



# Strategy to improve the performance of dye-sensitized solar cells: Interface engineering principle

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Received 2 October 2009; accepted 2 October 2009

Communicated by: Associate Editor Yogi Goswami

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## Abstract

As next generation solar cells, dye-sensitized TiO<sub>2</sub> solar cells attract many scientists' attention throughout the world. Although currently there are no commercially available products on the market, construction of large modules and long-term stability tests have been carried out by many companies and laboratories worldwide; commercialized DSC products may be appearing in the near future. Improving DSC performance and long-term stability is a great challenge not only to the academic research but also for industrial applications. Here the interface molecular engineering principle is proposed as the main strategy to meet this challenge in view of recent progress in this domain.

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*Keywords:* Dye-sensitized TiO<sub>2</sub>; PEDOT hole conductor; Hybrid ruthenium dye; Nb<sub>2</sub>O<sub>5</sub> blocking layer; Photo-electro-polymerization;  $\pi$ -Stacking self-organization on interfaces

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## 1. Introduction

Developing clean energy alternatives to fossil fuels technology has become one of the most important tasks undertaken by modern science. So far, crystalline silicon solar cells dominate the photovoltaic market especially in Europe, leading to shortages of highly pure silicon throughout the world. The dye-sensitized mesoscopic TiO<sub>2</sub> solar cells have numerous advantages over silicon solar cells, such as low materials cost, ease of production, and efficiencies outperforming amorphous silicon solar cells. As a result, many researchers in both academia and industry are focusing their research on the development and the exploitation of the DSC devices. Since the first high performance dye-sensitized nanocrystalline TiO<sub>2</sub> solar cell (DSC) appeared in

1991 (O'Regan and Grätzel, 1991), many scientists around the world have taken great efforts to investigate the performance of DSC devices. However, from a practical application standpoint, organic liquid electrolytes are not a good choice due to shortcomings involving solvent evaporation and iodine sublimation resulting in long-term and high-temperature instability. Therefore, many attempts to form quasi-solid-state electrolytes by using gelators (Kubo et al., 2002, 2003), organic capped nanoparticles (Xia et al., 2004; Kato et al., 2005) or polymers (Wang et al., 2002) and application of low molecular oligomers (Kang et al., 2005) as polymer electrolytes have been investigated with interesting progress. Recently, a lot of attention (Wang et al., 2004, 2005b; Matsumoto et al., 2001; Yamanaka et al., 2007) has been given to improving the performance of the ionic liquids based DSC due to their high ionic conductivity, non-volatility, improved electrochemical stability, and non-flammability (Hagiwara and Ito, 2000; Welton, 1999; McEwen et al., 1999). In this paper, we will review recent progress based on ionic liquid and solid-state

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## Nomenclature

FF	fill factor	SAM	self-assembled monolayer
$I$	current density ( $\text{mA cm}^{-2}$ )	N3	cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)
$I_{sc}$	short-circuit current density ( $\text{mA cm}^{-2}$ )	$E_{cb}$	energy position of conduction band
$\eta$	overall conversion efficiency	EIS	electrochemical impedance spectroscopy
$V$	voltage (V)	SEM	scanning electron microscope
$V_{oc}$	open-circuit voltage (V)	PET	poly(ethylene terephthalate)
IPCE	incident photo to current conversion efficiency	PEN	poly(ethylene naphthalate)
$\eta_{lh}$	light harvesting efficiency	spiro-OMETAD	2,2',7,7'-tetrakis( <i>N,N</i> -di- <i>p</i> -methoxyphenyl-amine)9,9'-spirobifluorene
$\eta_{ei}$	charge injection efficiency	MEI-SCN	1-methyl-3-ethylimidazolium thiocyanate
$\eta_{et}$	charge transport efficiency	TBP	4- <i>tert</i> -butyl-pyridine
$\eta_{ec}$	electron capture efficiency	NMBI	<i>N</i> -methylbenzimidazole
$\eta_{hi}$	hole injection efficiency	EDOT	ethylenedioxythiophene
$\eta_{ht}$	hole transport efficiency	bis-EDOT	bis-ethylenedioxythiophene
$\eta_{hc}$	hole capture efficiency	PEDOT	poly(3,4-ethylenedioxythiophene)
$k_{et}$	rate constant for charge recombination	PEDOT-PSS	poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
DSC	dye-sensitized solar cells	PVP	polyvinylpyrrolidone
TCO	transparent conductive oxide electrode	P3HT	poly(3-hexylthiophene)
FTO	fluorine doped tin oxide	PCBM	1-(3-methoxycarbonyl) propyl-1-phenyl [6,6]C61
ITO	indium-tin oxide		
LED	light-emitting diode		
OLED	organic light-emitting diodes		

DSC by applying the interface molecular engineering principle, focusing on heterojunction interfaces in DSC as shown in Fig. 1. Additionally, modifications of nano-porous TiO<sub>2</sub> electrodes will be reviewed along with an overview of co-adsorbent at the molecular-level and the effects of additives in the electrolyte as well.

As far as DSC's parameters are concerned, short-circuit current density ( $J_{sc}$ ) depends on the incident photon to current conversion efficiency (IPCE). IPCE is the most important factor, which is determined by (1) light harvesting efficiency (LHE) of sensitizing dye molecules ( $\eta_{lh}$  in Fig. 1), (2) charge injection efficiency at diode-like dye-TiO<sub>2</sub> interfaces ( $\eta_{ei}$ ), and (3) charge transport efficiency in n-type nano-TiO<sub>2</sub> phases ( $\eta_{et}$ ). LHE is simply the ratio of the amount of incoming photons to that of absorbed photons. Thus, LHE can be improved by increasing the absorption coefficient of dye molecules, the density and arrangement of adsorbed dyes, or the thickness of dye-adsorbed nano-porous TiO<sub>2</sub> electrodes. Charge injection efficiency ( $\eta_{ei}$ ) is determined by several factors including the potential difference between the conduction band edge of TiO<sub>2</sub> and the lowest unoccupied molecular orbital (LUMO) of the adsorbed dyes, acceptor density in the TiO<sub>2</sub>, and spatial distance between the surface of TiO<sub>2</sub> and the dye. For charge transport efficiency ( $\eta_{et}$ ), the electron diffusion length is a measure of assessment. During charge diffusion in TiO<sub>2</sub>, photogenerated electrons may recombine with electron acceptors like I<sub>3</sub><sup>-</sup> and the oxidized dye molecules at interfaces as may be called as electron leakage of DSC devices. Thus, to extract the photogenerat-

ed electrons through an external load, the electrons must reach grids on the transparent conductive oxide electrode (TCO) faster than the recombination process. Meanwhile, to achieve higher energy conversion efficiency, higher open-circuit voltage ( $V_{oc}$ ) is also required.  $V_{oc}$  is derived from the difference between the Fermi level of the TiO<sub>2</sub> electrode and I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox potential (Pichot and Gregg, 2000). In particular, charge recombination at the device interfaces has a significant influence on  $V_{oc}$ . In this paper, we review recent progress in DSC in a strategic view of interface engineering and unidirectional electron flow principle.

## 2. Interfacial DSC mechanisms

Fig. 2 shows the internal structure of the DSC, electron flow from a Ru complex (N3) dye on nano-porous TiO<sub>2</sub>, and SEM images of nano-sized TiO<sub>2</sub> electrodes and TiO<sub>2</sub>/FTO interfaces. Nano-porous TiO<sub>2</sub> electrodes are commonly prepared by sintering TiO<sub>2</sub> nanoparticles with diameter preferable around 20 nm. It is worth noting that TiO<sub>2</sub> particles undergo necking during sintering without growth of the crystalline size and the necking between TiO<sub>2</sub> layer and FTO is not perfect. During light illumination, excited electrons in the adsorbed dyes are injected into the conduction band of TiO<sub>2</sub>.

Here we briefly review the mechanisms of charge recombination that directly determine the parameters of DSC devices. Some researches (Huang et al., 1997; Grätzel, 2000) have suggested that charge recombination at the

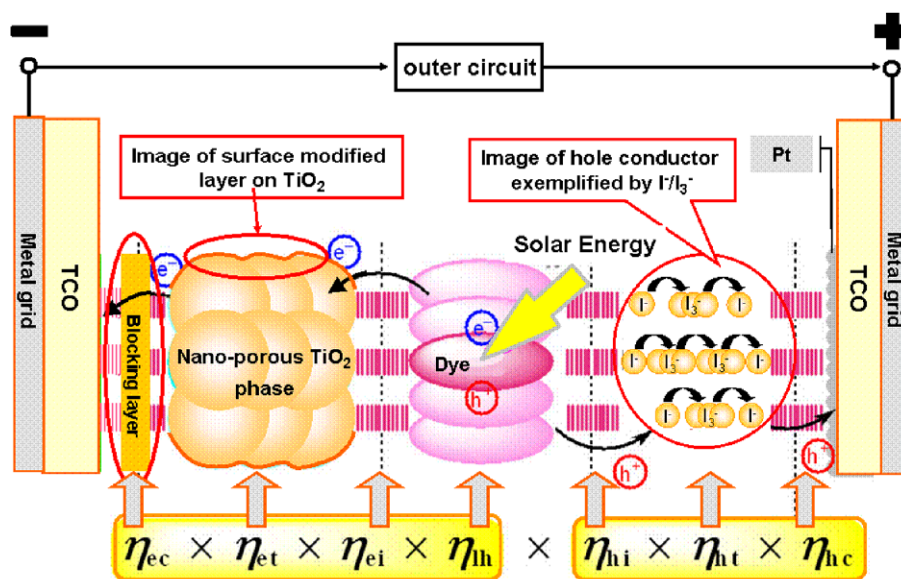


Fig. 1. DSC interface schematic and parameters for unidirectional charge flow.

