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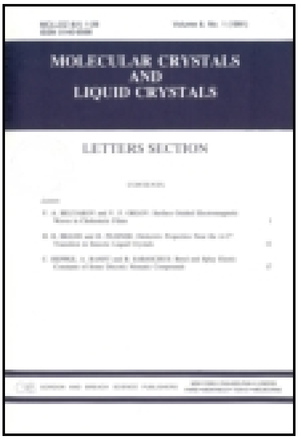

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Effects of Double Layer Coating on TiO_2Surface on the Photovoltaic Properties of Dye-Sensitized Solar Cells

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Effects of Double Layer Coating on TiO_2 Surface on the Photovoltaic Properties of Dye-Sensitized Solar Cells

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Double layer coating on TiO_2 surfaces was performed to improve the performance of dye-sensitized solar cells (DSSCs). Nanoporous TiO_2 electrode was first treated with $TiCl_4$ followed by sintering, and then a dilute aqueous solution of Li_2CO_3 was applied to doubly modify TiO_2 surface via a dip coating process. The DSSC with the doubly modified TiO_2 film showed a power conversion efficiency of 9.85%, enhanced from that (8.70%) of pristine TiO_2-based device, due to an improvement in short circuit current and open circuit voltage.

Keywords Double layer coating; dye-sensitized solar cell; lithium carbonate; surface modification

Introduction

Since the first report by O'Regan and Grätzel, dye-sensitized solar cells (DSSC) as promising and third generation solar cells have been intensively studied due to their low cost, ease of production, and high efficiency comparable with that of amorphous silicon solar cells [1–3]. The typical DSSC consists of a dye sensitizer, a nanoporous TiO_2 film, an electrolyte containing the I^-/I_3^- redox couple, and a platinum coated conductive glass. The power conversion efficiency (PCE) has been raised up to $>12\%$ through the great efforts of researchers working in the DSSC field [4], and various materials and process approaches have been still studied to further enhance PCE of DSSCs.

Meanwhile, TiO_2-based DSSCs suffer from charge recombination between photoinjected electrons and acceptors such as the oxidized dye cations and I_3^- ions in the redox electrolyte, because of the absence of significant band bending in the nano-sized particles [5]. To reduce the charge recombination, which will otherwise lead to remarkable electron loss and performance reduction, ultrathin layers of metal oxides, titanate and carbonate

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have been applied on the surface of the nanoporous TiO_2 electrode to improve the performance of DSSC [6–10]. Among those surface modifiers, $TiCl_4$ is one of the most effective materials, and is being mostly applied to modify the nanoporous TiO_2 electrode [11–13]. Although considerable improvements in PCE were achieved with $TiCl_4$-modified TiO_2, as compared to the unmodified TiO_2 electrode, the efficiency is not enough to successfully commercialize yet. Recently, double layer coating using strontium acetate [$Sr(OAc)_2$] and $TiCl_4$ on nanoporous TiO_2 layer has been reported by Wang et al. [14]. As compared to the typical $TiCl_4$-treated DSSC, the $Sr(OAc)_2$-$TiCl_4$ treated DSSC improved short-circuit photocurrent (J_{sc}) and open-circuit voltage (V_{oc}), leading to an enhancement in PCE by 20%.

In this study, we adopted the double layer coating to further improve the performance of DSSCs. The nanoporous TiO_2 electrode was first treated with $TiCl_4$ followed by sintering, and then a dilute aqueous solution of Li_2CO_3 was applied to doubly modify TiO_2 surface via a simple dip coating process. We could successfully introduce Li_2CO_3 on the $TiCl_4$-treated TiO_2 layer without calcination process to give $Li_2CO_3/TiCl_4$-coated TiO_2 photoelectrode and applied the resulting TiO_2 films to photoanode of DSSCs. The overall performance of DSSCs was investigated, and the effects of modified TiO_2 layers on the performance were discussed.

Experimentals

Materials

A commercial TiO_2 paste [T20/SP, Ti-nanoxide 300; Solaronix] and Li_2CO_3 [Sigma-Aldrich] were selected as the photoelectrode and the coating materials, respectively. Commercial N719 dye was employed as the sensitizer. An 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.

