

Dye sensitized solar cells - Present and future -

Shuzi Hayase (Kyushu Institute of Technology)

1. Introduction

Market of solar cells is growing sharply and the growing rate reached one and a half times each year. Most of the market is occupied with crystal Si-based solar cells including micro-crystalline Si, however, new types of solar cells, such as CdTe-based solar cells and CIGS-based solar cells have been put into practical uses. Dye-sensitized solar cells (DSC) are one of the next generation-solar cells, aiming at low-cost-type solar cells. In this report, where DSC is now and to where DSC researches go are discussed.

2. What is dye sensitized solar cells?

DSCs consist of titania nano-particles covered with dye molecules and electrolytes¹ (Figure 1). The working principle is summarized in Figure 2. When dyes are exposed to sun light, dyes is excited and electrons are injected into titania layers.

Electrons are carried in titania layers by diffusion force. On the counter electrode,

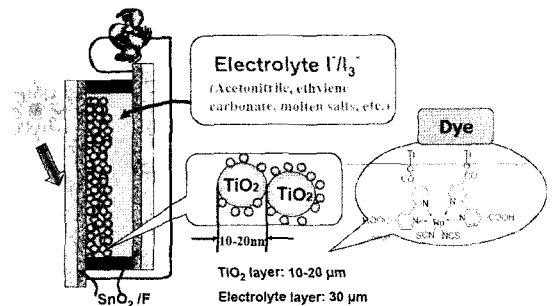


Fig. 1. Structure of DSC(dye sensitized solar cell)

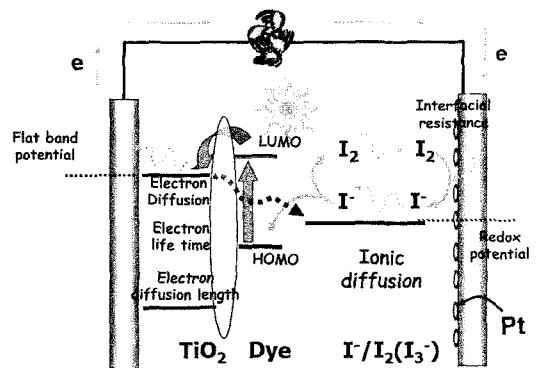


Fig. 2. Working principle of DSCs and measurable parameters

iodine molecules obtain electron to form iodide ions. Electrons diffuse in organic solvent as iodide ions. Iodide ions give electrons to dye molecules to form iodide molecules. Since these charges are carried by only diffusion process, it is crucial to control the diffusion in order to increase the photo-conversion efficiency. DSCs are prepared by coating titania paste, baking the substrate at 400~500 degree C, dipping the substrates into dye solutions, followed by injecting liquid electrolytes (Figure 3). Namely, the processes are composed of coating, baking and dipping processes, which are conventional and currently conducted technologies. The key process is similar to those of LCD and Li ion rechargeable batteries. Semi-conductive production lines are needed for manufacturing new type of solar cells such as thin film Si-solar cells, where, only big companies are able to join the competitions. However, production lines for DSCs have nothing to do with semi-conductive production lines and are similar to ones used so far. Companies not having Si-related semi-conductive technologies have opportunities to join the competitions.

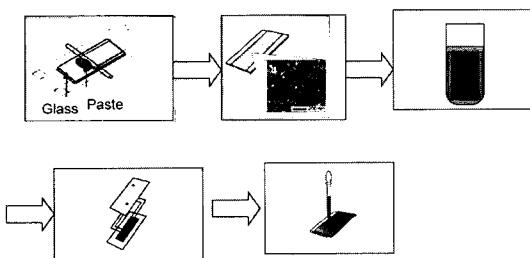


Fig. 3. Fabrication of DSC(dye sensitized solar cell)

3. DSC -Now-

Efficiency of the DSC reached 11[%] which is almost the same as those of amorphous Si solar cells[2-4]. 11[%] efficiency is surprisingly high, even though the fabrication processes contain simple coating and dipping processes. The efficiency is now lower than those of crystalline Si-based solar cells and CIGS-based solar cells (Figure 4). The Next target of the DSC researches is 15[%], efficiency (2020) which is described in a future plan (PV2030) made by New Energy and Industrial Technology Development Organization of Japan (NEDO). The reason why crystalline Si-based solar cells have high efficiency is because the cells are able to harvest lights with wide range of wavelength from 500~1,100[nm]. DSCs cover only wavelength of 400~700[nm], which is almost the same as that of amorphous Si-based solar cells. The spectral-matching between DSC and sun light is not enough, but DSCs can cover the wavelength region of fluorescence

