Aiming at High Efficiency Dye-Sensitized Solar Cells
–From the View Point of Photoconversion Interface–

Shuzi HAYASE*, Yuhei OGOMI, and Shyam S. PANDEY

Kyushu Institute of Technology (2-4, Hibikino, Wakamatsu-ku, Kitakyushu 808-0196, Japan)

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Researches aiming at high efficiency-dye-sensitized solar cells (DSC) are reviewed from the view point of photoconversion interfaces. Developments of dyes converting photons to electrons in near infrared regions are essential for increasing short circuit current (Jsc). Hybrid cells consisting of double dye structures and double titania layer structures are proposed. Leak currents at photoconversion interfaces decrease open circuit voltage (Voc) and fill factor (FF). Therefore, strategies for decreasing leak currents are essential, especially for all-solid DSCs and I−/I3− free DSCs. Structures of these interfaces are discussed in terms of surface passivation, self-organization, dye structures, interactions between dyes and I− in titania nanopores. Fundamental studies for tandem cells are also reported.

Key Words : Dye-Sensitized Solar Cell, Hybrid, Interface, Electron Injection

1 Introduction

Certified efficiency of dye-sensitized solar cells (DSC) having active area of more than 1 cm² is 10.4 % which is almost the same as that of amorphous Si solar cells (10.1%). Bulk hetero junction polymer solar cells (BHJOPV) with 8.3 % efficiency (certified) follow the DSC. These organic solar cells are fabricated by low cost printing technologies, which is one of advantages over Si based solar cells. However, certified efficiency of crystalline Si, poly Si, CuInGaSe(S), and CdTe based solar cells is 25 %, 20.4 %, 19.6 %, and 16.7 %, respectively, which are higher than those of DSCs and BHJOPVs. Therefore increase in efficiency for DSCs and BHJOPV is now desired. Solar cell efficiency (Eff) is expressed by the following equation.

\[ \text{Eff} = \text{Voc} \times J_{sc} \times \text{FF} \]  

(1)

where, Voc, Jsc and FF stand for open circuit voltage, short circuit voltage, and fill factor.

In order to increase efficiencies, Voc, Jsc, and FF have to be improved. Trials for increasing these factors are reported in this paper.

2 Results and Discussion

2.1 Increase in Jsc

Jsc increases with an increase in the number of harvested photons. Figure 1 shows the relationship between the number of photons in sun light and wavelength. Conventional Ru complexes can convert photons to electrons in the area from 400 nm to 800 nm. If all of the photons in this wavelength region are converted to electrons, 25-26 mA/cm² of Jsc is expected. Considering the fact that 10-15 % light is lost by an F-doped SnO₂ glass (FTO glass), the expected Jsc is about 22 mA/cm² which is close to 20.1 mA/cm² reported by Chiba and his coworkers. Small increase in Jsc in the area is still expected by optimizing dye structures, electrolyte compositions, and solar cell structures. If photons in an area from 400 nm to 900 nm can be harvested and covered to electrons, 32 mA/cm² is expected from Fig. 1. If 85 % of these photons is harvested, 15 % efficiency are expected by the following equation.

\[ 15% = 27.2 \text{ mA/cm}^2 \times 0.75 \text{ V} \times 0.735 \text{ (FF)} \]  

(2)

Therefore, developments of dyes covering wavelengths from 400 nm to 900 nm with high incident photon to current conversion efficiency (IPCE) are crucial. The potential gap between a conduction band of titania and a redox potential of I−/I3− species is reported to be 9 V. Supposing that 0.2 V of potential barrier is present for electron shifts from a dye to titania, and from redox species to a dye, a longest wavelength at which DSCs consisting of titania and I−/I3− can convert photons to electrons with maintaining high Voc, is 950 nm. New concepts are needed to convert light longer than 950 nm to electrons,
maintaining high Voc. One of these approaches is to design dyes which reduce these potential barriers. However, clear solutions for this approach have not been reported yet.

There are many reports on dyes which were directed to cover wide ranges of wavelengths by single dye. It has been reported that there is a conflicting factor, namely, an improvement of IPCE at a region of longer wavelengths results in decrease of IPCE in visible regions. Cocktail DSC has been reported, where a porous titania substrate is randomly stained by two dyes. This worked well when a dye covering a region of short wavelengths was coupled with Ru dyes. However, when dyes covering a region of long wavelengths were coupled with Ru dyes, the efficiency often decreases because of unfavorable interactions between these two dyes. Therefore, two dyes had better to be separated each other. In order to cope with this issue, multiple electron transfer processes have been reported.

