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The way forward for the modification of dye-sensitized solar cell towards better power conversion efficiency

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ABSTRACT

The power conversion efficiency (PCE) of TiO_2-based dye-sensitized solar cells (DSSCs) could be enhanced by modification of photoanodes. The effective blocking layer addition, one-dimensional nanostructure architecture, and scattering material design are the most important approaches to provide the high PCE of DSSCs and are critically reviewed in this work. The blocking layer generated the energy barrier can suppress the recombination of an electron in photoanode. One-dimensional (1D) nanostructures of a nanorod, nanotube and nanowire, promote the enhanced electron transport of DSSCs. The PCE of 1D nanostructure based DSSCs can potentially be improved by incorporating high surface area TiO_2 nanoparticles and constructing the multilayered 1D nanostructure arrays photoanodes. The scattering effect can be generated by mesoporous, core-shell and yolk-shell materials with the sizes architecture corresponding to the wavelength of incident light, enhancing the light harvesting. The high efficiency of TiO_2-based photoanodes could be realized by optimizing the composition, size of materials, and thickness of photoanodes.

1. Introduction

Since O'Regan and Grätzel introduced the dye-sensitized solar cell (DSSC) using TiO_2 films as photoanodes in 1991 [1], the performance of DSSCs has been improved by researchers to provide the device which is possible for commercialization. DSSCs are usually composed of photoanode, the dye molecule, electrolyte and the counter electrode. The photoanode architectures are among the most exciting developments in enhancing the power conversion efficiency (PCE) of DSSCs. Schematic illustration of the photoanode modification can be seen in Fig. 1. The principle of DSSC operational is as follows [2]: (1) a dye molecule adsorbed on semiconductor photoanode absorbs solar light, (2) the electrons in the excited state of dye are injected into the conduction band semiconductors diffuse through the array and collected by the transparent conductive glass, (3) the oxidized dye is regenerated by redox system in the electrolyte solution and (4) the redox system is regenerated through a counter electrode.

There are some review papers discussing the progress of DSSCs. Shalini et al. [3] highlighted the progress of sensitizer for DSSCs. Sengupta et al. [4] summarized the research effort of effect doping, morphology and film thickness of photoanodes. Raj et al. [5] highlighted the fabrication of efficient nanostructured photoanodes. However, photoanode modifications through a blocking layer, one-dimensional and scattering material design have not been comprehensively discussed. It is worthwhile to highlight that these modifications could provide the way forward for an improvement of dye-sensitized solar cell. In this review, recent progresses of TiO_2-based photoanode improvement works are critically discussed with particular regards to (1) effective of blocking layer design, (2) modification of one-dimensional nanostructure and (3) generation of high scattering effect.

There are four important factors that should be considered to improve the photoanode of DSSCs [6]: (1) a superior electron-transport characteristic for efficient charge collection, (2) a large specific surface area for sufficient dye-loading, (3) an excellent scattering effect for enhanced light harvesting, and (4) adequate porosity of the film for feasible diffusion of the electrolyte. These four factors can be accessed in semiconductor photoanodes of DSSCs. Consequently, to provide the best performances of DSSCs, researchers, in last decade, modified the photoanodes. The most highlighted investigation of photoanodes is TiO_2-based hybrid photoanodes [7–12].

TiO_2-based hybrid photoanodes can be classified as homogeneous hybrid or heterogeneous hybrid system. The homogeneous hybrid system has the electrodes which are composed of the same material such as TiO_2 nanoparticle/TiO_2 nanotube hierarchical structures [7], porous titania nanosheet-titania nanoparticle hybrids [8] and TiO_2@TiO core-shell nanowires [9]. The heterogeneous hybrid system uses

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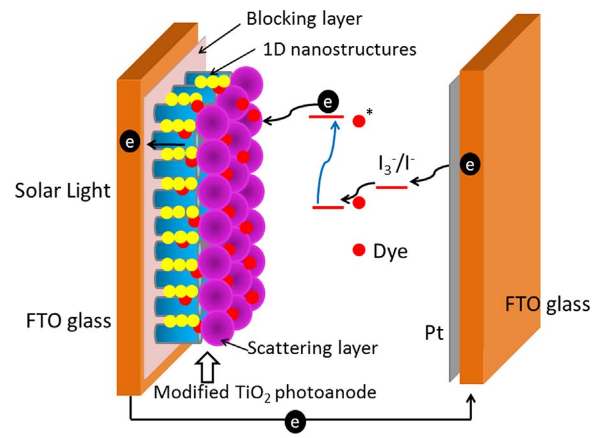

Fig. 1. Schematic illustration of photoanode modification using blocking layer, one-dimensional and scattering materials in the dye sensitized solar cell (DSSC).

the electrodes which are composed of different materials such as TiO_2/ZnO [10], SiO_2/TiO_2 [11], TiO_2/carbon nanotube photoanode [12].

Up to now, the highest power conversion efficiency (PCE) of DSSCs was demonstrated by Mathew et al. [13]. They reported that the molecularly engineered porphyrin dye (coded SM315) with the cobalt (II/III) redox couple resulted in PCE of 13%. The authors focused on sensitizer and electrolyte development to generate high PCE using TiO_2 photoanode at a thickness of 7 µm which consisted of 3.5 µm of TiO_2 transparent layer (32 nm) and 3,5 µm TiO_2 scattering layer (400 nm). Theoretically, the PCE of TiO_2 photoanode could be predicted to 31% [14]. However, the PCE of DSSCs photoanodes is low due to slow forward reaction or transport kinetics, the coupling of charge transfer to chemical steps and the catalysis of back-reaction from the defect structure of photoanodes [2]. Therefore, it is a great challenge for future researchers to develop the photoanode to achieve high PCE.