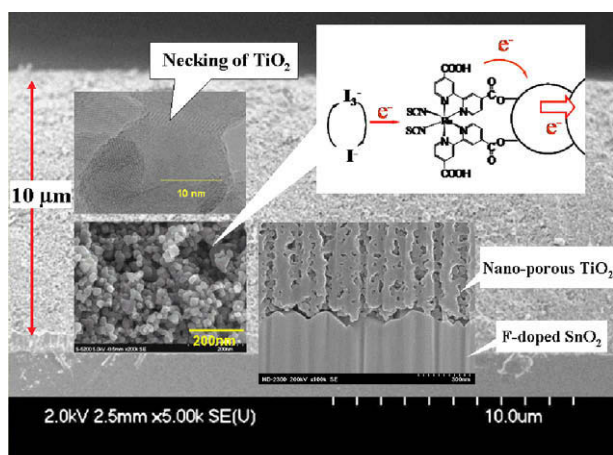


Fig. 2. SEM pictures of TiO<sub>2</sub> electrodes and interface in DSC.

interfaces of dye-vacant sites in nano-porous TiO<sub>2</sub> play a significant role in lowering photovoltage of DSC. There are two recombination pathways occurring at this interface (see Fig. 3). The injected conduction-band electrons may recombine with oxidized dye molecules or tri-iodide and

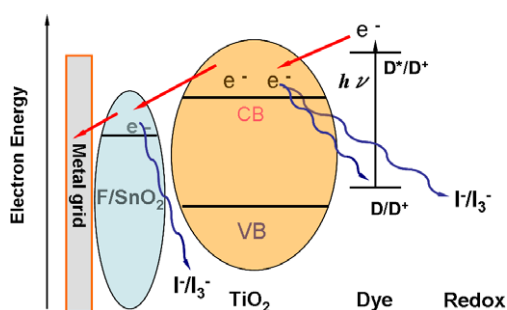


Fig. 3. Electron injection and leakage on nano-porous TiO<sub>2</sub>.

poly-iodide redox species in the electrolyte. Usually the former reaction is ignored because of the rapid rate of reduction of the oxidized dye molecules by I<sup>-</sup> ions. Many attempts have been done to suppress such back-electron transfer reactions taking place at dye-vacant nano-porous TiO<sub>2</sub> phases in recent years using surface treatment of porous TiO<sub>2</sub> electrode, which we will discuss in Section 3. On the other hand, the porous interfaces between FTO substrates and TiO<sub>2</sub> layers can act as electron recombination sites, i.e., electron leakage sites exist especially when solid or highly viscous redox species like ionic liquid iodides infiltrate into the poor necking airspace interfaces. It should be pointed out that those electrons caught by the SnO<sub>2</sub> phase of FTO might easily leak to redox electrolytes or solid-state hole conductors at the interfaces. In general, the TiO<sub>2</sub> compact layer between nano-porous TiO<sub>2</sub> and FTO is indispensable as a blocking layer in solid-state DSC employing CuI in place of liquid electrolyte or other organic p-type hole conductors systems.

### 3. Interfaces of nano-porous TiO<sub>2</sub>

#### 3.1. Electron leakage and electron blocking at interfaces

DSC is composed of a dye-sensitized nano-porous TiO<sub>2</sub> electrode on TCO (in most cases, fluorine doped tin oxide (FTO)), electrolytes containing I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple fill the pores of the electrode (anode), and the platinum counter electrode (cathode). The injected electrons diffuse through nano-porous TiO<sub>2</sub> into the TiO<sub>2</sub>/TCO interface, where electrons are extracted to the external grid and back through an outer circuit to the counter electrode. Meanwhile, electrons are transferred through Pt counter electrode to the electric conductive electrolyte system of the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple. Afterward the dye cations are eventually reduced back to

their ground state, receiving electrons from the electrolyte. This cycle continues as long as the device is illuminated and light energy is converted into electrical energy. Fig. 3 shows the unfavorable interfacial processes as electron leakage, which will put a ceiling on the eventual conversion efficiency of the DSC devices.

According to a simplified model of the unidirectional electron transporting principle of DSC, there are four important interfaces in the device as shown in Fig. 1. These are: the interfaces of FTO/TiO<sub>2</sub>, TiO<sub>2</sub>/dye, dye/electrolyte (or dye/hole transporting material), and the electrolyte/counter electrode (usually platinized FTO electrode). These heterojunction interfaces (Yanagida et al., 2003) and their parameters ( $\eta_{ec}$ ,  $\eta_{ei}$ ,  $\eta_{hi}$ ,  $\eta_{hc}$  in Fig. 1) play a decisive role in the performance of DSC devices as well as light-emitting diode (LED) (Armstrong et al., 2003), electro-luminescence devices, and other photovoltaic devices (Kobayashi et al., 1993; Nanu et al., 2005).

### 3.2. Surface modification of nano-porous TiO<sub>2</sub> phases

As far as the n-type porous TiO<sub>2</sub> electrodes are concerned, most of the work is focused on the modification of nano-porous TiO<sub>2</sub> electrodes. The most famous strategy is surface modification of mother TiO<sub>2</sub> electrode by dip-coating of diluted precursors of selected materials.

The pioneering work was done by Zaban et al. in 2000 by first proposing a core-shell double structure to form TiO<sub>2</sub>/Nb<sub>2</sub>O<sub>5</sub> electrode. Shell materials, such as Nb<sub>2</sub>O<sub>5</sub> with band structure of 100 mV higher than TiO<sub>2</sub>, can effectively suppress back-electron transfer at the interface of the nano-porous TiO<sub>2</sub> and dye molecules, leading to great improvements of  $V_{oc}$  and  $J_{sc}$ . Following this strategy, SrTiO<sub>3</sub> (Yang et al., 2002; Diamant et al., 2003), Al<sub>2</sub>O<sub>3</sub> (Taguchi et al., 2003; Palomares et al., 2003), SiO<sub>2</sub> (Spivack et al., 2006) even CaCO<sub>3</sub> (Wang et al., 2006a) have been employed as shell materials in surface modification of nano-porous TiO<sub>2</sub> films. Through mechanism study, transient decay of the injected electrons indicated that the charge recombination rate is retarded after the formation of Al<sub>2</sub>O<sub>3</sub> layers as a shell material (Campbell et al., 1997). In addition, the shell materials CaCO<sub>3</sub> (Wang et al., 2006a) or Nb<sub>2</sub>O<sub>5</sub> (Ahn et al., 2006) are interpreted to behave as a barrier to energetically separate the injected electrons from oxidized dye molecules and I<sub>3</sub><sup>-</sup> ions (Palomares et al., 2003) in electrolytes and thus to increase electron lifetime compared to the case of bare nano-porous TiO<sub>2</sub> electrodes.

For further interpretation of this phenomenon, subsequently Zaban et al. tried to probe the relationship between TiO<sub>2</sub> and the effective shell materials based on their physical and chemical properties (Diamant et al., 2004). Fig. 4 presents the percentage change of  $V_{oc}$  upon coating as a function of the isoelectric point and the electron affinity of the shell materials. When the isoelectric point of the shell is higher than that of the TiO<sub>2</sub>, the shell material maintains a more positive surface with respect to the core TiO<sub>2</sub>. Thus, a surface dipole directed towards the TiO<sub>2</sub> layer is gener-

ated. In this figure, a good correlation between the  $V_{oc}$  changes and the isoelectric point is observed. Although lower electron affinity shell materials yield improvements in  $V_{oc}$ , the correlation between the change in  $V_{oc}$  and the difference of electron affinity to that of TiO<sub>2</sub> is poor. Therefore, it seems that the acidity of the material is an important factor as far as these chemical-made specific core-shell systems.