A DSC consists of nano-titania particles/Dye 1/ alumina thin layers/dye 2. A porous titania substrate is dipped in a dye A solution, an alumina precursor solution, and a dye B solution consecutively. Dye 1 is adsorbed on the surface of a parent porous titania layer and dye 2 is adsorbed on the surface of alumina thin layers. It has been reported that electrons are injected from both dyes 1 and 2 to titania nanoparticles. Since dye 1 is separated from dye 2, interactions of dye 1 with dye 2 can be inhibited.

We have reported a DSC consisting of a double dye structure where two dyes are molecularly and linearly linked, and bonded to porous metal oxide surfaces. Figure 2 shows the double dye structure. TiN(IV) 2,11,20,29-tetra-tert-butyl-2,3-naphthalocyanine (NeSn) was adsorbed on SnO2 nanoparticles through a Sn(p)-O-Sn(n) bond, where Sn(p) and Sn(n) stands for Sn in SnO2 nanoparticles and Sn in naphthalocyanine, respectively. Cis-diisothiocyanato-bis(2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium(II) bis(tetra-n-butylammonium) (N719) was bonded to Sn(n)-OH through Sn-O-CO linkages. Almost all dyes including phthalocyanine and naphthalocyanine derivatives reported for DSCs so far have anchor groups such as carboxylic acids. It has been reported that a naphthalocyanine derivative consisting of Si adsorbs on titania nanoparticles through Ti-O-Si linkages. Despite the fact that NeSn does not have carboxylic groups, representative anchor groups, the dye clearly adsorbed on a porous SnO2 layer. Figure 3 shows incident photon to current efficiency (IPCE) curves with error bars for three cells, namely, a DSC consisting of SnO2 layers stained with only N719 (cell-N719), a cell stained with only NeSn (cell-NeSn), and a cell consisting of a double dye structure(cell-NeSn-N719). The photovoltaic performance was monitored with a Bunko-Keiki model solar simulator KHP-1 equipped with a xenon lamp (XLS-150A). The exposure light was adjusted to be AM1.5 (100 mW/cm²). An IPCE curve for cell-N719 and cell NeSn had a single peak at 500-600 nm (IPCE:63%) and 900 nm (IPCE:39%), respectively. The IPCE curve of cell-NeSn-N719 had two peaks at 500-600 nm (IPCE:59%) and 900 nm (IPCE:30%), which correspond to those of NeSn and N719, respectively. In addition, the IPCE curve for the double dye cell was almost the same as those of the sum of the two single dye cells. demonstrates that electrons were injected from both N719 and NeSn, and there were no interactions between these two dyes which decrease the photoconversion efficiency. Figure 2 also shows an energy diagram for the double dye cell, suggesting that electrons can be injected stepwise from N719 to NeSn and to SnO2 nanoparticles. Shen and Toyo-da have analyzed the ultrafast photoexcited electron dynamics using a transient absorption (TA) and an improved transient grating (TG) technique. They proved that the stepwise electron injection shown in Fig. 2 actually occurred with a time scale of a few ps. These fundamental studies strongly demonstrated that the double dye system has a potential to cover a wide range of wavelengths.

Multiple electron transfers were also realized by double titania layer systems, where each titania layer is stained with two dyes, respectively, as shown in Fig. 4. The hybrid cell (hyb-cell) consists of top and bottom...
Fig. 4  Structure of hybrid cell consisting of double titania structure stained with two dyes, respectively. X: I /I; redox potential, Y: TiO_2 conduction band, Za: LUMO of dye A, Zh: LUMO of dye B, Wa: HOMO of dye A, Wb: HOMO of dye B. Dye A: 345-carboxyl-(1-dodecyl-1,3-dihydro-3,3-dimethyl-2H-indole-2-ylidene)methyl-4-hydroxy-cyclobutene-1,2-dione, Dye B: bis45-carboxyl-1-dodecyl-2,3,3-Trimethyl-Indolium-2-ylidene]squaraine.

