Chromopore-Linked Conducting Polymers Attached to Semiconductor Surfaces: A Strategy for Development of Dye-Sensitized Solar Cells

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It is suggested that attaching chromopores to a conducting polymer chain anchored to a semiconductor surface is a good strategy for development of dye-sensitized solar cells. A model system that illustrates this principle is constructed by bonding mercurochrome to poly(vinyl alcohol) films adsorbed onto nanocrystalline TiO$_2$ films. The dye−polymer structure enables transport of electrons (released in excitation of the dye) along the polymer chain to TiO$_2$ as states in the lowest unoccupied molecular orbital of the polymer. By attaching several chromopores to a polymer chain, panchromatic sensitization can be achieved in principle by avoiding concentration quenching and the insulation by thick dye layers.

Introduction

Researchers all over the world are engaged in development of cheap devices for the conversion of solar energy to electricity. In this context, the dye-sensitized (DS) solar cells receive a great deal of attention as an economically viable alternative to the conventional photovoltaics.[1,2] Although efficiencies of the order of 10% have been achieved, wide applicability of DS solar cells depends on further enhancement of the efficiency. The two factors limiting the efficiency of DS photovoltaic devices are the recombination losses[3,4] and the narrow spectral response. In DS photoelectrochemical cells (DS PECs), the reaction of electrons injected to the nanocrystalline matrix with acceptor species in the redox electrolyte happens to be the main route of recombination, which become important under operating conditions with a load (at short-circuit, recombination is less important as its rate is slower compared to the collection rate). Geminate recombination also exists and becomes important under open-circuit conditions at higher intensities or if the redox couple happens to be inefficient in scavenging the positive charge on the dye cation. Compared to DS PECs, dye-sensitized solid-state cells (DS SSCs) have lower efficiencies due to the faster recombination rate in these devices. In a DS PEC dye chelation to the semiconductor surface ensures fast injection of carriers competing with the recombination. The nature of the electronic states (i.e., conduction band states and/or trap states) participating in the recombination and details of the mechanism involved are not fully understood. Presumably, surface trap states play an important role in mediating recombination in both DS PECs and DS SSCs. In this situation, the surface chelation of the dye would have the additional advantage of passivating the surface states. DS SSCs have low efficiencies because of the faster recombination at the n-type-semiconductor/dye/p-type-semiconductor interfaces.[4−7] In the present form of DS SSCs, dye molecules attached to the n-type substrate are not intentionally bonded to the p-type surface to facilitate the injection of holes. Thus slow injection of holes to the p-type material favors recombination. Furthermore, when the dye is not chelated at the p-type interface, surface states could not be passivated. A strategy attempted to mitigate recombination of both DS PECs

and DS SSCs has been the coverage of the nanocrystalline n-type surface with a thin layer of a high band gap semiconductor or an insulator.[8−15] Combinations of dyes and polymers have also been attempted as a means of achieving photoinduced charge separation for photovoltaic conversion.[16,17] In this paper we describe construction of DS PECs and DS SSCs with poly-(vinyl alcohol)-coated (PVA-coated) nanocrystalline films of TiO$_2$. Mercurochrome (MC) readily adsorbing on PVA surface is selected as the sensitizers. It is found that the cells based on TiO$_2$/PVA/MC films have significantly higher efficiencies and open-circuit voltages compared to the cells made from the TiO$_2$/MC films, where the dye is coated on TiO$_2$. The dye−polymer structure enables transport of electrons (released in excitation of the dye) along the polymer chain to TiO$_2$ as states in the LUMO of the polymer. The attachment of MC to PVA induces n-type conductivity to PVA as there is a finite probability of thermal delocalization of electrons in the MC cation to the LUMO of the polymer.