Other methods such as doping with metal ions to prepare composite electrodes can improve conversion efficiency as well. Interestingly, among shell materials as mentioned above, most doping ions such as Zn<sup>2+</sup> (Wang et al., 2001), Mg<sup>2+</sup> (Jung et al., 2005), Nb<sup>5+</sup> (Imahori et al., 2006), and N (Ma et al., 2005) gave similar effects as a surface modification. Meanwhile, Yum (Yum et al., 2006) in our group developed an electrophoresis method to prepare Mg<sup>2+</sup> coated nano-porous TiO<sub>2</sub> electrode, achieving superior performance than that of mother TiO<sub>2</sub> electrode. We regard that these methods are similar to the above-mentioned surface modification methods because the electrophoresis method improves  $J_{sc}$ , fill factor (FF), and conversion efficiency as a result of effective unidirectional electron transport in the DSC devices. In fact, the surface modification in TiO<sub>2</sub> anodes can improve the lifetime of electrons in TiO<sub>2</sub> layers, which suggests a decrease of electron leakage at the interfaces of nano-porous TiO<sub>2</sub> and FTO/TiO<sub>2</sub> to a significant extent.

Currently, a core/shell double structure of ZnO/SnO<sub>2</sub> (Tennakone et al., 1999) composite electrodes are the only type showing around 7% conversion efficiency comparable to that of the TiO<sub>2</sub> electrode. Recently, one of our group members, Niinobe (Niinobe et al., 2005), investigated ZnO/SnO<sub>2</sub> electrode system and found that the enhancement of  $V_{oc}$  was mainly caused by the shift of the conduction band or surface dipolar, leading to a decrease in the chemical capacitance of the electrode by the difference in the chemical capacitance of ZnO and SnO<sub>2</sub>.

A TiCl<sub>4</sub> surface treatment of porous TiO<sub>2</sub> electrode is a common method employed during DSC fabrication (Nazeeruddin et al., 1993). Usually such treatment induces necking the nano-TiO<sub>2</sub> particles during calcination. Although such treatment will lead to a reduction of surface area, it can improve dye loading and eventually  $J_{sc}$  (Ito et al., 2005). A more detailed analysis (Sommeling et al., 2006) was carried out based on this treatment and it was found that the TiCl<sub>4</sub> treatment can improve electron injection efficiency leading to improvement of  $J_{sc}$ , which was attributed to the improvement of dye adsorption. However, when the photocurrent of the device is already high without the treatment (corresponding to cell efficiencies around 10%), the improvements with TiCl<sub>4</sub> are limited because the dye molecules must be effectively adsorbed on the nano-porous TiO<sub>2</sub> layers. Generally, the trace amount of effective doping ions and the improved necking of nano-porous TiO<sub>2</sub> electrodes can improve electron injection and charge separation efficiency because of the formation of polar states on the surface of the nano-porous TiO<sub>2</sub>.

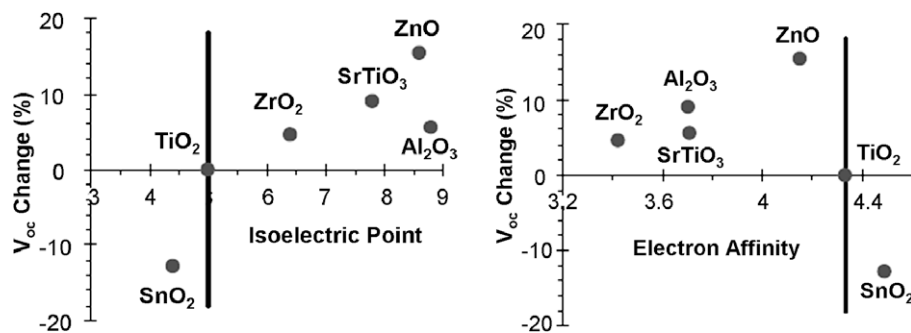


Fig. 4. The percentage of  $V_{oc}$  change upon coating as a function of the isoelectric point and the electron affinity of the shell material. A shell with higher isoelectric point or lower electron affinity than  $\text{TiO}_2$  generates a surface dipole directed toward the  $\text{TiO}_2$ , thus shifting the  $\text{TiO}_2$  conduction band negatively.

### 3.3. Effects of co-adsorbents and 4-*tert*-butyl-pyridine

Since DSC is three-dimensional nano-electronic device, we need to think about the three-dimensional interaction during the fabrication of DSC devices. One of the key processes is the sensitization by the adsorbed dye molecules. Dye adsorption conditions, i.e., time, temperature, and solvents would have great influence on effective dye absorption, but the selection of co-adsorbent is also very important to get high conversion efficiencies.

The first observation of co-adsorbent effect in DSC is based on chlorophyll and natural porphyrins derivatives (Kay and Grätzel, 1993). Along with the amphiphilic Ru-dye Z-907 (Wang et al., 2003b), K-19 (Zhang et al., 2005) were developed, many groups reinvestigated the mechanism and effectiveness of different co-adsorbents. It seems that the co-adsorbents are more effective on amphiphilic Ru-dye compared with N3 because of the favorable interaction between flexible chains of co-adsorbents and alkyl chains attached to these amphiphilic Ru-dyes. Generally, it is regarded that co-adsorbents with alkyl chains can prevent aggregation of sensitizing dye molecules on  $\text{TiO}_2$  and enhance dye's electron injection efficiency when excited. Fig. 5 shows the structures of Z-907, K-19, and typical co-adsorbents. In most cases, the co-adsorbents can improve the performance of the devices.

Recently, Grätzel et al. (Zhang et al., 2005, 2007) examined a series of guanidinoalkyl acids as co-adsorbents in order to tune the downward shift of the  $\text{TiO}_2$  conduction band and to eliminate dye-vacant sites on nano-porous  $\text{TiO}_2$  electrodes. Through photo-transient measurements, they found that the increase in open-circuit voltage for guanidinoalkyl acids is a collective effect of suppression of surface recombination and negative band edge movement. Interestingly, 3-guanidinopropylphosphonic acid at low concentration only suppresses the surface recombination, whereas at a higher concentration it also induces a negative band shift to 30 mV, which is opposite the effect of decylphosphonic acid (Wang et al., 2003c) that leads to a positive band-edge shift of 40 mV.

Another important point for realizing the high-efficiency of DSC is optimization of electrolyte composition. Usually

LiI, imidazolium iodide, 4-*tert*-butyl-pyridine (TBP),  $\text{I}_2$ , and organic solvent are essential components in organic liquid electrolyte. Among these components, frequently used additive in the electrolyte, TBP (Huang et al., 1997) plays a significant role in the process of the electrolyte development history because TBP (Huang et al., 1997) can improve  $V_{oc}$  greatly with a small decrease of  $J_{sc}$ . Although recently it seems that *N*-methylbenzimidazole (NMBI) (Wang et al., 2003b) will replace such low boiling point additives in DSC, here we briefly discuss the effect of TBP.

The effect was initially interpreted as retardation of charge recombination due to the adsorption of TBP at the dye-vacant  $\text{TiO}_2$  surface (Huang et al., 1997). The interpretation was derived by analyzing  $I$ - $V$  characteristics of the solar cells using the equation of

$$V_{oc} = \frac{kT}{qu\alpha} \ln \left( \frac{AI_0}{n_0^{u\alpha} k_{et} c_{ox}^m} \right), \quad (1)$$

where  $k_{et}$  is the rate constant for charge recombination,  $I_0$  is the incident photon flux,  $c_{ox}$  is the concentration of  $\text{I}_3^-$ ,  $n_0$  is the electron density in the dark, and  $m$ ,  $u$ , and  $\alpha$  are constants. When different electrolytes are employed, the  $E_{cb}$  may differ depending on the adsorbed species. Eq. (1) does not take into account the  $E_{cb}$ , and thus, the effects of recombination and the potential shift cannot be ruled out. Later, the influence of TBP was investigated by measuring electron lifetime and no significant change was found, suggesting that the  $V_{oc}$  was improved by the change of  $E_{cb}$  (Schlichth et al., 1997; Nakade et al., 2005). The effect of TBP on  $V_{oc}$  becomes significant when  $\text{Li}^+$  is dissolved in the electrolyte. Higher  $V_{oc}$  observed with TBP seems to be caused by the suppression of the specific adsorption of  $\text{Li}^+$  through the formation of complex with TBP, retarding the positive shift of the conduction band edge (Nakade et al., 2005). In addition, basicity of TBP itself induces the negative shift of the conduction band edge potential, increasing  $V_{oc}$ .

