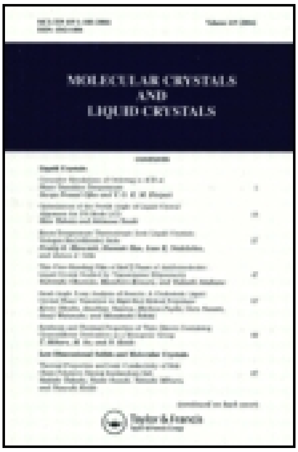

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Enhanced Performance of Dye-Sensitized Solar Cells with Surface-treated Titanium Dioxides

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Enhanced Performance of Dye-Sensitized Solar Cells with Surface-treated Titanium Dioxides

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This work reports on the preparation of lithium acetate (LA)-incorporated TiO_2 *electrodes by a very simple dip coating process and the effects of the modified electrode on the photovoltaic properties of dye-sensitized solar cells (DSSCs). The DSSC with a LA-modified* TiO_2 *layer exhibited an increase in both open circuit voltage and fill factor, resulting in a power conversion efficiency of 7.69% compared to that of a reference device with bare* TiO_2 *(6.82%). By monitoring the changes in electrochemical impedance spectra, dark current-voltage characteristics and incident photon-to-current conversion efficiency, it was revealed that the incorporated LA functioned as a surface dipole on the* TiO_2 *electrode.*

Keywords lithium acetate; dip coating; dye-sensitized solar cell; surface dipole

Introduction

Since the introduction of the photosensitized nanocrystalline TiO_2 electrode [1], dye-sensitized solar cells (DSSCs) have become a low cost alternative to the conventional p-n junction solar cells [2–6]. However, further improvements in the power conversion efficiency (PCE) are necessary to successfully commercialize DSSCs. The cell performance is influenced by parameters that include the morphology and optical properties of the nanocrystalline oxide films, the electrochemical characteristics of the redox electrolytes and the photochemical properties of the molecular sensitizers. Thus, if all of the parameters, including the short circuit current (J_{sc}), open circuit current (V_{oc}) and fill factor (FF), are optimized, the performance of the DSSCs can still be considerably improved. Because the J_{sc} value is strongly related to the light absorbance of the dye molecules, many studies have been focused on the synthesis of new dyes that are able to absorb longer wavelengths of light [7–10]. Meanwhile, as a well-known method to improve V_{oc}, interfacial modifications to the TiO_2 layer have been conducted, resulting in the conduction band edge shift of the TiO_2 or suppression of charge recombination. There are three cases in which surface modifications can influence the V_{oc} value of DSSCs with a surface-modified TiO_2 layer. In the first case, materials such as $CaCO_3$ and Nb_2O_5 form an energy barrier [11,12]. The electrons injected into the TiO_2 layer may transfer back to the sensitizer or to the electrolyte

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due to an electron recombination phenomenon. The energy barrier causes deceleration in the recombination rate for a given electron population, resulting in a larger concentration of electrons in the TiO_2 layer. This increase induces a more negative Fermi level in the TiO_2 and thus a larger V_{oc}. In the second case, the surface dipoles could be shaped instead of the energy barriers, depending on the modification process. Some oxide compounds, such as $SrTiO_3$ and ZnO, have been reported to make surface dipoles [13,14]. Surface dipoles have been shown to shift the conduction band edge of TiO_2 toward a negative potential. In this case, a back electron transfer is not hindered, but overall conversion efficiency is improved due to the enhancement of V_{oc} [15,16]. In the last case, surface-coating materials passivate the surface states, which are considered to be the recombination centers, leading to an enhancement of V_{oc} [17].

Meanwhile, several works have shown that addition of $LiClO_4$ [18] or acetic acid [19] into electrolytes leads to an adsorption of lithium ions or acetic acids on the TiO_2 surface, resulting in an enhanced performance of DSSCs. In this paper, we selected lithium acetate (LA) to incorporate both lithium ions and acetate group onto the TiO_2 layer. The TiO_2 surfaces were directly modified via a very simple dip coating process using aqueous LA solution, and the resulting electrodes were applied to the photoanodes of DSSCs. We expected the LA on the electrodes to possibly behave as surface dipoles or as an insulation layer on the TiO_2 layers, resulting in an improvement in the performance of the DSSCs. Thus, we examined whether LA is successfully deposited onto the TiO_2 layers by simple dip coating, and the effects of the surface treatment on the improvement in the performance of the DSSCs were also investigated.