Fabrication of DSSC

DSSCs with a layer structure [11–13] of transparent electrode/modified-TiO_2:Dye/electrolyte/platinized counter electrode were fabricated. To prepare working electrodes, TiO_2 films composed of TiO_2 nanoparticles (~20 nm) were fabricated on FTO (fluorine-doped tin oxide) substrates using a doctor-blade method and sintered at 500 °C for 60 min. The $TiCl_4$ -treated electrodes ($TiCl_4/TiO_2$) were obtained by dipping the as-prepared TiO_2 films in 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min followed by washing with deionized water and sintering at 500 °C for 1 h. For the additional surface modification with Li_2CO_3, $TiCl_4/TiO_2$ films were immersed in 50 mM lithium carbonate aqueous solution for 60 sec followed by washing with deionized water and drying at 100 °C for 30 min to give $Li_2CO_3/TiCl_4/TiO_2$ films. The three kinds of films, pristine TiO_2, $TiCl_4/TiO_2$, and $Li_2CO_3/TiCl_4/TiO_2$ films, were separately immersed in 0.5 mM N719 solution (in acetonitrile/*tert*-butanol, volume ratio of 1/1) for 24 h. To prepare the counter electrode, a drop of 3 mM H_2PtCl_6 solution (in 2-propanol) was placed on the FTO glass, and then it was calcined at 400 °C for 30 min. The working electrode and the counter electrode were sealed together using a 60 μm thick hot-melt Surlyn spacer under heat. The electrolyte was introduced into the cells through one of the two small holes drilled on the counter electrodes to give DSSCs with 25 mm^2 active area.

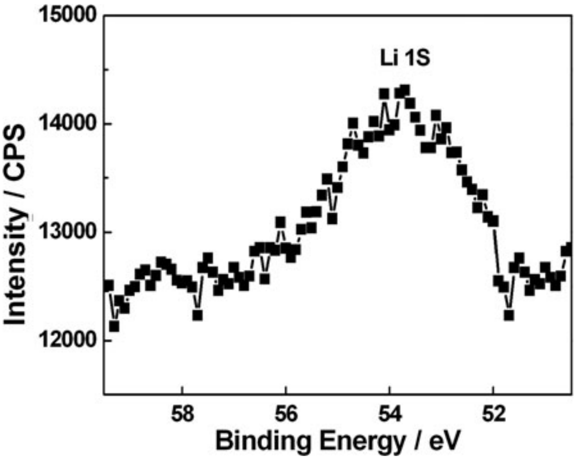

Figure 1. XPS spectrum for Li 1s from the $Li_2CO_3/TiCl_4/TiO_2$ film.

Measurements

X-ray photoelectron spectroscopy (XPS) was performed using VG Multilab ESCA 2000 (ThermoVG scientific) with Al Kα radiation. The C 1s photoelectron peak (binding energy at 284.6 eV) was used as the energy reference. The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were measured with a Nicolet 380 FT-IR spectrometer (Thermo Electron Corporation). The photovoltaic current-voltage characteristics were performed under 1 Sun illumination (100 mW/cm^2, AM 1.5) verified by an AIST-calibrated Si-solar cell. The UV-Visible absorption spectra were obtained from a Lambda 750 UV-Vis spectrophotometer (PerkinElmer).

Results and Discussion

When the TiO_2 film was treated with $TiCl_4$, a fresh TiO_2 layer was formed after sintering, leading to denser TiO_2 layers [11–13]. In order to additionally modify, $TiCl_4/TiO_2$ films were dipped in the aqueous Li_2CO_3 solution for 60 sec, and then rinsing with water and drying. The Li^+ and $CO_3{}^{2-}$ ions penetrate the porous TiO_2 film, and then they are adsorbed onto the surface of $TiCl_4/TiO_2$, resulting in $Li_2CO_3/TiCl_4/TiO_2$ films. Incorporation of Li_2CO_3 onto the $TiCl_4/TiO_2$ surface was verified by the XPS and ATR-FTIR measurement. XPS spectrum of the $Li_2CO_3/TiCl_4/TiO_2$ film is shown in Fig. 1. A broad peak detected at 54 eV agrees with the binding energy of 1s in Li, indicating the existence of Li. To further confirm the presence of Li_2CO_3, ATR-FTIR spectra were recorded. Figure 2 shows the ATR-FTIR spectra of $Li_2CO_3/TiCl_4/TiO_2$ and pristine TiO_2 films. When $TiCl_4/TiO_2$ film was dipped into the Li_2CO_3 solution for 60 sec, any peaks were not detected because of the small amount of Li_2CO_3. Thus, we provide the ATR-FTIR spectrum for the $Li_2CO_3/TiCl_4/TiO_2$ film that was dipped into the solution for 60 min in comparison with that for the pristine TiO_2 film. In contrast to the pristine TiO_2 film, the broad peak at 1400 cm^{-1}, assignable to the O—C—O stretching vibration, appeared in the spectrum of the $Li_2CO_3/TiCl_4/TiO_2$ film, supporting the presence of O—C—O moieties which are from carbonate [15].