The addition of a blocking layer into photoanode could retard the electron back transmission from the semiconductor photoanodes to the oxidized dye molecules or electrolyte. The blocking layer is proven to be acting as the energy barrier which is pivotal for the enhancement of PCE. Many type of blocking layers have been invented so far by researchers such as TiO_2 [15], ZnO [16], Nb_2O_5 [17], Al_2O_3[2] and HfO_2 [18]. It is very useful to comprehensively understand the materials of working principles of the blocking layer for further research activities.

One-dimensional TiO_2 nanostructures of nanorods [19], nanotubes [20] and nanowire [21] could also be used as photoanodes of DSSCs. These materials can facilitate high electron transport which is very crucial for enhancing the PCE. However, these materials usually have low surface area which decreases dye-loading. Therefore, modification of one-dimensional TiO_2 nanostructure to increase surface area should be attempted. Choi et al. [7] modified the nanotube to create TiO_2 nanoparticles/TiO_2 nanotubes hybrid photoanodes. The PCE of these photoanodes could be improved up to 11.3%. Attaching TiO_2 nanoparticles on TiO_2 nanotubes could be a promising strategy to enhance the energy-conversion efficiency. This invention brought to the objective of generating the high direct electron pathway with high harvesting light energies.

The PCE of photoanodes could also be enhanced by generating the scattering effect. The scattering material could extend optical path length of the photon within the photoanode which enhances the light harvesting of DSSCs. Many researchers presented the modification of photoanodes using mesoporous TiO_2 microspheres [22], TiO_2/SiO_2 core-shell [23] and mesoporous TiO_2 yolk-shell microspheres [24] for generating the scattering effect. Introducing these materials into one-dimensional structure and blocking layer can boost the PCE of DSSCs.

Based on the investigation on TiO_2-based hybrid photoanodes, many researchers have successfully enhanced the PCE of DSSCs using the effective blocking layer, modified one-dimensional and scattering material design. However, in the last decade, there has been no report on improvement efficiency higher than 13%. Therefore, the results focused on TiO_2-based photoanodes development should be reviewed to highlight the invention of more superior DSSCs. Thus, their commercialization could be realized in the very near future.

2. Blocking layer design

The problem of DSSCs is mainly due to the electron recombination within photoanode which leads to decreased PCE. To suppress the electron recombination, the compact layer or blocking layer should be attempted. Therefore, the goal of this section is to highlight the blocking layer preparation to reduce the electron recombination and to find out the way forward for its improvement. Up to now, researchers have developed the blocking layer to improve the PCE of DSSCs. The blocking layer of TiO_2 [25–30], ZnO [31,32], Nb_2O_5 [33,34], HfO_2 [35,36], Al_2O_3-TiO_2 [37], Nb-TiO_2 [38], g-C_3N_4[39] and SnO_2 [40,41] were successfully prepared within photoanodes. These blocking layers are essential to maintain the efficient charge generation under light irradiation. The structures of various blocking layers reported are listed in Table 1.

2.1. Ultrathin layer preparation

The preparation of effective ultrathin blocking layer is the fundamental criterion to allow the efficient injection of electron from the excited state of the dye into the TiO_2 [42]. Various methods have been developed by researchers to create the ultrathin blocking layer material. The method of spin-coating [15], soaking/dip-coating [27], atomic layer deposition [29], radio-frequency (RF) magnetron sputtering [28], have been applied for ultrathin blocking layer preparation on transparent conductivity oxide (TCO) glass. $TiCl_4$ is the most popular precursor material for the thin layer. The thickness [15] and roughness [27] of TiO_2 blocking layer can be controlled by changing the concentration of $TiCl_4$. The organic titanium (IV) butoxide [26] could also be used as a source of TiO_2 blocking layer through TiO_2 sol preparation. The thin layer could be deposited on the surface of transparent conductive oxide (TCO) glass by dip-coating method followed by calcination. A specially tailored index TiO_2 blocking layer (arc-TiO_2) can also be prepared by long-throw radio-frequency (RF) magnetron sputtering [28]. With this layer, the reflection loss could be minimized, and the efficiency could be enhanced. Chandiran et al. [42] reported that the atomic layer deposition (ALD) in ultrathin layer preparation was better than the sol-gel, chemical deposition, or physical vapor deposition. This method can prevent the formation of an uneven or thicker oxide layer.

Because of the toxicity of the $TiCl_4$ solutions, the ZnO ultrathin layer preparation could be the alternative to the $TiCl_4$ treatment. The particle size and the thickness of this layer could be easily controlled by polyvinyl alcohol and deposition times under chrono amperometric (CA) technique, respectively [31]. With this technique, the optimized amount of ZnO deposition was achieved and enhanced the electron lifetime and cell performance. Meanwhile, ZnO thin layer could also be prepared by the spray pyrolysis technique which was better than the spin-coating or dip-coating [32]. Moreover, the blocking layer using this technique was more efficient than $TiCl_4$ treatment. The ultrathin ZnO layer could also be prepared by atomic layer deposition (ALD) [16]. The thickness of 15 nm as the optimum performance was successfully prepared by this technique. This blocking layer could effectively suppress the recombination of electron at the interface of FTO/electrolyte. The DSSCs employing the ZnO for blocking layer was highly promising.