Fig. 5 IPCE curves for hyb-cell, sing-A-cell, and sing-B-cell. Hyb-cell: hybrid cell consisting of double titania layer shown in Fig. 4, sing-A-cell: single DSC cell stained with dye A, sing-B-cell: single DSC cell stained with dye B, Sub-top-A and Sub-bottom-B were pressed at 2300 kg/cm^2. Dye A and B: see Fig. 4. Electrolyte: E-1 electrolyte (composition: see text). AM1.5, 100 mA/cm^².

Electrodes. Electrons are expected to be injected from a top electrode as well as a bottom electrode.

Model dyes, 345-carboxyl-(1-dodecyl-1,3-dihydro-3,3-dimethyl-2H-indole-2-ylidene)methyl-4-hydroxy-cyclobutene-1,2-dione (A) and bis45-carboxyl-1-dodecyl-2,3,3-Trimethyl-Indolium-2-ylidene]squaraine (B) were employed to verify the work as hybrid cells. These two dyes were selected because the absorption of dye A (λ max 429 nm) was completely different from that of dye B (λ max 646 nm), and fundamental cell performances are evaluated easily. The top layer consists of a porous titania layer stained with dye A fabricated on a transparent conductive glass (TCO glass). The bottom layer consists of a porous titania layer stained with dye B on a glass mesh sheet. The bottom layer and the top layer were pressed mechanically to obtain the hybrid anode electrode shown in Fig. 4. A concern is whether a top electrode has good contact with a bottom electrode by the mechanical pressing. Single cells for a reference cell consist of the following compositions: single cell stained with only dye A (sing-A-cell): FTO glass/titania layer stained with dye A/E-1 electrolyte/counter electrode; single cell stained with only dye B (sing-B-cell): FTO glass/titania layer stained with dye B/E-1 electrolyte/counter electrode, where E-1 electrolyte has following composition: 0.5 M LiI, 0.05 M I_2, 0.58 M 4-tert-butylpyridine, and 0.6 M 1-methyl-3 ethyl-imidazolium dicyanoamide (EMIDCA, Solaronix) in acetonitrile. Figure 5 shows IPCE curves for hyb-cell, sing-A-cell, and sing-B-cell. The IPCE curve of the hyb-cell had two peaks (450 and 660 nm) that correspond to those of single cells (sing-A-cell: 450 nm, and sing-B-cell: 660 nm). J_sc of hyb-cell was 6.89 mA/cm², which was higher than those of the single cells, namely, 4.5 mA/cm² for sing-A-cell, and 2.09 mA/cm² for sing-B-cell. The IPCE curve for hyb-cell is almost the same as that of sum of sing-A-cell and sing-B-cell. The efficiencies of hyb-cells were 1.96, 2.54, 3.11, and 3.19 % when they were pressed at 0, 770, 1550, and 2300 kg/cm², respectively. The increase in the efficiency was mainly due to the increase in J_sc as the pressure increased. The IPCE peaks of sub-top-A did not change considerably, but those of sub-bottom-B increased from 3 to 36 % as the pressure increased from 0 to 2300 kg/cm². The diameter of a semicircle associated with titania layers in the Cole-Cole plot before pressing was 14.88 Ω, which decreased to 6.06 Ω after pressing at 1550 kg/cm². The results demonstrate that an interface between sub-top-A and sub-bottom-B was connected electronically well, and electrons were collected from both the top and bottom electrodes. The explanation is also supported by the report that necking between titania nanoparticles is strengthened by mechanical pressing. This is fundamental results to prove the work of hybrid DSCs. The double titania structure was fabricated by portion-selective dye adsorption in pressurized CO_2 atmosphere. They were also prepared by dipping a porous titania substrate in a cocktail solution in a specific combination of two dyes. We have to wait for forthcoming near IR dyes for a bottom electrode to realize high efficiency cells.

2.2 Increase in open circuit voltage (Voc)

Maximum Voc is determined by a potential difference between conduction band of titania (d) and redox potential (c) shown in Fig. 6. One of approaches for increasing Voc is to lower the redox potential (c). As far as I /I is employed, the maximum Voc is limited to 0.9 V. Recently, high efficiency DSCs consisting of Co complex, Fe complex, disulfide compounds, and so on, have been reported. These redox potentials can be tuned by changing these chemical structures. Because of the fast charge recombination between electrons in titania and these redox species, optimizations of photoconversion in-
interfaces are needed, such as fabrication of a blocking layer against charge recombination, employing high extinction coefficient-organic dyes to make a titania layer thin, and so on. Recently, 67% efficiency has been reported using a Co complex.93 9.3% efficiency has been reported in IPS 18 (Seoul) by Graetzel and his coworkers. To use hole conductors which give all-solid dye-sensitized solar cells is another option. In this case, charge recombination between electrons in titania layer and holes in p-type compounds is very fast. 51% efficiency has been reported by optimizing photoconversion interfaces.30

