



Effects of a TiO₂:CaO barrier layer on the back electron transfer in TiO₂-based solar cells



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ABSTRACT

A TiO₂:CaO mixed overlayer was formed on TiO₂ photoelectrodes, and the resulting photoelectrodes were applied to dye-sensitized solar cells (DSSCs). DSSC with the mixed overlayer showed an increase in short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF), resulting in a 17% enhancement in photovoltaic performance, compared to that of reference cell. It was found that, by incorporating the mixed overlayer, light harvesting and electron collection efficiency were enhanced, thereby increasing J_{sc} . The enhancement in V_{oc} resulted from a reduced back electron transfer, and the increased FF was attributed to a decreased series resistance and an increased shunt resistance.

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Introduction

A dye-sensitized solar cell (DSSC) based on a TiO₂ semiconductor is composed of a photoelectrode, an electrolyte, and a Pt counter electrode, and it has various advantages, such as reasonable photovoltaic efficiency, low production cost, brief fabrication process, semi-transparency, and flexibility [1–3]. Recently, a power conversion efficiency (PCE) of 14.3% in a co-sensitized solar cell with a cobalt (II/III) complex redox electrolyte solution and graphene nanoplates as a counter electrode has been achieved [4]; however, DSSCs still cannot compete with Si- or inorganic semiconductor-based solar cells in the market of large-scale energy production due to insufficient PCE and reliability.

In DSSCs, photon-to-current conversion is achieved through the injection of electrons from photoexcited dyes into the conduction band of TiO₂ (the photoelectrode), a subsequent completion of dye regeneration, and a hole transportation to the counter electrode. The electrons and holes are eventually collected in the front and counter electrodes, respectively. Unlike other solar cells, in DSSCs, an n-type semiconductor (TiO₂) electrode is in direct contact with the hole conductor (electrolyte). This causes the back electron transfer between the photoinjected electrons and ions in the electrolyte, leading to a reduction in the photovoltaic performance. To reduce the back electron transfer, metal oxides have been coated

using their precursor on the surface of TiO₂ photoelectrodes [5–10]. In addition, organic/inorganic acids, insulating/semiconducting blocking layer, and coadsorbates have also been incorporated on the photoelectrodes to get a higher PCE of DSSCs [11]. Among various surface modifiers, TiCl₄ is one of the most effective materials [12,13]. The treatment of TiCl₄, which eventually converts to TiO₂ due to sintering, leads to an increase in the PCE, which results from an improvement in electron injection efficiency and a reduction of the recombination rate. It has also been reported that a CaO overlayer on the nanoporous TiO₂ electrode can also increase the photovoltaic performance by slowing down the back electron transfer [7].

In this study, a TiO₂:CaO mixed overlayer as a surface modifier was incorporated onto the TiO₂ surface to reduce the back electron transfer in DSSCs. The TiO₂ films were immersed in a mixed solution of TiCl₄ and CaCl₂ and then sintered to produce the mixed overlayer. DSSCs with the surface-modified photoelectrodes were fabricated, and their photovoltaic properties were compared to those of a reference device with a TiO₂-only overlayer.

Experimental

Materials

Commercial fluorine-doped tin oxide (FTO; sheet resistance ~7 Ω/square) glass (TCO22-7), TiO₂ pastes for the photoelectrodes (Ti-nanoxide T/SP), N719 dye (Ruthenizer 535-bisTBA), hot melt adhesive (SX1170-60PF, Surlyn), and an iodide-based electrolyte

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(AN-50) were purchased from Solaronix. TiCl_4 and CaCl_2 (Sigma-Aldrich) were selected as precursor materials of the surface modifier. Platinum paste (PT-1, Dyesol-Timo) was selected as a source for Pt counter electrodes. All chemicals were used without any further purification.