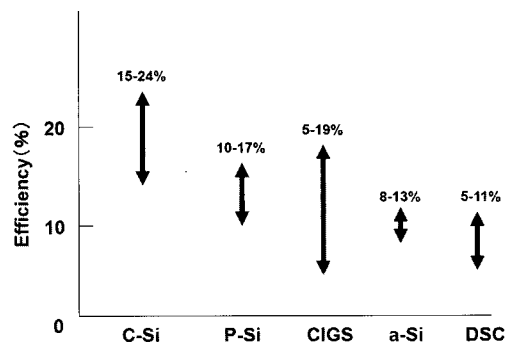


Fig. 4. Current status of DSC against Si-base solar cells

light. This is why inner-use is discussed for one of the entrances for DSC-commercialization. SONY has reported that the efficiency of the Si-solar cells is about 12[%] under a certain fluorescence light and that of DSC is about 21[%] under the same condition.

Many companies such as Fujikura, Toyota-Aishin, Hitachi, and so on have reported large DSC modules. They are accumulating KNOW-HOW to make large modules and give durability to the modules. Fabrication of DSC cells is simple, but, many problems have to be resolved in order fabricate large modules, for example, structures of modules, encapsulations and the protection of grids. Figure 5 shows DSC modules reported by Fujikura (Fujikura Homepage).

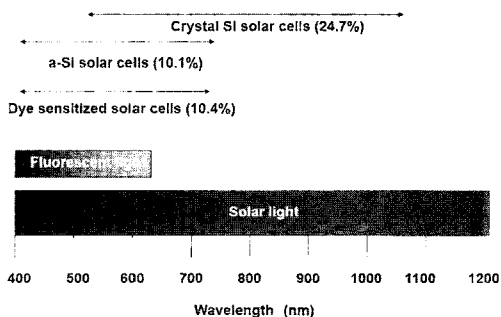


Fig. 5. Spectrum matching

4. DSC -from now on-

DSC researches are now focused on the fabrication of large modules, increase in efficiency and improvement of stability.

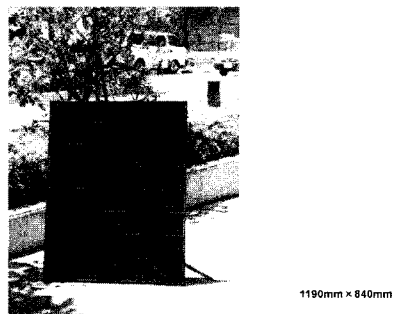


Fig. 6. DSC module reported by Fujikura(2006)
From Fujikura homepage

4.1 Trials to increase in efficiency(15[%])

In order to increase efficiency, light harvesting and electron collection are focused on in this paper.

4.1.1 Light harvesting

Many trials have been done to prepare dye molecules extending the absorption edge up to IR regions[5-12]. In addition, various tandem cells are reported. Figures 7 and 8 show one of tandem cells, where anode consists of conventional titania nano-particles covered with dye molecules and cathode are composed of p-type NiO covered with dye molecules. Dye molecules on the anode cover different wavelength from those on the cathode, which enable the cell to cover wide range of wavelength. Increase in Voc is expected in this type of the cells. Figure 9 shows an example of parallel cells[13]. Cathode and anode consist of titania nano-particles covered with dye molecules, but dye molecules on the anode cover

