SCIENCE CHINA
Chemistry

• REVIEWS •

August 2010 Vol.53 No.8: 1669–1678
doi: 10.1007/s11426-010-4042-8

Recent progress in interface modification for dye-sensitized solar cells

MA BeiBei, GAO Rui, WANG LiDuo*, ZHU YiFeng, SHI YanTao, GENG Yi, DONG HaoPeng & QIU Yong

Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education; Department of Chemistry, Tsinghua University, Beijing 100084, China

Received April 2, 2010; accepted April 25, 2010

Interface modification on the TiO_2/dye/electrolyte interface of dye-sensitized solar cells (DSCs) is one of the most effective approaches to suppress the charge recombination, improve electron injection and transportation, and thus ameliorate the conversion efficiency and stability of DSCs. Conventional research focusing on the photoanodes interface modification before sensitization in dye-sensitized solar cells has been carried out and reviewed. However, recent studies showed that post-modification after sensitization of the TiO_2 electrode also plays a significant role on the TiO_2/dye/electrolyte interface. This post-modification using the immersing method could deprotonate dye molecules, prohibit the dye aggregation and retard the recombination reaction. As a result, it has great influence on the devices' photovoltaic performance. This interface modification could also provide an approach to broaden the response of the solar spectrum by introducing an alternative assembling structure. An *in-situ* meaning of using a co-adsorbent is employed to modify the interface in the DSCs, which could retard the aggregation of the dye molecules and enhance the conversion efficiency. In addition, electrolyte additives can be used to modify the TiO_2/dye/electrolyte interface through some unique mechanisms. Based on the background of interface modification of photoanodes before sensitization, this review introduces various interface modifications after sensitization of dye-sensitized solar cells and their mechanisms.

dye-sensitized solar cell, TiO_2 electrode, interface modification, electron recombination

1 Introduction

Since the dye-sensitized solar cells (DSCs) based on mesoporous TiO_2 nanocrystalline were first reported in 1991 by Grätzel *et al*. [1], this new type of solar cells with considerable efficiency has been regarded as a promising alternative to the conventional silicon solar cells for their relatively low production cost and simple manufacturing technique [2, 3]. After about two decades of development, the overall conversion efficiency over 11% has been achieved by DSCs [4]. Despite the discovered advantages, enhancing the conversion efficiency above 12% seems to be exceptionally difficult. The DSCs still suffer from the stability problem. Therefore, attempts are still in need to improve the conversion efficiency and stability for future industrial production and application [5–7]. TiO_2 mesoporous electrode with high surface area is the most critical component in DSCs. This special structure enables both efficient light harvesting and electron injection by a dye monolayer, while the compact electrode can solely achieve optical density with a few dye molecules and has poor cell performance [8–11]. As shown in Figure 1, there are three major processes in DSCs [12]: (1) light harvest and generation of the dye excited states (process 1 in Figure 1), (2) the electron injection and transmission (processes 2 and 3 in Figure 1), (3) reduction of the

*Corresponding author (email: chldwang@mail.tsinghua.edu.cn)

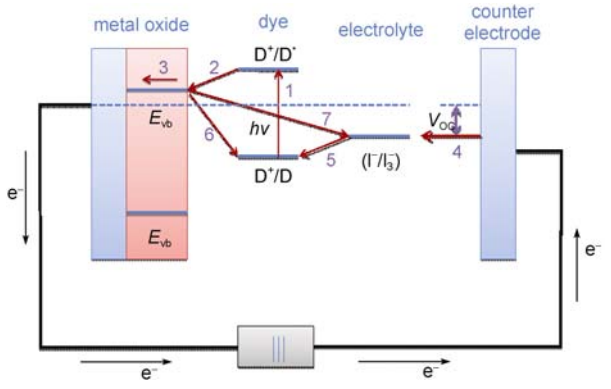

Figure 1 Principle of operation in DSCs.

excited dye (process 5 in Figure 1). All these three processes occur at the dye/TiO_2, dye/electrolyte, and TiO_2/electrolyte interfaces [13]. Nevertheless, the high surface area results in a series of problems, such as increased electron recombination, surface reaction, and dye aggregation. Therefore, modifications of TiO_2/dye/electrolyte interface may be a breakthrough to improvement of the conversion efficiency and stability of DSCs.

