

# High efficiency 3D dye sensitized solar cells and the nano-surface control.

Shuzi Hayase

Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology,  
2-4 Hibikino, Wakamatsu-ku, Kitakyushu 808-0196

**ABSTRACT:** Dye-sensitized solar cells consisting of tandem and hybrid structures are reported. It was proved that these new structures have a potential to harvest light with wide range of wavelength and increase open circuit voltage. In addition, modification of charge separation interfaces with organic molecules and dyes are discussed in terms of trap passivations which bring about high efficiency.

## 1. INTRODUCTION

Since O'Regan and Grätzel reported dye-sensitized solar cells (DSCs) with a relatively high photoconversion efficiency, DSCs have emerged as potential candidates for next-generation solar cells [1]. The efficiency of the DSC is reported to be 10.4 % (DSC with active area of more than 1 cm<sup>2</sup>) which is almost the same as that of amorphous Si solar cells. However, the efficiency was still lower than those of other solar cells. To parallel the efficiencies of crystalline silicon-based solar cells, further improvement of the efficiency is desired. In order to increase the efficiency, we focus on light harvesting properties and electron collection properties. In this report, directions to high efficiency cells as well as cost-effective cells are discussed in terms of cell structures and nano-surface modification.

## 2. TRANSPARENT CONDUCTIVE OXIDE LAYER-LESS DSC (TCO-LESS DSC)

### 2.1 TCO-LESS DSC WITH POROUS Ti ELECTRODE

TCO-less DSCs have attracted interest because these FTO-glasses are expensive [2-4]. In addition, solar light reaches a titania/dye layer effectively because a TCO glass has light absorption in the range of visible and IR. Figure 1 shows the comparison of a TCO-less DSC and a conventional TCO-DSC. Electrons are collected by a TCO layer in the TCO-DSC and by a Ti electrode layer in the TCO-less DSC. Kroon et al. have reported a TCO-less DSC [2]. Instead of the TCO layer, they fabricated a secondary metal electrode on the porous TiO<sub>2</sub> layer and have reported 3.6%

efficiency without any precise description in their review article [2]. Fuke et al., have

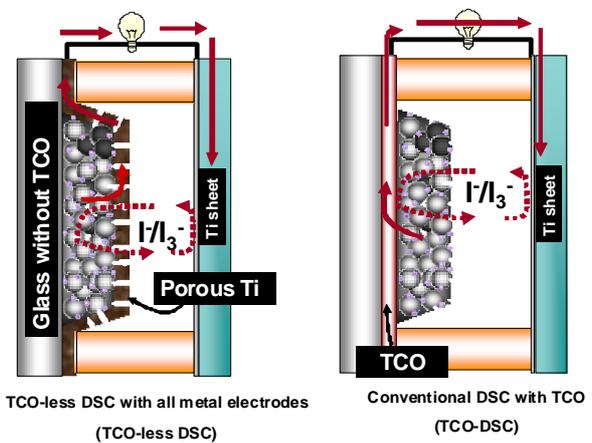


Figure 1. Structure of TCO-less DSC and TCO-DSC

reported a TCO-less DSC structure named “back contact DSC” [3, 4]. They used a vacuum evaporation process to prepare the Ti electrode and reported an efficiency of 8.4 %.

Both high conductivity and high diffusion of

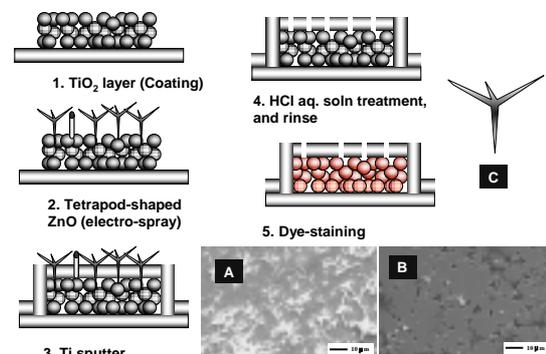


Figure 2. Fabrication of porous Ti electrode on titania layer

A: Before HCl treatment, B: After HCl treatment, C: Tetrapod shaped ZnO

ions passing through the Ti electrode are required for the Ti electrode, because I<sup>-</sup> diffuses

