Review

Solid-state dye-sensitized solar cells

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Abstract: All solid-state dye-sensitized solar cells (DSSCs), which have been pursued just in the past ten years, are reviewed here in terms of the historical background, the present situation and the developmental outlook. Recent efforts to fabricate high-efficiency solid-state DSSCs are summarized in this paper, as well as studies on the long-term operational stability of such solar cells. Studies on the extremely-thin-absorber solar cell (ETA-solar cell) are also reviewed. The operational mechanisms of solid-state DSSCs are compared to those of the liquid counterparts (dye-sensitized photoelectrochemical cells, DSPECs). Two main obstacles to high conversion efficiency of solar energy are highlighted herein for solid-state DSSCs, i.e., insufficient light absorption and large internal recombination loss. Possible resolutions for these obstacles are pointed out.

Key words: Solid-state dye-sensitized solar cell; photoelectrochemical cell; ETA-solar cell; solar energy conversion efficiency; long-term stability; interfacial charge recombination.

Introduction. The all solid-state dye-sensitized solar cell (DSSC) has been a subject of research just in the past ten years (Tennakone *et al*. 1995; O'Regan *et al*. 1998; Bach *et al*. 1998).[1)-3)] This work has appeared as an offshoot of that on dye-sensitized photoelectrochemical cells (DSPECs); thus, the solid-state cell always exhibits a structure similar to the latter except for the replacement of the liquid electrolyte with a p-type semiconductor or organic hole conductor materials. It inherits the advantage of the DSPEC in terms of separating charge generation from charge transport. Therefore, the quality of the electrode material (purity and crystallinity) for either n-type or p-type semiconductors, is not as critical as that for classical photovoltaic cells, which have to provide good photo-response as well as good charge mobility within the same compound. Moreover, being a kind of solid-state device, it could be manufactured with simpler, less expensive technology than that for PECs, since problems such as leakage, packaging, and corrosion, which exist for liquid electrolytes, could be avoided.

Despite these advantages, the development of solid-state DSSCs in the past decade has been less than satisfactory. The best reported efficiency for solar energy conversion for solid-state DSSCs was below 4%, far lower than the efficiency (~10-11%) reported for DSPECs. More and more evidence has shown that a solid-state DSSC is not equivalent to a solidified DSPEC. The PEC is in principle a molecular electronic device on the base of chemical conversion on the molecular scale, while the solid-state DSSC works like a p-n heterojunction, whose behavior should be described in terms of semiconductor physics. Thus far, studies on solid-state DSSCs have been mainly based on the knowledge already developed for DSPECs, which might be a factor contributing to the unsatisfactory progress. In this review paper, we will look into the historic background and the recent developments of solid-state DSSCs, discuss the main problems, and try to find a resolution for further improving the solar energy conversion efficiency.

Historic background: Photoelectrochemical cells. Research on PECs started in the late 1960s, and

went through a frantic period after the oil crisis in 1973, since it was recognized at that time that the gigantic supply of solar energy, 3×10^{24} Joules per year, could, in principle, meet the energy needs of all the people in the world. It was also recognized that solar energy was a clean energy source, which could relieve the environmental problems arising from the use of fossil fuels.

In the late 1960s, one of the authors of this paper (AF) began to study oxide semiconductors that would respond to light, while he was still a graduate student at the University of Tokyo. The author was able to obtain a single crystal of the rutile form of titanium dioxide, a wide band-gap semiconductor. The crystal was transparent, like glass, and most importantly, it was an extremely stable material in the presence of aqueous electrolyte solutions. The author connected a complete electrochemical circuit, with titanium dioxide and platinum black as the two electrodes, as illustrated in Fig. 1. When the surface of the TiO_2 electrode was irradiated with light ($\lambda < 415$ nm), photocurrent flowed from the platinum counter electrode to the TiO_2 electrode through the external circuit. The direction of the current revealed that the oxidation reaction (oxygen evolution) occurred at the TiO_2 electrode and the reduction reaction (hydrogen evolution) at the Pt electrode. The overall reaction was the photo-splitting of water into hydrogen and oxygen in the photoelectrochemical cell (Fujishima et al., 1972).[4]

The discovery of photo-splitting of water was a very important event in the history of photoelectrochemistry, since it demonstrated the possibility of chemical conversion of solar energy into clean fuel of H_2 by means of PECs. However, TiO_2 only absorbs the ultraviolet part of the solar emission and so has low solar energy conversion efficiency. In the same period, the concept of the DSPEC was put forth after the discovery of dye sensitization of the photocurrents on semiconducting electrodes (Tributsch, 1972).[5] Light, via the light-absorbing and sensitizing activity of dyes, was found to be able to drive electrochemical cells for photoelectric power generation. The concept of the DSPEC was rather promising, since such a cell could operate with visible light and thus should exhibit good solar energy conversion. In 1976, Tsubomura et al.[6] reported an approximately 1.5% energy conversion efficiency (for light incident within the dye spectrum) for Rose Bengal sensitized zinc oxide ceramic electrodes. Later, the same group reported (Matsumura et al., 1980) an energy efficiency of 2.5% (also for light incident within the dye spectrum) by
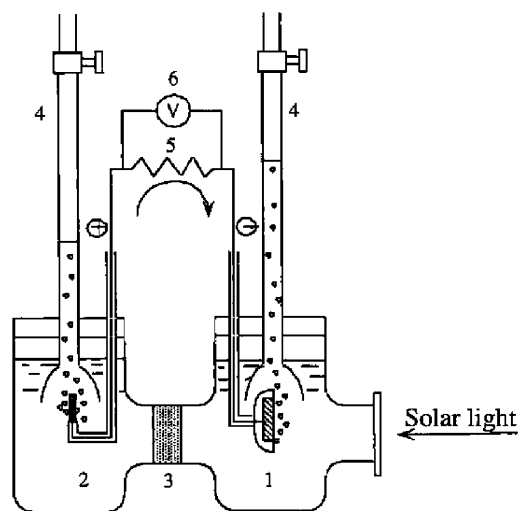