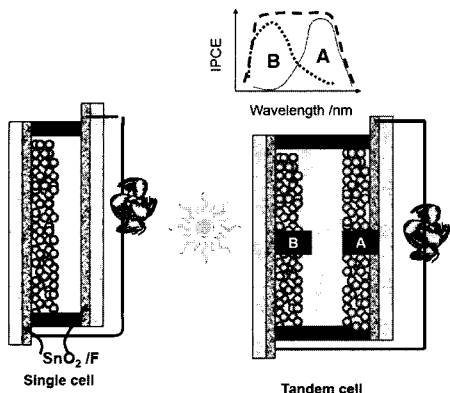


Fig. 7. Comparison of single cell and tandem cell

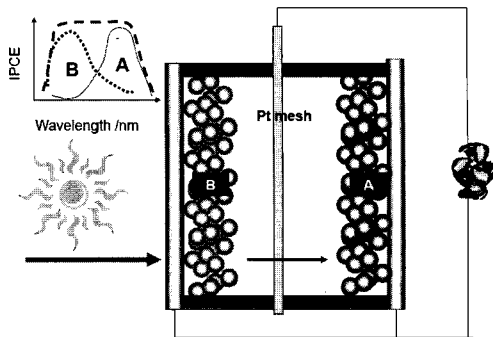


Fig. 9. DSC with parallel structure

See ref. 13

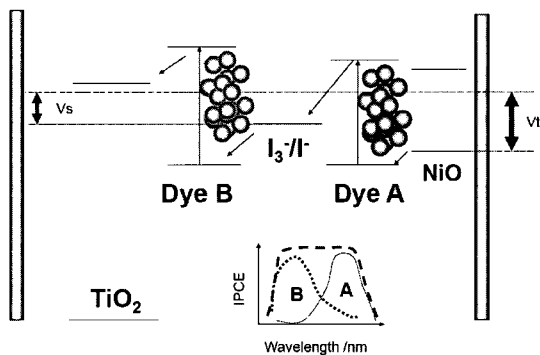


Fig. 8. Working principle of tandem cells

See ref. 15

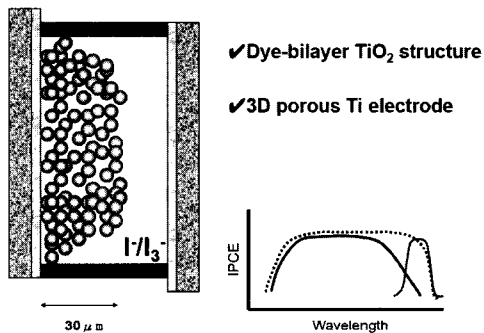


Fig. 10. DSC with dye-bilayer structure

different wavelength from those on the cathode. In the same way, increase in J_{sc} is expected. Figure 10 shows the simplest structure of parallel cells, where titania layers are stained with dye molecules separately. Position-selective dye-staining and preparation of DSC consisting of dye-bilayer structure have been reported by us. In this report, reports on merely accumulating two cells are omitted(14-16). Since improvement of light harvesting is crucial to increase efficiency, the research on light harvesting becomes one of the most

important items.

4.1.2 Electron collection.

Electron diffuses in titania layers by hopping electron trapping sites (Figure 11). Surface states become a center for charge recombination. Therefore, trap density or surface state density should decrease. The surface state density can decrease by passivating surfaces of titania nano-particles with organic molecules. The best way is to passivate the surface state with dye molecules, however, too may adsorption of dye molecules on titania surface causes dye

aggregation which inversely decreases photovoltaic performance. We found that the surface state density decreased and dye aggregation was suppressed by staining titania layers under pressurized CO₂ conditions[17]. Both of open circuit voltage (Voc) and short circuit current (Jsc) were improved by the CO₂ process as shown in Figure 12. Decreases in the number of grain boundary between titanium nano-particles are also needed. Nanofibers and nanotubes of titania were added in order to suppress the

undesirable effects associated with the grain boundaries[19].

4.2 Solidification

4.2.1 All-solid-DSC

One of the curical problems on module fabrications is the corrosion of metals by iodide and iodide. They react with Au, Ag and Al metals employed conventionally s grids. Therefore, extra protection layers on these metals are needed. Solidification is one of the methods to avoid the use of iodine. Figure 13

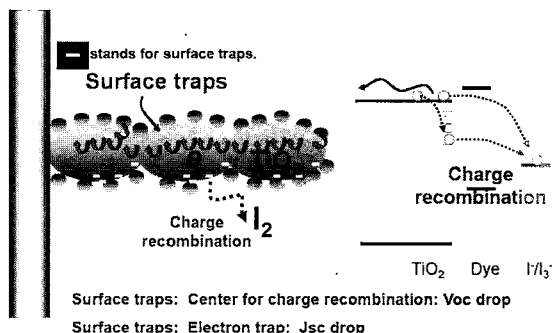


Fig. 11. Relationship among surface states, electron diffusion and electron life time