The recombination of the photocarrier [14] is one of the most challenging issues for improving the conversion efficiency of DSCs. As an effective approach to suppress the charge recombination, and thus ameliorate the conversion efficiency and stability of DSCs, interface modification was first introduced into DSCs in 1993 [15]. As the recombination may cause loss of nearly 300 mV of the open-circuit voltage (V_{oc}) from the theoretical value [14], the conversion efficiency may be optimized to 14% by solving the recombination issue through interface modification [16].

Since then, a great deal of work has been carried out concerning photoanodes interface modification, which has been reviewed in past years. However, it has unduly ignored the interface between the dye and the electrolyte. The interface modifications after sensitization have recently been shown of great significance for improving the conversion efficiency and stability of DSCs: post-modification after sensitization of TiO_2 electrode could deprotonate dye molecules, prohibit the dye aggregation and retard the recombination reaction, and thus has great influence on the devices' photovoltaic performance. Electrolyte additives can be considered as a modification method after sensitization to influence the electrode/dye/electrolyte interface.

Overall, as the photoanodes/dyes and dye/electrolyte interfaces are the focus of DSCs study, by taking sensitization of photoanodes as a standard, the interface modification was divided into pre-modification (referred to as photoanode modification) and post-modification. In addition, as some electrolyte additives can affect both the interfaces, the modification effect from electrolyte additives is taken as a separate category for interface modification. All the three parts of the interface modification are shown in Figure 2. There is no good general overview of them yet.

2 Photoanodes interface modification

The recombination in DSCs mainly occurs between the injected electron and the dye cation or the acceptor such as I_3^- in the electrolyte, during the transit of the electrons through the nanocrystalline (processes 6 and 7 in Figure 1). During the injection and transfer process of photoinduced electrons, the distance between the injected electrons and I_3^- ions in the electrolyte is less than 10 nm [17]. The small size of the TiO_2 particles cannot establish a significant electric field that spatially separates the injected electrons from the acceptors from the dye or electrolyte. The above causes lead to the high recombination rate in DSCs [18–21]. Consequently, the interface modification at the photoanode surface can suppress the electron recombination effectively by improving the electron injection and transfer.

2.1 Photoanodes modification to improve electron injection and suppress electron recombination

Three different mechanisms have been proposed for the photoanodes modification to improve electron injection and suppress electron recombination: (1) forming an energy barrier that allows electron injection but hinder the recombination reaction; (2) forming a "surface dipole" that shifts

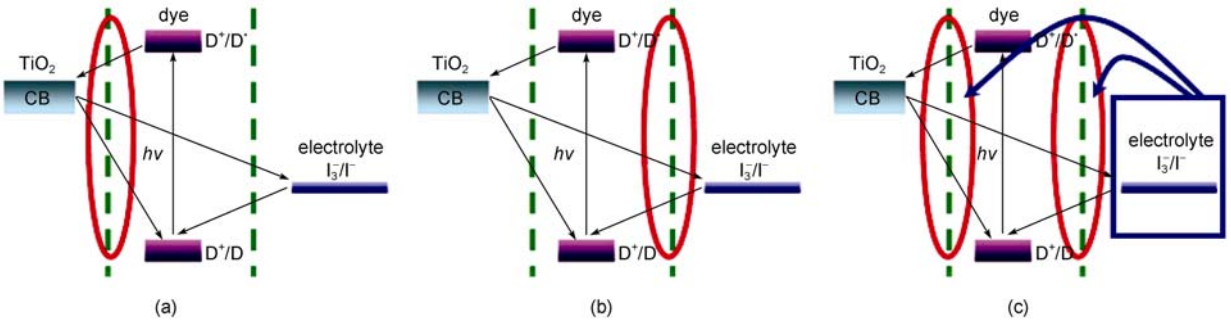

Figure 2 Illustration of the three different parts of interface modification of DSCs. (a) Photoanodes interface modification. (b) Post-modification after sensitization. (c) Interface modification effect from additives in the electrolyte.

the conduction band potential of the TiO_2 electrode; (3) passivating the surface states, which are considered to be the recombination centers (as shown in Figure 3).

