

# Surface Modification of SnO<sub>2</sub> Electrodes for Highly Efficient Dye Sensitized Solar Cells

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## 1. Introduction

Ever since Grätzel *et al.* reported highly efficient, low-cost dye-sensitized solar cells (DSCs) using cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4''-dicarboxylate) ruthenium(II) (N719) with a photovoltaic efficiency of 11% [1], many researchers have tried to reproduce the solar cell. Many papers have been published regarding TiO<sub>2</sub> fabrication to achieve larger surface areas for dye adsorption, in which nanoparticle TiO<sub>2</sub> films [1-3] have been reported. As these surfaces with extremely large surface areas allowed for highly efficient power generation with a high density adsorption of the sensitizing dye, most researchers have been trying to achieve high density adsorption as much as possible. In a previous paper [see Ref. 4], however, we reported surface modification of the TiO<sub>2</sub> surface by a UV treatment is also effective in improving power generation, where the dye adsorption was enhanced with intentional generation of adsorption site (TiOH)[4].

In previous papers of Refs. 4 and 5, we observed the adsorption states of N719-sensitizing dye on anatase TiO<sub>2</sub> surfaces with a variety of adsorption densities using infrared absorption spectroscopy (IRAS) with a multiple-internal-reflection (MIR) geometry. It was found that chemisorbed and physisorbed dyes coexisted on the dye-adsorbed surface. We found that the ratio of the chemisorbed and the physisorbed dye densities was dependent on the exposure of the TiO<sub>2</sub> surface to N719 dye, and overexposure generated a physisorbed state. Test fabrications of DSCs with various N719 exposures suggested that the degeneration of the physisorbed N719 is effective in enhancing power generation. We discussed how to promote the power conversion efficiency of DSCs without interference of the physisorbed N719 dye in the photovoltaic operation.

As we mentioned above, we consider that there are rooms for improvement not only in the preparation of TiO<sub>2</sub> nanoparticle films, but also in modification of their interfaces. In this paper, we clearly show an effective measure for highly efficient DSCs by inserting chemical vapor deposition (CVD) grown TiO<sub>2</sub> between TiO<sub>2</sub> nanoparticle and SnO<sub>2</sub> transparent conducting films. We discuss how the interface modification with the CVD grown film works for the improvement.

## 2. Experimental

We fabricated DSCs by inserting interfacial layers of TiO<sub>2</sub> between nanoparticle and SnO<sub>2</sub> films. The schematic

is shown in Fig.1. The TiO<sub>2</sub> films were deposited on SnO<sub>2</sub>-coated glass plates by CVD [6]. Nanoparticle TiO<sub>2</sub> films with pores with a thickness of 15  $\mu$ m with an area of 0.5 $\times$ 0.5 cm<sup>2</sup> were formed on the CVD grown TiO<sub>2</sub> by a screen printing method. The TiO<sub>2</sub> paste was made from TiO<sub>2</sub> powder manufactured by Ishihara Sangyo (ST-01), deionized water, acetic acid solution with a pH of 3.5, and polyethylene glycol. The TiO<sub>2</sub> films were baked in air at a temperature of 500°C for 1 h. The N719 adsorption was performed by immersing the TiO<sub>2</sub> particle surface in N719 solution. The redox electrolyte was 0.1M LiI, 0.05M I<sub>2</sub>, 0.6M dimethyl propyl imidazolium iodide and 0.5M tert-butylpyridine in dried acetonitrile. The photovoltaic properties of the DSCs were measured using an I-V measurement system and a 5000 K-300 W-xenon lamp was used as a light source. The light intensity at the DSC surface was set at 80 mW/cm<sup>2</sup> with a standard Si solar cell manufactured by Peccell Technologies.

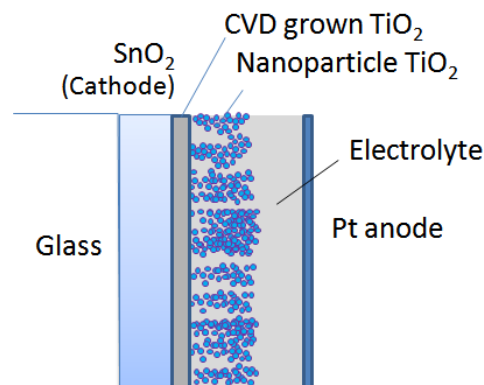


Fig. 1 Schematic of dye-sensitized solar cell with a CVD grown TiO<sub>2</sub> film.

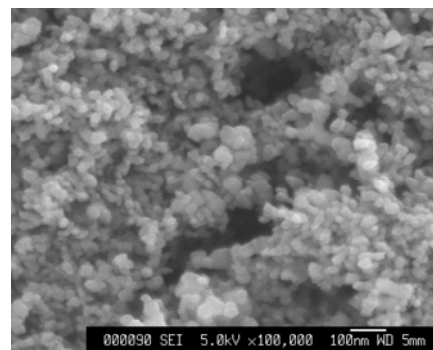


Fig. 2 SEM micrograph of nanoparticle TiO<sub>2</sub> with pores.

### 3. Results and Discussion

A typical current density-voltage characteristics obtained from DSCs with and without the TiO<sub>2</sub> interfacial layer is shown in Fig. 3. The short circuit current density (J<sub>sc</sub>), open circuit voltage (V<sub>oc</sub>) and power conversion efficiency (η) of the DSCs are summarized in Table.1. It is clear that the CVD grown TiO<sub>2</sub> interfacial layer enhanced the power conversion efficiency by 0.4 %. The short circuit current density was also improved by 0.4mA/cm<sup>2</sup>. To discuss the mechanism of the TiO<sub>2</sub> interfacial layer, we have analyzed series resistance (R<sub>s</sub>) and shunt resistance (R<sub>sh</sub>) with the characteristics. It was found that R<sub>sh</sub> was improved from 4 to 40 kΩ cm<sup>2</sup> by inserting the TiO<sub>2</sub> interfacial layer, although R<sub>s</sub> remained unchanged. This fact strongly suggests that the TiO<sub>2</sub> interfacial layer prevented the recombination of I<sub>3</sub><sup>+</sup> ion and electron on the SnO<sub>2</sub> surface.