Fig. 1. Schematic diagram of an electrochemical photocell. (1) n-type TiO_2 electrode; (2) platinum back counter electrode; (3) ionically conducting separator; (4) gas buret; (5) load resistance and (6) voltmeter.

increasing the specific surface area of ZnO electrodes.[7] A significant breakthrough in DSPECs was reported in 1991 by Grätzel and his research group (O'Regan et al., 1991).[8] They prepared mesoporous TiO_2 film electrodes with very large inner surface area, and developed a ruthenium bipyridyl complex that could be adequately bonded to the surface of TiO_2 electrodes and exhibited a wide absorption band in the visible spectrum. Based on these improvements, the energy conversion efficiencies of DSPECs were lifted to 7%.

Since then, the Grätzel cell has become the standard model for DSPECs and has aroused worldwide attention on DSPECs. Very recently, Grätzel et al. have reported an energy conversion efficiency of 10.6% in full sunlight, very close to that of the amorphous silicon solar cell (Grätzel, 2003).[9] Figure 2 shows the operational principle of the Grätzel cell. The TiO_2 film electrode, typically 10 μm thick and with a porosity of 50%, has a surface area available for dye chemisorption over a thousand times that of a flat electrode of the same size. Ruthenium dye molecules are firmly bonded to the surface of the porous TiO_2 electrode as a monomolecular layer. The vast surface area of the TiO_2 film electrode ensures the sufficient absorption of incident light by the dye monolayer. Under light excitation, ruthenium dye molecules inject electrons within femtoseconds to picoseconds into the conduction band of TiO_2 with a quantum yield of near unity, while the oxidized dye mol-
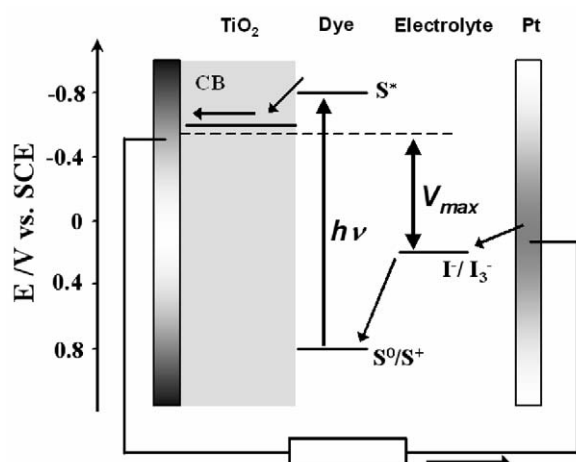
Fig. 2. Principle of operation and energy level scheme of the dye-sensitized photoelectrochemical solar cell.

Fig. 3. Principle of operation of the solid-state dye-sensitized solar cell.

ecules can be reduced by the iodide/triiodide couple in the electrolyte, which is in turn regenerated on the platinum counter-electrode. After a full cycle, incident light is converted into electric power, leaving behind no net chemical change. Charge generation is separated from charge transportation in such a device, and only majority carriers are involved in the photo-to-electric conversion. This allows the use of inexpensive, low quality materials in the device.

Interestingly, TiO_2, whose photo-function were discovered by one of the authors of this paper (AF) in the experiment of the photoelectrochemical splitting of water, has become the semiconductor of choice for the mesoporous electrode in the Grätzel cell. This material has many advantages for sensitized photochemistry and photoelectrochemistry: it is a low cost, widely available, nontoxic material; it is highly stable in electrolyte solution; and it also has almost ideal energy band positions for the PEC. Again, TiO_2 has also become the dominant material for environmental photocatalysis.

The Grätzel cell is rather efficient for solar energy conversion. The ruthenium dye can sustain 10^8 redox cycles without noticeable loss of performance, corresponding to 20 years of continuous operation in natural sunlight (Grätzel, 2003).[9] However, since it contains organic solvent and highly corrosive iodine inside, the Grätzel cell meets with the problems of dye desorption, leakage, and packaging. In addition, the incomplete regeneration of the iodide/triiodide couple during oper-
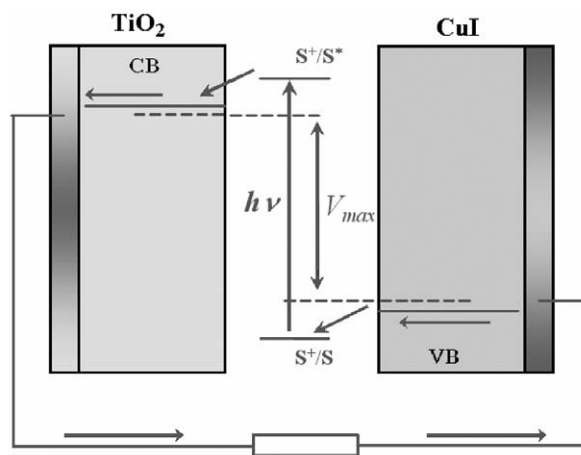
ation also raises the question of long-term operational stability. Much effort has been devoted to overcome the above problems, including the use of gel electrolyte and high boiling point molten salt electrolytes (Wang *et al.*, 2003).[10] Some progresses have been made. However, an alternative path, i.e., to replace the liquid electrolyte with a solid hole conductor, might provide a complete resolution for the problems of DSPECs.