2.1.1 *Modification as an energy barrier*

Many studies have tried to modify the exposed TiO_2 electrode surface by the materials that have higher conduction band energy level than TiO_2 [24–29] or are the insulation materials directly [30–33]. It is expected that these materials can form an energy barrier between the TiO_2 electrode and the electrolyte. Because the modification material has higher conduction band, the injected electrons have to overcome this barrier to recombine with the I_3^- ions in the electrolyte. Thus the barrier layer reduces the recombination rate, and then increases the V_{oc} of the DSCs. Research by using inorganic oxide semiconductors to modify the TiO_2 electrode surface tends to be active since the first inorganic oxide semiconductor Nb_2O_5 was used [23, 27, 29, 34]. Besides Nb_2O_5 [21, 26, 27, 35], ZnO [14, 34, 36, 37], MgO [14, 38], Al_2O_3 [14, 22, 34, 39, 40], and other inorganic oxide semiconductors, such as In_2O_3 [41], SnO_2 [34] and ZrO_2 [22], were also used as modification materials. Diamant *et al*. [34] compared a series of inorganic oxide semiconductors when they were used as the modification materials for TiO_2 electrode. In addition, other insulating materials such as $CaCO_3$ [16, 42] and insulating polymers such as polymethylsilane [33] are also effective in blocking recombination and increasing the conversion efficiency of DSCs.

2.1.2 *Modification as "surface dipole"*

In 2002, $SrTiO_3$ was used by Diamand *et al.* to modify the TiO_2 electrode [23]. They found that $SrTiO_3$ modification shifted the conduction band of the TiO_2 in the negative direction rather than formed an energy barrier at the TiO_2 surface. This type of photoanode modification cannot suppress the back recombination rate as a function of the electron density, but can suppress the back recombination as a function of the applied potential. Consequently, despite the slightly reduced I_{sc} of the cell, the forming "surface dipole" with modification increased the V_{oc} significantly and the devices conversion efficiency was still improved notably. As shown in Figure 3(b), the formation of a potential step subjected to the surface dipole shifted the conduction band of TiO_2 in the negative direction [43]. In our previous work [44], $BaCO_3$ was applied to modify the TiO_2 electrode in quasi-solid-state DSCs.

2.1.3 *Modification for passivating surface states*

The surface state sites on the TiO_2 electrode are presumed to be the center of the electron recombination [9, 17, 45–47], so passivating the recombination centers by photoanode modification to diminish the density of the surface state sites is an effective way to suppress the recombination [22, 48, 49]. According to our previous work [50, 51], 3–10 nm nanosized PbS particles which were fabricated on the TiO_2 electrode by an *in-situ* method fill the surface states of TiO_2 electrode effectively. The conversion efficiency was improved by 20%. The similar mechanism was demonstrated when the TiO_2 electrode was modified by alizarin [52].

2.2 Photoanodes modification for improving electron transportation

Some photoanodes modification is concerned with improvement of the electron transportation. Because the macroscopic electric field across the film is negligible at normal solar light intensities due to the screening effect by electrolyte [53], the transport of injected electrons to the collecting back contact is believed to occur by diffusion [54]. Generally, the diffusion length is 10–20 μm in anatase TiO_2 film [55], and the thickness of most electrodes in DSCs is confined within this range. Such a long diffusion distance makes the competition between collection of injected electrons by conductive glass and recombination become fierce, which in turn affects the overall conversion efficiency of DSCs considerably [56, 57]. In 1993, Nazeeruddin *et al.* [15] modified the TiO_2 electrode with aqueous solution of $TiCl_4$. This modification formed a pure TiO_2 layer on the surface of TiO_2 particles. This thin layer can increase the connectivity between adjacent TiO_2 particles and then improve electron transportation. In this way, the transportation rate of injected electrons was increased with reduction of the

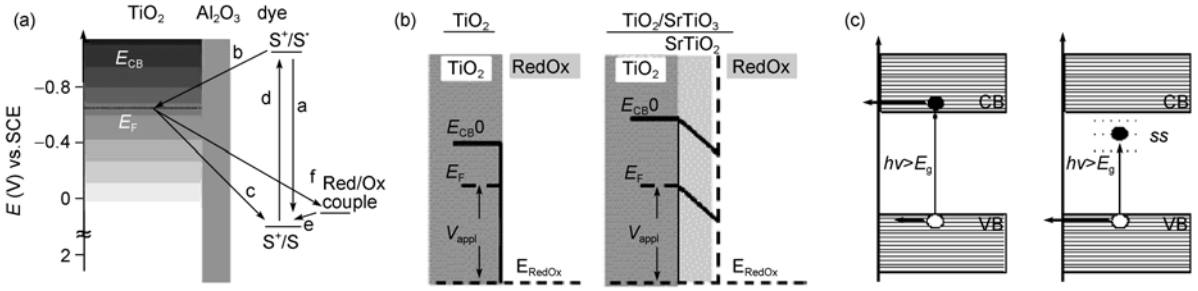

Figure 3 Three mechanisms for the photoanodes modification to improve electron injection and suppress electron recombination. (a) Energy barrier modification of the photoanodes to improve electron injection [22]. (b) Surface dipole modification for the photoanodes to improve electron injection [23]. (c) Passivating the surface states for the photoanodes to suppress electron recombination [9].

recombination rate relatively. As a result, the devices I_{sc} and efficiency were increased. $TiCl_4$-modification has been widely studied and used as one of the most effective modification methods [58–60].

