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Improving the efficiency of dye-sensitized solar cells by photoanode surface modifications

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ABSTRACT Dye-sensitized solar cells (DSSCs) provide a promising alternative solar cell technology because of their high efficiency, environmental friendliness, easy fabrication, and low cost. Power conversion efficiency is an important parameter to measure the performance of DSSCs, but the severe charge recombination that occurs at the photoanode hinders the future improvement of power conversion efficiency. Therefore, one of the key goals for achieving high efficiency is to reduce the energy loss caused by the unwanted charge recombination at various interfaces. From this perspective, surface modification of the photoanode is the simplest method among the various approaches available in the literature for enhancing the performance of DSSCs by inhibiting the interfacial charge recombination. After some brief notes on DSSCs, in this review, we present a comprehensive discussion on surface modifications of different photoanodes that have been adopted in the literature not only for reducing recombination but also for enhancing light harvesting. Depending on the electrode materials, we discuss surface modifications of binary oxides such as TiO₂ and ZnO and ternary oxides, including Zn₂SnO₄, SrSnO₃, and BaSnO₃. We also talk about methods of surface modification and the materials suitable for surface treatment. Finally, we end with a brief future outlook of DSSCs.

Keywords: surface modification, photoanode, power conversion efficiency, dye-sensitized solar cell

INTRODUCTION

Today, with rapid population growth and the wide use of a large amount of fossil fuels, an important and urgent global problem is our enormous appetite for energy, serious environmental pollution, and severe energy shortages. Under the threat of increasing environmental pollution and energy shortages, it is clear that the utilization of clean energy is essential for the development of a globally sustainable

society. Clean and renewable energy, which has a much lower environmental impact than conventional energies, has been the focus of recent attention. Various energy storage and conversion systems aimed at utilization of different clean energy sources are being developed [1].

In addition to fusion, solar energy has the largest potential to satisfy future global need for renewable energy sources [2]. In 1954, Chaplin, Fuller, and Pearson gave birth to the so-called “first generation” of solar devices, which generated great interest throughout the scientific community and related commercial interests [3]. The key to the breakthrough in 1991 was the use of mesoporous TiO₂ electrodes, invented by O'Regan and Grätzel, which had a high internal surface area to support the sensitizer monolayer. These devices had a power conversion efficiency (PCE) of 7.1% [4]. This breakthrough was the origin of dye-sensitized solar cells (DSSCs). Since then, DSSCs have presented a viable alternative to the standard silicon photovoltaic devices, which made this new photovoltaic technology attractive to both the scientific community and commercial interests [5–7].

As third-generation photovoltaic devices, DSSCs have received extensive attention as prospective alternatives to conventional silicon solar cells due to their low production cost, ease of fabrication, and high PCE [4]. In addition, DSSCs can offer numerous versatile properties such as transparency with tunable colors and mechanical flexibility. DSSC performance is also relatively better as compared to other solar cell technologies under diffuse light conditions and at higher temperatures [8].

A typical DSSC has a sandwich-type structure and is composed of three primary components: a photoanode, counter electrode, and electrolyte. The photoanode is a

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dye-sensitized mesoporous nanocrystalline semiconductor (nc-SC) film printed on a fluorine-doped tin oxide (FTO) conductive glass substrate. The most commonly used counter electrode in DSSCs is prepared by deposition of a thin catalytic layer of platinum onto a conducting glass substrate. The liquid electrolyte traditionally contains an iodide/triiodide (I^-/I_3^-) redox couple and acts as a conductor to electrically connect the photoanode and counter electrode. Fig. 1 shows the structure of DSSCs. The basic electron transfer processes in a DSSC, as well as the potentials for a state-of-the-art device based on an N3

Figure 1 Schematic overview of a dye-sensitized solar cell. Reprinted with permission from Ref. [8], Copyright 2010, the Royal Society of Chemistry.

dye adsorbed onto TiO_2 and I^-/I_3^- as a redox couple in the electrolyte, is shown in Fig. 2 [8].

When the adsorbed dye molecules absorb sunlight, they are excited (0). Electrons jump from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) state. Photoexcitation of the dye results in the rapid injection of photoelectrons into the conductive layer of the mesoporous photoanode, leaving the dye in its oxidized state (2). The injected electrons diffuse across the photoanode to be collected and then pass through an external circuit to the counter electrode (4). The excited dye molecules are reduced by I^- (3), and the I_3^- ions formed by oxidation of I^- diffuse a short distance through the electrolyte to the counter electrode, where the regenerative cycle is completed by electron transfer to reduce I_3^- to I^- (7). In addition to the desired pathway of the electron transfer processes described above, decay of the excited state of the dye to the ground state (1) and recombination of electrons in the semiconductor with oxidized dyes (5) or acceptors in the electrolyte (6) have a negative effect on the performance of DSSCs [8].

The development of DSSCs is devoted to the enhancement of the light-to-electric energy conversion efficiency and the long-term stability. Up to now, the highest PCE reported in DSSCs is 14.3% [9], which is far lower than the theoretically predicted efficiency of ~20% [10]. All the approaches to achieve higher DSSC efficiencies look for improvement in the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF).

Figure 2 Simple energy level diagram for a DSSC. The basic electron transfer processes are indicated by number (0–7). The potential for a DSSC based on the N3 dye, TiO_2 , and the I^-/I_3^- redox couple are also exhibited. Reprinted with permission from Ref. [8], Copyright 2010, the Royal Society of Chemistry.

The current-voltage (I - V) characteristics of a solar cell under illumination are used to measure the PCE (η). From the I - V curve, J_{sc} is determined at the $V = 0$ V intercept, whereas V_{oc} is found at the $I = 0$ intercept. FF is a value between 0 and 1 that describes the shape of the I - V curve, where a high value indicates a more preferable rectangular shape. The PCE is given as $\eta = J_{sc} V_{oc} FF / P_{in}$, where P_{in} is the power density of the incident light.