Other additives also play effective role in achieving respectable performance of DSC devices. For instance, Frank et al. (Kopidakis et al., 2006) found that guanidinium cations in the electrolyte can passivate recombina-

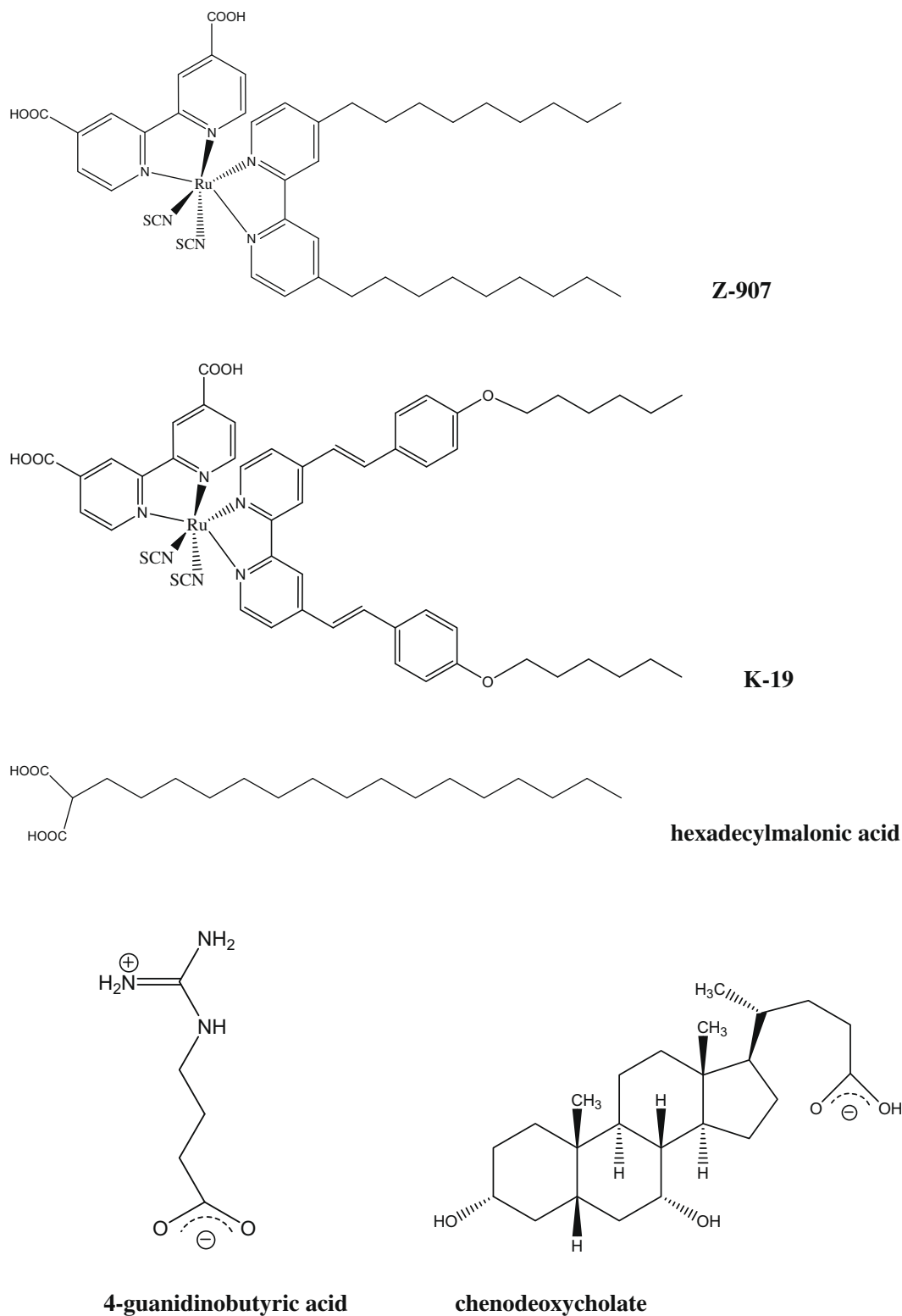


Fig. 5. The structures of Ru-dye as Z-907, K-19, and typical co-adsorbents.

tion, which was largely compensated by a downward shift in the band edge of the conduction band of  $\text{TiO}_2$ , resulting in a small overall gain of 20 mV in  $V_{oc}$ . As discussed above, such effects are similar to guanidinoalkyl acids co-adsor-

bent because the nano-porous  $\text{TiO}_2$ , especially dye-vacant  $\text{TiO}_2$  surfaces can adsorb the additive molecules in the electrolyte. In a word, the electrolyte behavior is so complicated that we need to think about its multiphase

interaction with dye molecules, TiO<sub>2</sub> surfaces and in particular the interface of FTO and nano-porous TiO<sub>2</sub> phases (see Fig. 2, inset SEM).

#### 3.4. Important interface at FTO and nano-porous TiO<sub>2</sub> phases

Because of the merit of keeping lower sheet resistance after thermal treatment, fluorine doped tin oxide (FTO) is preferable in DSC fabrication compared with the widely used highly conductive, indium-tin oxide (ITO). However, the latter has been attracted by many researchers to modify its surface for higher performance in organic light-emitting diodes (OLEDs) (Wang et al., 2003a) or organic solar cells (Krüger et al., 2000). For instance, a silanization reaction and formation (Ho et al., 1998; Choi et al., 2001) of self-assembled monolayers (SAMs) (Campbell et al., 1997; Appleyard et al., 2000; Morgado et al., 2002) are carried out to change the ITO electrode's work function. However, few groups gave much attention to the modification of FTO in DSC. One reason might be the inevitable step of sintering and annealing the FTO/nano-TiO<sub>2</sub> electrode at high temperature (>400 °C).

In the early 1990s, a TiO<sub>2</sub> compact layer had been introduced as a blocking layer at interfaces of FTO and nano-porous TiO<sub>2</sub> layers (FTO/nano-TiO<sub>2</sub>) in DSC fabrication by spray pyrolysis or by spin-coating method using Ti-isopropoxide solution. However, such a compact layer has no dramatic influence on the conversion efficiency of liquid electrolyte-based DSC. Therefore, most groups ignore such blocking layer during the preparation of wet DSC. On the other hand, some groups studied the interface of FTO/TiO<sub>2</sub> in order to establish models (Pichot and Gregg, 2000; Levy et al., 1997; Zaban et al., 1997; Cahen et al., 2000; Lagemaat et al., 2000; Fabregat-Santiago et al., 2003) of DSC or to characterize (Kavan and Grätzel, 1995; Gregg et al., 2001) and investigate the effectiveness (Ito et al., 2005; Peng et al., 2004; Hore and Kern, 2005) of the compact TiO<sub>2</sub> layer on conversion efficiencies. There are, however, few intense investigation on methods used to cope with poor necking at TiO<sub>2</sub>/FTO interface in DSC before 2005 (see Fig. 3, inset SEM picture).

Until 2003, Peter et al. (Cameron and Peter, 2003, 2005; Cameron et al., 2005) investigated the TiO<sub>2</sub> blocking layer in viewpoint of reaction mechanisms of back-electron transfer. They found that the TiO<sub>2</sub> blocking layer could significantly influence transient photovoltage and current decay by using electrochemical impedance spectroscopy (EIS) and simulations. From then on, many researchers started to notice this interface. For instance, in 2005 Grätzel et al. (Ito et al., 2005) investigated TiO<sub>2</sub> blocking layers with high performance DSC in detail and found that it can suppress dark current significantly. Meanwhile, our group paid considerable attention to this interface by introducing different oxides (Xia et al., 2006) by the spray pyrolysis method in viewpoint of fabrication of ionic liquid-based DSC devices. We found that not only TiO<sub>2</sub> but also

Nb<sub>2</sub>O<sub>5</sub> can work well as a blocking layer in such systems. Subsequently, in order to form a more homogeneous blocking layer, we developed a sputtering method (Xia et al., 2007a) which has good reproducibility, homogeneous coverage, and suitability for large-scale production. The improvement should come from the Nb<sub>2</sub>O<sub>5</sub> that may create 100 mV (Sayama et al., 1998) potential barrier between the Nb<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> particles, which can suppress back-electron transfer from FTO to electrolytes without lowering conductivity between them as shown in Fig. 6. A typical example of the Nb<sub>2</sub>O<sub>5</sub> effect is shown in Table 1, indicating that the combination of the surface treatment and blocking layer techniques should give better results.

Interestingly, we found that only a trace amount of Nb<sub>2</sub>O<sub>5</sub> (thickness 3–5 nm) works well while thicker Nb<sub>2</sub>O<sub>5</sub> leads to poor performance. However, compared with TiO<sub>2</sub> compact blocking layer, such thinner layered interface can suppress electron leakage through electronic control because Nb<sub>2</sub>O<sub>5</sub> diffuses to FTO and nano-TiO<sub>2</sub> layer completely during calcination (Xia et al., 2007b). Nevertheless, a very small amount of Nb<sup>5+</sup> at the interface of FTO/nano-TiO<sub>2</sub> can improve electron capture efficiency ( $\eta_{ec}$ ), leading to unidirectional electron flow, which is a very important point when designs and fabricates efficient and effective DSC devices.

On the other hand, we also prepared thin TiO<sub>x</sub> (Xia et al., 2007c) blocking layer by sputtering Ti target. Electrochemical analysis indicated that the electron leakage was perfectly suppressed compared with the case of conventional TiO<sub>2</sub> blocking layers as follows:

- (1) The resulting TiO<sub>x</sub> layer is more dense than nano-porous TiO<sub>2</sub> due to their different lattice structures.
- (2) Titanium metal is very reactive with the SnO<sub>2</sub> in FTO, which favors tight attachment to the FTO layer at thermal treatment during fabrication of DSC devices.