Voc decreases by the charge recombination between electrons in a titania layer and redox species and between electrons in a titania layer and oxidized dyes. Figure 6 shows charge recombination of only the former case. The charge recombination occurs via surface traps (route 1) or directly from conduction band (route 2). In order to inhibit route 1, surface traps has to be passivated. We evaluated the surface traps using a thermally stimulated current method (TSC). A TSC peak which is associated with trap depth, appeared at 0.2 eV and has a tail up to 0.5 eV. After a Ru dye, N719, was adsorbed on a titania layer, the number of surface traps (10⁻¹⁵-10⁻¹⁶/cm²) decreased by 10 times (10⁻¹⁴-10⁻¹⁵/cm²), suggesting that dyes adsorbed on a porous titania layer decrease the number of surface traps.31 We have already reported that black dye absorbed well on a TiO₂ layer under a pressurized CO₂ atmosphere because of activation of titania surfaces by CO₂ and the photovoltaic performance was improved.32 We expect that the surface of the titania was well passivated by dye molecules under the pressurized CO₂ conditions.33 Introduction of sterically hindered substituents into dye molecules is effective to separate I⁻ from the surface of titania. It has been reported that an introduction of long alkyl groups into dyes increases photovoltaic performances.34 We prepared several model molecules bearing alkyl groups as shown in Fig. 7 and examined the role of alkyl groups.40-42 The amount of dyes adsorbed on a titania layer increased as a chain length increases due to self-organization of the long alkyl groups as shown in Fig. 7. This brought about well organized surface passivation of a titania layer and retarded route 1 in Fig. 6. In addition, the self-organized long alkyl group inhibited I⁻ from coming close to a titania surface spatially (route 2 in Fig. 6). The results are well explained by the fact that electron life time measured by intensity modulated photovoltage spectroscopy (IMVS) became longer as the chain length increased.36,37 Actually, the Voc and the efficiency increased as the alkyl chain length increased. Surface passivation is needed, however, dye-aggregation arising charge recombination centers has to be avoided.

Charge recombination between electrons in titania layer and I⁻ takes place in nanopores in a titania layer. I⁻ diffuses from a bulk electrolyte layer to nanopores whose diameter is around 30 nm and length is about 20000 nm. I⁻ gives electrons to oxidized dyes, where I⁻ oxidized to I⁺. I⁺ has to diffuse out through long nanopores as shown in Fig. 6. When I⁻ moves close to titania surfaces and receives electrons from a titania surface during I⁻ diffusions in the long nanopores, Voc decreases. It is important to know how I⁻ diffuses in titania nanopores. We measured relative I⁻ diffusion coefficients in nanopores of a titania layer by using a porous titania sheet supported by a stainless metal sheet.43 Dyes bearing different substituents as shown in Fig. 8 were adsorbed on the wall of these nanopores. I⁻ diffusion rate in nanopores modified with dyes with long alkyl groups (SQ4, SQ18) was largest and decreased in nanopores modified with polar substituents such as F and O (SQ4F6, SQ4F3, SQ4O4, SQ4O2) as shown in Fig. 9.43 I⁻ interacts with polar substituents of dye molecules in nanopores, resulting in slow diffusions in the nanopores. The phenomena are similar to those of column chromatography. Voc decreased as relative diffusion coefficients of I⁻ in nanopores decreased as shown in Fig. 9.43 The slow diffusion increases the opportunities for charge recombination between electrons in titania and I⁻. It has been reported that long alkyl chains substituted on dye molecules retards charge recombination between electrons in titania and I⁻ of electrolyte.45-47 Actually, SQ18
showed highest Voc. However, the fact that Voc of SQ4 is higher than those of SQ4F6, SQ4F3, SQ4O2, and SQ4O4 is not explained by the retardation of the charge recombination by the steric hindrance of these substituents, because SQ dyes except for SQ18 have almost the same molecular size (2.20–2.23 nm). The lower Voc of SQ4F6, SQ4F3, SQ4O2, and SQ4O4 is explained by slow $I_-$ diffusion in nanopores of a titania layer, where these surfaces are modified with dye molecules bearing alkyl groups consisting of polar atoms such as O or F. It is most likely that $I_-$ interacts with O or F atoms in alkyl chains, which lowers diffusion coefficients. The results show a direction for designing dyes. Introduction of polar substituents to portions close to titania surface should be avoided and dyes covered with hydrophobic substituents such as long alkyl groups are preferable for high Voc.\textsuperscript{43} Mori and his coworkers have also reported that spherical and large dye structure and two adsorption sites to decrease the reorganization energy, wider distribution of charged atoms to control $I_-$ concentration at the TiO$_2$ surface, and packing density of dyes to block the approaches of $I_-$ are essential to give long electron life times and increase photovoltaic performances.\textsuperscript{53}