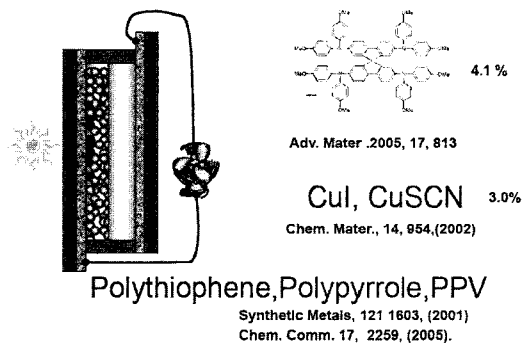


Fig. 13. All-solid DSCs

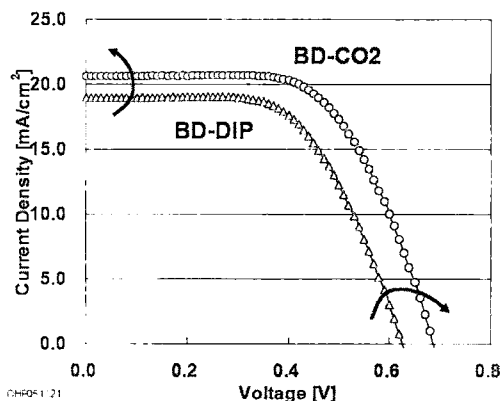


Fig. 12. I-V curves of DSCs prepared by dipping (BD-DIP) and CO₂ process (BD-CO₂)

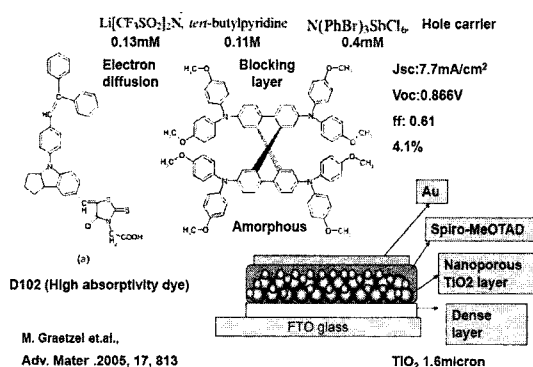


Fig. 14. All-solid DSCs containing additives
 See ref. 25

shows research trends on solidification [19-24]. When liquid electrolytes are replaced with organic p-type semi-conductive materials, defects such as short electron diffusion length, short hole diffusion length and fast charge recombination appear, which are suppressed in use of liquid electrolytes. The cells shown in Figure 14 cope with the defects properly[25]. In order to solve the problem, the thickness of the titanium layer was decreased to 1~3 micron, compared with 10~20 micron thickness for liquid type DSCs. Organic dyes with high absorbance were used instead of Ru dyes because of efficient light harvesting irrespective of thin titania layers. In addition, t-butylpyridine is added in the hole conductor in order to avoid charge recombination at the interface between titania and p-type semiconductor. In order to increase electron diffusion length in titania, Li salt is added. In addition, in order to increase hole diffusion length, Sb complex is added. Graetzel and his co-workers have reported 4.1[%] using the all-solid DSC. Much effort is needed for improving the efficiency[25].

4.2.2 Ionic-liquid type-Quasi-solid DSC

In order to avoid spilling from the DSC and volatilization of organic solvents, quasi-solidification using non-volatile ionic liquid has been reported. Quasi-solidification is carried out by adding solidification agents into ionic liquid type electrolytes. They are visually