Due to the different affinity toward FTO and nano-porous TiO<sub>2</sub> layer, the appropriate blocking materials should tune their affinity well to lead unidirectional electron flow at the interfaces. Therefore, good electronic matching is necessary at the interfaces. In fact, similar interface control is very important in silicon solar cells, heterojunction solar cells and even in OLEDs. In addition, recently flexible solar cell based on flexible PET-ITO or PEN-ITO (poly(ethylene

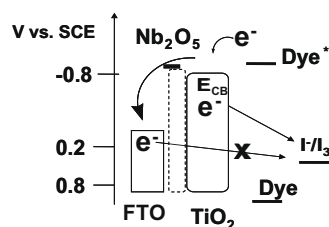


Fig. 6. Scheme of the electron transfer at the Nb<sub>2</sub>O<sub>5</sub> as blocking layer devices.

Table 1  
Comparison of the parameters of the ionic liquid DSC devices fabricated by mesoporous TiO<sub>2</sub> electrodes with or without Nb<sub>2</sub>O<sub>5</sub> blocking layers (BL) on FTO before and after optimization with the NbCl<sub>5</sub> surface treatment.

Electrodes	$V_{oc}$ (mV)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF	$\eta$ (%)
Nano-TiO <sub>2</sub> /dye (non-blocked electrode)	663	7.91	0.66	3.5
Nb <sub>2</sub> O <sub>5</sub> -BL(5 nm)/nano-TiO <sub>2</sub> /dye	710	9.32	0.68	4.5
Nano-TiO <sub>2</sub> /treated with NbCl <sub>5</sub> /dye	675	9.12	0.67	4.2
Nb <sub>2</sub> O <sub>5</sub> -BL/nano-TiO <sub>2</sub> /treated with NbCl <sub>5</sub> /dye	720	9.73	0.68	4.8
Nano-TiO <sub>2</sub> /scattering layer/dye	682	11.2	0.66	5.0
Nb <sub>2</sub> O <sub>5</sub> -BL/nano-TiO <sub>2</sub> /scattering layer/dye	719	11.4	0.67	5.5

terephthalate) or poly(ethylene naphthalate) coated with indium-tin oxide) or metal substrates is a popular trend in DSC. Due to the cost-effective and lightweight merits, PET or PEN and metal substrates are employed to replace traditional FTO glass substrates. In order to improve the attachment between nano-porous TiO<sub>2</sub> layers and these flexible substrates, pretreatment of the flexible substrates is indispensable. So far, very thin (thickness 100 nm) layers of SiO<sub>2</sub> (Kang et al., 2007), ITO (Jun and Kang, 2007), or TiO<sub>2</sub> (Ito et al., 2006a) have been pre-coated on the flexible substrate. Such techniques exemplify a successful application of the interface engineering principle.

#### 4. Interfaces in solid-state DSC devices

##### 4.1. Design of solid-state hole conductors for robust DSC

Since stability and reliability of DSC devices are still the most important issues for practical use of DSC devices, solid-state DSC, and especially the development of I<sub>2</sub>-free DSC attracts great interest in industry. The following aspects are essential for adoption of solid-state p-type semiconductors for the DSC devices.

- (1) Solid materials should be able to transfer holes from the photoexcited dye to the counter electrode as well as I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox electrolytes. Thus, its band level should match the oxidation potential of the dye molecules well.
- (2) For electronic unidirectional communication, the solid hole-transport molecules must interact through bonds or through space with the sensitizing dye molecules on mesoporous TiO<sub>2</sub> phase.
- (3) The hole transport materials must fill into the nano-space of the three-dimensional TiO<sub>2</sub> layer
- (4) Ionic species must be incorporated into the three-dimensional TiO<sub>2</sub> layers to enhance the electron diffusion in the nano-porous TiO<sub>2</sub> phase.

As mentioned in Section 1, the photovoltaic DSC devices consist of two principle processes, namely the photo-formed carrier from excited dye molecules and the separation of hole–electron pairs by TiO<sub>2</sub> as n-type (electron) conductors and electrolytes as p-type (hole) conductors, respectively. In the case of solid-state DSC, the

latter hole separation process is very important as well as in bulk heterojunction solar cells.

In order to achieve effective charge separation efficiency, the electronic interaction of dye molecules with liquid electrolyte or solid-state hole conductors is very important. In the case of liquid I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox electrolyte, such interaction is plausible due to high fluidity of the electrolyte and easy penetration into three-dimensional porous dyed TiO<sub>2</sub> phase. However, in the case of more viscous ionic liquids, the difficulty of smooth infiltration into porous space constructed by nano-porous TiO<sub>2</sub> framework results in lower  $V_{oc}$ ,  $J_{sc}$ , and FF. The case is also true for the solid-state DSC. In fact, other investigations on interfaces of dye/electrolytes (or dye/hole transporting materials) are in progress on the basis of so-called interface engineering combined with molecular self-assembly method (Haque et al., 2004).

##### 4.2. Solid-state DSC devices using CuI or spiro-OMETAD

As far as the typical trend is concerned, inorganic p-type semiconductors such as CuI and organic p-type conductive polymers serve as hole transporting materials in solid-state DSC. Developed in 1995 by Tennekone et al., CuI was used in one of the first successful solid-state DSC as well as the use of 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)9,9'-spirobifluorene (spiro-OMETAD). However, the stability of the devices were very poor until Kumara et al.(2002a,b) introduced a small amount (10<sup>-3</sup> M) of 1-methyl-3-ethylimidazolium thiocyanate (MEI-SCN) in the coating solution. In this case, such material serves as CuI crystal growth inhibitor and maintains nano-sized CuI for a longer time so as to maintain good contact with dyed TiO<sub>2</sub> phase, which improves the stability and energy conversion efficiency of the devices. Meanwhile, Fujishima et al. (Taguchi et al., 2003; Meng et al., 2003) optimized such kind of solid-state DSC by introducing ZnO- or MgO-modified TiO<sub>2</sub> electrodes, which has previously discussed in Section 3.

Usually the efficiency of solid-state DSC devices is only one third or even much lower than that of liquid-based DSCs because of the lower hole mobility of these p-type materials and their insufficient penetration into three-dimensional porous dyed TiO<sub>2</sub> layer. To date, the highest efficiency achieved has been about 5% (Snaith et al., 2007) based on spiro-OMETAD with a novel Ruthenium dye, which was the first small molecular hole conductor employed in solid-state DSC in 1998 (Bach et al., 1998).



### 4.3. Introduction of PEDOT as a solid-state hole conductor

Fig. 7 shows the p-type organic semiconductors studied to date for solidification of DSC (Haque et al., 2004; Park et al., 2003; Murakoshi et al., 1997; Saito et al., 2004a; Tan et al., 2004; Wang et al., 2006b). In consideration of commercial availability of nicely conductive PEDOT derivatives, we choose PEDOT as a typical hole conductor for solid-state DSC. Although the invention of nano-porous

TiO<sub>2</sub> layers as electron conductors in DSC was the most important breakthrough in 1991 (O'Regan and Grätzel, 1991), such nano-porous structures are the most difficult obstacle for polymeric hole conductors to penetrate into the nanospaces in the TiO<sub>2</sub> layer of solid-state DSC. In order to get perfect charge separation between dye molecules and hole conductor phase, we should organize hole conductors nicely to contact with dye molecules on nano-porous TiO<sub>2</sub> surface. Therefore, in order to achieve