Fabrication of DSSCs

To prepare working electrodes, FTO glasses were cleaned in a detergent solution by sonication for 20 min and then thoroughly rinsed with deionized water and ethanol. An active TiO_2 layer, which formed on the FTO glass (TiO_2/FTO), was prepared via a doctor-blade coating of the TiO_2 paste, followed by a calcination process at 500°C for 60 min. The bare TiO_2/FTO photoelectrodes were soaked in a mixed aqueous solution (40 mM) of TiCl_4 and CaCl_2 with various molar ratios of 10:0, 7:3, 5:5, 3:7, and 0:10 at 70°C for 30 min. This was followed by washing with deionized water and then sintering at 500°C for 60 min to produce the surface-modified photoelectrodes, i.e., $\text{Ti:Ca}(10:0)$ -, $\text{Ti:Ca}(7:3)$ -, $\text{Ti:Ca}(5:5)$ -, $\text{Ti:Ca}(3:7)$ -, and $\text{Ti:Ca}(0:10)$ - TiO_2/FTO , respectively. All solutions for surface modification were prepared prior to use. The surface-modified photoelectrodes were separately immersed in a 0.5 mM N719 solution (in acetonitrile/*tert*-butanol, volume ratio of 1/1) for 24 h to obtain working electrodes.

To prepare counter electrodes, two holes were formed in the FTO glass with a drill, and then they were cleaned using the method described above. A Pt layer was formed on the FTO glass via a doctor-blade method using Pt paste followed by a calcination process at 400°C for 30 min. Thermally treated platinum counter electrodes were placed on the photoelectrodes and sealed with a $60\ \mu\text{m}$ -thick sealing material. The electrolyte was introduced into the cells through one of the two small holes drilled on the counter electrodes to give DSSCs with $25\ \text{mm}^2$ active area.

Measurements

X-ray photoelectron spectroscopy (XPS) was performed using VG Multilab ESCA 2000 (ThermoVG scientific) with $\text{Mg K}\alpha$ radiation. The C 1s photoelectron peak (binding energy at 284.6 eV) was used as an energy reference. The photocurrent-voltage measurement was performed using a CompactStat (Ivium Technologies B.V.) and a PEC-L01 solar simulator system (equipped with a 150W xenon arc lamp, Peccell Technologies, Inc.). Light intensity was adjusted to 1 sun ($100\ \text{mW}/\text{cm}^2$) with a silicon photodiode (model PEC-SI01, Peccell Technologies, Inc.). The UV–vis absorption spectra were obtained from a SINCO NEOSYS-2000 spectrophotometer. Electrochemical impedance spectroscopy (EIS) was performed using an electrochemical analyzer (CompactStat, Ivium Technologies B.V.). The active areas of the dye-adsorbed TiO_2 films were estimated using a digital microscope camera (OLYMPUS SZ61) with image analysis software.

Results and discussion

Performance variations with a ratio of TiCl_4 and CaCl_2

To incorporate the overlayer composed of both TiO_2 and CaO , bare TiO_2 films (photoelectrodes) were soaked in a $\text{TiCl}_4:\text{CaCl}_2$ mixed aqueous solution, and then sintered. As a result of sintering, the precursors adsorbed on the TiO_2 surface were converted to their metal oxide forms, i.e., TiO_2 and CaO in this case [7,12,13]. To confirm the incorporation of Ca, an XPS measurement was conducted; however, for the TiO_2 film dipped in a CaCl_2 solution for 30 min at 70°C , the peaks attributed to Ca were not detected. This could have occurred because the concentration of Ca on the TiO_2 surface is below the detection limit of the XPS instrument.

Thus, the XPS spectra for the Ca that was introduced on the TiO_2 surface were provided by dipping it in the CaCl_2 solution for 6 h at 70°C . Fig. 1 compares the XPS spectra measured from the photoelectrode with $\text{Ti:Ca}(10:0)$ - and $\text{Ti:Ca}(0:10)$ - TiO_2/FTO . Unlike the $\text{Ti:Ca}(10:0)$ - TiO_2/FTO electrode, the peaks detected at 347.14 and 350.75 eV agreed with the $2p_{3/2}$ and $2p_{1/2}$ binding energies in Ca, respectively, indicating the existence of Ca on the TiO_2 surface.