In the past two decades, rapid progress has been made on photoanodes modification. It seems to be generally considered that the interface modification can solely act on the bare photoanode surface. However, recent work indicated that some interface modification materials can influence the dye absorbed on the porous TiO_2 electrode. Therefore, photoanodes modification is just one aspect of interface modification. The post-modification after sensitization is also a significant aspect of interface modification, which could be used through soaking the dyed photoanode in the solution of modification materials and adding the modification material into the electrolyte.

3 Post-modification after sensitization using immersing method

tert-Butyl pyridine (TBP) was first used to modify electrode/electrolyte interface by immersing the sensitized electrode into it [15]. This modification could improve the device's V_{oc} and fill factor. This can be considered as the first modification after sensitization. However, this was not proposed as a post-modification, and no one indicated that this modification can have effect on the dye. In the subsequent research, *tert*-butyl pyridine was usually added into the electrolyte as a regular component instead of modification.

Some previous work has partly focused on the basic property of the electrode surface and found its influence on the dye adsorption [22, 30, 38, 61]. Because the carboxylate substituents on the bipyridine ligands of ruthenium dye are covalently bound to the surface of the electrode, the modification may favor higher dye adsorption sites, thus yielding higher light-harvesting efficiency when the modification materials are more basic than TiO_2. The aforementioned $BaCO_3$-modification can be taken as an example. Some other materials can also stabilize the connection between dye molecules and TiO_2 electrode. For example, acidic compounds containing hydroxyl or mercapto can also reinforce the covalent bond of the dye to the surface of the electrode. Nilsing *et al.* [62] used H_3PO_3 to modify the TiO_2 electrode and improve the stability of the cell.

This phenomenon indicates that these modification materials may also have significant impact on the dye. The structural models of sensitizer molecules anchoring to the TiO_2 anatase surface show that there are two or three free carboxylic groups that do not connect with the surface, when the N3-dye molecule was absorbed on TiO_2 films [63]. These free carboxylic groups may cause the H-bonding aggregates, which in turn reduced the performance of DSCs by increasing the recombination centers [64]. Dye molecules that cover the TiO_2 surface can hardly achieve a closely-packed monolayer, even at saturated absorption [65, 66], which may give more charges for the electrolyte to recombine with the injected electrons in TiO_2. The electrolytes can be separated by increasing the coverage ratio of the TiO_2 surface, which is achieved by adsorbing more dye or applying coatings, such as modification materials, after dye-sensitization.

3.1 Post-modification for the dye/electrolyte interface

In our previous studies [67], Al_2O_3 post-modification after sensitization was carried out in the quasi-solid state DSCs through hydrolysis of aluminum isopropoxide by immersing dye-sensitized TiO_2 electrodes into its solution. Spectroscopic characterization showed that Al_2O_3 post-modification not only acted as an insulator barrier to retard the recombination between the TiO_2/electrolyte and dye/electrolyte interfaces, but also prohibited the dye aggregation. The FT-IR measurement is presented in Figure 4. After Al_2O_3 post-modification, the peak of COOH at 1700 cm^{-1} was weakened, while the peaks of COO^- at 1600 and 1380 cm^{-1} were significantly enhanced, which indicated that the H-band aggregation of the COOH group was prohibited.

As a result, the Al_2O_3 post-modification at the dye/electrolyte interface caused the improvement both in the overall photo-to-electrical conversion efficiency and the stability of DSCs.

However, because the alkalinity of aluminum isopropoxide was too strong, the modification process was difficult to control. To avoid this problem, a new material $Mg(OOCCH_3)_2$ was introduced into post-modification, whose alkalinity was much weaker than that of aluminum isopropoxide, and there was no hydrolysis reaction. The modification process of $Mg(OOCCH_3)_2$ was much more gentle.