To discuss why the prevention of the recombination enhances J<sub>sc</sub>, we constructed a simplified nanoporous TiO<sub>2</sub> electrode model as shown in Fig. 4. This illustrates flows of I<sub>3</sub><sup>-</sup> and I<sup>-</sup> ions between the nanoporous TiO<sub>2</sub> electrodes. When the sun light induces to N719 dye, electron and hole are generated. Holes oxidize I<sup>-</sup> ions to generate I<sub>3</sub><sup>-</sup> ions. If I<sub>3</sub><sup>-</sup> ions flow to the Pt anode, power generation takes place. However, if electrons and I<sub>3</sub><sup>-</sup> ions are recombined with each other at the surface of SnO<sub>2</sub>, a reverse flow of the I<sub>3</sub><sup>-</sup> ion might appear. This reverse flow would deteriorate the short circuit current density.

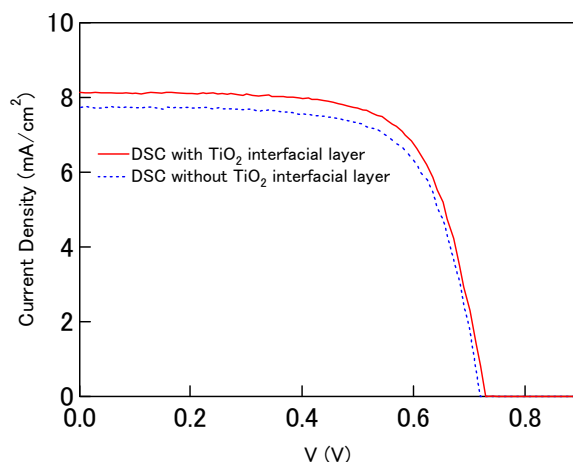


Fig. 3 I-V characteristics obtained from DSCs with and without a TiO<sub>2</sub> interfacial layer.

Table 1 Summary of electrical characterization of DSCs with and without a TiO<sub>2</sub> interfacial layer.

Sample	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	η (%)
With TiO <sub>2</sub> interfacial layer	8.13	0.72	4.8
No TiO <sub>2</sub> interfacial layer	7.73	0.71	5.2

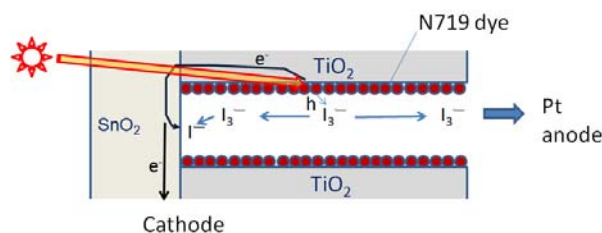


Fig. 4 Schematic illustrating I<sub>3</sub><sup>-</sup> and I<sup>-</sup> ion flows between porous nanoparticle TiO<sub>2</sub> electrodes.

We have obtained a result supporting the above explanation; variation of J<sub>sc</sub> as a function of thickness of the porous TiO<sub>2</sub> nanoparticle electrode. The result is shown in Fig.5. The TiO<sub>2</sub> interfacial layer is effective to suppress the variation of J<sub>sc</sub>. If the porous TiO<sub>2</sub> nanoparticle electrode becomes thinner without the interfacial layer, the negative flow of the I<sub>3</sub><sup>-</sup> ion to SnO<sub>2</sub> may occur, where the impact of the recombination of electrons and I<sub>3</sub><sup>-</sup> ion on J<sub>sc</sub> must be larger. The suppression of the variation suggests that the interfacial layer plays a role to limit the consumption of I<sub>3</sub><sup>-</sup> ions at the SnO<sub>2</sub> surface, where it might enhance the flow of I<sub>3</sub><sup>-</sup> ions toward the Pt anode and J<sub>sc</sub> might be improved.

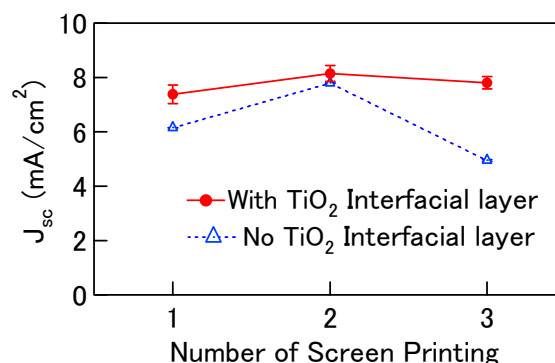


Fig. 4 Variation of short circuit current density as a function of thickness of the porous TiO<sub>2</sub> nanoparticle electrode. The thicknesses at the screen-printing numbers of 1,2 and 3, are 7.4,15.5 and 23.0 μm, respectively.

### 3. Conclusions

We successfully demonstrated that the interface modification of SnO<sub>2</sub> electrode with CVD grown TiO<sub>2</sub> promotes the power generation in DSCs. The CVD grown TiO<sub>2</sub> interfacial layer prevents the recombination of electron and I<sub>3</sub><sup>-</sup> ion on SnO<sub>2</sub> surface.

### References

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