The DSSCs with the surface-modified photoelectrodes were fabricated, and their photovoltaic properties were characterized. The resulting photovoltaic properties of the DSSCs as a function of CaCl_2 content in the mixed solution are presented in Fig. 2. As can be seen from Fig. 2(a), the J_{sc} value was improved due to the incorporation of both TiO_2 and CaO on the photoelectrode surface compared to the device with a TiO_2 - or CaO -only overlayer. The V_{oc} values were also increased with increasing the content of CaCl_2 in the mixed precursor solution, as shown in Fig. 2(b). The fill factor (FF) values were slightly increased when the CaCl_2 content was over 70 mol%.

Because the PCE exhibited the highest value when the TiO_2/FTO electrode was modified with the mixed solution with a molar ratio of 3:7 ($\text{TiCl}_4:\text{CaCl}_2$), the device with the $\text{Ti:Ca}(3:7)$ - TiO_2/FTO electrode as well as the reference device with $\text{Ti:Ca}(10:0)$ - TiO_2/FTO , i.e., a TiO_2 -only overlayer, were the primary focuses.

Effects of the mixed overlayer on J_{sc}

Fig. 3 shows the current density (J) and voltage (V) curves of the DSSCs with $\text{Ti:Ca}(10:0)$ - TiO_2/FTO and $\text{Ti:Ca}(3:7)$ - TiO_2/FTO electrodes, and the device performance is compared in Table 1. The overall PCE of the cell increased from 5.54% for $\text{Ti:Ca}(10:0)$ - TiO_2/FTO to 6.48% for $\text{Ti:Ca}(3:7)$ - TiO_2/FTO , corresponding to an improvement of about 17%. The enhanced PCE in the DSSCs with $\text{Ti:Ca}(3:7)$ - TiO_2/FTO was caused by an increase in all parameters, including J_{sc} , V_{oc} , and FF .

By introducing the mixed overlayer, J_{sc} increased from 12.49 to $13.66\ \text{mA}/\text{cm}^2$ (Table 1), corresponding to a contribution of around 57% to the enhancement in PCE. It is necessary to clarify the origin of this enhancement in J_{sc} . The J_{sc} value is generally influenced by four efficiency factors, as shown in Eqs. (1) and (2), i.e., light harvesting (LHE), electron injection (Φ_{inj}), dye-regeneration (Φ_{reg}), and electron collection (Φ_{coll}) efficiency of the injected electrons to the transparent electrode [14].

$$J_{sc} = \int \text{IPCE}(\lambda) e \Phi_{ph,AM1.5G}(\lambda) d\lambda \quad (1)$$

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda) \Phi_{inj}(\lambda) \Phi_{reg} \Phi_{coll}(\lambda) \quad (2)$$

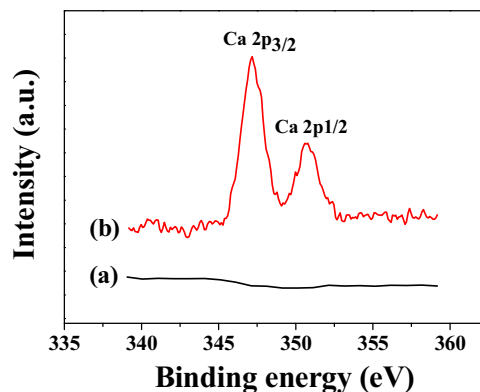


Fig. 1. XPS spectra measured from (a) $\text{Ti:Ca}(10:0)$ - TiO_2/FTO and (b) $\text{Ti:Ca}(0:10)$ - TiO_2/FTO electrodes.

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