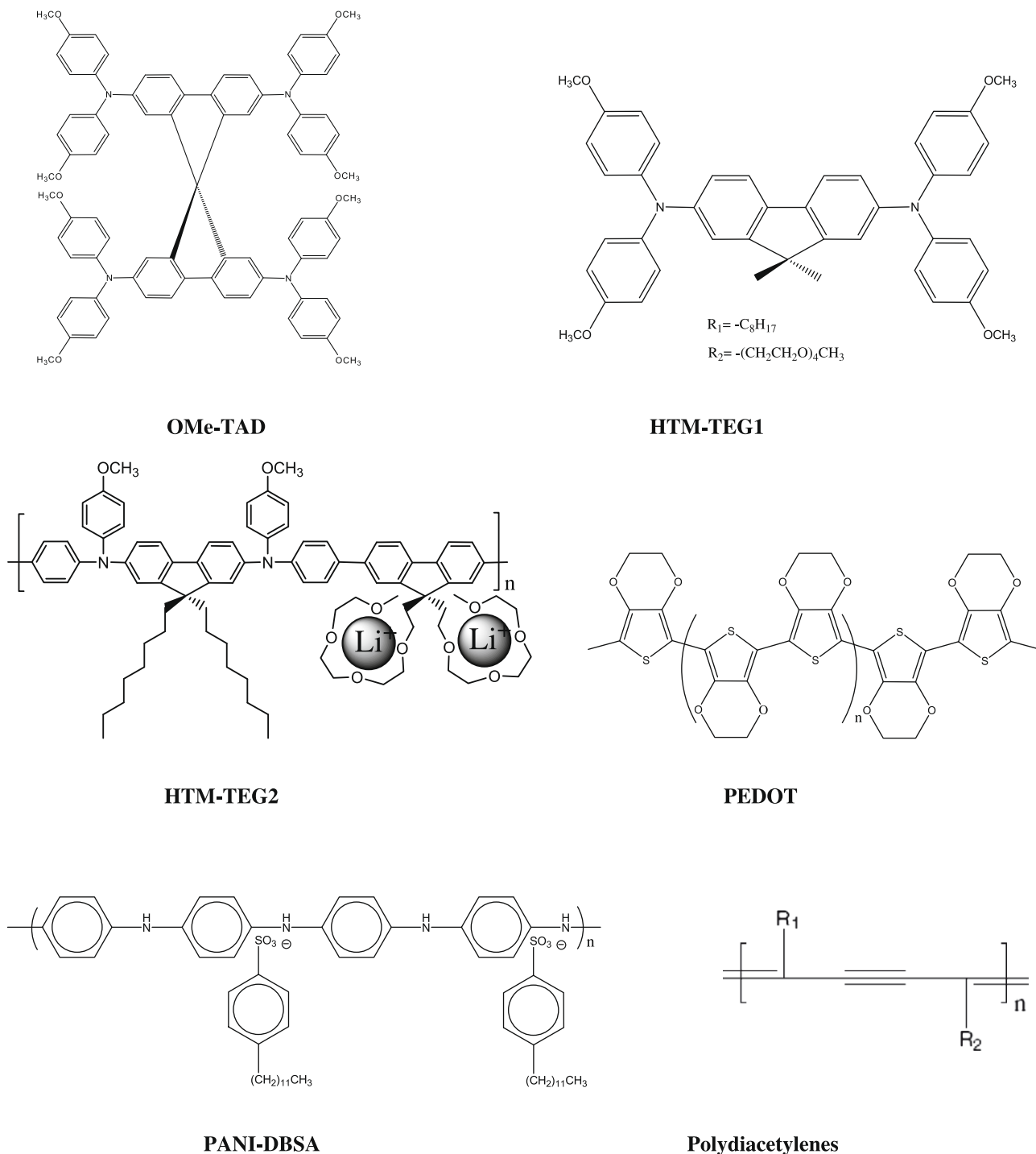


Fig. 7. Some commonly used p-type organic semiconductors in solid DSC.

effective filling of PEDOT in the DSC nanospace, we first proposed the photo-polymerization of bis-ethylenedioxythiophene (bis-EDOT) for fabrication of PEDOT-based solid-state DSC. Namely, the photo-polymerization was carried out using Z-907 as the dye and bis-EDOT as the monomer under potentiostatic conditions (0.2 V vs Ag/AgCl). Because bis-EDOT has lower oxidation potentials than that of ethylenedioxythiophene (EDOT), it can be successfully photo-electropolymerized on dyed TiO<sub>2</sub> film without damaging the Ru-dye. During this process, under irradiation by visible light, the oxidized dye molecules work as active sites, triggering the polymerization of bis-EDOT in the three-dimensional nanospace. Along with investigation of this system, we found that the dye-excitation from cathode-side illumination gave better conversion efficiency than from the anode-side illumination (Fukuri et al., 2006).

Fig. 8 shows the set up of the experiments and their respective  $I$ - $V$  curves for FTO/blocking layer/TiO<sub>2</sub>/Z-907/PEDOT/Au cells are shown in Fig. 9. Table 2 summarizes their parameters for the two illumination modes. The enhancement of  $J_{sc}$  seems to be attributed to improvement of the electric contact between the dye molecules, the resulting PEDOT chains and the Au-sputtered counter electrode. Such excellent interface contact will result in the smooth unidirectional electron transfer in the devices. In addition, the short-circuiting between PEDOT and FTO glass substrate due to the direct contact between them has hardly occurred in the case of cathode-side illumination. Both the enhancement of  $V_{oc}$  and FF and the reduction of dark current in cathode-side illumination indicate that the back-electron transfer and the electron leakage from both the conduction band of TiO<sub>2</sub> and FTO to PEDOT should be suppressed. In other words, the enhancement of shunt resistance and the reduction of series resistance of the PEDOT-based DSCs can be rationalized due to unidirectional electron flow at the interfaces. The cathode-side illumination method in the polymerization of bis-EDOT into the nanospaces of the dyed TiO<sub>2</sub> layer should lead to rectifiable improvement of the PEDOT-

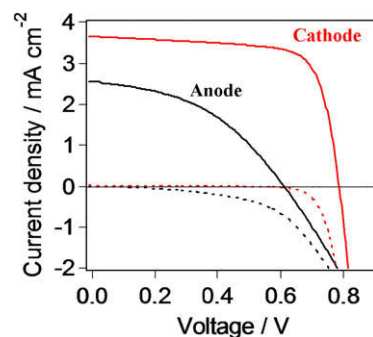


Fig. 9. Photocurrent–voltage characteristic for PEDOT/DSCs fabricated by cathode-side illumination (bold curve) and anode-side illumination (solid curve) under AM1.5 irradiation and their dark currents (dotted curves). The best performances of the cells are chosen.

Table 2

Polymerization charge and the cell performance of solid-state PEDOT/DSCs.

	Polymerization charge (mC cm <sup>-2</sup> )	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	FF	$\eta$ (%)	$\eta_{max}$ (%)
Anode side	20.8	2.76	660	0.36	0.64	0.67
Cathode side	15.2	3.20	770	0.50	1.25	2.09

based DSC. The molecular-controlled impregnation of PEDOT in nano-porous TiO<sub>2</sub> electrodes is essential for achieving high efficiency of the solid-state PEDOT-based DSC.

As demonstrated above, controlling the photo-electropolymerization process can optimize the interaction between PEDOT and the dye molecules, resulting in improved performance of the DSC devices. However, when Z-907 was employed as sensitizer in organic p-type solid-state DSC, the hydrophobic interaction between Z-907 and PEDOT seems a little inefficient.

#### 4.4. Development of sensitizing dyes for PEDOT-based DSC

We recently succeeded in developing a novel hybrid Ru-complex sensitizer (HRS) by hybridizing the advantages of N3 dye and metal-free organic  $\pi$ -conjugation sensitizers. Two advantages of N3 dye are (1) a dc bpy (2,2'-bipyridine-4,4'-dicarboxylic acid) ligand is indispensable for adsorption on TiO<sub>2</sub> for effective photoelectron injection. (2) Ru ion and SCN<sup>-</sup> ligands are essential for efficient light energy harvest in long wavelength range. The organic  $\pi$  conjugation dyes have two different advantages (1) the  $\pi$  conjugation leads to an increase of molecular extinction coefficients through self-organization of the molecules, (2) it is easy to control the redox potential and energy gap of the  $\pi$  conjugation moiety and to introduce hydrophobic alkyl group. Keeping these facts in mind, our group (Jiang et al., 2006) recently developed a novel ruthenium dye (HRS-1) with hydrophobic 2-thiophen-2-yl-vinylconjugated bipyridyl ligand, which gives a 30% improvement of molar

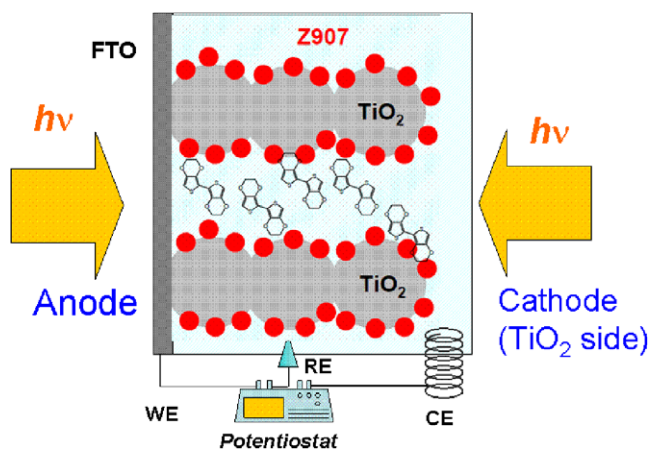


Fig. 8. Graphic illustration of light illumination direction in situ photo-electrochemical polymerization of bis-EDOT.

extinction coefficient at visible region with 10 nm red-shift to longer wavelength when compared with N-719. The energy structure of HRS-1 is shown in Fig. 10, showing the excellent energy matching with the conduction band and the redox potential of  $I^-/I_3^-$ . The solid-state HRS-1-sensitized PEDOT/DSC showed better performance than the solid-state Z-907-sensitized PEDOT/DSC as shown in Table 3 (Mozer et al., 2006).