Experimental Section

TiO$_2$ films for DS PECs were prepared using Degussa P25 TiO$_2$ powder (median particle size, 30 nm) as follows. TiO$_2$ (500 mg), 85% ethanol (100 mL), acetic acid (2 mL), and poly-(ethylene glycol) (5 mg) were mixed and agitated ultrasonically for 1 h. The mixture is again ground, allowing a part of the alcohol to evaporate until a thick paste is formed. The paste is screen-printed on fluorine-doped conducting tin oxide glass (sheet resistance = 16 Ω/sq; area = 1.5 × 1.0 cm^2) and fired in air at 430 °C for 35 min. TiO$_2$ films of the type needed for fabrication of DS SSCs (i.e., films largely free of interconnected pores going up to the back-contact, which causes short-circuiting when the film is coated with the hole collector) were prepared by the following method.[18] Titanium tetraisopropxide (5 mL) mixed with propan-2-ol (15 mL) and acetic acid (6 mL) was hydrolyzed by addition of water (5 mL), keeping the mixture vigorously stirred. The dispersion was ultrasonically agitated and sprayed onto the conducting glass plates heated to 150 °C and sintered in air at 450 °C for 10 min. The plate was allowed to cool, and the loose crust of unsintered TiO$_2$ particles was removed by brushing with cotton wool. The process was repeated until the film grows to a thickness of ∼12−14 μm.
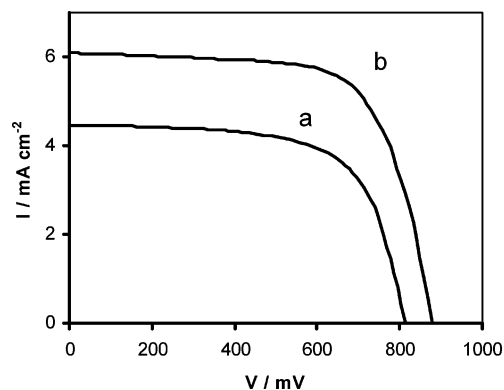
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Figure 1. $I-V$ characteristics of the cells (a) $TiO_2/MC/I^--I_3^-$ and (b) $TiO_2/PVA-MC/I^--I_3^-$.

TABLE 1: Open-Circuit Voltage (V_{oc}), Short-Circuit Current (I_{sc}), Fill Factor (FF, %), Efficiency (η, %), and Incident Photon to Photocurrent Conversion Efficiency (IPCE (%) at 530 nm) of Cells with $I^--I_3^-$ Redox Couple

	V_{oc}/mV	I_{sc}/ (mA cm^{-2})	FF/%	η/%	IPCE/%
$TiO_2/I^--I_3^-$	780	$\sim10^{-2}$			
$TiO_2/PVA/I^--I_3^-$	800	$\sim510^{-2}$			
$TiO_2/MC/I^--I_3^-$	815	4.4	66	2.4	77.3
$TiO_2/PVA-MC/I^--I_3^-$	879	6.1	68	3.6	80.1
$TiO_2/PVA-MC$ (mixed)/ $I^--I_3^-$	769	1.9	68	1.0	
$TiO_2/MC-PVA/I^--I_3^-$	736	2.5	66	1.2	

The TiO_2 films prepared by the two methods described above were coated with PVA (molecular weight, 31 000) by soaking them in aqueous PVA (4.1×10^{-3} g/L) for 40 min and rinsing with water followed by 98% ethanol. The amounts of PV adsorbed was determined by spectroscopic ($\lambda = 278$ nm) estimation of the depletion of PV in the coating solution. Films were dried and soaked in mercurochrome solution (5×10^{-3} M in 99% ethanol) for 90 min. In some experiments PVA and MC were coadsorbed from aqueous solution (PVA $\sim 4.1 \times 10^{-3}$ g/L; MC $\sim 5 \times 10^{-3}$ M). DS PECs were made by clamping a platinized counter electrode against the dyed surface and introducing the $I-I_3^-$ redox electrolyte (0.5 M 4-*tert*-butylpyridine, 0.5 M tetrapropylammonium iodide, 0.1 M iodine, in a 4:1 ratio mixture of ethylenecarbonate and acetonitrile). DS SSCs were made by depositing CuSCN on the dyed surface using a solution of CuSCN in *n*-propyl sulfide.[19] The outer surface of CuSCN was painted with graphite and a gold-plated conducting glass plate was pressed to form the cell. The IV characteristics of the cells at 1.5 AM 1000 W m^{-2} illumination (simulated sunlight) were recorded using a Keithly source meter. A Nikon monochromator was used to record the photocurrent action spectra. The dark rectification curves of DS SSCs were recorded with HJ instruments potentiostat. Mott–Schottky plots of PVA and PVA/MC films were recorded using a Hewlett-Packard, 4276A LCZ Meter.