DSSCs with pristine TiO_2, $TiCl_4/TiO_2$ and $Li_2CO_3/TiCl_4/TiO_2$ electrodes were fabricated, and their photovoltaic properties were characterized. Figure 3 shows the current density (*J*) and the voltage (*V*) curves of DSSCs with pristine TiO_2, $TiCl_4/TiO_2$, and

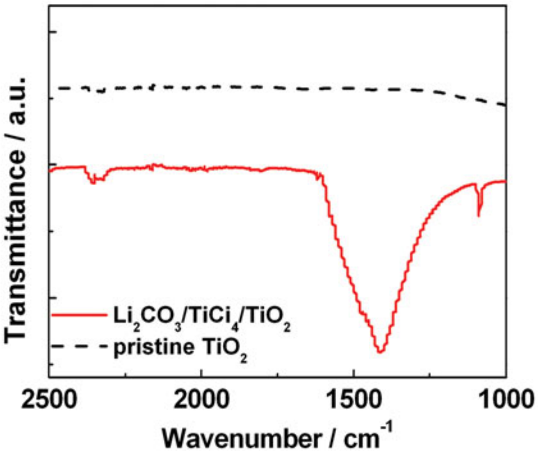

Figure 2. ATR-FTIR spectra of pristine TiO_2 and $Li_2CO_3/TiCl_4/TiO_2$ films.

$Li_2CO_3/TiCl_4/TiO_2$ films, and the device performance is compared in Table 1. The pristine TiO_2-based DSSC exhibited J_{sc} of 16.6 mA/cm^2, V_{oc} of 738 mV, fill factor (FF) of 71.0% and PCE of 8.70%, whereas the PCE of $TiCl_4/TiO_2$-based DSSC was improved to 9.14% due to an increase in J_{sc}. This tendency, i.e, improvement in J_{sc} by $TiCl_4$ treatment, was well consistent with the literatures [11,12]. For the device with $Li_2CO_3/TiCl_4/TiO_2$ electrode, the efficiency was further increased to 9.85%. Thus, the double layer coating led to an enhancement of 13.2% in PCE, compared to that of pristine TiO_2-based DSSC, due to an increase in J_{sc} and V_{oc}.

In order to investigate the physical origins of the improved J_{sc} value, the influence of the double layer coating on the dye adsorption was investigated. The dye molecules on the electrodes were desorbed by soaking the electrodes in a 0.1 M NaOH solution. The dye adsorptive capacity was determined by the molar absorption coefficient for N719 in basic

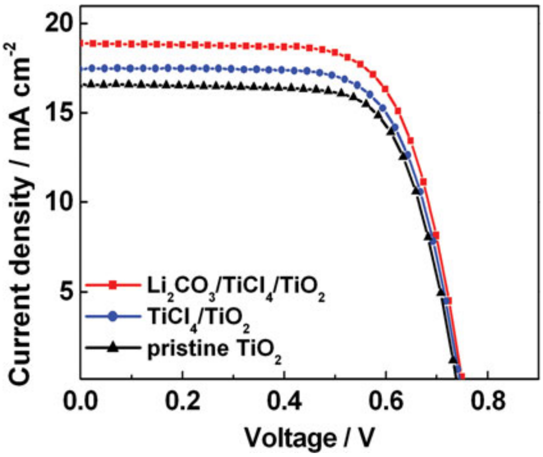

Figure 3. J-V curves of the DSSCs employing pristine TiO_2, $TiCl_4/TiO_2$, and $Li_2CO_3/TiCl_4/TiO_2$ electrodes.