In our previous study [68], we discovered that $Mg(OOCCH_3)_2$ was an excellent modification material for

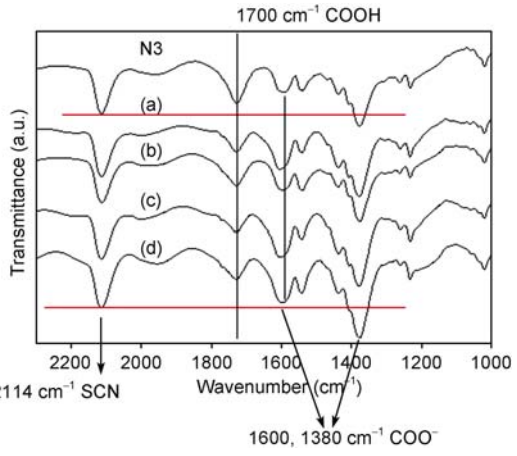

Figure 4 IR spectra for N3-TiO_2 film (N3), N3-TiO_2 films with different immersion times in the aluminum isopropoxide solution. (a) 30 s, (b) 2 min, (c) 5 min, and (d) 15 min [67].

post-modification. Aside from the effects that were similar to Al_2O_3, such as separating the TiO_2 film and electrolyte to retard the charge recombination, $Mg(OOCCH_3)_2$ had novel features. It could interact with N3 dye through intermolecular force, which changed the electron static of the dye molecule, and then raised the LUMO of N3 dye to a higher energy level as evidenced by the results of the cyclic voltammetry test and the blue shift of the optical band gap. The cyclic voltammograms of the N3 dye and N3/$Mg(OOCCH_3)_2$ in pure CH_3CN solvent are shown in Figure 5(a). Their respective oxidation potential was found to be 0.95 and 0.92 V, with almost no change taking place, and the reduction potential was −1.07 and −1.33 V, respectively, which changed more negatively. From this result, the energy levels of the TiO_2 and the N3 dye without and with $Mg(OOCCH_3)_2$ modification are shown in Figure 5(b). It shows that the modification benefited the electron injection from N3 dye to the conductive band of TiO_2.

Thus the modification of $Mg(OOCCH_3)_2$ improved the conversion efficiency of DSCs. With the modification of $Mg(OOCCH_3)_2$, the conversion efficiency significantly increased from 4.69% to 5.37% under AM1.5 irradiation.

3.2 Alternating assembly structure of the dye and modification material

Because post-modification has great influence on the dye-adsorption, the aforementioned results indicate that these post-modification materials could be used to modify photoanodes before sensitization to improve the quality of dye-adsorption. Based on the thinking to combine the mechanisms of photoanodes interface modification and post-modification, some modification materials, such as Al_2O_3 or $Mg(OOCCH_3)_2$, can serve as dye-carriers to adsorb different dyes with different spectral response ranges after the TiO_2 film was sensitized. It is expected to be one of the research directions so as to broaden the spectral response through the method of this dye/modification material alternating assembly structure.

Thus, an alternating assembly structure of dye and modification material was developed for DSCs [69]. As shown in Table 1, the Al_2O_3 modification and sensitization process was repeated several times in the alternating assembly process.

In this structure, at first, Al_2O_3 served as a photoanode interface modification material to suppress electron recombination as an energy barrier (Figure 6).

At the same time, it served as a post-modification material to prohibit the dye aggregation. In addition, Al_2O_3 also served as a carrier layer to increase the adsorption of N3-dye (Figure 7). Thus, the alternating assembly structure of N3/Al_2O_3 increased the dye adsorption and maintained the modification effects at the same time.