Results and Discussion

Figure 1 shows the $I-V$ characteristics of the DS PECs of configurations $TiO_2/PVA/MC/I^--I_3^-$ and $TiO_2/MC/I^--I_3^-$. The $I-V$ parameters (I_{sc} = short-circuit photocurrent, V_{oc} = open-circuit voltage, η = efficiency, FF = fill factor) are summarized in Table 1. The cell with an overlayer of PVA on TiO_2 gives significantly higher values for all the $I-V$ parameters with an efficiency of 3.65% compared to 2.40% for the cell without PV. In absence of the dye, cells based on TiO_2 and TiO_2/PVA (Table.1) show nearly the same feeble photoresponse,
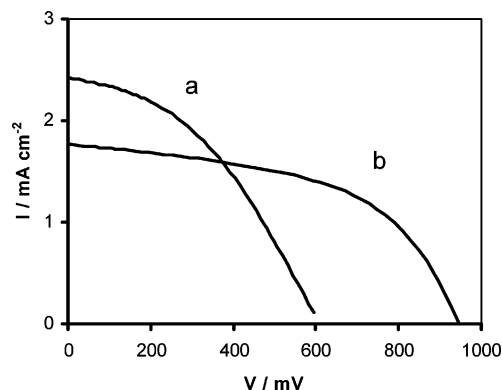

Figure 2. $I-V$ characteristics of the cells (a) $TiO_2/MC/CuSCN$ and (b) $TiO_2/PVA-MC/CuSCN$.
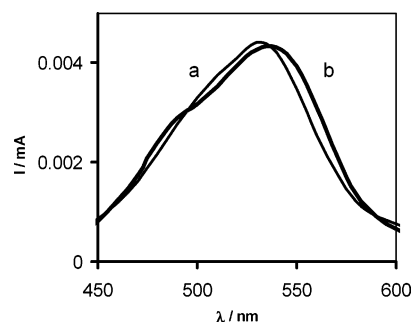
Figure 3. Photocurrent action spectra of the cells (a) $TiO_2/MC/I^--I_3^-$ and (b) $TiO_2/PVA-MC/I^--I_3^-$.

TABLE 2: Open-Circuit Voltage (V_{oc}), Short-Circuit Current (I_{sc}), Fill Factor (FF, %), Efficiency (η, %), and Incident Photon to Photocurrent Conversion Efficiency (IPCE (%) at 530 nm) of Cells with p-CuSCN as the Hole Collector

	V_{oc}/mV	I_{sc}/ (mA cm^{-2})	FF/%	η/%	IPCE/%
$TiO_2/CuSCN$	380	$\sim10^{-2}$			
$TiO_2/PVA/CuSCN$	512	$\sim210^{-3}$			
$TiO_2/MC/CuSCN$	602	2.4	41	0.6	25.7
$TiO_2/PVA-MC/CuSCN$	948	1.8	52	0.9	20.6
$TiO_2/PVA-MC$ (mixed)/ CuSCN	798	1.4	55	0.6	
$TiO_2/MC-PVA/CuSCN$	825	0.8	60	0.4	

indicating that PVA has no sensitization influence. The corresponding results for the DS SSCs of configurations $TiO_2/PVA/MC/CuSCN$ and $TiO_2/MC/CuSCN$ are given in Figure 2 and Table 2. Here again the cell with the PVA-coated TiO_2 film yields a higher efficiency with an impressively high V_{oc} of 948 mV compared 602 mV for the cell without PV. Table 1 also gives the $I-V$ parameters of cells where MC and PVA are coadsorbed into the TiO_2 film. Although, not as conspicuous as in the previous case, improvements above the TiO_2/MC systems were clearly noticeable (Table 1). However, when PVA is coated above MC (i.e., film configuration $TiO_2/MC/PVA$), we could not observe any improvement of the $I-V$ parameters (Table 1). The photocurrent action spectra of MC sensitized PECs with and without PVA are presented in Figure 3. Photon to photocurrent efficiencies (IPCEs) of different cells are given in Tables 1 and 2.