Experimental details

Materials

Commercial TiO_2 pastes [T20/SP (20 nm), Ti-nanoxide 300 (400 nm); Solaronix] and LA (CH_3COOLi; Sigma-Aldrich) were selected as photoelectrode and coating material, respectively. Commercial N719 dye [$RuL_2(NCS)_2(TBA)_2H_2\dot{c}4H_2O$, L = 2,2'-bipyridyl-4,4'-dicarboxylate, TBA = tetrabutylammonium; Solaronix] was employed as the sensitizer. Iodide-based commercial electrolyte (AN-50; Solaronix) and a Pt source ($H_2PtCl_6{\cdot}5.5H_2O$; KOJIMA CHEMICALS) were selected. All of the chemicals were used without any further purification.

Preparation of DSSCs

To prepare the working electrodes, fluorine-doped tin oxide (FTO, sheet resistance: ∼10 Ω/□) glasses were cleaned in a detergent solution using sonication for 20 min, and then thoroughly rinsed with deionized water (DI) and ethanol. After treatment with UV-O_3 for 20 min, the FTO glasses were immersed into a 40 mM $TiCl_4$ solution at 70°C for 30 min and then washed with DI and ethanol. An active TiO_2 layer was formed on the FTO glass via a doctor-blade method followed by a calcining process at 500°C for 60 min. An additional TiO_2 layer composed of ca. 400-nm particles was then deposited and subsequently calcinated. Finally, the TiO_2 films were treated with 40 mM $TiCl_4$ solution again and annealed at 500°C for 60 min to prepare the TiO_2/FTO electrodes. The electrodes were soaked in aqueous solutions (5×10^{-2} M) of LA for 5∼20 min to deposit the LA onto the TiO_2 layers. The resulting electrodes were rinsed with DI and ethanol, and dried at 65°C for 10 min to prepare the LA-modified TiO_2 layer (LA-TiO_2/FTO). Both bare TiO_2/FTO and LA-TiO_2/FTO electrodes were separately immersed in a 0.5 mM N719 dye solution (acetonitrile/tert-butyl alcohol, v/v = 1/1) for 24 h. To prepare the counter electrode, two holes were drilled in the FTO glass and cleaned with the method described previously. A drop of 0.7 mM H_2PtCl_6/isopropanol solution was placed on the rinsed FTO glass, and then the glass was calcined at 400°C for 30 min. Thermally treated platinum counter electrodes were placed on the TiO_2/FTO electrodes, and these were then sealed with a 60 μm-thick sealing material (SX1170–60PF; Solaronix). The electrolyte was introduced into the cells through one of the two small holes drilled in the counter electrodes to give DSSCs with 25 mm^2 active area.

Measurements

X-ray photoelectron spectroscopy (XPS) was performed using a VG Multilab ESCA 2000 (ThermoVG Scientific) with Mg Kα radiation. The C 1s photoelectron peak (binding energy at 284.6 eV) was used as an energy reference. The amount of LA introduced onto the TiO_2 layer was measured using inductively coupled plasma mass spectrometry (ICP/MS, Elan 6100, PerkinElmer). The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were measured with a Nicolet 380 FT-IR spectrometer (Thermo Electron Corporation). To calculate an amount of absorbed dye molecules, UV-Vis diffuse reflectance spectra (UV-Vis DRS) were obtained from a Lambda 750 UV-Vis spectrophotometer (PerkinElmer) equipped with an internal diffuse reflectance integrating sphere. Photocurrent-voltage measurements were performed using a Keithley model 2400 Source Meter and a Newport 91192 solar simulator system equipped with a 1 kW xenon arc lamp (Oriel). Light intensity was adjusted to 1 sun (100 $mWcm^{-2}$) with a Radiant Power Energy Meter (model 70260, Oriel). The incident photo-to-current conversion efficiency (IPCE) results were acquired using an IPCE G1218a (PV Measurement). This system applies monochromatic light from a 75W xenon arc lamp (Ushio UXL-75XE), which is filtered by a dual-grafting monochromator and individual filters, onto the test devices. An ellipsoidal reflector collects light from the lamp and focuses it on the monochromatic entrance slit via a mechanical chopper to produce a small, modulated signal. As the modulated, monochromatic light was applied to the test devices, a continuous bias light (1 sun) was also applied.