Consequently, compared to the blank sample, the photon-

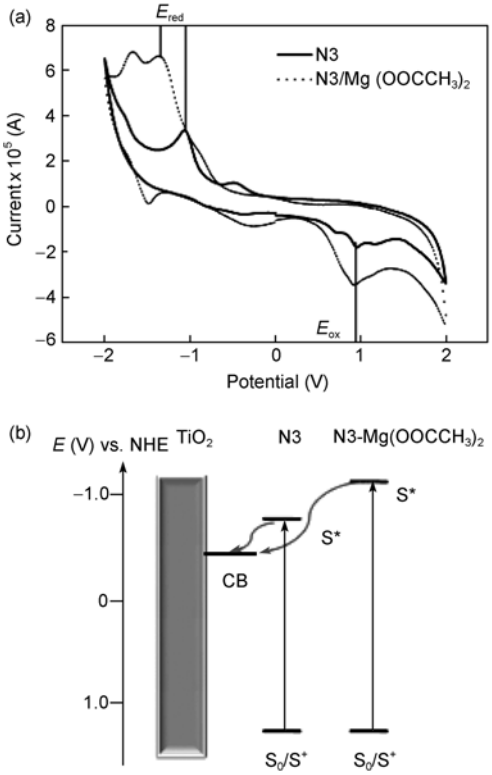

Figure 5 Post-modification by $Mg(OOCCH_3)_2$ [68]. (a) Cyclic voltammograms of N3 and N3/$Mg(OOCCH_3)_2$ in CH_3CN. (b) The energy levels of the TiO_2 and the N3 dye without and with $Mg(OOCCH_3)_2$ modification.

Table 1 Alternating assembly structure on the nanoporous TiO_2 films [69]

Sample number	Structure
N3-dye only	N3-dye
1 circle	$Al_2O_3/(N3/Al_2O_3)_1$
3 circles	$Al_2O_3/(N3/Al_2O_3)_3$
5 circles	$Al_2O_3/(N3/Al_2O_3)_5$

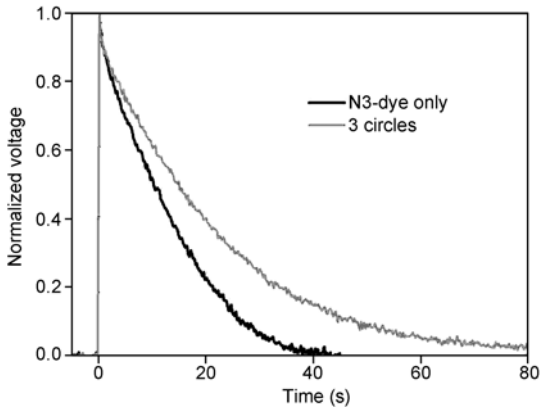

Figure 6 Normalized transient photovoltage spectra for cells with different circles alternating assembly structure [69]. The decay was slower in the cell with 3 circles of alternating assembly structure, indicating that the Al_2O_3 layer can retard the recombination between the injected electrons and the electrolytes.

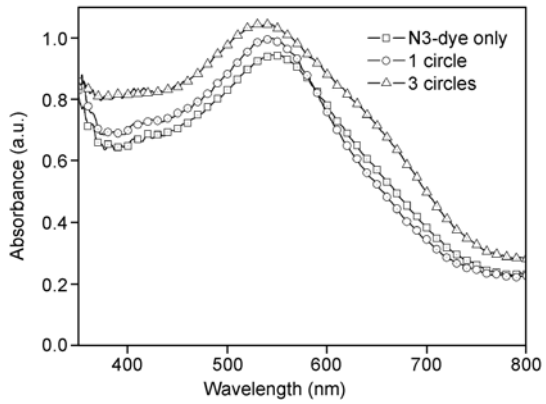

Figure 7 UV-vis absorption spectra of TiO_2 films with different circles of alternating assembly structure [69].

electron conversion efficiency of the cell with three circles of alternating assembly structure of N3-dye/Al_2O_3 increased from 3.86% to 4.49% by 16% under AM1.5 irradiation. The cell stability was also improved (Figure 8).

To truly broaden the spectral absorption, different dyes need to be added into this multilayered dye sensitization structure. Durrant *et al.* [70] reported novel co-sensitization based on the controlled construction of the film architecture in which a primary monolayer of the dye is spatially separated from a secondary monolayer of another dye using a layer of Al_2O_3, resulting in the configuration TiO_2/Dye1/Al_2O_3/Dye2. However, the attempts resulted in unimpressive power-onversion efficiency compared to the single-dye device.

In 2008, Choi *et al.* reported a stepwise co-sensitization based on two organic dyes having complementary spectral absorption in the visible region [71]. These two organic dyes are 3-[5′-{*N*,*N*-bis(9,9-dimethylfluorene-2-yl)phenyl}-2,2′-bisthiophene-5-yl]-2-cyanoacrylic acid (JK-2) and 5-carboxy-2-[{3-[(1,3-dihydro-3,3-dimethyl-1-ethyl-2*H*-indol-2-ylidene) methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene}methyl]-3,3-trimethyl-1-octyl-3*H*-indolium (SQ1) [72]. Al_2O_3 was employed as the intermediate layer to form the structure

