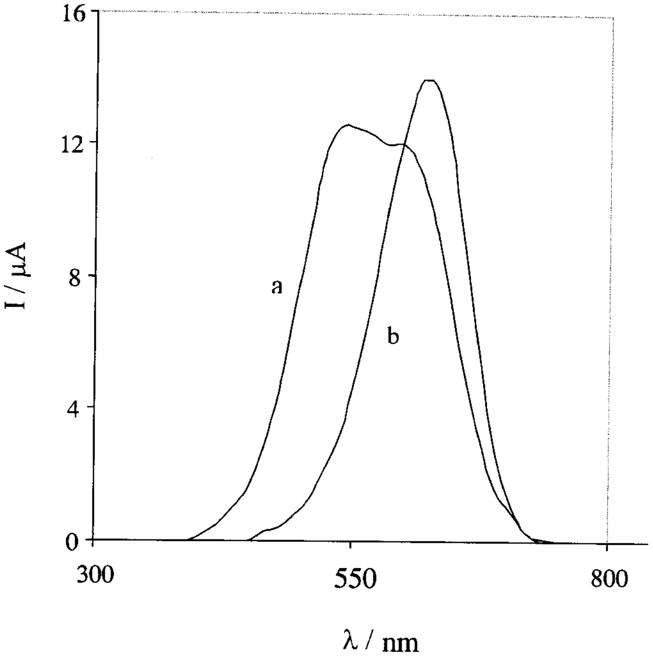

Fig. 6. Photocurrent spectrum of the cell n-SnO_2/Al_2O_3/Ru-dye/p-CuI: (a) front side illumination (b) back side illumination.

ential absorption of shorter wavelength light by the film and the distance electrons in SnO_2 will have to travel in reaching the back contact, with some probability of exposure to the interface where they can recombine with the holes in CuI. The probability that an electron in SnO_2 will recombine with a hole in CuI is less, when the electron-hole separation occurs close to the CTO back contact, because here the electrons need to travel only a short distance. Consequently if the cell is illuminated from the FS, the photoresponse is stronger at shorter wavelengths compared to red light. When the illumination is from the BS, the shorter wavelengths are less effectively utilized and the absorption peak is red-shifted. This effect is also noticeable in wet cells made from thick films of TiO_2.[10–12] The fact that this effect is not noticeable in the wet cells made from SnO_2/Al_2O_3 films used in this investigation (thickness ~10–12 μm) indicate that the recombinations are higher in case of the solid-state cell. A difference between FS and BS spectra could also originate from preferential absorption of short wavelength radiation by CuI.

CONCLUSION

The above investigation is not intended for construction of a practical DS solid-state cell. Efficiency of the cell is insignificant and the low fill factor is an indication that recombinations and/or short-circuiting at the CTO glass surface and CuI contacts are still occurring. However, the observation that deposition of a thin film of Al_2O_3 on SnO_2 and coating dye on Al_2O_3 effectively sensitizes SnO_2 suppressing recombinations is fundamentally important. This clearly demonstrates that an excited dye molecule on the surface of a thin insulating layer in contact with a semiconductor is able to inject electrons to the semiconductor via tunneling. In dye-sensitization energetic hot carriers are injected to the substrate and therefore tunneling across a barrier is facilitated.[13] Thus, heterojunctions N/I/D/P, N/D/I/P, or N/I/D/I/P (where I is an insulating barrier) could show very low permeability to electrons and holes under an external bias, whereas the photoexcitation of the dye is able to cause efficient injection of carriers to the two semiconductors (N and P). When these carriers relax to the bands of the semiconductors, the insulating barrier assists suppression of recombinations. A practical difficulty of fabricating heterojunctions of the above type is the difficulty of depositing thin crystalline films of insulators on semiconductor particles without formation of voids. In the present system, the dye itself seems to close these voids at least partly. We have observed that the efficiency and the fill factor of DS solid-state cell made from nanocrystalline film of TiO_2 (with CuI as the hole conductor) is also improved, when TiO_2 is coated with Al_2O_3 and the same mechanism seems to be operative here. The details of this work will be presented elsewhere.

ACKNOWLEDGEMENTS

The authors wish to thank Prof. Kenji Murakami, The Department of Material Science, Shizuoka University, Japan; and Ashigara Research Laboratories, Fuji Photo Film for conducting SEM and TEM measurements, respectively.

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