Results and discussion

TiO_2/FTO electrodes were soaked in aqueous solutions of LA, and the rinsed electrodes were dried at 65°C to produce the LA-TiO_2/FTO. The soaking time was adjusted because it determines the coating amount in the dip coating process. We prepared three different LA-TiO_2/FTO electrodes by varying the soaking time from 5 to 20 min. The amount of LA incorporated onto the TiO_2 layer was calculated using the data from the ICP measurements, where the results confirmed that the amount of LA was increased by extending the soaking time (Table 1). XPS measurements of the LA-modified electrode were also conducted. As an evidence of LA incorporation, the characterization peak for the Li 1s was clearly detected at 55.6 eV (Fig. 1).

To further confirm the formation of LA on TiO_2 surface, ATR-FTIR spectra were recorded for the LA-modified TiO_2 film. However, for the TiO_2 film dipped into the LA solution for 5∼20 min, the ATR-FTIR peaks were difficult to detect because of the small amount of LA. Thus, we provide the ATR-FTIR spectrum for the LA that was formed on the TiO_2 film by dipping into the LA solution for 60 min. Figure 2 shows the IR spectra of LA-TiO_2/FTO and bare TiO_2/FTO films. The peak at 1640 cm^{-1} can be attributed to

Table 1. Amount of LA coated onto the TiO_2 layer.

Applied electrodes		dipping time (min)	Amount of LA (wt%)
TiO_2/FTO		0	0
LA-TiO_2/FTO	LA(5)-TiO_2/FTO	5	1.01
	LA(10)-TiO_2/FTO	10	1.12
	LA(20)-TiO_2/FTO	20	1.20

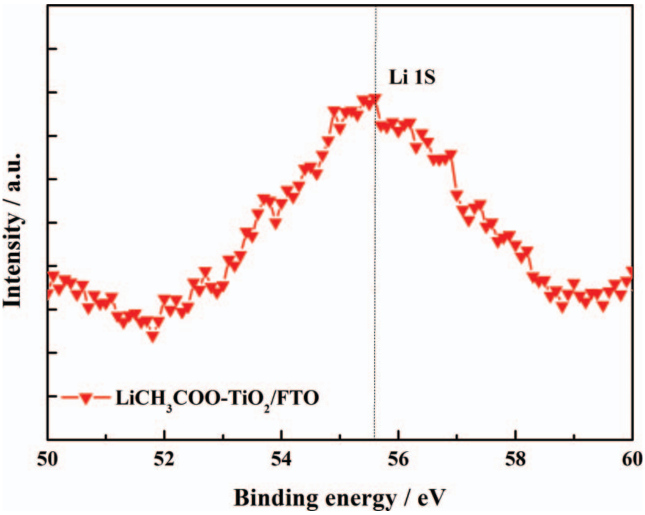

Figure 1. X-ray photoelectron spectrum for the Li 1s peak in LA-TiO_2/FTO.

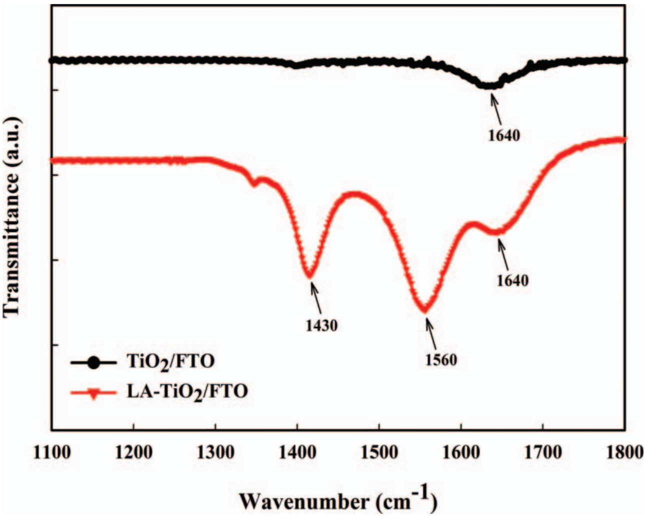

Figure 2. ATR-FTIR spectra of TiO_2/FTO and LA-TiO_2/FTO.