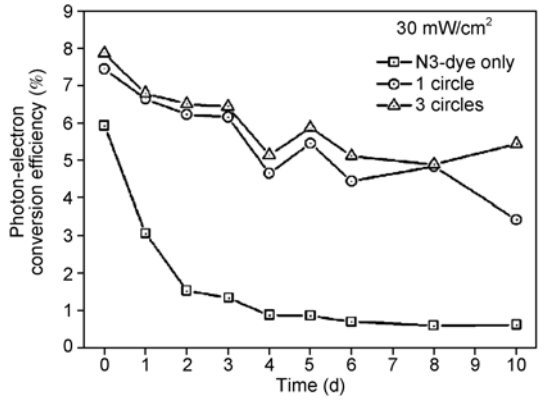

Figure 8 Stability of the cells with different circles of alternating assembly structure during 10 d testing [69].

TiO_2/JK-2/Al_2O_3/SQ1. This structure formed an appropriate energy level gradient, and the Al_2O_3 layer effectively retarded the interfacial recombination, resulting in an impressive improvement of conversion efficiency from respectively 7.48% and 4.02% to 8.65% totally.

3.3 Interface modification of the coadsorbent

A coadsorbent was added to the dye solution to retard the dye aggregation during the sensitizing process. The adsorbent was used to modify TiO_2 surface by coadsorbing with dye molecules. It could separate the dye molecules spatially when adsorbing onto the TiO_2 film. As a result, the dye aggregation was retarded, which caused the decreasing of the recombination reaction in DSCs. Then the conversion efficiency was enhanced. The coadsorbent acted as a modification material when the photoanode was sensitized, which is an in situ modification method.

The commonly used efficient coadsorbents are chenodeoxycholic acid (CDCA) [73] and pivalic acid (PVA) [74]. Tamiaki *et al.* reported that compared to the blank sample, the CDCA coadsorbent enhanced the conversion efficiency from 6.2% to 6.6% at AM1.5, 100mW/cm^2 [73]. The same effect could be found when the PVA was used as a coadsorbent. The conversion efficiency increased from 5.77% to 6.25%. It was shown that the efficiency enhancement was mainly caused by the increasing of V_{oc}, indicating the recombination was retarded by the coadsorbent [73].

The *in situ* modification of using a coadsorbent could reduce the recombination reaction in DSCs by weakening the aggregation of the dye molecules when the photoanode was sensitized. As a result, it improved the devices photovoltaic performance.

4 Interface modification effect of additives in electrolyte

In recent years, some components in the electrolyte known as additives have been recognized to impact the performance of DSCs by affecting the TiO_2/dye/electrolyte interface. With these additives, the J_{sc}, V_{oc} and the devices conversion efficiency can be improved.

4.1 TBP additive

As mentioned above, TBP was first used to modify the electrode/electrolyte interface by immersing the sensitized electrode into it [15]. However, in the subsequent research, *tert*-butyl pyridine was usually added into the electrolyte as a regular component. This additive improves the device's V_{oc} and fill factor according to two mechanisms: (1) *tert*-butyl pyridine can coordinate with the Ti^{3+} to passivate the surface states on the TiO_2 electrode through N atom on the pyridine ring, in this way, the recombination rate was re-

duced; (2) the adsorption of the *tert*-butyl pyridine formed a Helmholz blocking layer to suppress the recombination between the injected electrons and I_3^- in electrolyte [75]. These effects are strikingly similar with the effects of interface modification materials as mentioned above. Like *tert*-butyl pyridine, other pyridine derivatives or imidazole derivatives can also coordinate with the Ti^{3+} state on the TiO_2 electrode surface. These surface state sites are presumed to be the center of the electron recombination, so many of them, such as *N*-methyl-benzimidazole (NMBI) [76], amino-triazole [77], and polyvinyl pyridine, were also used as electrolyte additives to modify the TiO_2 electrodes.

4.2 NMBI additive and $Mg(OOCCH_3)_2$/NMBI additive

As an excellent additive in electrolyte, NMBI has been reported to have similar beneficial effect as TBP to suppress the charge recombination and increase V_{oc}, for which it has been widely used in electrolyte for DSCs [78–80]. In 2005 Hayase *et al.* found that adding NMBI into quasi-solid electrolyte could reduce the change transfer resistance from counter electrodes to I_3^-. It was the first report that additives in electrolyte could modify the electrolyte/counter electrode interface [81].

Most electrolyte additives are organic additives. Only a few inorganic additives, such as KI, have partial effect on the interface.