The thickness of PVA films estimated from the knowledge of the roughness factor of the TiO_2 films (i.e., thickness = wweight of PVA adsorbed/film area × roughness factor × density of PVA) turned out be ~2.0 and 3.5 nm for DS PEC and DS SSC films. Scanning electron microscopy (SEM) pictures of TiO_2 and TiO_2/PVA films did not show a distinctive
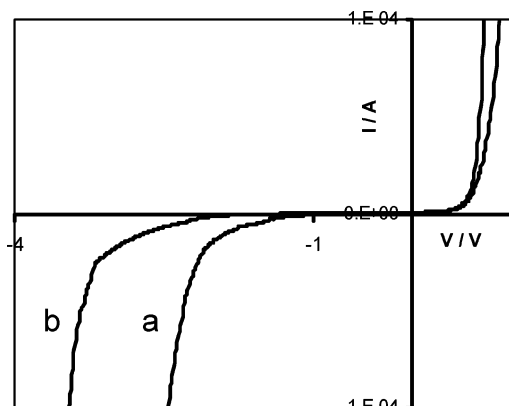
Figure 4. Dark $I-V$ curves of the cells (a) TiO$_2$/MC/CuSCN and (b) TiO$_2$/PVA−MC/CuSCN.

difference because of the thinness of the PVA film. However, the following observation proves that the PVA coverage on TiO$_2$ is free of voids. We found that TiO$_2$/PVA films do not adsorb N3 dye from moisture-free alcoholic solutions. Unlike MC, N3 dye is not adsorbed on PVA films deposited on glass. Hence, if there are voids in the PVA film, N3 would certainly penetrate and get deposited directly on TiO$_2$. It is not very clear as to why the latter type of films turned out be thicker, when estimated by the method described above. Presumably, PVA, clogging smaller pores of the latter film, remain firmly bound and are not removed during washing. Cells where the MC is coated above the PVA films have much higher open-circuit voltages. In both cases (i.e., DS PEC and DS SSC), the poly(vinyl alcohol) barrier effectively suppresses recombinations of the separated carriers, improving cell performance. The dark rectification curves of the DS SSCs in the presence and the absence of PVA are shown in Figure 4. Clearly, the latter system shows better rectification, the respective rectification ratios at $|V| = 0.8$ V being 217 and 2984, respectively. Thus this cell generates an exceptionally high V_{oc}, i.e., 948 mV, which is quite high for a DSSC.

PVA film thickness of 2.0 and 3.5 nm for TiO$_2$/PVA/MC/ I$^-$−I$_3^-$ and TiO$_2$/PVA/MC/CuSCN corresponds to the optimum efficiency. An increase of PVA thickness beyond the optimum initially raises V_{oc}, dropping I_{sc} and η, but on further increase of the PVA film thickness a point is reached beyond which all the $I-V$ parameters begin to decrease. Although the thicker films are more effective in mitigating recombination, they also decrease the efficiency of electron injection. Consequently, the cells perform optimally for a critical thickness of the PVA film.

It is known that PVA adsorbs onto oxide surfaces via hydrogen bonding of OH groups in PVA to those groups on the oxide surface.[20] Molecules with OH groups will also readily form hydrogen bonds with PVA.[21,22] Figure 5 schematically illustrates the bonding of PVA to the TiO$_2$ surface and MC to PVA adsorbed on TiO$_2$. In the TiO$_2$/PVA/MC film, some of the hydroxyl groups in the PVA strand could get hydrogen bonded to hydroxyl groups in MC (MC adsorbed on PVA is not leached by dilute NaOH; this indicates that the attachment of MC to PVA is not through its carboxylate ligands). The peak absorption wavelength of MC coated PVA films is 522 nm compared to 514 nm of the MC aqueous solution and the red shift suggests a bonding of MC to PVA. Again, the peak (540 nm) of the photocurrent action spectrum (Figure 3) of the cell where dye is coated on PVA is slightly red-shifted with respect to the cell with the dye on TiO$_2$ (530 nm), indicating the difference of bonding. On excitation of the chromopores in MC, electrons enter the conduction band of TiO$_2$ "across" the bridge
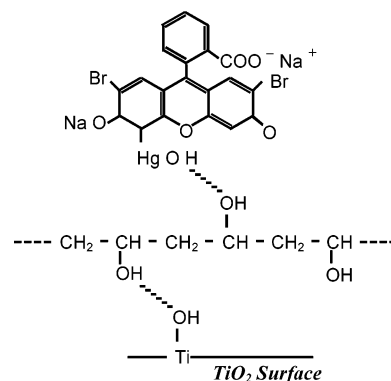