Charge recombination between electrons in a titania layer and oxidized dyes depends on dye structures. It has been reported that the recombination is very slow for conventional Ru complexes because the distance between titania surface to Ru is large. In some organic dyes, the recombination occurs fast and designs of photovoltaic conversion interfaces are needed to avoid the recombination.\textsuperscript{23}

It has been reported that dye dipole is associated with Voc as shown in Fig. 10.\textsuperscript{60} In some cases, the dipole may be compensated with ions in electrolytes.\textsuperscript{43} We measured surface potential of some dyes adsorbed on a titania layer and found that Voc increased with an increase in positive surface potential of dyes,\textsuperscript{47–49} which is consistent to the explanation in Fig. 10.

\subsection*{2.3 Tandem cell}

Tandem structures are needed to convert light longer than 1000 nm. There are several reports on tandem cells, where two single cells are merely piled up.\textsuperscript{52,54} However, these cells are not practical because they require more than three transparent conductive oxide layered glasses. Tandem or hybrid cells with two electrodes in one cell have been reported,\textsuperscript{13,22,53,59} in which two metal oxide layers were stained with different dyes, respectively. For example, Suzuki and Mori have issued a patent application on a tandem cell consisting of a transparent conductive oxide (TCO) layered glass/dye-stained porous titania layer (top electrode)/electrolyte/Pt/TCO/dye-stained porous titania (bottom electrode)/composite electrolyte/substrate. In these tandem cells, the bottom electrode was fabricated on a counter electrode and the surface of the bottom layer was covered with a TCO layer, which acts as an interlayer connecting the top cell and the bottom cell electrically.\textsuperscript{50} We have reported another tandem cell consisting of a floating electrode (a flexible porous titania sheet) which is employed as a bottom electrode.\textsuperscript{59} The floating electrode (bottom electrode) is composed of a porous TiO$_2$/dye layer supported by a protected stainless-steel mesh sheet or a glass mesh. The tandem cell has the following structure: a transparent conductive oxide (TCO) layered glass/dye-stained porous titania layer (top electrode)/gel electrolyte sheet 1/Pt island layer/dye-stained porous titania sheet (bottom electrode)/gel electrolyte sheet 2/conductive substrate layer (counter electrode). Voc of the tandem cell was 0.88 V which was higher than that of the corresponding single cell (0.6 V). This demonstrated that the structure has a potential for tandem cells even though the Voc increase is not satisfactory.

In order to complete the tandem structure, a floating electrode consisting of metal oxides with a low conduc-
tion band level, such as SnO$_2$ is needed. Of course, development of new dyes which harvest infrared light and convert the light effectively to electrons are crucial.

3 Conclusion

Some directions to high efficiency cells were shown in terms of $J_{sc}$ and $V_{oc}$. In order to increase $V_{oc}$, new iodine free electrolytes or hole conductors are needed, where, charge-recombination-blocking layers has to be optimized. Constructions of interfaces are needed for decreasing charge recombination between electrons in a titania layer and redox species. Surface passivation, dye dipole, diffusions of $I_3^-$ in nanopores which are affected by dye structures have to be considered. Hybrid cells and multiple electron transfer dyes were proposed. Tandem cells were needed to harvest light in IR area. Development of new dyes harvesting near IR light (from 400 nm up to 900 nm) for hybrid cells or IR light covering wavelength longer than 1000 nm for tandem cells is needed. In any cases, optimizations of interfaces are crucial for achieving high efficiency DSCs.

References

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