from a counter electrode to a titania/dye layer through the Ti electrode. Figure 2 shows the preparation process of the nano-porous Ti electrode fulfilling the requirement. Tetrapod-shaped ZnO was used as a sacrifice material for the ionic path. Figure 3 shows the relationship between the thickness of the Ti electrode and the photoconversion efficiency. The efficiency of the DSC-Porous-Ti increased as the Ti thickness increased. However, in the case of DSC-Dense-Ti which was prepared without these ZnO particles, the efficiency decreased as the thickness increased. In order to make a thick and porous Ti electrode layer,

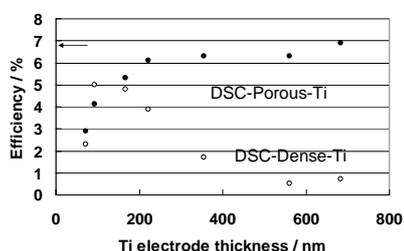


Figure 3. Relationship between Ti electrode thickness and efficiency for DSC with porous Ti or dense Ti.

DSC-Porous-Ti: DSC consisting of a porous Ti electrode, DSC-Dense-Ti: DSC consisting of a dense Ti electrode. An arrow stands for an efficiency of a TCO-DSC. Electrolyte: LiI:500mM, TBP:580mM, I<sub>2</sub>:50mM, EMImDCA:600mM in Acetonitrile, 0.25 cm<sup>2</sup> cell. AM 1.5, masked. Active area was corrected by a photograph.

sacrifice materials such as tetrapod-shaped ZnO particles were essential. We have already reported that ionic diffusions in straight ion paths were much faster than those of curved ionic paths [5]. Tetrapod-shaped ZnOs have four hands which always penetrate the Ti layer at any conditions and link the porous titania layer with the electrolyte layer. When the Ti electrode thickness was more than 300 nm, the efficiency became almost the same as that of a TCO-DSC (an arrow in Figure 3). One of our best results of the TCO-less DSC was 7.98 %.

## 2.2 TCO-LESS DSC WITH FLOATING ELECTRODE

A TCO-less DSC, where a porous titania/dye layer is fabricated on a stainless mesh electrode, was shown in Figure 4 [6,7]. Since the electrode is inserted into space between a counter electrode and a glass substrate (or a plastic substrate), we denote this titania electrode as “a floating electrode (FE)” in this report. Fan *et al* have reported a DSC based on a stainless mesh electrode, however,

the efficiency was quite low (1.49%) [6]. They employed a dense and thin TiO<sub>2</sub> layer as a charge-recombination-blocking layer (CRBL) which is commonly used for DSCs. The CRBL protects the surface of the stainless mesh metal in order to suppress the back electron transfer

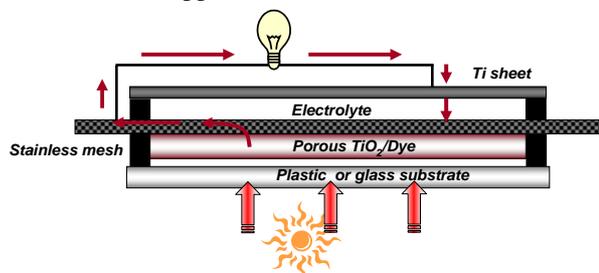


Figure 4. DSC consisting of floating electrode

from the metal to an electrolyte. The conventional thin TiO<sub>2</sub> layer did not work effectively as the CRBL. We found that a new CRBL consisting of a gradient structure of TiO<sub>x</sub> works well as the CRBL, where x was changed gradually from 0 to 2, namely Ti metal layer to TiO<sub>2</sub> layer. The floating electrode (FE) was prepared by coating a titania particle paste on the stainless mesh sheet covered with the TiO<sub>x</sub> CRBL layer, followed by baking at 450 °C. Dye (N719) was adsorbed on the porous titania layer.