solid but charges are carried by diffusion in ionic liquids. Therefore, the addition of electrochemically-inactive solidification agents suppresses somehow the diffusion of ionic liquids and decreases photovoltaic performances. One of the most convenient solidification agents is nano-particles. However, photo-voltaic performances decreased linearly with the amount of nano-particles added. We have reported quasi-solid DSCs with straight ionic paths as shown in Figure 15[26]. Anodically oxidized alumina was used for the solidification agent. The anodically oxidized alumina films have many nanopores and the nanopores are penetrating from one side to another side straightly. The straight-pass helps swift ion diffusions. In addition, the nano pore surfaces were modified with organic molecules which are self-organized on the alumina nano-pore-wall. Iodine and iodide are concentrated on the self-organized imidazolium moieties and make ion paths. The photovoltaic properties of the quasi-solid-DSC were surprisingly larger than that of the parent ionic-liquid type solar cells (Figure 16). We are expecting Grotthuss type charge diffusion mechanism which is observed when charge carriers are making networks[28]. When one charge comes to the networks, another charge goes out from the networks. Therefore, charges are carried without diffusion of the charge carriers, which exhibit best performances in solidified media.

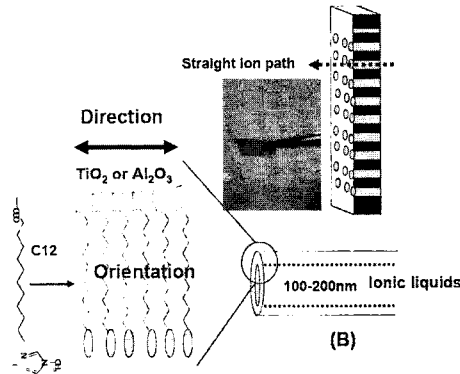


Fig. 15. Nano-hybrid charge carrier composite

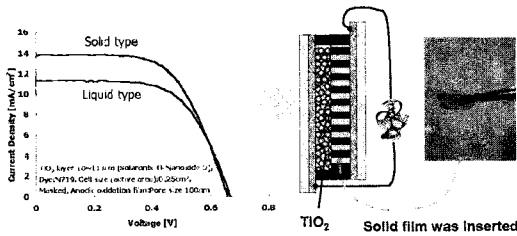


Fig. 16. I-V curves before and after quasi-solidification

4.3 Module

Figures 17~20 shows modules structures of DSC reported so far. Most simple one is shown in Figure 17. Because of insufficient conductivity of transparent conductive oxides (TCO) ($10(\text{ohm}/\text{cm}^2)$), grids have to be on the TCO glasses. However, iodide and iodine corrode metals such as Ag, the grid has to be protected perfectly. Low melting glass is one of the best selections for protecting the iodide/iodine corrosion.

4.4 TCO-less DSC

Conventional DSCs have two TCO glasses.

