Highly efficient sensitization of nanocrystalline TiO_2 films with styryl benzothiazolium propylsulfonate

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Near 100% of maximum incident photon-to-electron conversion efficiency (IPCE) and >15 mA cm^{-2} of short-circuit photocurrent under 94.6 mW cm^{-2} simulated solar light from a xenon lamp were obtained from a thin layer sandwich-type solar cell based on a 2-[4-bis(methyl)aminostyryl]benzothiazolium propylsulfonate (BTS) sensitized nanocrystalline TiO_2 film.

Dye-sensitized nanocrystalline TiO_2 is a promising material for solar cell applications since it is expected to be fabricated at a relatively low cost and can generate efficiencies of up to 10%.[1–3] The most efficient charge transfer sensitizers employed so far are polypyridyl-type complexes of ruthenium[2–4] that have been widely studied in the past ten years.[5,6] Pure organic dyes, owing to their small size, large extinction coefficients and much lower cost, are also promising sensitizers. However, with poor solar energy conversion efficiency (η) below 1%, they are insufficient for solar cell applications.[7,8] Recently Arakawa and coworkers reported that some efficient merocyanine dyes generated 4.2% overall yield on a porous TiO_2 electrode,[9] which suggests good application prospects of these organic dyes on Grätzel cells. Our previous work centered on the photoelectric conversion of hemicyanine derivatives with a π-conjugation bridge between the donor and acceptor groups (D-π-A), and some promising dyes have been selected by molecular design and use of the Langmuir-Blodgett technique.[10–12] In order to advance the development of the Grätzel cell, it is worthwhile to investigate the sensitization of nanocrystalline TiO_2 with pure organic dyes, such as hemicyanine derivatives. Here, we report an outstanding organic sensitizer for nanocrystalline TiO_2 films. A thin layer sandwich-type solar cell fabricated with this dye-modified nanocrystalline TiO_2 film generated an exceptional, high IPCE near unity between 480 and 500 nm and 15.1 mA cm^{-2} of short-circuit photocurrent, amongst the highest values reported so far.[1–3,7–9]

2-[4-Bis(methyl)aminostyryl]benzothiazolium propylsulfonate (BTS) (Fig. 1) was synthesized[12,13] by condensing its methyl azolium propylsulfonate precursor with 4-[bis(methyl)-amino]benzaldehyde. [Elemental analysis: found (calc. for $C_{20}H_{22}N_2S_2O_3{\cdot}H_2O$): C, 56.73 (57.12); H, 5.86 (5.75); N, 6.54 (6.66)%]. The absorption and fluorescence emission spectra of BTS were measured in chloroform solution. While the absorption peak in the visible region is at 557 nm, the maximum of the fluorescence is located at 590 nm. Interestingly, the emission is entirely quenched when BTS is adsorbed onto a nanocrystalline TiO_2 film, indicating efficient electron injection from the excited singlet state of the dye into the conduction band (CB) of TiO_2. Cyclic voltammetry of BTS in MeCN was measured using $LiClO_4$ as supporting electrolyte. The oxidation and reduction potentials are 0.87 and 0.80 V (*vs.* SCE), respectively, from which $E_{1/2}$ is derived to be 0.84 V (*vs.* SCE). When BTS is adsorbed onto a TiO_2 film, the absorption threshold is extended to *ca.* 700 nm. Combining the redox potential with the absorption threshold of BTS, the first excited state level of BTS is estimated to be −0.93 V (*vs.* SCE), above the flat band potential (−0.90 V *vs.* SCE) of nanocrystalline TiO_2 film in aprotic solvent containing no less than 0.1 M Li^+ ion.[14] Therefore, one can conclude that electron injection from the excited dye molecules to the CB of TiO_2 is thermodynamically possible. A 7 μm-thick nanocrystalline TiO_2 film,[2] coated onto conducting glass (fluorine doped SnO_2 sheet, resistance 20 Ω per square), was protonated by soaking for 2 h in a HCl solution at pH 2 and dried in a hot air flow before dipping it in a 1×10^{-4} M solution in chloroform for 4 h. The visible band in the absorption spectrum of BTS on TiO_2 film is red shifted by 12 nm with the half width increased from 55 to 90 nm upon previous treatment of the TiO_2 film with HCl solution, as seen in Fig. 2(a) and (b). These changes are favorable to photoelectric conversion. It is of note that HCl treatment does not significantly affect the adsorbed quantity of BTS on the TiO_2 [Fig. 2(a) and (b)]; the height of the absorption peak remains almost the same while the shape of spectrum changes drastically upon treating the TiO_2 film with HCl solution.