$Mg(OOCCH_3)_2$ has been demonstrated as an effective post-modification material. In our latest work [82], we found that when it was put into the electrolyte, a new co-additive of $Mg(OOCCH_3)_2$/NMBI improved the efficiency of DSCs by acting on the interface.

By introducing $Mg(OOCCH_3)_2$ additive into electrolyte with fixed content of NMBI, interface behavior shows that $Mg(OOCCH_3)_2$ could suppress the charge recombination and similarly enhance the excited energy level of the modified dye molecules like post-modification, thus electron injection was greatly facilitated. As a coagent with NMBI in electrolyte, $Mg(OOCCH_3)_2$ plays a significant role of modification at TiO_2/dye/electrolyte interfaces. Thus it can further improve the devices photovoltaic performance.

4.3 Polyethylene oxide (PEO) additive

Li^+ is usually added into the electrolyte as the cation in response to I^-, but it has been observed that the addition of bis(trifluoro-methyl-sulfonyl)amine lithium salt to some solid-state electrolyte such as spiro-MeOTAD retards the electron recombination [83]. It was explained by the Coulombic repulsion to the hole in the electrolyte caused by the lithium cation adsorbed on the TiO_2 surface [84].

PEO is an additive that is very suitable for fabricating all solid or quasi-solid state electrolyte for DSCs, except that PEO can form a Helmholz blocking layer. Furthermore, PEO is an ion-conducting polymer and it was found that it could form a potential step at the surface of TiO_2 electrode, which caused a dipole layer like $SrTiO_3$ or $BaCO_3$ modification [78]. According to our previous work [85], adding PEO into liquid electrolyte not only increased the mobility of Li^+, but also improved the devices photovoltaic performances. Li^+ in an electrolyte has negative and positive effects on DSCs photovoltaic performance. For example, adsorption/intercalation of Li^+ into the porous TiO_2 electrode shifts the conduction band edge downwards, lowering the V_{oc} value [86, 87]. In addition, it is noteworthy that the transport of injected electrons through TiO_2 films occurs by diffusion [17], and Li^+ in the electrolyte is helpful to the diffusion of electrons through TiO_2 films. This effect was interpreted by Kopidakis *et al.* with ambipolar diffusion mechanism [54]. By optimizing the dye adsorbing time and the thickness of the TiO_2 film, a quasi-solid DSC based on a polymer gel electrolyte with a PEO weight ratio of 10.0% showed a considerable conversion efficiency, which was 6.12% and 10.11% under 100 and 30 mW/cm^2 illumination, respectively. The research results of PEO additive in the quasi-solid electrolyte showed that PEO additive could enhance the conversion efficiency of DSCs through the interface effect of Li^+.

5 Conclusions

This paper mainly reviewed the interface modification after sensitization, which was found a vital factor to the interface reactions in the DSCs. It could be achieved by the immersing method and additives in the electrolyte. The effects of modification after sensitization could improve the performance of the devices through special mechanisms, which are different from the modification before sensitization.

Conventional photoanodes modification can improve electron injection and suppress electron recombination by forming energy barriers, serving as “surface dipole” or passivating the surface states. Some photoanodes modifications can also improve electron transportation.

Recent work introduced post-modification after sensitization into DSCs, which could deprotonate the free carboxylic groups of dye molecules and raise the LUMO of the dye to a higher energy level, resulting in higher conversion efficiency and better stability of DSCs. By combining the mechanisms of photoanodes interface modification and post-modification, Al_2O_3 was used as the intermediate layer for multi-layered dye sensitization. A coadsorbent was also used to modify the interface of TiO_2/dye/electrolyte after sensitization. Electrolyte additives act as a modification material after sensitization, too. The effects of these additives in electrolyte are similar with those of the modification materials, such as creating an energy barrier or surface dipole and passivating the surface states. Some other additives can modify the TiO_2/dye/electrolyte interface through eliminating photonation, establishing coulomb repulsive

field and reducing the resistance of the interface between the counter electrode and the electrolyte.

In summary, interface modification is a significant approach to solve the problems for practical applications of DSCs. Many problems remain to be studied. Some mechanisms of the modification are still under discussion. Therefore, interface modification, especially the modification after sensitization, as an effective approach to improve the performance of DSCs, requires further research in the future.

This work was supported by the National Natural Science Foundation of China (50873055), and the National Key Basic Research and Development Program of China (2006CB806203, 2009CB930602).

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