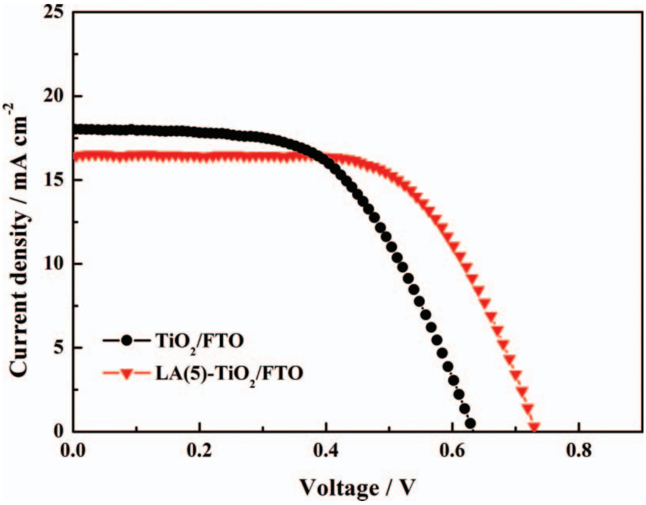

Figure 3. Current-voltage characteristics of DSSCs with pristine and LA-coated TiO_2 layers.

bending mode of the O-H groups of the adsorbed water. The two strong peaks at 1560 and 1430 cm^{-1}, assignable to the asymmetric and symmetric O-C-O stretching vibration, appear in the spectrum of the coated film, strongly supporting the presence of O-C-O moieties which are from acetate group [20,21].

The DSSCs were fabricated with LA-TiO_2/FTO and bare TiO_2/FTO electrodes, and their photovoltaic properties were characterized. To optimize the amount of LA that were incorporated, the soaking time was varied from 5 to 20 min, and the resulting photoelectrodes were applied to DSSCs. The DSSCs with LA(5)-TiO_2/FTO electrodes that incorporated LA at about 1 wt%, corresponding to a soaking time of 5 min, showed the better performance due to an increase in both V_{oc} and FF, resulting in an improvement in the PCE (7.69%) compared to that of the reference device with a bare TiO_2/FTO electrode (6.82%). Because the PCE exhibited the highest value when the TiO_2/FTO was treated with LA for 5 min, we focused on this device to reveal the origin of an enhancement in the PCE. Figure 3 shows the current density (J) and voltage (V) curves of DSSCs with LA(5)-TiO_2/FTO and bare TiO_2/FTO electrodes, and the device performances are compared in Table 2.

Electrochemical impedance spectroscopy (EIS) has been widely used for investigating the kinetics and energetics of transport and recombination in DSSCs [22,23]. Figure 4a shows the Nyquist plots of the electrochemical impedance spectra of the DSSCs in an open-circuit condition under the illumination of simulated AM 1.5 solar light (100 mA/cm^2). The arcs are assigned to the resistances at the transparent conducting layer/TiO_2 (ω_1),

Table 2. Performance comparison of the DSSCs employing TiO_2/FTO and LA(5)-TiO_2/FTO as photoanodes.

Applied electrodes	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	η (%)	R_{sh} (Ω cm^2)	R_{se} (Ω cm^2)	Loaded dye (mol cm^{-2})
TiO_2/FTO	0.63	18.02	60.10	6.82	311	18.5	1.80×10^{-7}
LA(5)-TiO_2/FTO	0.73	16.45	64.06	7.69	746	10.3	1.82×10^{-7}

