Interface Modification of Dye-sensitized Solar Cells with Pivalic Acid to Enhance the Open-circuit Voltage

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Pivalic acid (PVA) was used as a new coadsorbent to dye-sensitized solar cells (DSCs) to modify the interface between the TiO_2 films and electrolyte. The addition of PVA improved the light-to-electricity conversion efficiency of devices by 8% by enhancing the open-circuit voltage.

Dye-sensitized solar cells (DSCs) have attracted much attention owing to its lower cost and shorter pay-back time compared to conventional silicon solar cells.[1] A typical DSC employs TiO_2 nanocrystal film to form a "bulk" junction with a large surface area at the semiconductor/electrolyte interface and thus provides sufficient anchoring sites for sensitizers to realize light harvesting and electron injection.[2,3] However, such large interface also increases the recombination between the photon-induced electrons inside the TiO_2 film and oxidized species of the redox couple in the electrolyte, which impairs the DSCs photovoltaic performance greatly.[4] To restrain such recombination, several classes of small molecules, such as pyridine derivatives,[5] phosphonic acids,[6] and carboxylic acids,[7,8] have been used to modify TiO_2 surface by coadsorbing with dye molecule. Those coadsorbents have been proven to be effective to alter the TiO_2/electrolyte interface and improve the DSCs photovoltaic performance. Nevertheless, the search for new coadsorbent molecules is still active field of research. In this paper, an amphiphilic molecule, pivalic acid (PVA) as shown in Figure 1, is reported as a new kind of coadsorbent. Furthermore, the adsorption condition of PVA was also varied to scrutinize its effect on the self-organization of dyes and influence on the photovoltaic performance of the DSCs.

All chemicals and solvents used in the present work were purchased from Fluka of puriss quality. Transparent films (5-µm thick layer) of 20-nm TiO_2 particles were used as photoanodes and prepared as described earlier.[7] The amphiphilic ruthenium dye $NaRu(2,2'\text{-bipyridyl-4-carboxylic acid-4'-carboxylic acid})(4,4'\text{-dinonyl-2,2'-bipyridine})(NCS)_2$, coded as Z-907Na was used as the sensitizer.[9] The dye and PVA solutions were prepared in a mixed solution of *tert*-butanol/acetonitrile (1:1, v/v).

TiO_2 electrode was first sintered at 500 °C for 25 min and cooled to about 100 °C in air. Then two different sensitizing conditions called as PVA pretreatment and cotreatment were adopted. In PVA pretreatment condition, TiO_2 electrodes were firstly immersed into PVA solution for 16 h, after that washed with acetonitrile, and then transferred to Z-907Na dye solution for 9 h. In PVA cotreatment, TiO_2 electrodes were immersed overnight in a dye solution containing a Z-907Na to PVA molar ratio of 4:1 and 1:1. After sensitising process, the photoanode electrodes were assembled into devices with thermally platinized conducting glass as counter electrode. The cell fabrication and characterization details are given in the Supporting Information.[14] UV–vis spectra were recorded on the surface of TiO_2 using a Cary 5 spectrophotometer. The light source for the photocurrent–voltage (I–V) measurement was a 450-W xenon lamp (Oriel, USA), simulating AM 1.5 solar light. Photovoltage transients were measured by using an exciting pulse generated by a ring of red-light-emitting diodes (LEDs, Lumiled) controlled by a fast solid-state switch.

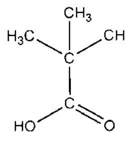

Figure 1. The molecular structure of PVA.

Figure 2 shows the absorption spectra of TiO_2 electrodes stained with dye and/or PVA under different treatment conditions. The peak at 518 nm corresponding to the MLCT transition of Z-907Na adsorbed on the surface of TiO_2 can be used to determine the dye loading.[10] PVA molecule has a carboxyl group that binds to the surface of TiO_2. In case of PVA treatments there will be a competion for dye adsorption on the surface of TiO_2 with PVA, and the dye loading was decreased. As PVA is weekly bound to the surface of TiO_2, it is readily replaced by the dye molecules which bind more strongly. The rational for using the PVA pretreatment is that PVA molecules that are not replaced by the dye will protect surface sites that otherwise would be exposed to the electrolyte. Note that a PVA-pretreated film after staining in a Z-907Na solution for 9 h showed a dye loading of 90% compared to the film stained in dye solution for 16 h without PVA pretreatment.