Studies on solid-state dye-sensitized solar cells. *1. Overview.* The concept of the solid-state DSSC was reported by Tennakone and his research group in 1995.[1] In their pioneering work, they assembled the solid-state solar cell from a flower pigment (cyanidin)-sensitized TiO_2 nanoporous electrode and a p-type CuI semiconductor. CuI was filled into the voids of the TiO_2 film by solution deposition. The operational principle (Fig. 3) of the solar cell was explained as follows: the cyanidin molecule injects an electron into the TiO_2 electrode conduction band under light excitation, the reduced state of the oxidized cyanidin molecule is regenerated by injecting a hole into p-type CuI, and the injected electron and hole are transported through the TiO_2 electrode and the CuI electrode, respectively, to the external circuit. The energy conversion efficiency of the cell was estimated to be about 0.8% in direct sunlight, a rather low value. However, it was an exciting result, since it demonstrated the possibility to fabricate all solid-state dye-sensitized photovoltaic devices from inexpensive, low quality materials.

The advantages of a solid-state dye-sensitized

photovoltaic device are apparent in manufacturing and operational stability. However, in such a device, the p-type semiconductor and the dye are required to have special properties. As summarized by Tennakone: (1) the p-type material must be transparent to the visible spectrum, where the dye absorbs light; in other words, the p-type material must have a wide band gap; (2) a method must be available for depositing the p-type material without dissolving or degrading the monolayer of dye on the TiO_2 nanocrystallines; (3) the dye must be such that its LUMO level is located above the bottom of the conduction band of TiO_2 and its HOMO level is located below the upper edge of the valence band of the p-type material. CuI is a good candidate for the solid-state DSSC, because it has a wide band-gap (3.1 eV) and can be easily dissolved in organic solvents for deposition. The valence band edge of CuI (–5.3 V vs. the vacuum level) also matches the HOMO level of the ruthenium bipyridyl dye used in the Grätzel cell. In a later report, Tennakone et al. (1998) reported an energy conversion efficiency greater than 3% by assembling the cell from ruthenium dye-sensitized TiO_2 porous film and CuI.[11]

Many p-type semiconducting materials besides CuI have been applied to solid-state DSSCs. One such material is CuSCN, a stable Cu(I) p-type semiconductor. This material has a band gap of 3.6 eV and a valence band edge of –5.1 V with respect to the vacuum scale, which fits the requirements of solid-state dye-sensitized devices. The only shortcoming of CuSCN is its weak solubility in organic solvents. So far, the best solvent for CuSCN is dipropyl sulfide, an odorous and poisonous chemical. An energy conversion efficiency over 2% has been reported recently for a cell assembled from ruthenium dye-sensitized TiO_2 mesoporous film and CuSCN (O'Regan, 2004).[12]

Spirobisfluorene-connected arylamine (spiro-OMeTAD) is another important p-type material for solid-state DSSCs. The material was first used in electroluminescent devices as a hole transmitter. The Grätzel group reported the application of this material in solid-state DSSCs (Bach et al., 1998).[3] The material is amorphous so that it can contact well with the dye monolayer. Transient spectroscopic data showed that spiro-OMeTAD reduced the oxidized ruthenium dye on the ns scale (Bach et al., 1999).[13] Energy conversion efficiency over 3% has been reported recently for a cell using spiro-OMeTAD as hole conductor (Krüger et al., 2002).[14]

2. Fabrication of solid-state DSSC. Figure 4 illustrates the profile of a solid-state DSSC using p-CuI as hole conductor. The cell is made up, from left to right, of
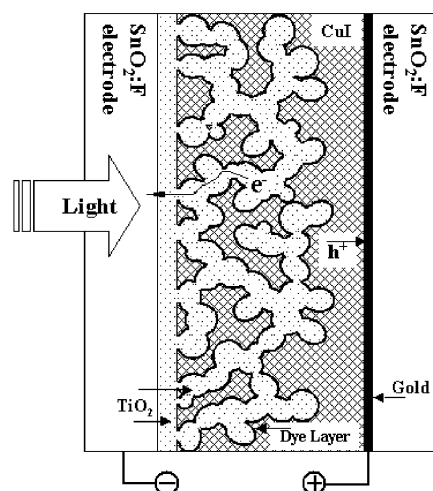

Fig. 4. Schematic of a cross section of a solid-state DSSC using CuI as hole conductor.

a conductive glass electrode, a compact TiO_2 thin film, a nanoporous TiO_2 film and dye monolayer, a CuI layer interpenetrated with TiO_2 porous film, and a gold-coated conducting glass electrode. The 100-nm thick compact TiO_2 thin layer is necessary for solid-state DSSCs to avoid the direct contact between CuI and the conducting glass cathode, which would short-circuit the cell. The compact TiO_2 layer, however, is not needed for DSPECs. CuI is deposited into the dye-coated TiO_2 nanoporous film by repeatedly applying droplets of the CuI solution. Gold film is always used as the anode for solid-state DSSCs, but other conducting materials, such as platinum and graphite, also work well.

The cell structure shown in Fig. 4 is a common one for all kinds of solid-state DSSCs. It is based on the same concept as that of DSPECs, i.e., the use of a mesoporous TiO_2 film to enhance the light absorption of the dye monolayer. Also as for the DSPEC, the solid-state DSSC is a device driven by majority carriers; electrons flow in n-type TiO_2, while holes flow in p-type materials. This point is very important, and ensures the use of inexpensive and low quality materials in the fabrication of solid-state DSSCs. In contrast, classical p-n junction solar cells, driven by minority carriers, must use very high purity semiconductor materials and adopt high-cost manufacturing technology.