J_{sc} is determined by the light-harvesting efficiency, electron injection efficiency, and charge collection efficiency at the counter electrode. V_{oc} is determined by the quasi-Fermi level and the potential of the redox couple in the electrolyte [11]. It can be enhanced either by increasing the rate of electron injection or by reducing the recombination. FF can be enhanced by reducing the series resistance by increasing the conductivity of the FTO and optimizing the thickness of the nc-SC film.

To obtain higher PCE, some general strategies have been found to be efficient in optimizing the above parameters and can be defined as follows:

1. Synthesis of new dyes. Based on some essential characteristics dyes must have, many different photosensitizers, including metal complexes, porphyrins, phthalocyanines, and metal-free organic dyes, have been designed and applied to DSSCs in order to reduce the interfacial recombination along with enhanced light harvesting [12,13]. Also, the addition of a co-sensitizer has been proven to be very useful [14,15].

2. Synthesis of nc-SCs with new architectures. Varying morphologies and architectures (nanoparticles (NPs), nanotubes, nanowires, and core-shell structures), including those with alternative types of semiconductors (e.g., ZnO or SnO₂), have been developed to improve the efficiencies of DSSCs [16].

3. Synthesis of new redox couples. Attempts have been made to replace the I^-/I_3^- redox couple with alternative faster redox couples such as Br^-/Br_3^- and Co^{+2}/Co^{+3} . Use of a LiBr/Br₂ mixture as redox in a series of electrolytes led to rather low efficiencies [17]; however, the Br^-/Br_3^- redox system was shown to give better results using eosin as a sensitizer [18]. As for transition metal systems, the diffusion constant of a cobalt-based redox couple $Co(DTB)_3^{2+/3+}$ was found to be at least one order of magnitude lower than that for the triiodide ions inside the pores of dye-sensitized TiO₂ [19]. Finding a good way to block recombination reactions or alternatively to identify new one-electron redox systems with inherent slow recombination appears to be the current challenge [8].

4. Surface modification of the photoanode. The pho-

toanode is responsible for both light harvesting and electron injection by a dye monolayer, and therefore its various interfaces, such as nc-SC/dye and nc-SC/electrolyte, play a very important role in determining the efficiency of DSSCs. A multiple trapping/de-trapping electron diffusion process occurs in conventional photoanode-based DSSCs, which results in slow electron transport properties. Owing to the above behaviors, electrons would be lost by recombination with oxidizing agents in the electrolyte and oxidized dyes on the surface of the photoanode [20].

Among all the methods available for improving efficiency, surface modification of the photoanode is a relatively simple method for enhancing the PCE by reducing the charge combination losses and improving light harvesting [7]. Therefore, various approaches for the surface modification of photoanodes have been developed to reduce the interfacial charge recombination, including modification of the mesoporous nc-SC layer, either through various acid treatments or by adding an insulating/semiconducting blocking layer on its surface, and modification of the nc-SC/dye and nc-SC/dye/electrolyte surfaces by employing different adsorbents and additives, respectively.

SURFACE MODIFICATIONS OF PHOTOANODE

The electrode material is a critical factor determining the performance of DSSCs. The electronic states below the conduction band edge (CBE), which is located at the photoanode nanocrystal surface, act as recombination centers and traps, which slow electron transport. Up to now, many semiconductors have been applied as electrode materials for DSSCs: TiO₂ [21], ZnO [22], Nb₂O₅ [23], SnO₂ [24], WO₃ [25], and so on. Among them, nanocrystalline TiO₂ and ZnO have been found to be the best materials owing to their high performance in DSSCs. In addition to these binary oxides, ternary oxides such as Zn₂SnO₄ [26], BaSnO₃ [27], and SrTiO₃ [28] have been investigated because of the ease of modifying their chemical properties and band structures. Different surface modifications of different photoanodes are described in detail in the following sections.

Surface treatment on TiO₂ photoanode

For DSSCs, the most common material for the photoanode is TiO₂ NPs. TiO₂ is a stable, nontoxic oxide, and anatase TiO₂ is widely used in DSSCs. Since 1991, there has been a significant effort to improve TiO₂ electrodes in DSSCs in terms of light absorption, light scattering, charge transport,

and suppression of charge recombination. At the heart of a DSSC is the mesoporous oxide layer, which is composed of a network of TiO_2 NPs that have been sintered together to establish electronic conduction. Typically, the film thickness is ca. 10 μm , with a NP size of 10–30 nm and a porosity of 50%–60%. The mesoporous layer is deposited on a transparent conducting oxide on a glass or plastic substrate [29].

The recombination reaction between electrons in the TiO_2 and the electron acceptors in the electrolyte can be suppressed in various ways: by thin blocking layers covering the TiO_2 surface, by TiCl_4 treatment, by acid treatment, or by the use of additives in the electrolyte and co-adsorbents. In this section, we focus our discussion on the first three methods.

Blocking layer

Most efforts in creating thin blocking layers have been devoted to coating a thin layer of large-band-gap metal oxides or insulating materials on the surface of the mesoporous electrode to inhibit recombination losses by forming a core-shell structure and energy barrier [30]. Insulating materials with conduction bands higher than that of TiO_2 , such as Al_2O_3 , SiO_2 , ZrO_2 , and SrO , have been coated onto TiO_2 photoanodes to enhance the performance of DSSCs [31,32]. Palomares *et al.* [31] deposited SiO_2 , Al_2O_3 , and ZrO_2 onto the surfaces of TiO_2 electrodes by a dip-coating technique using an organic solution of their respective alkoxides. They found that recombination between electrons and oxidized dye molecules was slowed in all cases, whereas an overlayer coating of Al_2O_3 was optimal for slowing the charge recombination without compromising other photovoltaic parameters. In many cases, the Al_2O_3 overlayer showed its effectiveness in improving the efficiency of DSSCs by forming a core-shell structure. Hamann *et al.* [33] prepared ultrathin Al_2O_3 blocking layers on TiO_2 by atomic layer deposition (ALD) to control the thickness of the blocking layer. The electron lifetime increased exponentially as the number of ALD cycles increased, but the photocurrent significantly decreased at the same time. Li *et al.* [32] reported the utilization of ALD to passivate surface trap states in mesoporous TiO_2 NPs for solid-state DSSCs. The mesoporous TiO_2 was coated by depositing ZrO_2 films with angstrom-level precision, producing a more than two-fold enhancement in short-circuit current density. The impedance spectra shown in Fig. 3 provides evidence that the ZrO_2 coating produced a barrier between the electron and hole transport media, which decreased recombination and suppressed the activity of sur-

