

Transparent conductive oxide layer-less dye-sensitized solar cells consisting of floating electrode with gradient TiO_x blocking layer

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A transparent conductive oxide less dye-sensitized solar cell (TCO-less DSC) consisting of a glass/a floating electrode (FE)/a stained nanoporous titania layer/a gel electrolyte sheet/a Pt layer/a Ti sheet is reported. The FE is composed of a stainless mesh sheet covered with a gradient TiO_x layer, which suppressed back-electron transfers from the stainless to electrolytes. The efficiency increased from 2.87% to 4.68% by replacing a conventional dense TiO_2 blocking layer with the gradient TiO_x layer. The cell in this architecture gave the efficiency of 5.56% after optimization. © 2009 American Institute of Physics. [DOI: 10.1063/1.3089845]

Dye-sensitized solar cells (DSCs) have shown their competence as one of the potential candidates for the next generation solar cell.¹ Reproducible efficiency of the DSC reaching 11% has paralleled them in the category of amorphous Si solar cells.²⁻⁴ A transparent conductive oxide-less (TCO-less) DSC consisting of a back-contacted Ti electrode has been reported recently⁵⁻⁷ aiming toward the reduction of the DSC production cost. These Ti electrodes are fabricated on nanoporous TiO_2 layers by sputtering or vacuum deposition. A TCO-less DSC where a stained porous titania layer is fabricated on a stainless mesh electrode, has been shown in Fig. 1.^{8,9} Since the electrode is inserted into space between a counterelectrode and a glass substrate (or a plastic substrate), we denote this titania electrode as “a floating electrode (FE)” in this letter. Fan *et al.* have also reported the DSC based on stainless mesh electrode, however, the efficiency was quite low (1.49%).⁸

One of these reasons behind the decreased efficiency of the DSC based on the stainless mesh electrode was cracking of the dense TiO_2 layer [charge-recombination-blocking layers (CRBL)] when they were subjected to baking at 450–500 °C. Thermal expansion coefficient of the stainless steel is $16.0 \times 10^{-6}/^\circ\text{C}$, which is about two times larger than that of the dense TiO_2 ($7.7 \times 10^{-6}/^\circ\text{C}$).^{10,11} This difference in these thermal expansion coefficients is actually responsible for the cracking of the CRBL. The aim of the present report is to propose a structure of the CRBL layer, which effectively blocks the back-electron transfers from the stainless metal to the electrolyte.

Figure 2 exhibits a stainless mesh structure bearing an electron-blocking layer. Ti was first deposited on a stainless mesh sheet (SUS316, diameter of 25 μm and space between two stainless wires is 25 μm) using a high-rate sputtering apparatus (ULVAC SH-250-T04, room temperature, 100 W, 40 min). Thickness of the prepared Ti layer was 200 nm (S-Ti, B in Fig. 2). The Ti sputtered mesh sheet was then protected with a TiO_x layer (200 nm thick, PAD- TiO_x) using an arc plasma deposition apparatus (ULVAC APG-1000, 3.4

kV, 200 μA , shot 1000 pulse at room temperature, C in Fig. 2) using Ti metal as the target. The arc-plasma deposition occurs by reacting vaporized Ti with oxygen in the chamber to form TiO_x layers (PAD- TiO_x), where x can be varied by the oxygen pressure in the chamber.¹² The stainless mesh covered with the S-Ti and the PAD- TiO_x is abbreviated as stainless- TiO_x (Fig. 2). Precise experimental conditions on the arc-plasma deposition have been reported previously.¹²⁻¹⁶ A stainless mesh covered with a dense TiO_2 layer [stainless- TiO_2 (conventional CRBL)] was prepared by dipping the titania mesh sheet into ethanol solution of tetra-propoxytitanium, followed by baking the sheet at 450 °C for 30 min.

A DSC consisting of a stainless mesh electrode protected with a dense TiO_x (DSC-stainless- TiO_x) was fabricated as follows. Ti-Nanoxide DSP paste (Solaronix SA) was coated on the mesh substrate by a doctor blade method, followed by its baking at 450 °C. It was then stained with *cis*-bis-(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutyl ammonium (Solaronix SA, Ruthenium 535-bisTBA abbreviated as N719, $3 \times 10^{-4}\text{M}$ in *t*-butylalcohol and acetonitrile (1:1 vol/vol). A Pt sputtered Ti sheet was employed as the counterelectrode. A porous polymer film (Membrane filter, Poreflon HP-045-30, Sumitomo Electric Fine Polymer INC., thickness of 30 μm) was