In solid-state DSSCs, p-type materials replace the iodide/triiodide couple in DSPECs to regenerate the oxidized dye molecules. One might imagine that it would be very difficult for the deposited p-type materials

to achieve intimate contact with the dye monolayer covering the mesoporous TiO_2 electrode; such contact is very important for the efficient regeneration of oxidized dye molecules. The p-type semiconductors, CuI and CuSCN tend to crystallize inside the mesoporous TiO_2 film, which destroys their contact to the dye molecules. However, the results are rather encouraging for the ruthenium dye-based solid-state DSSCs. One possible reason is the firm bond between the thiocyanate group of the ruthenium dye and the cuprous ion (Mahrov *et al.*, 2004),[15] which may affect the nucleation and growth of CuI or CuSCN microcrystals inside the porous film. The organic hole conductor, *spiro*-OMeTAD, can contact the dye monolayer intimately, since it forms an amorphous solid inside the TiO_2 porous film due to its special molecular structure.

However, the problem of contact between the dye monolayer and the p-type material is a real one for the solid-state DSSC. A solid-state cell prepared from a thin Grätzel-type mesoporous TiO_2 film (<2 µm) could produce an output comparable to that of a cell that used liquid electrolyte, while a thicker film worked poorly for the solid-state solar cell (O'Regan *et al.*, 2002).[16] The reason was that the filling of the p-type material into the void volume of the mesoporous film became worse, as a thicker film was used. This is a drawback of the solution deposition method. However, no better method has been developed to replace the solution deposition method until now. Tennakone *et al.* (1998) developed another type of TiO_2 nanoporous film for solid-state DSSCs.[11] The film was prepared by repeated deposition of a colloidal TiO_2 solution on a heated conductive glass electrode. Large pores from the surface down to the conductive glass substrate can be formed in the film due to the vigorous evaporation of solvent during preparation. This kind of film was found suitable for the solution deposition method, since a thick film (~10 µm) was used for the fabrication of the solar cell. However, the method is rather time-consuming and is unsuitable for large-scale manufacturing. Moreover, the roughness of a 10-µm thick Tennakone-type film was about 300, which was not large enough for the effective absorption of incident light, and this restricted the energy conversion efficiency of the solid-state DSSC. In contrast, the mesoporous TiO_2 film used in the DSPEC always exhibits a roughness greater than 1000.

3. Interfacial recombination in solid-state DSSCs. Another problem of the solid-state DSSC is the serious interfacial recombination, especially when CuI or CuSCN is used the hole conductor. To understand this problem, we must look back at the structure and the operational principle of solid-state DSSCs. Perhaps it is better to describe the cell here as a dye-sensitized heterojunction, for a better understanding of the serious recombination problem. Such a heterojunction has two features: an extremely large interface and very weak interfacial electric field, due to its mesostructured interpenetrating nature. As we know, a substantial built-in electric field at the interface is a necessary condition for a high-quality heterojunction. Moreover, the physical heterojunction device always adopts a planar structure instead of the interpenetrating structure with extremely large interface. What would happen to the solid-state DSSC under operation is clear: after the initial interfacial charge generation, the interfacial recombination between the electrons in the TiO_2 phase and the holes in the hole conductor is unavoidable. The DSPEC does not meet with such a serious recombination problem, since it is basically a molecular device, and the iodide/triiodide redox couple is used as charge mediator. The iodide/triiodide couple exhibits irreversible charge transfer kinetics. The reduction of triiodide to iodide on the surface of TiO_2 and conducting glass electrode is very sluggish.

The serious interfacial recombination is equivalent to an internal short-circuit for the solid-state DSSC. One may be surprised at the reported considerable output of the cell. However, it is the truth that the solid-state DSSC works well, despite the disastrous recombination that always threatens to ruin the cell performance. The answer is the existence of a ruthenium dye monolayer at the interface. This monolayer, with a thickness of about 1 nm, behaves as a physical barrier layer at the interface and blocks the interfacial recombination (Tennakone, *et al.*, 1998).[11] Supposing that the monolayer were ideally compact, it would be possible to completely suppress the interfacial recombination between the TiO_2 and the hole conductor. However, such a compact dye monolayer is impossible to form, due to the large size of the dye molecule and the electrostatic repulsion between the molecules. Thus, the direct contact between TiO_2 and the hole conductor is nearly unavoidable for solid-state DSSCs.

There is another kind of interfacial recombination between the oxidized dye molecule and the injected electron in TiO_2. However, this type of recombination can be neglected in the solid-state DSSC, since the oxidized dye molecule is regenerated by the hole conductor at a rate much higher than that for the recapture of an electron from TiO_2. The recapture of the electron may happen in
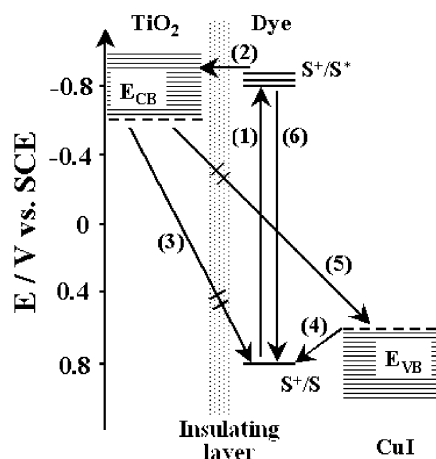
Fig. 5. Illustration of the interfacial charge-transfer processes occurring in the TiO$_2$/dye/CuI solid-state DSSC. Also shown is the blocking function of the insulating interlayer on interfacial recombination.

Fig. 6. Two configurations for the insulating layer-coated TiO$_2$ porous film electrode.

the time scale of microseconds to milliseconds; however the regeneration of oxidized dye molecule with *spiro*-OMeTAD has been reported on the time scale of nanoseconds (Bach *et al.*, 1999).[13] No dynamical data of dye regeneration by CuI or CuSCN have been reported, but this charge transfer should occur at a very high rate, considering the firm bond between the cuprous ion and the NCS group of the dye molecule, whose orbitals mainly contribute to the HOMO of the ruthenium dye molecule.