The DSC consisting of FE was prepared simply by inserted the FE between a Ti counter electrode and a glass or a plastic sheet. It can be clearly seen in Figure 5 that all of J<sub>sc</sub>, V<sub>oc</sub>, ff

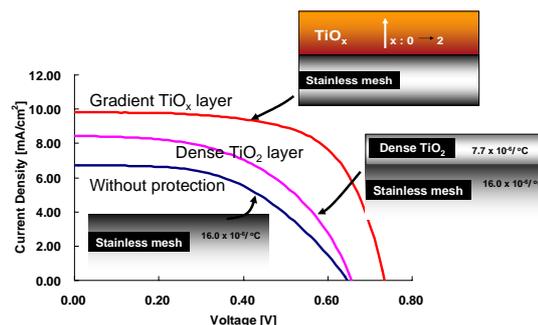


Figure 5. Photovoltaic performances of DSCs consisting of floating electrode

and efficiency for the DSC consisting of the gradient TiO<sub>x</sub> CRBL were better than those for the DSC consisting of a dense TiO<sub>2</sub> CRBL (a conventional CRBL) and a DCS without the CRBL. It can be explained by better suppression of back electron transfers from the metal electrode to the electrolyte in the presence of the TiO<sub>x</sub> CRBL. One of our best

results after optimization gives  $J_{sc}$ ,  $V_{oc}$ ,  $ff$  and efficiency as  $12.26 \text{ mA/cm}^2$ ,  $0.72 \text{ V}$ ,  $0.63$ , and  $5.56\%$ , respectively.

### 3. HYBRID CELLS AND TANDEM CELLS

Conventional Ru dyes absorb the light from 400 to 800 nm. If all of these photons are converted to electrons, short circuit current ( $J_{sc}$ ) of  $23.0 \text{ mA/cm}^2$  is expected. Supposing that fill factor (FF) is  $0.75$  and open circuit voltage ( $V_{oc}$ ) is  $0.75 \text{ V}$  (ideally  $0.9 \text{ V}$ ), photoconversion efficiency of  $12.9 \%$  is expected. If DSC absorbs light from 400- 900 nm,  $J_{sc}$  of  $29 \text{ mA/cm}^2$  and  $16.3 \%$  efficiency are expected. Supposing that light loss caused by the surface refraction of a glass substrate and by light absorption of a transparent conductive oxide layer (TCO) are  $15 \%$ ,  $13.9 \%$  efficiency is expected for the latter case (400-900 nm).

DSCs prepared by adsorbing dye mixtures covering a short wavelength and a long wavelength are called cocktail-type DSCs and are expected to cover a wide range of wavelengths [10-15]. A crucial concern for the cocktail-type adsorption is that unfavorable interactions between neighboring dye molecules often lead to a decrease in photovoltaic performance. We proposed a dye-bilayer DSC shown in Figure 6 [16]. It

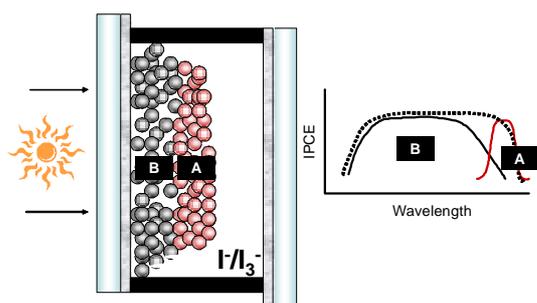


Figure 6. Dye-bilayer DSC

was difficult to stain the titania layer portion-selectively in a conventional dipping condition. We found that the selective dye-staining was able to be carried out in a pressurized  $\text{CO}_2$  condition. In the pressurized  $\text{CO}_2$  condition, the dye adsorption occurred from the top to the bottom of the titania layer because the titania nanoparticle surface is activated by carbon dioxide under the pressurized condition [16]. The model cell

was fabricated with using black dye (BD, Solaronix SA) covering 450-800 nm and NK3705 (Hayashibara) converting 400-450 nm. To begin with, a titania substrate on a TCO-less glass was stained with BD under the pressurized  $\text{CO}_2$  condition to obtain the titania substrate, where a half top of the titania layer was stained with the BD. The half bottom of the unstained titania layer was stained with NK3705 under a dipping condition. The double dye-layer was observed clearly by a confocal laser scanning microscope. The IPCE curve of the dye-bilayer DSC was the sum of that of the single cell stained with the BD and