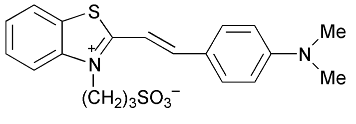

Fig. 1 Schematic structure of BTS.

The photocurrent action spectra are shown in Fig. 2(c) and (d) where IPCE is plotted as a function of wavelength. After HCl treatment, IPCE values are increased by more than 50% between 400 and 700 nm with respect to the untreated TiO_2 film, but remain almost unchanged above 700 nm. Obviously, IPCE is improved remarkably upon HCl pretreatment of the TiO_2 film. The surface of nanocrystalline TiO_2 is hydroxylated

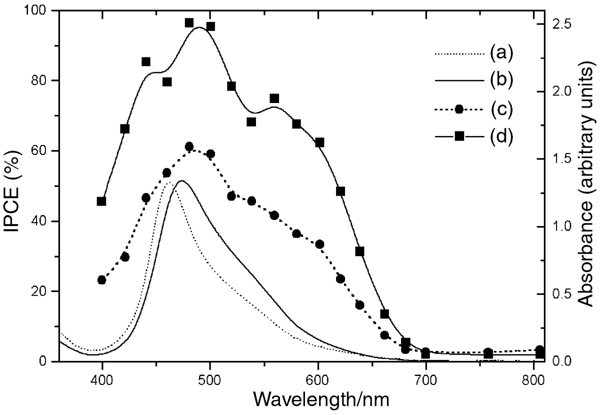

Fig. 2 Absorption spectra of BTS on nanocrystalline TiO_2 film (2 μm), corrected for the absorption of TiO_2 film and the conducting glass support: (a) untreated TiO_2 film and (b) HCl pretreated TiO_2 film. Photocurrent action spectra for BTS-coated nanocrystalline TiO_2 film (7 μm): (c) untreated TiO_2 film and (d) HCl pretreated TiO_2 film. A sandwich-type cell configuration was used to measure the action spectra. The redox electrolyte was 0.5 M LiI–0.05 M I_2 in propylene carbonate solvent. IPCE data were corrected for the absorption of the conducting glass.

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under preparation conditions.[15] BTS, which is adsorbed onto TiO_2 *via* coordination bonds between RSO_3^- and Ti^{4+},[2] may show a weakened interaction due to the repulsive force between RSO_3^- and deprotonated hydroxyl groups on neutral TiO_2. However, after pretreatment of the nanocrystalline TiO_2 film with HCl solution, the surface of nanocrystalline TiO_2 is protonated which enables BTS to adsorb onto the TiO_2 surface more strongly, which is consequently favorable for electron injection.[15] Another reason for the improvement in performance is that the decrease of flat band potential of nanocrystalline TiO_2 film due to the adsorption of H^+ ion can increase the driving force for electron injection.[14] Under illumination of simulated solar light from a 500 W Xe lamp (Ushio Electric, Japan), while a sandwich-type solar cell fabricated with this dye-sensitized nanocrystalline TiO_2 film in conjunction with a 0.5 M LiI–0.05 M I_2 redox electrolyte in propylene carbonate (PC) generated 9.0 mA cm^{-2} of short-circuit photocurrent (I_{sc}), 413 mV open-circuit photovoltage (V_{oc}) and 0.410 for the fill factor (FF) with an overall yield (η) of 1.6%, a value of 2.1% for η (15.1 mA cm^{-2} I_{sc}, 410 mV V_{oc} and 0.315 FF) was obtained from a HCl treated film under the same conditions. It is interesting that while V_{oc} remains almost unchanged, I_{sc} is increased by 68% upon HCl pretreatment of the nanocrystalline TiO_2 film. It is believed that the overall yield will be greatly improved after optimization of FF and V_{oc}.[2] The maximum IPCE and short-circuit photocurrent are the highest values among pure organic sensitizers so far studied.[9] For stability examination, this solar cell was illuminated with 94.6 mW cm^{-2} white light from a xenon lamp for 10 h, and the short-circuit photocurrent was almost unchanged after this period. Longer-term tests will be studied in detail.

Our results indicate that hemicyanine derivatives are promising sensitizers for solar cell applications. The notable improvement of photoelectric properties upon treating nanocrystalline TiO_2 film with HCl solution indicates that surface treatment is very important in photoelectric conversion. Preliminary experimental results show that this method for surface treatment of TiO_2 can also improve performance parameters for other hemicyanine dyes containing SO_3^- groups. Therefore, these findings open up a new pathway for designing new efficient sensitizers and aid the development of the Grätzel cell. As the cost of hemicyanine-group dye is much lower than that of ruthenium polypyridine complexes, the overall cost of dye-sensitized solar cells could be further reduced. Detailed study of BTS is now in progress.

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