Figure 3 Impedance spectra of solid-state DSSC at 0.4 (a) and 0.75 V (b–d) forward bias with increasing number of cycles of ZrO_2 deposition. c and d are magnifications of b.

face recombination sites. As a consequence, increases in both the current density and FF of the solid-state DSSCs were observed.

Semiconductor materials such as ZnO , SrTiO_3 , BaTiO_3 , and Nb_2O_5 have also been employed to modify the TiO_2 surface [34–36]. Chen *et al.* [34] found improved DSSC performance with Nb_2O_5 -coated TiO_2 electrodes. Chen *et al.* [37,38] compared the effects of SrTiO_3 and Nb_2O_5 shells on the electronic properties of TiO_2 cores. They found that in both cases, V_{oc} increased. The coating layer of Nb_2O_5 formed an energy barrier at the TiO_2 /electrolyte interface, whereas the SrTiO_3 layer shifted the conduction band of the TiO_2 in the negative direction. Depositing In_2O_3 and Nb_2O_5 onto TiO_2 by ALD also resulted in significantly improved performance, thus enhancing the DSSC efficiency [39]. In addition to providing an energy barrier against the electron transfer from TiO_2 to I_3^- , a BaTiO_3 blocking layer resulted in enhanced dye absorption, leading to an enhanced J_{sc} and improving the efficiency from 5.46% to 7.52% [40].

In addition to the methods discussed above, carbonates such as CaCO_3 , BaCO_3 , and SrCO_3 have also been used to suppress charge recombination. Zhan *et al.* [41] synthesized alkaline-earth carbonate (CaCO_3 , BaCO_3 , and SrCO_3)-modified TiO_2 electrodes by dipping TiO_2 electrodes into alkaline-earth hydroxide or alkaline-earth acetate aqueous solutions. Wang and co-workers [42] reported prolonged electron lifetimes and increased V_{oc} and J_{sc} by using CaCO_3 for surface passivation. Gregg *et al.* [8,43] formed a blocking layer on the mesoporous

electrode after dye adsorption by a silanization treatment. Their aim was to block parts of the electrode not covered by the dye from the electrolyte so that they could use fast one-electron redox couples. They demonstrated for the first time a working mesoporous TiO_2 solar cell using ferrocene as the redox mediator.

Emerging as a new class of porous crystalline materials, metal-organic frameworks (MOFs) are good candidates for DSSCs owing to their flexible fabrication and highly porous nature [1]. In 2011, we first used a zeolitic imidazolate framework, ZIF-8, to coat TiO_2 with different thicknesses for use as electrode materials in DSSCs by immersing TiO_2 in a fresh methanol solution containing $1 \text{ mmol L}^{-1} \text{ Zn}(\text{NO}_3)_2$ and 2 mmol L^{-1} 2-methyl imidazole for 0–40 min. After a growth time of 30 min, a very thin ZIF-8 layer with a thickness of approximately 2 nm was coated on the TiO_2 . A linear relationship between the thickness of the ZIF-8 coating layer and V_{oc} was found and the value of V_{oc} was increased, which could be ascribed to the inhibited interfacial charge recombination due to the introduction of the ZIF-8 shell material [30]. We then presented the first report of a post-treatment approach to decorate a TiO_2 photoanode interface with ZIF-8. In this strategy, the TiO_2 photoanode was first sensitized by dyes and then further treated by ZIF-8 overlayer growth and dye sensitization. Fig. 4 shows a comparison between photoanodes from the pretreatment and post-treatment procedures. When using the pretreatment step, a ZIF-8 overlayer existed between the TiO_2 and the dye, which hampered the injection of photo-excited electrons into the conduction band of TiO_2 and thereby reduced J_{sc} . Although electron injection also hampered dyes adsorbed on the ZIF-8 overlayer created by post-treatment, the dyes tightly anchored onto the TiO_2 surface ensured the efficiency of photocurrent output. The

Figure 4 The possible photoanode statuses after sensitization in pretreatment and post-treatment approaches.

additional dyes adsorbed onto the ZIF-8 contributed to the enhancement of J_{sc} , thereby resulting in markedly enhanced performance. The results illustrated in Fig. 5 suggest that the use of MOFs as blocking layers could improve the overall performance of DSSCs [44].

TiCl₄ treatment

TiCl_4 surface treatment of nanocrystalline TiO_2 has been frequently applied to improve the performance of DSSCs since the publication of a paper by Nazeeruddin *et al.* in 1993 [15]. In that study, TiCl_4 surface treatment was used to improve the performance of relatively impure Degussa P25 TiO_2 NPs. Sommeling *et al.* [45] studied the influence of TiCl_4 post-treatment on nanocrystalline TiO_2 photoanodes. As a result of this post-treatment, cell efficiencies were improved due to higher photocurrents. The TiCl_4 treatment leads to the deposition of an ultrapure TiO_2 shell ($\sim 1 \text{ nm}$) on the mesoporous TiO_2 , which results in increased dye adsorption owing to increased roughness. It also improves the injection efficiency by lowering the acceptor levels in TiO_2 in energy and significantly improves the electron lifetime [46,47]. Fig. 6 shows SEM images of the TiO_2 nanotube layers before (left) and after (right) TiCl_4 treatment [47]. Clearly, the samples after TiCl_4 treatment are uniformly decorated with TiO_2 NPs approximately 3 nm in diameter. From the cross-section views after TiCl_4 treatment in Figs 6c and 6e–f, it can be seen that the wall thickness uniformly increased by ~ 25 –40 nm. Most importantly, the SEM images show the drastically more corrugated surface area of tubes, which allows for significantly higher dye adsorption.