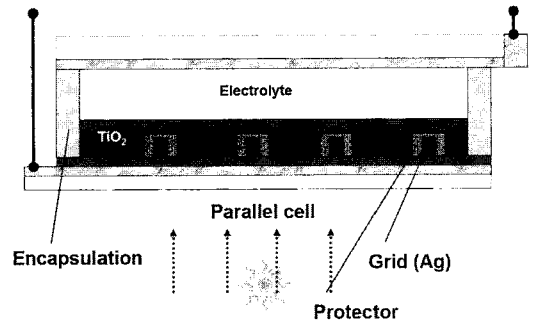


Fig. 17. DSC modules-parallel

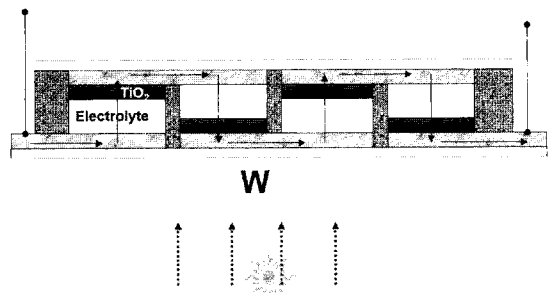


Fig. 18. DSC modules-W

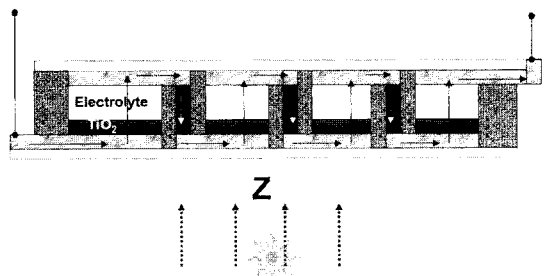


Fig. 19. DSC modules-Z

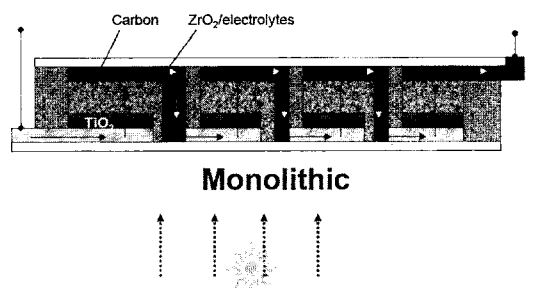


Fig. 20. DSC modules-Monolithic

However, TCO glasses is very expensive in this moment. TCO-less DSCs have been desired. Some TCO-less structures have been reported so far. Our all-metal-electrode-DSCs are shown in Figure 21[27]. The cell consists of glass/porous titania covered with dye molecules/porous Ti/electrolytes/Ti sheet. Electrons generated in the porous titania layer are collected in the porous Ti electrodes. The key to success is the preparation of thick and porous Ti electrodes,

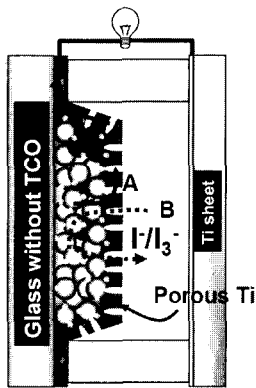


Fig. 21. DSC with All-metal-electrode (TCO-less DSC)

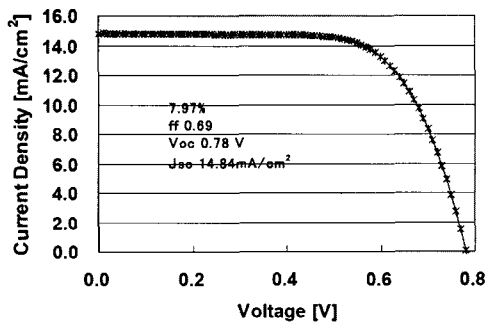


Fig. 22. I-V curves for DSC with All-metal-electrode(TCO-less DSC)

which fulfills the contradict requirements on thick Ti layers for higher conductivity and porous structure for not suppressing the ionic diffusions thorough the Ti electrode. Figure 22 shows the I-V curves of the DSC with all-metal-electrodes (TCO-less-DSC). The 8[%] efficiency was almost the same as that of conventional DSC using TCO-glasses, leading the conclusion that the porous Ti acts as electron collectors.

5. Conclusions

The efficiency of DSCs is about 11[%] which is almost the same as amorphous Si-based solar cells. The next target is 15[%] efficiency in order to catch up microcrystalline Si-based solar cells. Light harvesting and charge collections are key research items for achieve the target. Another research trend is the fabrication of large modules. The KNOW-HOW is still in companies and the details are not open yet. Encapsulations and protection layers of grids should be the key research items. Stability is related largely to electrolyte compositions. The relationship between the stability and electrolyte compositions, and degradation mechanisms should be made clear. Indoor use as well as outdoor use has been focused on. DSC performances exceed that of Si-based solar cells under fluorescence light exposure. DSCs would be put into practical uses before long.