The photovoltaic performance parameters (short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and photon-to-electron conversion efficiency (η)) of the DSCs

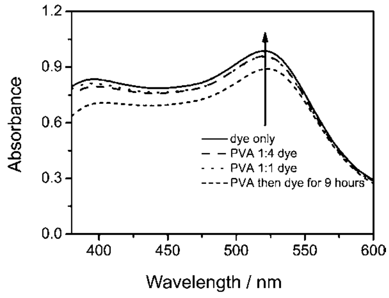

Figure 2. UV–vis spectra of TiO_2 film stained with dye and/or PVA under different treatment conditions.

Table 1. Photovoltaic characteristics of the DSCs made with different treatments of PVA under illumination of AM 1.5 full sunlight[a]

Device	TiO_2 electrodes treatment	J_{sc} /mA·cm^{-2}	V_{oc} /mV	FF	η /%
a	Dye only, 16 h	11.8	682	0.72	5.77
b	PVA 16 h, then dye 9 h	11.8	735	0.72	6.25
c	PVA and dye (1:4)	11.8	724	0.72	6.13
d	PVA and dye (1:1)	11.4	727	0.73	5.98

[a] The cell active area was 0.158 cm^2.

employing Z-907Na alone (Device **a**) or with different PVA treatments (devices **b** to **d**) are listed in Table 1. The parameters obtained with device **a** are 11.8 mA·cm^{-2}, 682 mV, 0.72, and 5.77%, respectively. As shown in Figure 2, the amount of dye adsorbed on the surface of TiO_2 depends on the staining conditions. It was clearly shown that in devices **b**–**d** certain amount of dye was replaced by PVA on the TiO_2 surface, but in all these cases the J_{sc} is almost the same indicating that the loss in light harvesting was well compensated by increasing the carrierr collection efficiency by the adsorption of PVA on the surface of TiO_2 which decreases the dark current.[11] The decrease in the dark current of devices **b**–**d** is reflected in an increase in the V_{oc} (42 to 53 mV than device **a**) contributing to the the high performance of devices. Such increase should be attributed to the passivation of TiO_2 surface or the shift of the TiO_2 conduction band.[8,10,12] Hence, devices **b**–**d** show higher efficiency than that of device **a** owing to a combinatorial effect of J_{sc} and V_{oc}. In this study we found that the pretreatment of PVA followed by 9-h dye adsorption gave the best result. With device **b** obtained an increase of efficiency by 8.3% compared to device **a** efficiency.

Phototransient measurements were used to scrutinize the effects of PVA treatments on the DSCs. Devices **a**, **b**, and **c** corresponding to no treatment, pretreatment and cotreatment of PVA on TiO_2 electrodes, respectively. Figure 3a shows the effect of different treatments of PVA on the short-circuit current as a function of photoinduced charge density accumulated in the TiO_2 nanoparticles at open circuit. It is clear that pretreatment and cotreatment of PVA on devices **b** and **c** lead to higher photoinduced charge densities at a given J_{sc} than that of device **a**, which implies a suppression of recombination.[13] Figure 3b represents the influence of different PVA treatments on the open-circuit voltage. It shows that devices **b** to **d** with PVA treatments gave higher V_{oc} at a fixed photoinduced charge density than that of device **a**, which indicates an upward shift of the TiO_2 band edge due to PVA coadsorption.[13] The band edge of TiO_2 in devices **b** and **c** shift more negatively than that of device **a** with respect to the redox potential of electrolyte. Considering that the recombination in devices **b** and **c** is suppressed and that the band edge is shifted upward simultaneously, V_{oc} values increased by 53 and 42 mV, respectively (Table 1). It is interesting to see that pretreatment with PVA followed by dye adsorption for 9 h gave the best performance, and one has to do more optimization in this direction.

In summary, PVA as a coadsorbent, was found to improve the photovoltaic performance of the DSC. Pretreatment of TiO_2 film with PVA before dyeing improved the photovoltaic performance by increasing the open-circuit potential without sacrificing the short circuit current.

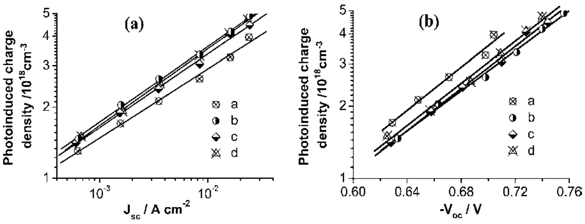

Figure 3. Effect of different PVA treatments on the photoinduced charge density at open circuit with respect to (a) short-circuit current density (J_{sc}) and (b) open-circuit voltage (V_{oc}).

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14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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