Figure 5 *I*-*V* curves of uncoated electrode and ZIF-8 coated electrode by post-treatment. Reprinted with permission from Ref. [44], Copyright 2014, WILEY-VCH.

Figure 6 SEM images of 20 μm long TiO_2 nanotubes before (left) and after TiCl_4 treatment (right). Reprinted with permission from Ref. [47], Copyright 2009, Elsevier.

Acid treatment

In the literature, acids have been used primarily for modifying TiO_2 surfaces. Acid treatment affects the movement of the CBE of nc-SC surfaces depending upon the pH of the acid and the isoelectric point (IEP) of the nc-SC. The IEP is the pH at which the nc-SC surface has a net zero charge. The IEP of TiO_2 is 5.5, which implies that acid treatment will result in the nc-SC carrying a net positively charged surface, which in turn would result in a negative movement of the TiO_2 CBE. Several acids, listed in Table 1, have been studied to determine the effect of such treatment on the charge recombination and light harvesting of DSSCs.

Wang *et al.* [56] studied the effect of HCl treatment on the photovoltaic properties of N749 DSSCs using intensity-modulated photovoltaic spectroscopy. The surface protonation of the TiO_2 film caused a positive shift of CBE by 28 mV, which corresponded to a decrease in V_{oc} of 28

mV. It also caused a reduction in recombination by a factor of 5, which corresponded to an increase in V_{oc} of 50 mV. Thus, the net change in V_{oc} was 22 mV, which was in good agreement with the experimental value (19 mV). These data indicate that surface protonation of TiO_2 can simultaneously improve J_{sc} as a result of the positive shift of CBE and V_{oc} due to the suppression of charge recombination. Balraju *et al.* [57] showed that an improvement in the PCE could be achieved by a simple acid treatment of the TiO_2 photoanode. The acid treatment could enhance dye adsorption by surface protonation, leading to the enhancement of J_{sc} . The PCE of a DSSC based on an HNO_3 -treated TiO_2 photoanode was higher than that of an HCl-treated one, which resulted from the suppression of backward electron transfer by uptaking NO_3^- anions to the TiO_2 surface, thereby collecting more charge carriers. These results indicate that anion adsorption onto a TiO_2 surface, as well as

Table 1 Several acids used to modify the TiO₂ photoanode in DSSCs

Photoanode	Acid	Dye	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	η (%)	Reference
TiO ₂	HCl	IDS	14.95	0.44	0.70	4.80	[48]
	HCl	N3	3.00	0.60	0.62	1.11	[49]
	HCl	N719	9.31	0.75	0.74	5.20	[50]
	HCl	N3	13.70	0.64	0.65	5.70	[51]
	HNO ₃	N3	14.80	0.65	0.65	6.20	[52]
	HNO ₃	N719	15.40	0.71	0.61	6.60	[52]
	Formic acid	N3+RhCL	6.97	0.64	0.53	4.70	[53]
	Acetic acid	N3	10.9	0.52	0.42	2.4	[54]
	Oxalic acid	N719	9.13	0.72	0.70	4.59	[55]

surface protonation, can improve the performance of DSSCs. From the results of their experiments, Hao *et al.* [49] found that a TiO₂ photoanode treated by hydrochloric acid had better performance than those treated by sulfuric acid, nitric acid, and phosphoric acid. In addition to inorganic acids, several organic acids have been used to modify a photoanode. Based on equivalent circuit analysis, Murayama *et al.* [58] concluded that acetic acid treatment not only improved the electrical contact between TiO₂ NPs but also blocked the charge transfer from the TiO₂ surface to the electrolyte. Sakaguchi *et al.* [54] treated TiO₂ electrodes with a dilute solution of carboxylic acid and fabricated DSSCs with quasi-solid electrolytes containing ionic liquids. Large increases in J_{sc} and small increases in V_{oc} were observed as compared to their previous results, in which acetic acid was added directly to the electrolyte. Interfacial resistance relating to the TiO₂ layers decreased after the acetic acid treatment. In addition, an increase in J_{sc} has been observed after TiO₂ was treated with other aliphatic and aromatic carboxylic acids such as hexanoic acid, lactic acid, and benzoic acid. Singh *et al.* [59] investigated the anchoring mechanism of N719 dye molecules on oxalic acid-treated TiO₂ electrodes. Also, DSSCs fabricated using N719 dye sensitized onto oxalic acid-treated TiO₂ showed an efficiency of ~4.6%, which is significantly higher than that based on untreated TiO₂ electrodes.

Surface treatment on ZnO photoanode

Historically, ZnO was one of the first semiconductors used in DSSCs [8]. As a semiconductor, ZnO possesses a band structure and physical properties similar to those of anatase TiO₂, but it has higher electron mobility and more accessible morphologies. For these reasons, many studies have been devoted to the fabrication of ZnO photoanodes.