O'Regan *et al.* (2004) have measured the recombination rate in a solid-state DSSC using CuSCN as the hole conductor.[12] They found that the recombination in the solid-state DSSC was 10 times faster than in the DSPEC at the open circuit potential V_{oc} ($t_{1/2}$ ~ 150 μs), and 100 times at short circuit ($t_{1/2}$ ~ 450 μs), although both kinds of cells exhibited a similar charge transport rate ($t_{1/2}$ ~ 200 μs). The similarity of the charge transport and recombination rates in the solid-state DSSC results in a low fill factor, and photocurrent losses, both important limiting factors of the efficiency. No recombination data of CuI-based solid-state DSSC have been available up to now. However, the fact that CuI-based cells always exhibited a V_{oc} of 400-500 mV, much lower than the theoretical V_{oc} (~ 1 V) estimated from the flat band potentials of CuI and TiO$_2$, should provide evidence for the existence of serious interfacial recombination. Thus, it is apparent that the key for high-efficiency solid-state DSSCs is to suppress the interfacial recombination.
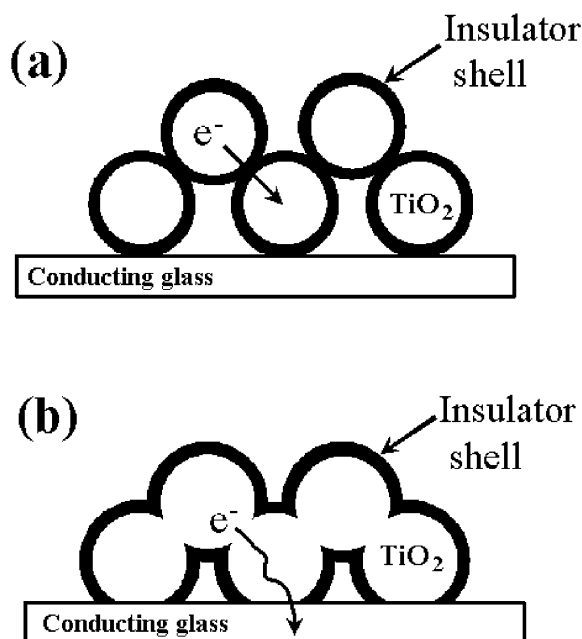
4. Interfacial blocking layers. We have proposed the idea of an interfacial blocking layer to suppress the interfacial recombination in the CuI-based solid-state DSSC (Fig. 5). This involves inserting an ultrathin insulating layer at the TiO$_2$/CuI interface. The insulating layer acts as a physical barrier to avoid the direct contact between TiO$_2$ and CuI. This layer must be very thin (< 1 nm) in order to keep the tunneling efficiency of electrons from the dye molecules to TiO$_2$. The idea seems reasonable for suppressing the interfacial recombination. The next question is how to prepare such a blocking layer at the interface. One method is to prepare a film from insulator-coated particles (Fig. 6a). However, it is more interesting to prepare an insulator layer on the porous film by means of a surface reaction (Fig. 6b), since the insulating layer prepared by this method will not increase the inner resistance of the film for electron transportation.

We coated the TiO$_2$ nanoporous film with an ultrathin Al$_2$O$_3$ layer by the surface sol-gel method and assembled solar cells (Zhang *et al.*, 2003 and 2004).[17),18)] We investigated the effect of the Al$_2$O$_3$ layer on the interfacial recombination by means of transient photovoltage measurements. This measurement provides a direct investigation on the interfacial recombination, since all the charges generated in the cell by the light pulse will recombine through the interface under
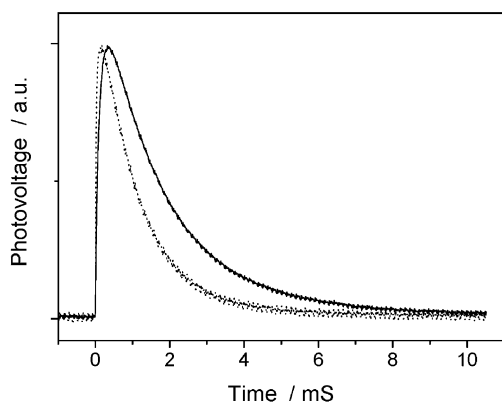
Fig. 7. Photovoltage transients of the solid-state DSSCs prepared from TiO$_2$ (dotted line) and Al$_2$O$_3$-coated TiO$_2$ (straight line) films.

open circuit conditions. The result was promising. A 0.19-nm thick Al$_2$O$_3$ layer decreased the decay rate of the photovoltage transient (Fig. 7). The lifetimes for the decay were calculated to be 1.19 ms for the conventional cell and 1.78 ms for the cell containing the Al$_2$O$_3$ layer. Thus, we can conclude that the blocking function of the Al$_2$O$_3$ layer exists.

The improvement in the cell performance due to the Al$_2$O$_3$ layer was very apparent, as shown in Table I (Zhang et al, 2004).[18] The blocking layer improved all the cell parameters, including the open-circuit voltage (V$_{oc}$), the short-circuit current (J$_{sc}$), the fill factor and the conversion efficiency. The improvements in V$_{oc}$ and fill factor are direct evidence for the suppression of interfacial recombination. The two cells exhibited the same J$_{sc}$ under very weak illumination (4 mW cm^{-2}); however, the cell containing the Al$_2$O$_3$ layer exhibited a larger value under higher light intensity. This phenomenon also indicated the charge collection of cell was improved by the blocking function of the Al$_2$O$_3$ layer. The J$_{sc}$ of both cells increased linearly with illumination power in the range of 4.1-31.4 mW cm^{-2}, yet both deviated from the linear function under higher light intensity. Thus indicated that the quality of the 0.19-nm thick Al$_2$O$_3$ layer was not high enough to resolve the recombination problem.