The high  $V_{oc}$  suggests effective suppression of electron recombination at the PEDOT interfaces by hydrophobic alkyl chain in HRS-1 as well as in Z-709. The high FF means that effective electron flow channel should form in the bulk and at the cathode/PEDOT/dye interfaces in HRS-1 as well as in Z-709. The improved  $J_{sc}$  implies an improved electron flow at the PEDOT/dye interfaces in HRS-1 due to improved dye absorption efficiency and high possibility of interaction between the dye and PEDOT. Namely, the thienyl groups in HRS-1 contact with PEDOT through intermolecular  $\pi$  stacking with EDOT units in PEDOT. Fig. 11 shows the schematic view of the interaction between HRS-1 and PEDOT.

Meanwhile, other groups obtained similar results. For instance, Wu et al. (Chen et al., 2006) developed a similar ruthenium dye with bis-thiophene moiety exhibiting supe-

rior performance compared with N-719. Such dye can be applied to the PEDOT/DSC as well. Thelakkat et al. (Karthikeyan et al., 2007) synthesized a novel ruthenium dye with triarylamine moiety in solid-state DSC showing over 3% of conversion efficiency when applied to spiro-OMETAD/DSC. According to these results which were based on interfacial molecular-level engineering principle in DSC, the introduction of hole transporting moiety into Ru-dyes to improve the interfacial contact with hole conductors in solid-state DSC is booming.

As another kind of solid-state photovoltaic devices, bulk heterojunction organic photovoltaic attracts some interests in solar cell research. Compared with  $I_2$ -free solid-state DSC, these two kinds of cells are very similar except that  $TiO_2$  serves as the electron carrier while commonly used 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C61 (PCBM) (Padinger et al., 2003) as the counterpart. The Ru-dyes absorb visible light, injecting charge into n-type  $TiO_2$  in the former, while charge formation as exciton and their separation occur at the interface between PCBM and regio-regular poly(3-hexylthiophene) (P3HT) in the latter. The hole transporting function are very similar. For instance, P3HT or its derivatives were applied in both two types of cells (Padinger et al., 2003; Lancelle-Beltran et al., 2006). Sariciftci (Hoppe and Sariciftci, 2004) pointed out that the research directions in these two kinds of cells are gradually merging together.

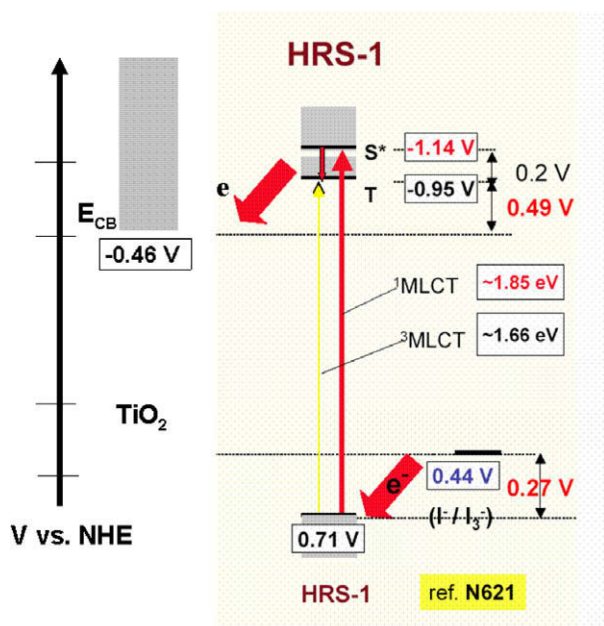


Fig. 10. Energy structures of HRS-1 matching with  $E_{cb}$  of  $TiO_2$  and redox potential of  $I^-/I_3^-$  ( $S^*$ , singlet state; T, triplet state estimated from N621 dye).

Table 3  
The comparison between Z-907 and HRS-1 sensitized solid-state PEDOT/DSCs.

	$J_{sc}$ ( $mA\ cm^{-2}$ )	$V_{oc}$ (mV)	FF	$\eta_{max}$ (%)
Z-709	3.70	790	0.73	2.1
HRS-1	4.50	780	0.74	2.8

## 5. Surface catalytic cathodes as counter electrodes of DSC

Another essential component in DSC devices, counter electrodes as cathodes must function to accept holes or release electrons through catalytic interaction with  $I^-/I_3^-$  redox electrolytes or hole conductors. At present, Pt on FTO exhibits the best performance for electrolyte-based DSC devices. However, its high cost and corrosive properties in combination with water and oxygen in the  $I^-/I_3^-$  redox electrolyte prompt DSC researchers to search for other substitute materials.

One possibility for counter electrodes is modified Pt counter electrode by formation of complex or alloy such as Pt-NiO or PtNi (Kim et al., 2006; Wang et al., 2005a; Katusic et al., 2006). Recently, polyvinylpyrrolidone (PVP) capped Pt nanoparticles (Wei et al., 2006) were employed as a counter electrode in DSC devices. These efforts might pursue the reduction of Pt loading on FTO. On the other hand, Pt-free electrodes such as nano-carbon (Kay and Grätzel, 1996; Papageorgiou et al., 1977; Suzuki et al., 2003; Imoto et al., 2003; Murakami et al., 2006) or PEDOT (Saito et al. 2002, 2004b; Shibata et al., 2003; Lenzmann et al., 2005) attract more interests. From an industrial and commercial production point of view, the latter direction has a more promising future. Interestingly, single wall carbon nanotube (Suzuki et al., 2003) showed 80% of the performance of Pt-activated counter electrode.

PEDOT-PSS is the only commercially available PEDOT polymer. Our group recently found that PEDOT deriva-

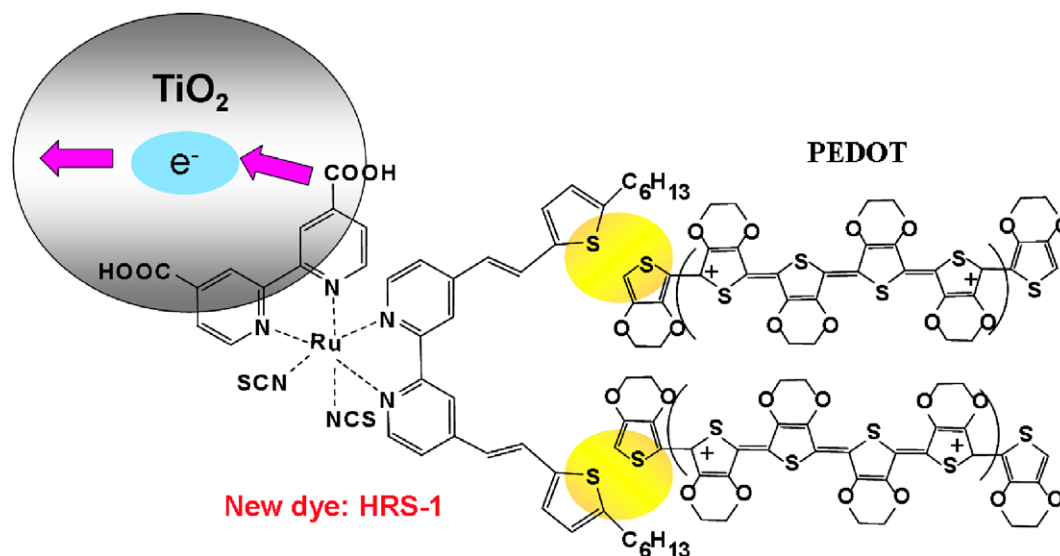


Fig. 11. The scheme of close contact of HRS-1 and the hole conductor PEDOT through  $\pi$ - $\pi$  interactions at interface.

tives work as a substitute of Pt on FTO. PEDOT-PSS on FTO gives moderate fill factor (FF) around 0.45–0.58 while employing case gel electrolytes (Shibata et al., 2003) was employed as electrolytes, while very poor FF (less than 0.3) was obtained when using general liquid electrolytes (Saito et al., 2002; Shibata et al., 2003). It was noted that these counter electrodes were fabricated by spin-coating an aqueous solution PEDOT-PSS. It is apparent that the interface-controllable methods for PEDOT-activated cathodes are essential for the improvement of FF. Fill factors higher than 0.65 can be obtained in DSC devices when using the chemical oxidation or electrochemical oxidation methods applied by our group (Xia et al., 2007d). We attribute the poor FF to the poor attachment of PEDOT on FTO surface when the spin-coating method was employed.

## 6. Improvement of fill factors in DSC

One of the surprises of DSC to solar cell researchers is the respectable FF of more than 0.65 which can be easily obtained. This is due to easily achievable large diffusion

length of  $\sim 20 \mu\text{m}$  in DSC, which in turn is due to the formation of the long-lived electron with high diffusion coefficients in nano-porous space  $\text{TiO}_2$  phases. The diffusion coefficients of nano-porous  $\text{TiO}_2$  layers are enhanced by adsorption of cationic species from the redox electrolytes on nano-porous  $\text{TiO}_2$  phases (Mori and Yanagida, 2006). Thus, it should be noted that the penetration of ionic species in nano-porous  $\text{TiO}_2$  improves the FF in DSC devices. In the case of solid-state DSC using p-type hole conductors, an ionic liquid additive (Senadeera et al., 2003) can greatly improve FF since the ionic liquid can penetrate into the interface and adhere well to the interface.