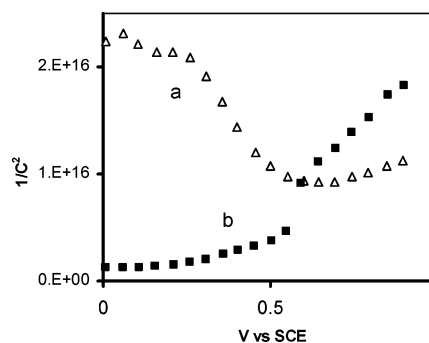**Figure 5.** Schematic diagram illustrating the bonding of PVA to TiO$_2$ and MC to PVA.

Figure 6. Mott−Schottky plots for (a) PVA and (b) PVA/MC.

structure composed of -CH−CH$_2$−CH- and H bonds (Figure 5). PVA has a feeble p-type conductivity (which is enhanced when doped with electron acceptors[23]), agreeing with the negative slope of the Mott−Schottky plot (Figure 6). When MC is adsorbed on PVA, the slope turns positive, indicating n-type conductivity. This can be understood as thermal delocalization of the electron in the MC anion (attached to PVA) to the LUMO (conduction band) of the polymer; i.e.,

$$PVA/MC^-Na^+ \rightarrow PVA^-/MC + Na^+ \qquad (1)$$

where, PVA$^-$ denotes PVA with an electron in the LUMO. The n-type conductivity of the polymer chain seems to facilitate electron transport to TiO$_2$. Presumably, the structure PVA/MC manifests molecular rectification and suppresses geminate recombination. The PVA barrier will also suppress nongeminate recombination of the separated carriers (i.e., electrons in TiO$_2$ with acceptors in electrolyte or holes in the hole collector).

Conclusion

We have shown that the I_{sc}, V_{oc}, and η of DS solar cells sensitized with MC are greatly enhanced when the TiO$_2$ surface is coated with a thin layer of PVA and the dye is attached to PVA. The model we have studied suggests the following strategy for enhancing the efficiencies of dye-sensitized solar cells. A conducting polymer chain is linked covalently to the semiconductor surface (Figure 7). If different chromopores are attached to the polymer chain (Figure 7), the excitation of each chromopore would cause fast electron injection to the semiconductor. A spatial separation of chromopore units avoids concentration quenching, and a built-in molecular rectification could suppress recombination. In principle this alleviates the problem of insulation by thick dye layers and concentration quenching, ensuring panchromatic sensitivity. Binding dyes to the semiconductor surface via ancillary molecular structures is
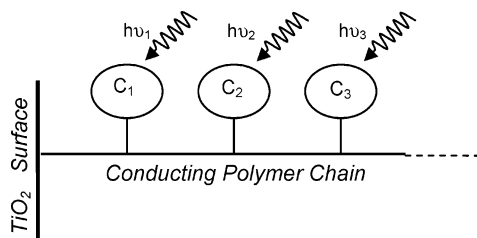
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Figure 7. Schematic diagram showing the attachment of a conducting polymer chain to a semiconductor surface (TiO_2) and different chromopore units (C_1, C_2, C_3, ...) linked to the polymer chain.

a promising way to enhance the effectiveness of the dye−semiconductor solar cell.[24−28] We believe that linking of chromopores to conducting polymer chains would be one of the most effective ways of achieving this objective.

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