MgO also did well as a blocking layer in solid-state DSSCs (Taguchi et al., 2003).[19] Other insulating materials, for example, SiO$_2$ and Y$_2$O$_3$, might also work well as the blocking layer for recombination. The blocking function should depend on the thickness and the density of the layer, instead of the materials used.

Interestingly, some wide band-gap semiconductors, such as ZnO, also showed a blocking function similar to that for an insulating layer (Meng et al., 2003).[20] One possible reason is the higher packing density of dye molecules on the ZnO-covered TiO$_2$ film.

It is better to discuss more on the effect of insulating layer on the photocurrent. As shown in Fig. 8, a cell containing a 0.33-nm thick Al$_2$O$_3$ layer exhibited a higher fill factor and V$_{oc}$ than a 0.19-nm thick Al$_2$O$_3$ layer, but its J$_{sc}$ became lower since the electron injection was exponentially dependent on the thickness of the insulating layer (Zhang et al., 2003).[17] As an extreme condition, a very thick MgO layer improved the V$_{oc}$ of a CuI-based cell up to 800 mV, with negligible J$_{sc}$ observed. The above discussion shows that the insulating layer in principle can increase the V$_{oc}$ of the cell greatly through suppressing recombination, but the problem is how to keep the J$_{sc}$ from decreasing at the same time. We have to point out that the present preparation method, the surface sol-gel method, is not an optimal one for preparing insulating blocking layers. It depends on the hydrolysis and condensation of metal alkoxide on the surface of the TiO$_2$ film, through the reaction with adsorbed water. It is possible to prepare an ultrathin insulating layer on the TiO$_2$ film by this method, but it is impossible to prepare a dense insulating layer, since the cleavage of bulky alkoxy groups will leave pores in the layer. As a result, the insulating layer can not cover the surface of TiO$_2$ completely.

If a better method is found for preparing dense insulating layers on the TiO$_2$ surface, it will be possible to resolve the interfacial recombination problem discussed above. A physical method, for example atomic layer chemical vapor deposition, might be a good choice for the preparation. In addition, post-treating a dyed TiO$_2$ nanoporous film with the precursor of insulating materials is also a promising method to resolve the recombination problem. Since the dye molecules are adsorbed on the TiO$_2$ film, the insulating material will not hinder the electron injection.

5. Long-term operational stability. The operational stability is a controversial issue for solid-state DSSCs. Stability data for the CuSCN- and *spiro*-OMeTAD-based solar cells have not been available. Previous studies suggested that the CuI-based solar cell was not stable for long-term operation or even for long-term storage, possibly due to the growth of CuI microcrystals inside the cell (Tennakone et al., 1995).[1] Recent studies showed that the growth of CuI microcrystals, however, could be suppressed by adding a

Table I. Comparison of the performance parameters of solid-state DSSCs based on TiO_2 and Al_2O_3-coated TiO_2 films under various intensities of simulated sunlight

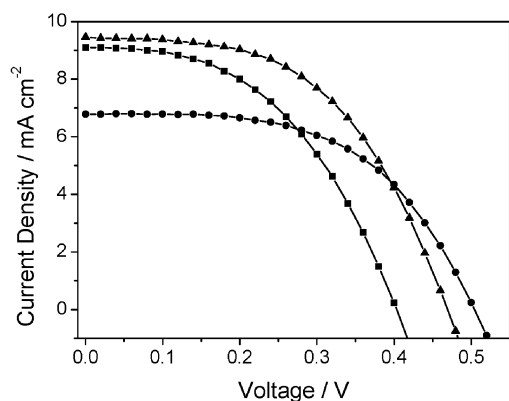|	Light intensity / mW cm^{-2}	Voc /V	Jsc / mA cm^{-2}	FF	Efficiency (%)
TiO_2	4.1	0.29	0.40	0.51	1.45
	17.6	0.35	1.97	0.58	2.27
	31.4	0.37	3.62	0.56	2.38
	89.0	0.40	9.10	0.48	1.94
TiO_2-Al_2O_3	4.1	0.35	0.40	0.56	1.92
	17.6	0.42	2.08	0.57	2.86
	31.4	0.45	3.77	0.57	3.03
	89.0	0.47	9.46	0.52	2.59

Fig. 8. Current-voltage curves of CuI-based solid-state dye-sensitized solar cells prepared from TiO_2 film (square), 0.19 nm-thick Al_2O_3-coated TiO_2 film (triangles), and 0.33 nm-thick-Al_2O_3 coated TiO_2 film (circles).
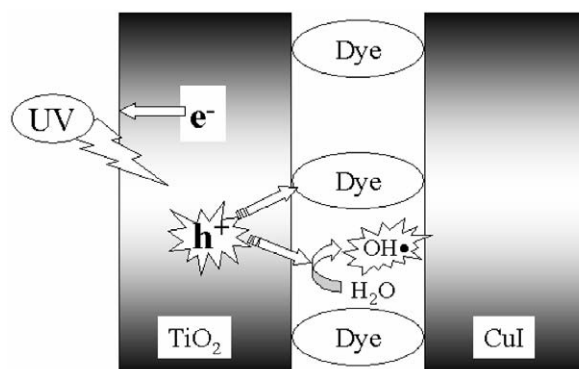

Fig. 9. Schematic illustration of the photodegradation mechanism for solid-state DSSCs. The highly reactive hydroxyl radicals, generated by the photocatalytic reactions on TiO_2, attack both dye molecules and CuI, which causes the degradation of the solid-state DSSC.

small amount of imidazolium thiocyanate, a crystal growth inhibitor for CuI (Kumara *et al.*, 2002).[21] The compound stabilized the surfaces of CuI microcrystals, by the strong interaction of the thiocyanate anion and the surface cuprous cation. Other thiocyanate salts also exhibited a similar effect (Kumara *et al.*, 2002).[22]

Operational stability is one of the most important factors for a photovoltaic device. It should be measured at the maximum output of the device. Previous studies on DSPECs always emphasized the stability under open circuit conditions, which could not provide a meaningful and accurate evaluation of the operational stability of the device (Grätzel, 2003).[9] Here, we will discuss the operational stability of the CuI-based solar cell under maximum output.