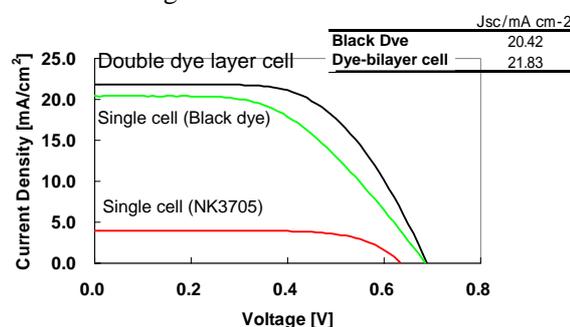


Figure 7. Photovoltaic performances for double dye layer cell and the corresponding single cell stained by each dye. Electrolyte: LiI:500mM, TBP:580mM, I2:50mM, EMImDCA:600mM in Acetonitrile,  $0.25 \text{ cm}^2$  cell. AM 1.5, masked. Active area was corrected by a photograph.

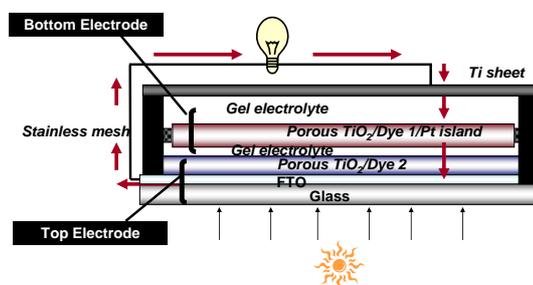


Figure 8. Tandem cells consisting of floating electrode as bottom electrode and TCO-electrode as top electrode

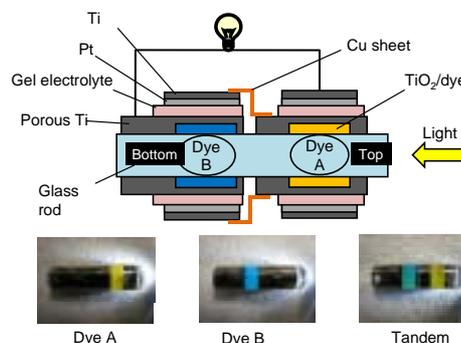


Figure 9. Tandem cells consisting of fiber DSC

that stained with the NK3705.  $J_{sc}$  of the double dye layer cell was higher than that of the single cell stained with the BD or that stained with the NK3705 as shown in Figure 7. These results strongly demonstrate that the double dye layer cell has a potential to cover wide ranges of wavelength without causing an unfavorable interaction between two dye molecules. In addition, photovoltaic performances of new tandem cells showing in Figures 8 and 9 would be presented in the presentation.

#### 4. $V_{oc}$ FROM THE POINT OF SURFACE POTENTIAL VIEW[17]

Overall photoconversion efficiency of a DSC is basically controlled by the short-circuit current density ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ) and fill factor.  $V_{oc}$  plays an important role in determining the photoconversion efficiency and is determined by the difference in the quasi-Fermi level of  $TiO_2$  and potential of  $I_3^-/I^-$  redox couple in DSC. We focused on the relative change of a conduction band level of titania caused by dipole moment of dye molecules adsorbed on the titania because differential shifting of  $TiO_2$  conduction band (CB) edge upon treatment of  $TiO_2$  surface by organic carboxylic and phosphonic acids has been reported by Rühle et al [18]. Our results implied that there is formation of different kind of dye dipoles at  $TiO_2$ /dye interface upon dye adsorption leading to differential nature of band alignments. Ruthenium dye having relatively positive shift in the dye surface potential compared to that of a bare  $TiO_2$  surface shifts the  $TiO_2$  local vacuum level and CB edge towards more negative potential leading to higher observed  $V_{oc}$ .