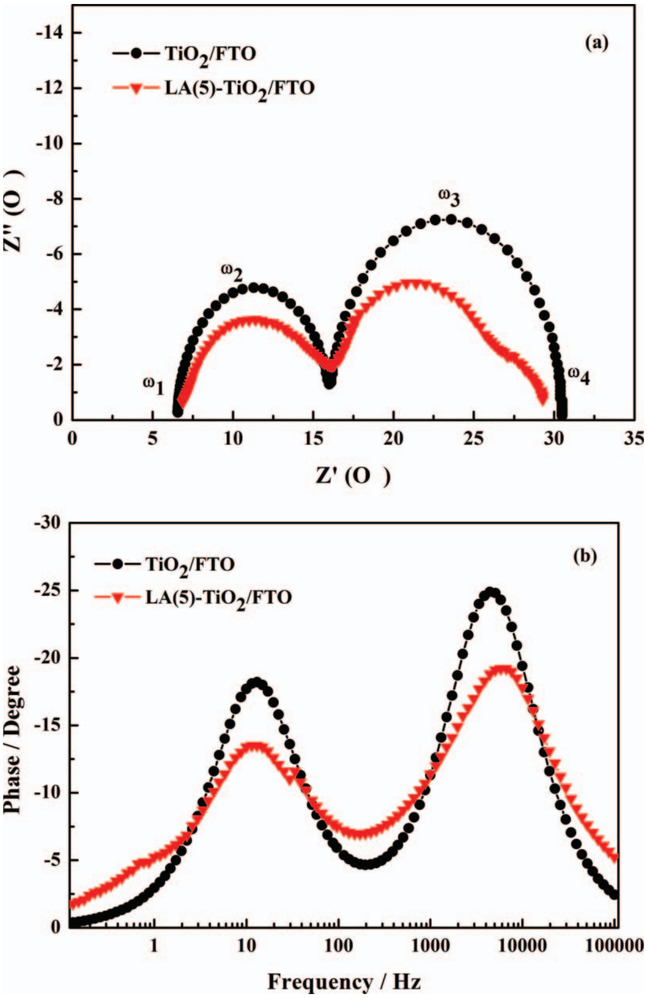

Figure 4. EIS spectra of (a) Nyquist and (b) Bode plots for DSSCs with pristine TiO_2 and LA-modified TiO_2 electrodes.

Pt/electrolyte (ω_2), TiO_2/dye/electrolyte (ω_3) interfaces and diffusion of the I_3^-/I^- redox electrolyte (ω_4) [24]. The Bode phase plots of the EIS spectra (mid frequency range) are shown in Fig. 4b. The frequency peak related to the LA-modified TiO_2 electrode was almost equivalent to that of bare TiO_2/FTO. The electron lifetime (τ_n) was estimated from the equation $\tau_n = 1/(2\pi f_{max})$, where f_{max} is the peak frequency. The electron lifetime was calculated to be 12.15 ms for DSSCs with bare TiO_2 and LA(5)-modified TiO_2. When we considered that the energy barrier causes an increment in the electron lifetime of the TiO_2 [25], we concluded that our LA modification of the TiO_2 does not induce formation of an energy barrier.

Although the dark current of the DSSCs does not directly reflect the recombination current under illumination, it can be used to measure a conduction band shift [13]. Figure 5 presents the dark current-voltage characteristics of the DSSCs with bare TiO_2/FTO and LA(5)-TiO_2/FTO as photoanodes. The onset potential of the dark current for the bare TiO_2/FTO electrode was measured to be ca. 0.48 V, whereas the dark current potential for

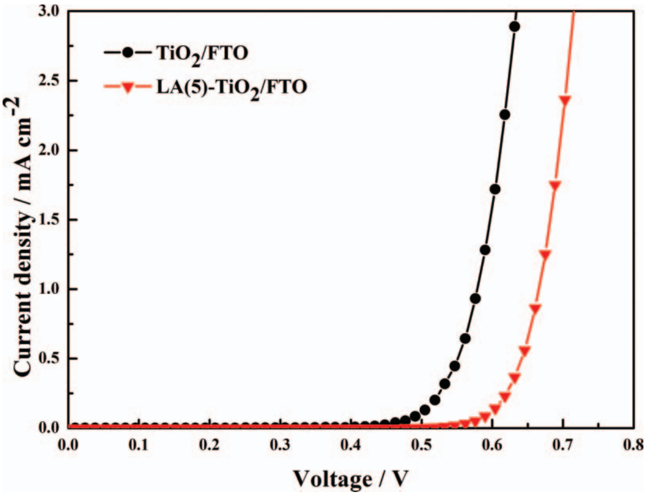

Figure 5. Dark current-voltage characteristics of DSSCs with pristine and LA-modified TiO_2 layers.

the LA(5)-TiO_2/FTO electrode was shifted to ca. 0.58 V. The LA modification induces a shift of the onset potential, but the curves maintain the same shape. This shape similarity implies that the modification does not form an energy barrier that prevents electron leakage to the electrolyte; instead, the LA modification shifts the conduction band potential in the negative direction, resulting in a lower electron density in the TiO_2 for any given applied potential [14]. Consequently, the back electron transfer at each applied potential in the LA(5)-TiO_2/FTO is lower than that in the bare TiO_2/FTO electrode, which can be inferred from Fig. 5, but modification does not change the amount of back electron transfer as a function of the electron density in TiO_2. In summary, the LA modification shifts the TiO_2 conduction band in the negative direction, thus leading to an increase in V_{oc}.