The CuI-based cell exhibited very fast degradation under simulated sunlight. The output became almost zero after 72 h of continuous illumination (Taguchi *et al.*, 2003).[19] The illuminated area turned from red (the color of the ruthenium dye) to black after the stability test, which was evidence for the existence of cupric oxide. However, when we carried out the stability test under the UV-free illumination ($\lambda > 435$ nm), the cell exhibited good operational stability. The cell retained more than 90% of the initial conversion efficiency after continuous illumination over 500 h.

XPS studies confirmed the oxidation of CuI to cupric compounds under ultraviolet light by TiO_2. The oxidation may involve TiO_2, ultraviolet light and residual water in the cell (Fig. 9). Water was oxidized to form OH· radicals, which reacted with CuI to form the cupric compounds. Since the reaction happened at the

interface, the oxidation of CuI might degrade the heterojunction directly and then finally degrade the cell. This mechanism suggests that the photocatalytic activity of TiO_2 should be purposefully suppressed, and the residual water should be kept to a very low level, in order to fabricate highly stable CuI-based DSSCs. Interestingly, the insulating blocking layer was found to improve the operational stability of the cell under simulated sunlight, possibly by blocking the photooxidative function of TiO_2 (Taguchi *et al.*, 2003).[19]

The results of the operational stability of the CuI-based DSSC were rather promising. It can be expected that the CuSCN-based DSSC should exhibit even better operational stability, since CuSCN in itself is more stable than CuI against oxidation.

Extremely-thin-absorber solar cell. Extremely thin absorber solar cells (ETA-solar cells) are conceptually close to solid-state DSSCs (Kaiser *et al.*, 2001).[23] In the ETA solar cell, an extremely thin (< 150 nm) layer of a small band gap semiconductor such as $CuInS_2$ and CdTe, replaces the molecular dye in the DSSC, to conformally cover the mesostructured transparent n-type semiconductor film, which is usually TiO_2. A void-filling transparent p-type semiconductor such as CuSCN and / or a reflecting metal layer is used for the back contact (Ernst *et al.*, 2003).[24] The structure of the ETA solar cell has the advantage of enhanced light harvesting due to the surface enlargement and multiple scattering. Because photo-induced charge separation occurs on a limited length scale, higher levels of defects and impurities can be tolerated than in flat thin film devices, where the minority carriers are required to diffuse several micrometers. Same as the solid-state DSSC, the operation of the ETA solar cell is also based on a heterojunction with an extremely large interface. Thus, the studies on the ETA solar cell can provide a valuable reference for the solid-state DSSC.

Theoretically, the ETA solar cell is promising for exhibiting high energy conversion efficiency. Previous studies (Ernst *et al.*, 2003) showed that electrochemical deposition techniques are suitable for the preparation of the ETA solar cell.[24] The TiO_2/CdTe ETA cell exhibited an open-circuit voltage of 0.67 V and a short-circuit current of 8.9 mA cm^{-2}, under 100 mW cm^{-2} simulated sunlight (Ernst *et al.*, 2003).[24] However, the cell exhibited a very low fill factor (22%), which limited its overall energy conversion efficiency. The low fill factor of the cell has been attributed to the large conduction band offset of approximately 0.6 eV for the TiO_2/CdTe junction. However, the fill factor did not show any improvement

when another material (CdHgTe), whose conduction band edge matched that of TiO_2 better than CdTe, was used (Ernst *et al.*, 2003).[24] Since the ETA solar cell is close to the solid-state DSSC in structure, the ETA cell should also encounter a problem in interfacial charge recombination, which would restrict its maximum output.

Very recently, Nanu *et al.* (2004) applied the atomic layer chemical vapor deposition technique (AL-CVD) to the fabrication of a TiO_2/$CuInS_2$ ETA solar cell.[25] The AL-CVD technique is very interesting, since it allows nanoporous matrices to be infiltrated in a controllable way. Interestingly, a 2-nm thick Al_2O_3 tunnel barrier and a 10-nm thick In_2S_3 buffer layer were inserted between TiO_2 and $CuInS_2$, to overcome the interfacial recombination problem. The as-prepared ETA solar cell showed an open-circuit voltage of 0.49 V, a short-circuit current of 18 mA cm^{-2}, a fill factor of 0.44, and an energy conversion efficiency of about 4% under 100 mW cm^{-2} simulated sunlight. If the Al_2O_3 layer and the In_2S_3 buffer were absent, the cell showed only a very moderate photoresponse. This study proved again that the interfacial blocking layer is necessary for a heterojunction with an extremely large interface.

Future outlook. It has already become clear that the study of solid-state DSSCs is encountering two problems: the insufficient light absorption due to the limited inner surface area of the TiO_2 film electrode, and the serious interfacial recombination due to the lack of a substantial interfacial electric field. The above two problems restrict the energy conversion efficiency of the solid-state DSSC to below 4%. The operational stability of the CuI-based solar cell was, however, unexpectedly good for a 500-h continuous test.

The interfacial recombination in the solid-state DSSC can be suppressed by a thin layer of an insulating material. However, the present preparation methods for this insulating layer are not satisfactory. A recent study on the ETA solar cell has suggested that the AL-CVD method is a possible candidate for the preparation of a thin, dense insulating layer on a porous structure. It can be predicted that a breakthrough in the energy conversion efficiency will occur for the solid-state DSSC when a preparation method for a high-quality insulating blocking layer is developed. Furthermore, the high-quality insulating layer will improve the operation stability of the solid-state DSSC.