Table 1. Photovoltaic properties of the DSSCs employing pristine TiO_2, $TiCl_4/TiO_2$, and $Li_2CO_3/TiCl_4$ as photoanodes

Applied electrodes	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)
Pristine TiO_2	738	16.6	71.0	8.70
$TiCl_4/TiO_2$	746	17.5	70.0	9.14
$Li_2CO_3/TiCl_4/TiO_2$	750	18.9	69.5	9.85

aqueous solution of 1.25×10^4 M^{-1}cm^{-1} at 500 nm. Figure 4 shows the UV-VIS absorption spectra of the desorbed dye molecules. The absorbance intensity was increased by the double layer coating on the TiO_2 surface. On the basis of the observed optical absorption spectra, the amount of adsorbed dye molecules were calculated [3,16]. The amount of adsorbed dye molecules on $Li_2CO_3/TiCl_4/TiO_2$ electrode was increased by 23.7% compared with that of $TiCl_4/TiO_2$ electrode (from 1.14×10^{-7} to 1.41×10^{-7} mol/cm^2), suggesting that the presence of Li_2CO_3 enhances the dye attachment to the TiO_2 surface. It is probably due to the more basic property of $Li_2CO_3/TiCl_4/TiO_2$ electrode than pristine TiO_2 [10], favoring higher dye adsorption and thus higher light harvesting efficiency. In addition, carbonate moieties on TiO_2 surface may be effective to physically separate the injected electrons and electron acceptors (i.e., I_3^- ions) and hence to retard charge recombination in DSSC, attributted to the insulating property of Li_2CO_3. The enhanced light harvesting efficiency and retarded charge recombination can contribute to the increase in J_{sc} value.

The V_{oc} value (750 mV) of DSSC with $Li_2CO_3/TiCl_4/TiO_2$ electrode was slightly increased from that (738 mV) of pristine TiO_2-based device. The increased V_{oc} can be explained by the formation of an energy barrier on the TiO_2 surface. Some semiconductors and insulators coated on the TiO_2 surface have been reported to form an energy barrier that allows the electron injection but hinders the recombination [17–20]. This barrier decreases the recombination rate constant for a given electron population. If the amount of electrons injected from the dyes is unchanged, then the electron concentration in the modified TiO_2

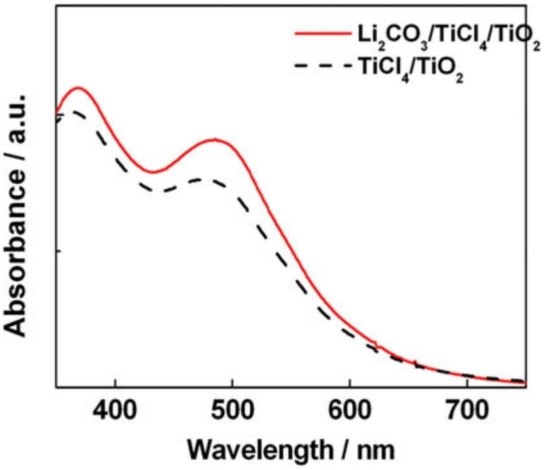

Figure 4. UV-VIS absorption spectra of the DSSCs employing $TiCl_4/TiO_2$ and $Li_2CO_3/TiCl_4/TiO_2$ electrodes.

layer will be higher than that in the unmodified TiO_2 layer. A larger electron concentration in the TiO_2 layer can cause a more negative shift of the Fermi level and thus a larger V_{oc} [21]. In our case, we believe that the carbonate groups on the TiO_2 surfaces serve as an insulator, and form an energy barrier between the TiO_2 layer and the electrolytes. This energy barrier in the device with $Li_2CO_3/TiCl_4/TiO_2$ electrode can induce a larger electron concentration in the TiO_2 layer, leading to a more negative Fermi level and thus a larger V_{oc}.

However, the V_{oc} enhancement was just 1.63%. It seems that the minute change in V_{oc} was attributed to low contents of carbonate moieties incorporated on TiO_2 surface. In this respect, further studies aimed at elucidating the cause of the small increment are currently in progress. By extending dipping time or using higher concentration of solution in the surface modification process, carbonate moieties on TiO_2 surface could be increased. We expect that increased contents could induce higher V_{oc} in the device with $Li_2CO_3/TiCl_4/TiO_2$ electrode.

Conclusions

In conclusion, a two-step surface modification was performed for improving the performance of DSSCs. The resulting $Li_2CO_3/TiCl_4/TiO_2$ film was applied to the photoanode of DSSC and compared with pristine TiO_2 and $TiCl_4/TiO_2$ films in terms of photovoltaic performance. We obtained ca. 13% improvement in PCE by adopting $Li_2CO_3/TiCl_4/TiO_2$ film as the photoanode of DSSC rather than pristine TiO_2 film. The experimental results indicate that the double layer coating on TiO_2 surface is effective method to further enhance the performance of DSSCs.

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