Although great effort has been made to improve the efficiency of dye-sensitized ZnO solar cells, it is still much

lower than that of TiO₂. There are two important factors restricting the performance of dye-sensitized ZnO solar cells. First, ZnO films are easily corroded in acidic dye solutions. The chemical stability of ZnO is rather poor compared to that of TiO₂, dissolving under both acidic and basic conditions. Second, the efficiency of ZnO photoanodes is restricted by its low open-circuit photovoltage [60]. Because of these disadvantages, it is highly desired to find a way to enhance the resistance of ZnO films toward acids and increase the V_{oc} of ZnO photoanodes without sacrificing the efficiency and J_{sc} . Similar to TiO₂, deposition of ultrathin metal oxide layers could improve the performance of ZnO DSSCs. SiO₂ blocking layers on mesoporous ZnO electrodes have been found to increase the chemical stability of the electrodes toward acidic dye molecules and enhance the PCE to 5.2% under AM 1.5G conditions [61]. Plank *et al.* [62] applied a MgO and ZnO shell deposition method to control the interface between two indole-based organic dyes in solid-state dye-sensitized ZnO solar cells. Transient absorption measurements indicated that the enhancement of photo-induced charge generation with a core-shell formation was the main factor leading to the improved device efficiency. We proposed a facile surface-treatment method by means of chemical-bath deposition (CBD) to improve the performance of dye-sensitized ZnO solar cells [60]. After the treatment, quantum dots of Zn₂SnO₄ were deposited onto ZnO NPs, accompanied by aggregation of the Zn₂SnO₄ NPs. The ZnO film had better resistance to an acidic dye solution and better light-scattering ability due to the deposited Zn₂SnO₄ NPs and their aggregates. The clearly increased V_{oc} was attributed to the elevated CBE of ZnO and the inhibited interfacial charge recombination. Although the adsorption amounts of N719 dye were decreased, the enhanced light-scattering ability led to an improved J_{sc} . By optimizing the thickness of the ZnO film, a top PCE of 4.38% was achieved. The *I*-*V* curves

are plotted in Fig. 7. Before surface treatment, the photovoltaic parameters of the cell were $J_{sc} = 8.66 \text{ mA cm}^{-2}$, $V_{oc} = 651 \text{ mV}$, $FF = 0.65$, and $\eta = 3.67\%$. After surface treatment, the performance of the cells clearly improved, with $J_{sc} = 9.49 \text{ mA cm}^{-2}$, $V_{oc} = 721 \text{ mV}$, $FF = 0.64$, and $\eta = 4.38\%$.

As for the acid treatment of ZnO photoanodes, although the ZnO surface is etched in the presence of acid owing to the dissolution of Zn^{2+} ions, some studies have reported improvement in the conductivity and mobility in ZnO upon acid treatment [63]. Chen *et al.* [64] found that the efficiency of a DSSC increased from 0.7% to 1.2% after treatment of vertically aligned ZnO nanowires with HAuCl_4 acid. ZnO nanorod arrays coated with gold NPs could enhance the optical absorption owing to surface plasmon resonance and reduce recombination by the interfacial ZnO–Au Schottky barrier.

Surface treatment on other binary oxide photoanodes

SnO_2 is a chemically stable binary oxide that has a conduction band edge approximately 0.5 eV lower than that of anatase TiO_2 [65]. Therefore, it can be used in combination with dyes with low-lying LUMO that inject poorly into TiO_2 . A significant improvement in V_{oc} and efficiency can be achieved by covering mesoporous SnO_2 with a very thin shell of another metal oxide, such as ZnO, MgO, and Al_2O_3 [66–68]. Kumara *et al.* [67] applied Al_2O_3 onto mesoporous SnO_2 and found a much increased V_{oc} and improved DSSC performance for small amounts of Al_2O_3 , whereas large amounts decreased the photocurrent. Kay and Grätzel [68] tested a number of insulating oxides such as ZnO, TiO_2 , ZrO_2 , and Al_2O_3 on SnO_2 and found that

Figure 7 *I*-*V* curves of the cells with a thickness of 10 μm . Inset: IPCE spectra. $\circ$ = ZnO-C1; $\bullet$ = ZnO. Reprinted with permission from Ref. [60], Copyright 2012, WILEY-VCH.

basic oxides improved the dye adsorption and the performance of DSSCs. As shown in Fig. 8, much better coloration and photocurrent/voltage characteristics were obtained with the basic oxides MgO (IEP at pH 12), Al_2O_3 (IEP at pH 9), and Y_2O_3 (IEP at pH 9). This change is ascribed to the inhibition of electron back transfer from SnO_2 to the redox electrolyte by the insulating oxide. The optimum coating thickness was found to be only a few angstroms. Sayama *et al.* [69] studied the photoelectrochemical properties of TiO_2 , Nb_2O_5 , ZnO, SnO_2 , In_2O_3 , and other porous semiconductor films sensitized by ruthenium dye. They found that the Nb_2O_5 semiconductor cell had the highest incident of monochromatic photon-to-current efficiency as compared to the TiO_2 cell. It also showed the highest V_{oc} .

Surface treatment on ternary oxide photoanode

In addition to these binary oxide materials, special attention has been paid to ternary oxides, which provide more freedom to modify their chemical properties and band structures. As compared to surface modification of TiO_2 photoanodes, surface modification of ternary oxide photoanodes such as Zn_2SnO_4 , SrSnO_3 , and BaSnO_3 has not been investigated intensively, and only a few examples have been demonstrated.

Zn_2SnO_4 is an interesting material for photoanode supports for DSSCs because the large band-to-band transition substantially diminishes photobleaching and presents a lower electron–triiodide recombination rate [70]. As an

Figure 8 Photocurrent-voltage characteristics of dye-sensitized nanocrystalline photoelectrochemical cells with modified SnO_2 photoelectrodes at an irradiance of 1000 W m^{-2} , AM 1.5 (lower curves in darkness): (a) unmodified SnO_2 , (b) SnO_2 coated with $12 \mu\text{mol}$ of MgO/m^2 or 0.13 nm , (c) SnO_2 coated with $6 \mu\text{mol}$ of $\text{Al}_2\text{O}_3/\text{m}^2$ or 0.16 nm , (d) SnO_2 coated with $6 \mu\text{mol}$ of $\text{Y}_2\text{O}_3/\text{m}^2$ or 0.27 nm . Reprinted with permission from Ref. [68], Copyright 2002, American Chemical Society.