The problem of insufficient light absorption may be overcome by replacing the ruthenium dye with another organic dye with a greater extinction coefficient. To

obtain a broad optical absorption extending throughout the visible and the near-IR region, one can use a combination of two dyes that complement each other in their spectral features. The semiconductor quantum dot is also a possible option for panchromatic sensitizers. The absorption spectra of the quantum dots, always II-VI and III-V semiconductor nanoparticles, can be adjusted to cover the visible and near-IR region by changing the particle size. Optical design can also improve the light collection in the solid-state DSSC and thus improve its solar energy conversion efficiency.

The morphology of the porous film electrode is also very important for the solid-state DSSC. A desirable morphology for the porous film used in the solid-state DSSC would have the mesoporous channels or nanorods aligned in parallel to each other and vertically with respect to the conducting glass substrate. Such a morphology would facilitate the pore-filling with p-type materials, allow the formation of a higher quality heterojunction, and exhibit faster charge transport in the film, compared to the random mesoporous morphology. Future studies should also be devoted to developing the fabrication technology for the solid-state DSSC. Recent progress in solution deposition (O'Regan *et al.*, 2002 and 2004) is encouraging. However, more efforts are required for the reproducible production of the solid-state DSSC.[12),16)]

References

1) Tennakone, K., Kumara, G. R. R. A., Kumarasinghe, A. R., Wijayantha, K. G. U., and Sirimanne, P. M. (1995) Semicond. Sci. Technol. **10**, 1689-1693.

2) O'Regan, B., and Schwartz, D. T. (1998) Chem. Mater. **10**, 1501-1509.

3) Bach, U., Lupo, D., Comte, P., Moser, J. E., Weissörtel, F., Salbeck, J., Spreitzer, H., and Grätzel, M. (1998) Nature **395**, 583-585.

4) Fujishima, A., and Honda, K. (1972) Nature **238**, 37-38.

5) Tributsch, H., (1972) Photochem. Photobiol. **16**, 261.

6) Tsubomura, H., Matsumura, M., Nomura, Y., and Amayma, T. (1976) Nature **261**, 402-403.

7) Matsumura, M., Matsudaira, S., Tsubomura, H., Takata, M., and Yanagida, H. (1980) Ind. Eng. Chem. Prod. Res. Dev. **19**, 415-421.

8) O'Regan, B., and Grätzel, M. (1991) Nature **353**, 737-740.

9) Grätzel, M. (2003) J. Photochem. Photobiol. C: Photochem. Rev. **4**, 145-153.

10) Wang, P., Zakeeruddin, S. M., Moser, J. E., Nazeerudin, M. K., Sekiguchi, T., and Grätzel, M. (2003) Nature Mater. **2**, 402-407.

11) Tennakone, K., Kumara, G. R. R. A., Kottegoda, I. R. M., Wijayantha, K. G. U., and Perera, V. P. S. (1998) J. Phys. D: Appl. Phys. **31**, 1492-1496.

12) O'Regan, B., and Lenzmann, F. (2004) J. Phys. Chem. B **108**, 4342-4350.

13) Bach, U., Tachibana, Y., Moser, J.-E., Haque, S. A., Durrant, J. R., Grätzel, M., and Klug, D. R. (1999) J. Am. Chem. Soc. **121**, 7445-7446.

14) Krüger, J., Plass, R., Grätzel, M., and Matthieu, H.-J. (2002) Appl. Phys. Lett. **81**, 367-369.

15) Mahrov, B., Boschloo, G., Hagfeldt, A., Siegbahn, H., and Rensmo, H. (2004) J. Phys. Chem. B **108**, 11604-11610.

16) O'Regan, B., Lenzmann, F., Muis, R., and Wienke, J. (2002) Chem. Mater. **14**, 5023-5029.

17) Zhang, X.-T., Sutanto, I., Taguchi, T., Tokuhiro, K., Meng, Q.-B., Rao, T. N., Fujishima, A., Watanabe, H., Nakamori, T., and Uragami, M. (2003) Solar Energy Mater. Solar Cells **80**, 315-326.

18) Zhang, X.-T., Liu, H.-W., Taguchi, T., Meng, Q.-B., Sato, O., and Fujishima, A. (2004) Solar Energy Mater. Solar Cells **81**, 197-203.

19) Taguchi, T., Zhang, X.-T., Sutanto, I., Tokuhiro, K., Rao, T. N., Watanabe, H., Nakamori, T., Uragami, M., and Fujishima, A. (2003) Chem. Commun. 2480-2481.

20) Meng, Q.-B., Takahashi, K., Zhang, X.-T., Sutanto, I., Rao, T. N., Sato, O., Fujishima, A., Watanabe, H., Nakamori, T., and Uragami, M. (2003) Langmuir **19**, 3572-3574.

21) Kumara, G. R. A., Konno, A., Shiratsuchi, K., Tsukahara, J., and Tennakone, K. (2002) Chem. Mater. **14**, 954-955.

22) Kumara, G. R. A., Kaneko, S., Okuya, M., and Tennakone, K. (2002) Langmuir **18**, 10493-10495.

23) Kaiser, I., Ernst, K., Fischer, Ch.-H., Könenkamp, R., Rost, C., Sieber, I., and Lux-Steiner, M. Ch. (2001) Solar Energy Mater. Solar Cells **67**, 89-96.

24) Ernst, K., Belaidi, A., and Könenkamp, R. (2003) Semicond. Sci. Technol. **18**, 475-479.

25) Nanu, M., Schoonman, J., and Goossens, A. (2004) Adv. Mater. **16**, 453-456.