Y. Diamant *et al*. reported that the improvement in V_{oc} by incorporation of ZnO [14] and $SrTiO_3$ [13] onto the TiO_2 layer was attributed to a surface dipole. The formation of a surface dipole was verified by comparing the normalized IPCE curves of the DSSCs with bare and modified TiO_2. They stated that the shapes of the two normalized IPCE curves were similar, such that an energy barrier was not formed in the modified TiO_2 layer. Figure 6 presents the normalized IPCE curves of the DSSCs with bare TiO_2/FTO and LA(5)-TiO_2/FTO as the photo-electrodes. This similarity in curve shape suggests that an enhancement in V_{oc} is due to the formation of a surface dipole in the TiO_2 layer not an energy barrier.

The *FF* values of the DSSC with the LA(5)-TiO_2/FTO electrode were also increased (ca. 14%) compared to the DSSC with a bare TiO_2 electrode. The *FF* value is known to be dependent on the series (R_{se}) and shunt (R_{sh}) resistances [26]. The DSSC with a LA(5)-TiO_2/FTO electrode had an R_{se} that was effectively reduced to 10.3 Ωcm^2 as compared with that of the device with a pristine TiO_2/FTO electrode (18.5 Ωcm^2). The R_{sh} value of the DSSC with the LA(5)-TiO_2/FTO electrode was increased by 746 Ωcm^2 from that of the reference device (311 Ωcm^2). Thus, we believe that the increased *FF* value is attributed to the lowered R_{se} and elevated R_{sh}.

The decrease in the J_{sc} values was observed in the device with a LA(5)-TiO_2/FTO electrode (Table 2). The J_{sc} values are largely influenced by the light-absorption capability of the dye and the electron injection efficiency into the TiO_2 layer. In this study, the amount

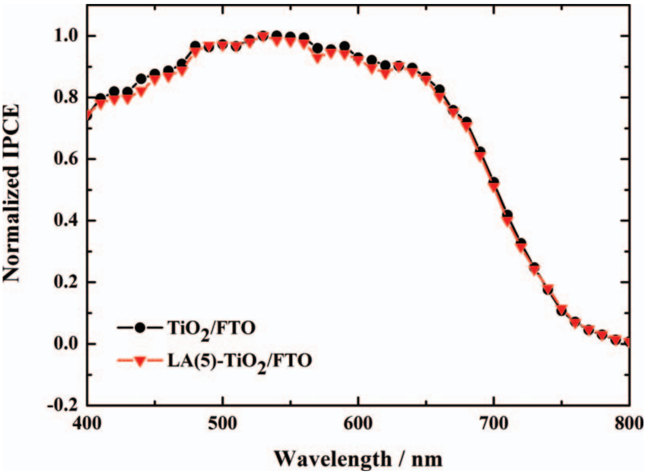

Figure 6. Normalized IPCE spectra for DSSCs with pristine and LA-modified TiO_2 electrodes.

of adsorbed dye molecules on the LA-TiO_2/FTO electrode was not changed when compared with that adsorbed on the bare TiO_2/FTO electrode, as presented in Table 2. This result suggests the decrease in J_{sc} for the LA-modified film could be primarily related to the poorer electron injection from the excited dye to the TiO_2 film. As mentioned previously, several groups have also shown decreases in J_{sc} by employing coating materials, such as $BaCO_3$, ZnO and $SrTiO_3$, on the TiO_2 surface; the decrease is likely due to the negative shift of the conduction band edge, and this shift could cause less efficient electron injection from the excited sensitizer into the conduction band of the modified TiO_2 [13–15]. Thus, the decrease in $J_{\rm sc}$ could be attributed to the lowered efficiency of electron injection from the excited dye to the modified TiO_2 film as a result of the negative (or upward) shift of the conduction band edge.

Conclusions

In summary, we have incorporated LA onto the surface of TiO_2/FTO electrodes via a simple dip coating process, and the resulting electrodes (LA-TiO_2/FTO) were used as the photoanode of DSSCs. When LA(5)-TiO_2/FTO was used as the photoanode of the DSSCs, the $V_{\rm oc}$ values were increased by ca. 16%. The $V_{\rm oc}$ increase was caused by the conduction band edge shift of the TiO_2 to a more negative potential; consequently, we propose that the incorporated LA functioned as a surface dipole on the electrode. Thus, we obtained an improved conversion efficiency of ca. 13% when LA(5)-TiO_2/FTO was employed as the photoanode instead of TiO_2/FTO, indicating that LA is a promising material that may be utilized to enhance the DSSC conversion efficiency by simple dip coating of the photoanode.

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