Figure 9 The process for the surface treatment of Zn_2SnO_4 with Al^{3+} ions, and the possible reaction mechanism. Reprinted with permission from Ref. [73], Copyright 2014, the Royal Society of Chemistry.

n-type semiconductor with a band gap of 3.6 eV, Zn_2SnO_4 is used as one kind of transparent conducting oxide material. We found that the efficiency of dye-sensitized Zn_2SnO_4 solar cells was obviously improved by the introduction of Al^{3+} ions onto the surface of the electrode [71]. The electrode was immersed in an ethanol solution containing 0.1 mol L^{-1} $\text{Al}(\text{NO}_3)_3$ for 10 min and then sintered at 510°C for 1 h. After calcination, Al^{3+} ions were introduced into the lattice of Zn_2SnO_4 and occupied the position of Sn^{4+} , resulting in a reduced conduction band edge and larger Zn_2SnO_4 NPs. It was observed for the first time that the efficiency of solar cells is improved by the doping of Al^{3+} ions rather than by the formation of an Al_2O_3 overlayer. Fig. 9 shows the reaction pathway in our $\text{Zn}_2\text{SnO}_4/\text{Al}$ -1 system. Pathway A is common for DSSCs based on binary oxides, whereas pathway B was first observed in our study. Although the adsorption amounts of dye decreased by 21%, the driving force for electron injection was greatly enhanced as a result of the decreased conduction band edge, resulting in significantly enhanced cell efficiency. The efficiency of CdS quantum dot-sensitized Zn_2SnO_4 solar cells was also improved by the same surface treatment method [72]. The electron lifetime was prolonged and the interfacial charge recombination was inhibited, which gave rise to a greatly improved short-circuit current and efficiency. In addition, we used the surface treatment of zinc tin oxide precursor solutions with a facile CBD method to enhance the performance of dye-sensitized Zn_2SnO_4 solar cells [73]. Typically, the electrodes were dipped into a 0.1 mol L^{-1} aqueous solutions of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{SnO}_3 \cdot 4\text{H}_2\text{O}$ in sequence for 3 min

at room temperature, and this two-step dipping procedure was defined as one CBD cycle. By optimizing the CBD cycle number, the surface state of the Zn_2SnO_4 film was promoted, which jointly led to an enhancement of 13.5% in the performance of Zn_2SnO_4 solar cells.

The effect of TiCl_4 treatment on a BaSnO_3 electrode has been reported [74]. The TiCl_4 treatment was found to form an ultrathin TiO_2 layer on the BaSnO_3 surface, leading to improved charge-collection efficiency by enhancing the charge transport and suppressing the charge recombination. However, the TiCl_4 treatment could reduce dye adsorption and light-harvesting efficiency. The trade-off effect between the charge-collection and light-harvesting efficiencies resulted in the highest quantum efficiency.

We also studied dye-sensitized SrSnO_3 solar cells, the efficiency of which was also greatly enhanced by introducing SrSnO_3 NPs through surface treatment using the CBD method [75].

METHOD FOR SURFACE MODIFICATIONS

Several methods have been developed that allow for surface modifications. The dip-coating sintering process is the simplest way to form an overlayer on the surface of a photoanode. CBD and reactive direct-current magnetron sputtering are also employed for surface modification. The ALD technique and pulsed laser deposition (PLD) technique are used for controlled thickness deposition [76,77]. As compared to ALD, PLD requires higher sintering temperatures and longer fabrication times. In this section, we will focus on discussing the following methods: the dip-

coating method, CBD, and ALD.

The dip-coating method

The dip-coating method is an extremely simple and low-cost method for forming a blocking layer on the surface of a photoanode. Palomares *et al.* [31] applied Al_2O_3 , SiO_2 , and ZrO_2 onto the surfaces of TiO_2 electrodes by a dip-coating technique using metal alkoxy precursors. Kato *et al.* [78] prepared TiO_2 coatings with different crystal structures from alkoxide solutions via the dip-coating technique. Chou *et al.* [79] prepared ZnO-coated TiO_2 electrodes using the dip-coating method and investigated the applicability of this photoanode in a DSSC. They fabricated a ZnO-coated TiO_2 electrode by immersing an FTO-glass substrate with a TiO_2 film treated with TiCl_4 into a solution of zinc acetate dehydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] and ethanol. They studied the effects of the concentration of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, the duration of dipping, and the dye loading on the PCE of a DSSC.

Chemical-bath deposition

CBD is a technique in which thin semiconductor films are immersed in dilute solutions containing metal ions and a source of hydroxide, sulfide, or selenide ions [80]. It is well suited for producing large-area thin films for solar energy-related applications, and it has been extensively applied in quantum-dot-sensitized solar cells to synthesize quantum dots (QDs) of a CdS sensitizer [81,82]. CBD has also been used to enhance the photovoltaic performance of ternary oxides in view of the characteristics of ternary oxides. The CBD approach demonstrates better coverage of QDs on the

surfaces of semiconductors [83]. We reported the fabrication of Zn_2SnO_4 photoanodes sensitized by CdS QDs via CBD [72]. In this typical CBD process, the electrodes were dipped in sequence into an ethanol solution of $\text{Cd}(\text{NO}_3)_2$ and an aqueous solution of Na_2S for 5 min at room temperature; this two-step dipping procedure is defined as one CBD cycle. We also deposited Zn_2SnO_4 (ZTO) QDs onto the surface of a ZnO photoanode by CBD, resulting in clear performance enhancement of dye-sensitized ZnO solar cells [60]. For the preparation of a TiO_2 /ZIF-8-based solar cell, the TiO_2 film was immersed in a fresh methanol solution containing $\text{Zn}(\text{NO}_3)_2$ and 2-methyl imidazole for a given time [30,84]. ZIF-8 was synthesized *in situ* on the surface of the TiO_2 film by CBD, which could improve the V_{oc} of DSSCs. The X-ray photoelectron spectroscopy (XPS) patterns of TiO_2 electrodes coated by ZIF-8, shown in Fig. 10a, exhibits the increase of Zn^{2+} content with increasing growth time, justifying the growth of the coating layer. The high-resolution transmission electron microscopy (HRTEM) image in Fig. 10b reveals a thin MOF layer with an approximate thickness of 2 nm coated on TiO_2 after 30 min, suggesting the successful preparation of a core-shell nanostructure.