#### 5. CONCLUSION

Directions to high efficiency DSCs were proposed from the view point of charge collection and light harvesting. Floating electrodes and porous Ti electrodes were proved to collect electrons efficiently. These electrodes are useful for fabrication of TCO-less DSCs aiming at economical cells and high efficiency cells. New hybrid and tandem cells using these electrodes were reported. It

was proved that these structures have a potential to harvest light with wide range of wavelengths. Dipole moment of dye molecules is expected to one of the items for improving  $V_{oc}$ . In order to realize a high efficiency DSC, development of dyes absorbing light sharply in the range from 800 to 900 nm are required.

#### REFERENCES

1. B. O'Regan and M. Grätzel: Nature 353 (1991) 737.
2. J. M. Kroon, N. J. Bakker, H. J. P. Smit, P. Liska, K. R. Thampi, P. Wang, S. M. Zakeeruddin, M. Graetzel, A. Hinsch, S. Hore, U. Wurfel, R. Sastrawan, J. R. Durrant, E. Palomares, H. Pettersson, T. Gruszecki, J. Walter, K. Skupien, and G. E. Tullloch: Prog. Photovolt. Res. Appl. 15 (2007) 1.
3. N. Fuke, A. Fukui, Y. Chiba, R. Komiya, R. Hamanaka, and L. Han: Jpn. J. Appl. Phys. 46 (2007) L420.
4. N. Fuke, A. Fukui, R. Komiya, A. Islam, Y. Chiba, M. Yanagida, R. Yamanaka, and L. Han: Chem. Mater. 20 (2008) 4974.
5. T. Kato, and S. Hayase: J. Electrochem. Soc. B. 154 (2007) 112.
6. X. Fan, F. Wang, Z. Chu, L. Chen, C. Zhang, and D. Zou: Appl. Phys. Lett. 90 (2007) 073501.
7. N. Namba, A. Kadota, Japanese Patent Application, P2001-283944A.
8. K. Miettunen, J. Halme, M. Toivola, and P. Lund, J. Phys. Chem. C 112 (2008) 4011.
9. J. Ramier, N. Da Costa, C. J. G. Plummer, Y. Leterrier, J. -A. E. Månson, R. Eckert, R. Gaudiana : Thin Solid Films 516 (2008) 1913.
10. J.-H. Yum, S.-R. Jang, P. Walter, T. Geiger, F. Nuesch, S. Kim, J. Ko, M. Graetzel, and M. K. Nazeeruddin: Chem. Commun. (2007) 4680.
11. A. Ehret, L. Stuhi, and M. T. Spitler: J. Phys. Chem. B 105 (2001) 9960.
12. K. Sayama, S. Tsukagoshi, T. Mori, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga, and H. Arakawa: Sol. Energy Mater. Sol. Cells 80 (2003) 47.
13. Y. Chen, Z. Zeng, C. Li, W. Wang, X. Wang, and B. Zhang: New J. Chem. 29 (2005) 773.
14. V. P. S. Perera, P. K. D. D. P. Pitigala, M. K. I. Senevirathne, and K. Tennakone: Sol. Energy Mater. Sol. Cells 85 (2005) 91.
15. J. He, H. Lindström, A. Hagfeldt, and S.-E. Lindquist: Sol. Energy Mater. Sol. Cells 62 (2000) 265.
16. S. Sakaguchi, S. S. Pandey, K. Okada, Y. Yamaguchi, and S. Hayase: APEX. 1 (2008) 105001.
17. N. R. Neale, N. Kopidakis, J. van de Lagemaat, M. Gratzel and A. J. Frank: J. Phys. Chem. B. 109 (2005) 23183.