In DSC devices, the large area cells usually show poorer FF compared with those of small size devices. Fig. 12 shows the relationship between cell area and FF (Ito et al., 2006b). High FF requires two things: (1) the shunt resistance should be increased to prevent electron leakage on TCO and (2) the series resistance should be minimized to get a sharp rise in the forward current. In most cases, the optimization of both series resistance and sheet resistance is an essential approach. Fujikula company (Kawashima et al., 2004) developed dou-

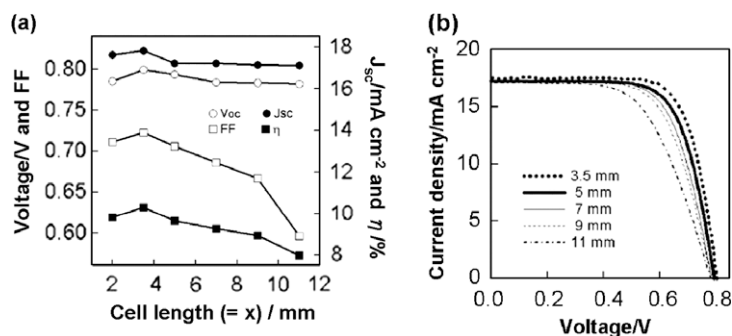


Fig. 12. (a) Effect of the side length ( $X = 3.5, 5, 7, 9,$  and  $11 \text{ mm}$ ) on the photovoltaic performance parameters of the DSC. The sensitized  $\text{TiO}_2$  electrodes having the quadratic shape. (b)  $I$ - $V$  curves for the same cells. The photocurrent densities and conversion efficiencies were calculated by using the total areas of the dyed  $\text{TiO}_2$  films. The size of mask was always  $1.5 \text{ mm}$  larger than  $X$ .

ble layer ITO/FTO substrate as TCO in order to minimize the sheet resistance of TCO of the dyed TiO<sub>2</sub> anode and successfully improved the FF. Due to its lower sheet resistance, use of highly conductive ( $\sim 2 \Omega/\square$ ) TCO substrate can increase up to 70% in FF of the devices (10 cm  $\times$  10 cm). Fig. 13 shows the structure of a double-layered substrate and their  $I$ - $V$  curves are shown in Fig. 14. Meanwhile, Ngamsinlapasathiana et al. (2006) developed ITO/SnO<sub>2</sub> substrate and observed similar behavior.

Another common method to improve FF is to embed metal grid such as Ni (Okada et al., 2004), Ag (Lee et al., 2006) on TCO like FTO. Taking into consideration the corrosive  $I^-/I_3^-$  redox electrolytes, we need to choose high conductive and stable metals for higher stability of DSC. After embedding such metal grid, the value of sheet resistance of the substrate would decrease to around  $1 \Omega/\square$ . Fig. 15 shows the effect of Ni grid in large area DSC devices.

## 7. Conclusions

The main goal of DSC devices is to optimize the performance with maintaining stability and cost-effectiveness of modules. The parameters for the conversion efficiencies are  $J_{sc}$ ,  $V_{oc}$ , and FF, which are dramatically influenced

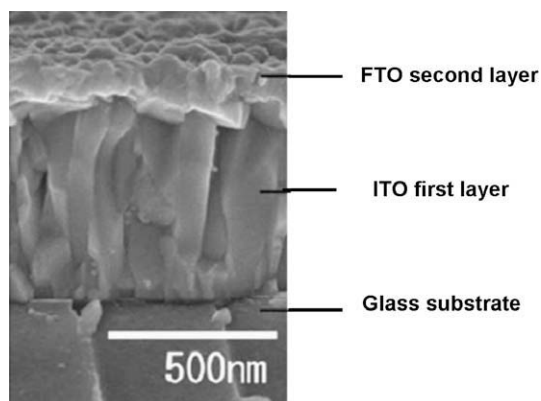


Fig. 13. Cross-sectional FE-SEM image of the double-layered film composed of ITO first layer and FTO second layer.

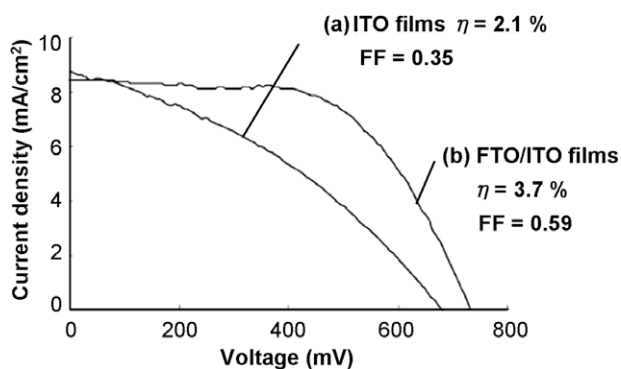


Fig. 14.  $I$ - $V$  characteristics of 100 mm  $\times$  100 mm sized cells using (a) ITO and (b) FTO/ITO films.

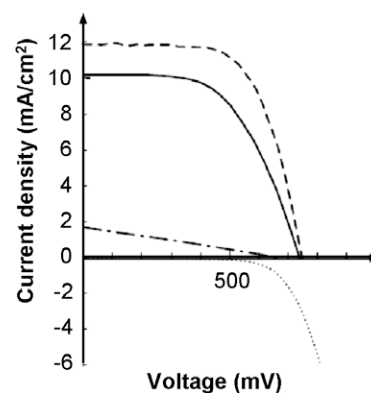


Fig. 15. Photocurrent–voltage characteristics of the 100 mm  $\times$  100 mm Ni grid large size cell (—), a 5 mm  $\times$  9 mm mini size cell (---), a 100 mm  $\times$  100 mm non-grid large cell (- · -), and dark current density of the Ni grid large cell (· · ·) under AM1.5, 100 mW/cm<sup>2</sup>. Conversion efficiency of the Ni grid large cell is 4.3% (5.1% in active area), the mini size cell is 5.7%, and the non-grid large cell is 0.3%.

by interface parameters as shown in Fig. 1. We must maximize each parameter at the same time. We cleared that  $J_{sc}$ ,  $V_{oc}$ , and FF can be optimized by designing the interface structures for unidirectional electron flow at semiconductor hetero-junctions ( $\eta_{ei}$ ,  $\eta_{ec}$ ,  $\eta_{hi}$ ) and by choosing catalytic or conduction materials for ohmic-contacting interfaces ( $\eta_{et}$ ,  $\eta_{hc}$ ), which will result in suppression of electron leakage at each interface. It appears that  $J_{sc}$  and  $V_{oc}$  sometimes trade off each other. However,  $J_{sc}$  correlates with  $V_{oc}$  and FF, hopefully being improved through optimization of  $V_{oc}$  and FF.

The optimization of  $J_{sc}$  will essentially be achieved by the most efficient photon absorption on dye molecules that function is as molecular diodes on nano-porous TiO<sub>2</sub> phases. The reason is that the energy level matching between adsorbed dye molecules, nanocrystalline TiO<sub>2</sub>, and electrolyte composition (or hole conducting molecules) is essential, and the introduction of scattering layer in the TiO<sub>2</sub> is desirable depending on the absorption property of the sensitizing dye molecules. Development of novel robust dye molecules with narrow band-gap and large molar absorption coefficient is an on-going DSC theme.

In summary, the interface optimization engineering principle is a powerful strategy to maximize the DSC performance. Superior unidirectional electron transport flow can be manipulated by greater control of interface contact at the molecular-level. With these in mind, one can design and fabricate cost-effective and durable DSC devices with higher conversion efficiency.

## Acknowledgements

This research was supported by the New Energy and Industrial Technology Development Organization (NEDO) under the Ministry of Economy, Trade and Industry. The authors acknowledge the financial support of the Japanese Society for the Promotion of Science. Additionally, the

authors acknowledge Dr. Tomoyoshi Mothiro of Toyota Central R&D Labs., Inc., Dr. Naruhiko Masaki, Dr. Kejian Jiang, Dr. Kazuharu Suzuki, Dr. A.J. Mozer, Mrs. Yukyeong Kim of Seoul National University, and Dr. Monica Lira-Cantu of Institut De Ciencia de Materials de Barcelona for helpful discussion and support.

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Osaka University in 1987, contributing to discovery of novel and efficient photocatalysis using nano-crystalline metal sulfides, and of photo-fixation of carbon dioxide using organic semiconductors. He also extended his research interest to microwave-assisted chemistry and remarkable luminescent lanthanide metal complexes. After retirement in 2004, he becomes emeritus and guest professors of Osaka University. He has just taken the chair of guest professor of “Kaneka Energy Solution Research” division that was newly established in 2008 at Center for Advanced Science and Innovation, Osaka University, and then continuing researches on dye-sensitization solar cells.



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