The atomic layer deposition technique

As mentioned in the second section, ALD has been used to prepare ultrathin blocking layers on mesoporous TiO_2 [33]. ALD enables controlled layer-by-layer deposition of metal oxides onto templates; however, it also facilitates deposition on NP and nanorod assemblies to form core-shell structures. The ALD technique allows for fast, low-temperature processing, fine control of the thickness, and high-

Figure 10 (a) High-resolution XPS spectra of Zn^{2+} for MOF coated TiO_2 electrodes with different growth times. (b) HRTEM image of TiO_2 with a thin coating layer of MOF, the scale bar is 2 nm. Reprinted with permission from Ref. [30], Copyright 2011, the Royal Society of Chemistry.

Figure 11 X-ray photoelectron spectra of the Ga $2p^{3/2}$ transition (1118.65 ± 0.1 eV) confirming the presence of the Ga^{3+} valence state expected for Ga_2O_3 . The transition peak intensity is found to increase together with the number of Ga_2O_3 ALD cycles. (Inset) Ti $2p^{3/2}$ and Ti $2p^{1/2}$ transitions (459.45 ± 0.15 , 465.05 ± 0.1 eV) for the Ti^{4+} oxidation state preserved after addition of the tunneling overlayer. Reprinted with permission from Ref. [86], Copyright 2012, American Chemical Society.

purity material precursors. Also, using the ALD technique may lead to low manufacturing costs due to the fast processing times and the small amount of material needed to grow the layers [85]. Chandiran *et al.* [86] presented the first use of a gallium oxide tunneling layer deposited by ALD to significantly reduce electron recombination in DSSCs. The surface of the porous TiO_2 photoanode for DSSCs was passivated using a subnanometer-thick Ga_2O_3 tunneling overlayer. As shown in Fig. 11, a peak at 1118.65 ± 0.1 eV observed for the surface-treated films was assigned to the Ga $2p^{3/2}$ transition, confirming the presence of the Ga^{3+} valence state expected for Ga_2O_3 . The inset indicates that the Ti^{4+} oxidation state is preserved after passivation. After ALD of only a few angstroms of Ga_2O_3 , the electron back reaction is reduced, whereas charge-collection efficiency and FF are increased by 30% and 50%, respectively.

MATERIALS SUITABLE FOR SURFACE TREATMENT

Many materials have been used for the surface modification of photoanodes. In the former part, we discussed three approaches for the surface modification of photoanodes: the addition of blocking layer, $TiCl_4$ treatment, and acid treatment. Depending on these three approaches, different materials are chosen for surface treatments.

The blocking layer forms a potential barrier to the recombination process, although in some cases, the blocking layer can increase the amount of adsorbed dye molecules as an additional effect. Materials for the blocking layer are thus restricted to insulators such as Al_2O_3 , SiO_2 , ZnO , and rare earth oxides. The CBE of the material should be more positive than that of nc-SC in order to create an energy barrier between the electrons present in the photoanode and the dye molecules. Also, the thickness of the blocking layer should be optimized. However, because of the quantum size effect, the electronic properties of a semiconductor can extend to the insulator regime. Also, the use of blocking layers made of narrow-band-gap semiconductors such as CdO may have some advantages because it widens the range of usable metals and provides the means to control the surface properties of the oxide electrodes [87]. Based on the types of materials for blocking layers, this approach can be divided into insulating blocking layers and semiconducting blocking layers. Table 2 lists several materials used as blocking layers in DSSCs.

In the studies listed in Table 2, the improved efficiency has been ascribed to the suppressed recombination, passivation of the surface state, and band edge shifting. In addition to inorganic insulators and semiconductors, organic insulators such as silane or siloxane derivatives have been used as blocking layers, which could passivate the surface of the TiO_2 layer and increase the surface area for dye loading, as well as shorten the electron transport pathway. Sewvandi *et al.* [94] modified TiO_2 electrodes with six different kinds of silane to decrease the back electron transfer on the TiO_2 surface. Among all silane molecules used, heptadecafluorodecyl trimethoxy silane showed the best performance. They found that the reduction of back electron transfer depended on the TiO_2 surface coverage by silane, the alkyl chain length, and the molecular structure of the silane. Also, a new approach, the sequential adsorption process of silane and dye, was introduced to enhance V_{oc} and FF without lowering J_{sc} . The improvements in V_{oc} and FF can be attributed to the increase in the amount of silane adsorbed onto the TiO_2 surface, which insulates the surface from the electrolyte solution, as shown in Fig. 12. An *et al.* [95] reported that tetraethyl orthosilicate (TEOS) treatment was an effective avenue in enhancing the photo-induced current and the PCE. The increased photocurrent density may be attributed to the effective charge injection from strongly anchored dyes by the equilibrium-shifting action of TEOS, as well as to a downward CBE shift. Moreover, the device showed a better long-term stability than the

Table 2. List of several semiconductors and insulators used as blocking layers in dye-sensitized solar cells [7]