References

- [1] B. O'Regan, M. Grätzel, Nature, 353, 737 (1991).
- [2] Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, and L. Han, Jpn. J. Appl. Phys., 45, L638 (2006).
- [3] M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Grätzel, J. Am. Chem. Soc., 123, 1613 (2001).
- [4] Z. -S. Wang, T. Yamaguchi, H. Sugihara, H. Arakawa, Langmuir, 21, 4272 (2005).
- [5] M. K. Nazeerudin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc., 115, 6382 (1993).
- [6] T. Renouard, R. -A. Fallahpour, M. K. Nazeeruddin, R. Humphry-Baker, S. I. Gorelsky, A. B. P. Lever, M. Grätzel, Inorg. Chem., 41, 367 (2002).
- [7] R. Amadelli, R. Argazzi, C. A. Bignozzi, F. Scandola, J. Am. Chem. Soc., 112, 7099 (1990).
- [8] Z. -S. Wang, C. -H. Huang, B. -W. Zhang, Y. -Y. Hou, P. -H. Xie, H. -J. Qian, K. Ibrahim, New J. Chem., 24, 567 (2000).
- [9] Z. -S. Wang, F. -Y. Li, C. -H. Huang, L. Wang, M. Wei, L. -P. Jim, N. -Q. Li, J. Phys. Chem., B, 104, 9676 (2000).
- [10] Z. -S. Wang, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, H. Arakawa, H. Sugihara, J. Phys. Chem., B, 109, 3907 (2005).
- [11] K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, New J. Chem., 27, 783 (2003).
- [12] Y. -G. Kim, J. Walker, L. A. Samuelson, J. Kumar, Nano Lett., 3, 523 (2003).
- [13] M. Murayama, T. Mori, J. Phys. D: Appl. Phys., 40, 1664 (2007).
- [14] P. Liska, K. R. Tampi, M. Graetzel, D. Bremaud, D. Rudmann, H. M. Upadhyaya, A. N. Tiwari, Appl. Phys. Lett., 88, 203103 (2006).
- [15] F. Vera, R. Schreiber, E. Muñoz, C. Suarez, P. Cury, H. Gómez, R. Córdova, R.E. Marotti and E.A. Dalchiele, Thin Solid Films 490, 182 (2005).
- [16] W. Kubo, A. Sakamoto, T. Kitamura, Y. Wada and S. Yanagida, J. Photochem. Photobiol. A: Chemistry 164, 33 (2004).
- [17] -15.Y. Ogomi, S. Sakaguchi, T. Kado, M. Kono, Y. Yamaguchi, S. Hayase, J. Electrochem. Soc., 153(12), A2294 (2006).
- [18] T. Kado, M. Yamaguchi, Y. Yamada and S. Hayase, Chem. Lett. 1056 (2003).
- [19] I. Schmidt-Mende, S. M. Zakeeruddin and M. Grätzel, Appl. Phys. Lett., 86, 013504 (2005).
- [20] N. Fukuri, N. Masaki, T. Kitamura, Y. Wada and S. Yanagida, J. Phys. Chem. B, 110, 25251 (2006).
- [21] J. Xia, N. Masaki, M. Uira Cantu, Y. Kim, K. Jiang, and S. Yanagida, J. Am. Chem. Soc., 130, 1258 (2008).
- [22] N. Ikeda and I. Miyasaka, Chem. Commun., 1886 (2005).
- [23] Q. B. Meng, K. Takahashi, X. -T. Zhang, I. Sutanto, T. N. Rao, O. Sato and A. Fujishima, Langmuir, 19, 3572 (2003).
- [24] G. R. A. Kumara, A. Konno, K. Shiratsuchi, J. Tsukahara and K. Tennakone, Chem. Mater., 14, 954 (2002).
- [25] L. S. Mende, U. Bach, R. H. Baker, T. Horiuchi, H. Miura, S. Ito, S. Uchida, and M. Graetzel, Adv. Mater. 17, 813 (2005).
- [26] T. Kato and S. Hayase, J. Electrochem. Soc., 154, B117, (2007).
- [27] Y. Kashiwa, Y. Yoshida and S. Hayase, Appl. Phys. Lett., 92, 033308 (2008).
- [28] K. Schmidt-Rohr, and Q. Chem, Nature Materials, Published online: 9 December 2007; doi:10.1038/nmat.2074.

◇ 저자 소개 ◇



Shuzi Hayase

He was born in Feb. 2, 1954.

Academic background : Graduated from Osaka University in 1978

Major : Polymer Chemistry

Degree : Received Ph.D from Osaka University in 1985

<Carrier>

1978 : Joined Toshiba Research and Development Center in 1978

1988~1990 : Joined the polysilane research group in Wisconsin University

1990 : Returned to Toshiba Research and Development Center

2001 : Professor of Kyushu Institute of Technology : Present Position : Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology

Award : In 1996 Award for Technological Development by The Japan Electrical Manufacturers' Association

In 1992 The Chemical Society of Japan Award for Technological Development : Awarded for distinguished contributions in technological development in chemical industry

In 1987 National Commendation for Invention by Japan Institute of Invention and Innovation
Specialty : Functional polymers, Material for LSI lithography

Polymers with opto and electrical properties,

Devices using functional polymers,

Development of materials for various batteries