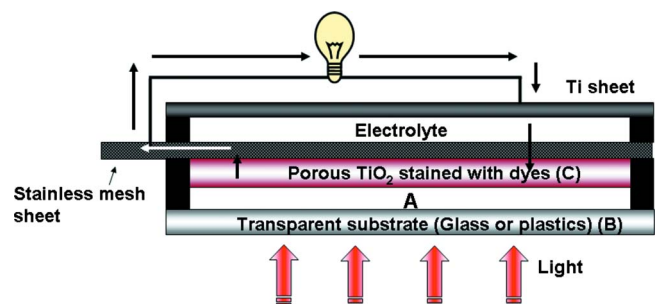


FIG. 1. (Color online) Schematic diagram of DSC architecture consisting of floating stainless steel mesh electrode. Here C actually contacts B. However, an area A is drawn in order to stress that the C is a floating electrode and the C is not glued with B.

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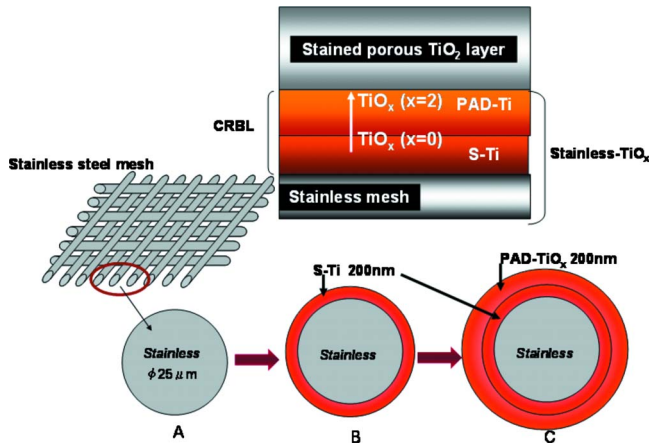


FIG. 2. (Color online) Fabrication process and structure of stainless- TiO_x . The S-Ti shows a sputtered Ti layer while PAD- TiO_x and CRBL represents an arc-plasma deposited TiO_x , and a charge recombination blocking layer, respectively.

soaked with an electrolyte solution consisting of 500 mM LiI, 50 mM I_2 , 580 mM *t*-butylpyridine, and 600 mM methylethylimidazoliumdicyanoamide in acetonitrile. The polymer film holding the electrolyte was inserted between the counter electrolyte and the stainless mesh anode. The film acts as a gel electrolyte and a spacer. Photoelectrochemical measurement was performed using a solar simulator (YSS-50A, Yamashita Denso Co. Ltd., AM 1.5, 100 mW/cm^2). The cell size was 0.25 cm^2 and a mask was used during the measurement of the solar cell performance. The exposed area was precisely recalculated by using photograph.

Figure 3 shows scanning electron microscopic (SEM) photographs of stainless- TiO_2 or stainless- TiO_x after their baking at 450 $^\circ\text{C}$. A perusal of Fig. 3(a) clearly corroborates that the dense TiO_2 layer of the stainless- TiO_2 peeled off because of the difference in the thermal expansion coefficient between the stainless metal and the dense thin TiO_2 layer. However, the stainless- TiO_x was not damaged by baking as shown in Fig. 3(b). Stoichiometry of Ti and O of the TiO_x layer can be varied depending on the pressure of oxygen in an arc-plasma chamber. The compositional analysis of the TiO_x layer using an Auger electron spectroscopy (ULVAC PHI-700) provided the stoichiometric composition of $\text{TiO}_{1.01}$ under 3.8×10^{-4} Pa, $\text{TiO}_{1.61}$ under 4.2×10^{-3} Pa, $\text{TiO}_{1.65}$ under 4.0×10^{-2} Pa, and $\text{TiO}_{1.8}$ under 1.6×10^{-1} Pa of oxygen pressure in the chamber. The x of the TiO_x layer increased from 0 (Ti metal) of the bottom layer to 2 (TiO_2) of

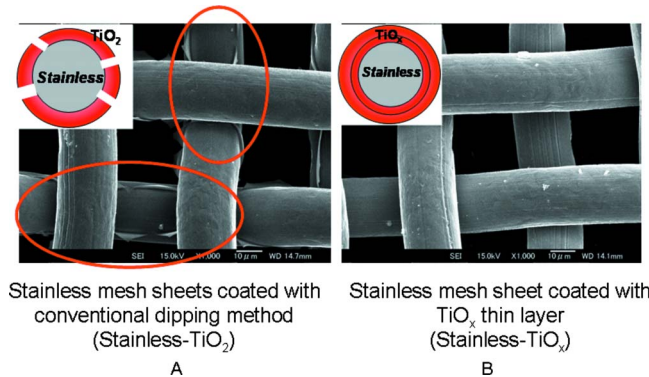


FIG. 3. (Color online) SEM micrographs of titania or TiO_x protected stainless mesh electrodes after its baking at 450 $^\circ\text{C}$.