nc-SC	Blocking layer	Dye	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	η (%)	Reference
	Inorganic insulators						
	SiO ₂	N3	10.6	0.71	0.58	4.40	[31]
	Al ₂ O ₃	N3	12.1	0.76	0.61	5.60	[31]
	ZrO ₂	N3	9.10	0.68	0.60	3.60	[31]
	SiO ₂	N719	8.91	0.79	0.70	4.97	[88]
	Al ₂ O ₃	Z907	4.74	0.80	0.73	2.74	[89]
	ZrO ₂	N719	2.30	0.70	0.66	1.08	[32]
	CaCO ₃	N719	12.41	0.85	0.76	7.90	[41]
	HfO ₂	N719	11.90	0.69	0.69	5.68	[90]
	MgO	N719	20.43	0.73	0.72	10.75	[91]
	Al ₂ O ₃	N719	20.41	0.73	0.72	10.75	[91]
	Mg(OH) ₂	N719	8.94	0.86	0.57	4.40	[92]
TiO ₂	Organic insulators						
	APTS	N3	14.82	0.67	0.64	7.04	[93]
	Heptadecafluorodecyl trimethoxy silane	N719	11.50	0.74	0.73	6.20	[94]
	Tetraethyl orthosilicate	Z907	11.00	0.72	0.70	5.60	[95]
	Semiconductors						
	Nb ₂ O ₅	N3	11.40	0.73	0.57	4.97	[34]
	In ₂ O ₃	WN1	7.13	0.88	0.56	3.49	[39]
	Sputtered-ZnO	N719	7.00	0.72	0.72	6.55	[35]
	SrTiO ₃	N719	5.81	0.70	0.73	5.91	[36]
	SrO	N719	16.02	0.78	0.50	6.27	[96]
	ZIF-8	N719	10.28	0.75	0.69	5.34	[30]
	BaTiO ₃	N3	16.29	0.77	0.61	7.52	[40]
	ALD Ga ₂ O ₃	Y123	5.10	1.10	0.71	4.00	[86]
	ZnO	N719	11.2	0.69	0.67	5.20	[68]
SnO ₂	TiO ₂	N719	10.9	0.66	0.54	3.90	[68]
	MgO	N719	12.6	0.60	0.51	3.80	[68]
	Ga ₂ O ₃	N719	11.3	0.58	0.49	3.30	[68]
	Al ₂ O ₃	N3	11.00	0.51	0.65	3.65	[97]
	MgO	D149	1.53	0.58	0.31	0.28	[62]
ZnO	SnO ₂	N719	16.3	0.66	0.59	6.31	[98]
	Sputtered-TiO ₂	N719	7.65	0.75	0.68	3.90	[99]
	CBD Zn ₂ SnO ₄	N719+D131	7.38	0.77	0.66	3.73	[60]
	Tetrabutyl titanate (TBT)	N719	6.65	0.68	0.65	2.94	[100]
Zn ₂ SnO ₄	Zn ₂ SnO ₄	N719	11.99	0.73	0.69	6.00	[101]

untreated reference cell.

Post-treatment of nanoporous TiO₂ films with a solution of TiCl₄ has been a very common method for fabricating a nanoporous TiO₂ films that serve both as a substrate for the dye and as the electron conductor. CBD of TiO₂ from TiCl₄ can improve the photocurrent of dye-sensitized TiO₂ solar cells. Usually, the TiCl₄ treatment is applied by soaking

the TiO₂ electrode in a 50 mmol L⁻¹ TiCl₄ solution for 30 min at 70°C, followed by a water rinse and an identical heat treatment.

As for acid treatment, several inorganic and organic acids have been studied to determine their effect on charge recombination and light harvesting of fabricated DSSCs. As mentioned in section *Acid treatment*, except HCl, H₂SO₄,

Figure 12 Schematic representation of self-assembled silane monomolecular layer formation on TiO₂ surface and blocking the back electron transfer. Reprinted with permission from Ref. [94], Copyright 2014, American Chemical Society.

HNO_3 , and HAuCl_4 , acetic acid, formic acid, and oxalic acid can also be utilized in the surface treatment of photoanodes. Carboxylic acids have recently been used to modify the TiO_2 surface for reduced recombination and enhanced light harvesting.

SUMMARY

Over the past two decades, great efforts have been made to improve the PCE of DSSCs through optimization of various components of the DSSCs, namely, photoanodes, electrolytes, and counter electrodes. The interfacial charge recombination between the photoanode and the electrolyte is recognized as the dominant loss process as compared to that between the photoanode and the oxidized dye. To minimize the recombination reaction, various methods for surface modification such as the use of novel dyes for efficient electron injection and light harvesting, new architecture of materials for photoanodes and counter electrodes, and new redox couples have been researched. Most of the work at the oxide/dye/electrolyte interface has focused on suppression of back electron transfer by forming a tunneling barrier and passivating surface states. Surface modification of a photoanode is a potential approach to reducing charge recombination losses at various interfaces and enhancing the efficiency of DSSCs. Surface modification plays an effective role in enhancing photovoltaic performance, which can reduce the density of surface traps, create an energy barrier for suppressing electron transfer to the electrolyte, and generate an interface dipole that shifts the semiconductor energy levels with respect to the redox potential.

Although many studies are devoted to increasing the performance of DSSCs, the physical chemistry of several of the basic operations of DSSC devices remains far from fully understood. For future study, it is important to understand and master this complexity, in particular at the oxide/dye/electrolyte interface, which offers a lot of room

for future research in higher power conversion efficiencies. How to enhance the efficiency and improve the stability of DSSCs remains the biggest challenge and goal for the present DSSC technology.

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Conflict of interest The authors declare that they have no conflict of interest.

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光阳极表面修饰以提高染料敏化太阳能电池效率

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摘要 染料敏化太阳能电池因其高效率、环境友好、制作工艺简单、生产成本低等优点而极具应用前景. 光电转换效率是衡量染料敏化太阳能电池性能的重要参数之一, 然而光阳极上发生的电子复合阻碍了光电转换效率的进一步提高. 因此, 减少由各个界面处不利的电子复合引起的能量损失是提高光电转换效率的关键之一. 从这个方面来说, 光阳极表面修饰是抑制界面电子复合以提高染料敏化太阳能电池光电转换效率的最简便方法之一. 这篇综述简单地介绍了染料敏化太阳能电池的工作原理, 综合讨论了目前文献中所采用的不同光阳极的表面修饰方法. 这些表面修饰方法不仅能减少电子复合, 还能提高对太阳光的吸收. 根据光阳极材料的特点, 本文讨论了二元氧化物, 例如TiO₂和ZnO, 以及包括Zn₂SnO₄、SrSnO₃和BaSnO₃在内的三元氧化物的表面修饰. 此外, 本文讨论了表面修饰的具体方法以及适用于表面处理的材料. 最后, 展望了染料敏化太阳能电池的发展前景.