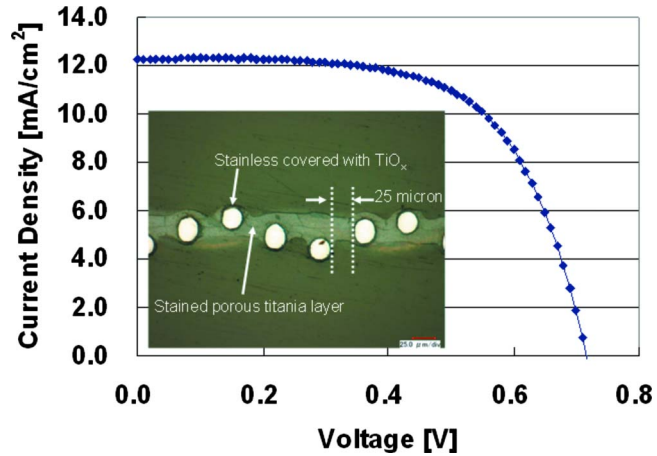


FIG. 4. (Color online) Photovoltaic performances of optimized cell based on DSC-stainless- TiO_x architecture under 100 mA/cm^2 simulated solar irradiation at AM 1.5. Active area after recalibration is 0.21 cm^2 . Inset: SEM cross section image of stainless- TiO_x /stained porous titania electrode.

the surface layer as shown in Fig. 2. Thermal expansion coefficients also varied gradually from $16.0 \times 10^{-6}/^\circ\text{C}$ of stainless, $8.4 \times 10^{-6}/^\circ\text{C}$ of Ti to $7.7 \times 10^{-6}/^\circ\text{C}$ of TiO_2 . The gradient structure of the TiO_x layer relieves the thermal stress caused by the difference in the thermal expansion coefficient between the stainless and the porous TiO_2 layer, leading to prevention of the CRBL from cracking.

The solar cell was fabricated by simply assembling a glass substrate without TCO, a stainless- TiO_x , an electrolyte film, and a counter Ti electrode with Pt catalyst. A SEM image of the cross section of the mesh electrode shows that the gap between the stainless wires was filled with titania nanoparticles, as shown in an inset of Fig. 4. It can be clearly seen from the Table I that all of J_{sc} , V_{oc} , fill factor (ff), and the efficiency for the DSC-stainless- TiO_x were better than those for the DSC-stainless- TiO_2 and the DCS without the CRBL. It can be explained by better suppression of back-electron transfer from the metal electrode to the electrolyte in the presence of the S-Ti and the PAD- TiO_x layers. This explanation was further supported by lower dark currents observed for the DSC-stainless- TiO_x than those of the DSC-stainless- TiO_2 and the DSC without the CRBL. We would like to emphasize here that photovoltaic performances of the DSC consisting of the stainless mesh electrode covered with the S-Ti only and the PAD- TiO_x only were 3.85% (ff of 0.59, V_{oc} of 0.75 V, and J_{sc} of 8.75 mA/cm^2) and 3.42% (ff of 0.52, V_{oc} of 0.67 V, J_{sc} of 9.82 mA/cm^2), respectively, which suggests the importance of the presence of both of the S-Ti and the PAD- TiO_x layers as indicated by the photovoltaic performance of the DSC-stainless- TiO_x . Figure 4 shows one of our best results after optimization giving J_{sc} , V_{oc} , ff, and efficiency as 12.26 mA/cm^2 , 0.72 V, 0.63, and

TABLE I. Photovoltaic performances of DSCs consisting of floating electrodes.

DSC structure	J_{sc} (mA/cm^2)	V_{oc} (V)	ff	Efficiency (%)
DSC-stainless- TiO_x	9.8	0.74	0.65	4.68
DSC-stainless- TiO_2	8.43	0.66	0.52	2.87
DSC without CRBL	6.74	0.65	0.51	2.21

5.56%, respectively. We fabricated five cells and the efficiency varied from 4.37% to 5.58% (4.37%, 5.58%, 5.52%, 5.20%, and 5.56%). Four out of five cells exhibited the efficiency more than 5%, which strongly demonstrated the effectiveness of the electron collection by the floating electrode.

The DSC consisting of the floating metal electrode protected with the graded TiO_x structure provided a way for fabricating a flexible DSC with improved device performance because the floating electrode is merely inserted into two substrates and the two substrates are not suffered from high temperature damages.

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