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Review

Layered-stacking of titania films for solar energy conversion: Toward tailored optical, electronic and photovoltaic performance

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ABSTRACT

Nanostructured TiO_2 with differentiate morphologies has attracted tremendous attention due to its wide band-gap nature as well as outstanding optical and electric properties for solar-driven light-to-electricity conversion application. Layered-stacking TiO_2 film such as double-layer, tri-layer, quadruple- or quintuplicate-layer, is highly desirable to the design of high-performance semiconductor material photoanodes and the development of advanced photovoltaic devices. In this minireview, we will summarize the recent progress and achievements on proof-of-concept of layered-stacking TiO_2 films (LTFs) for solar cells with emphasis on the tailored properties and synergistic functionalization of LTFs, such as optimized sensitizer adsorption, broadened light confinement as well as facilitated electron transport characteristics. Various demonstrations of LTFs photovoltaic systems provide lots of possibilities and flexibilities for more efficient solar energy utilization that a wide variety of TiO_2 with distinguished morphologies can be integrated into differently structured photoanodes with synergistic and complementary advantages. This key structure engineering technology will also pave the way for the development of next generation state-of-the-art electronics and optoelectronics. Finally, from our point of view, we conclude the future research interest and efforts for constructing more efficient LTFs as photoelectrode, which will be highly warranted to advance the solar energy conversion process.

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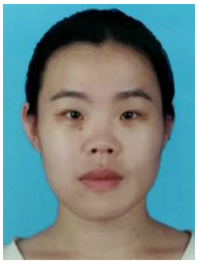

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1. Introduction

In modern-day society, the energy crisis has called for the efficient utilization of clean and renewable energy sources, such as solar energy, which has the greatest potential to create a more green and environmental-benign world [1]. Over the years, many efforts have been devoted to the conversion of solar energy into other usable energy by means of solar cells, photoelectrochemical cells, photocatalysis as well as water splitting, etc. [2–6]. In particular, dye-sensitized solar cells (DSSCs) using semiconductor metal oxides, for instance, TiO_2, SnO_2, ZnO and Zn_2SnO_4, have garnered considerable attention, as an era of smart and efficient energy utilization is rapidly coming toward us [7–10]. TiO_2 is one of the most widely used anode material in DSSCs owing to its suitable energy level bandgap, low-cost, low-toxicity, high chemical and optical stability as well as relatively high photovoltaic performance.

The photovoltaic performance of TiO_2-based DSSCs is strongly determined by crystal structure, surface area, light scattering ability as well as charge transfer characteristics of the films, which in general, are the extremely important requirements for the high-efficiency state-of-the-art devices [11–14]. Over the past few decades, tremendous efforts have been made on the optimization of TiO_2 with well-tuned geometries and morphologies, ranging from 0D nanoparticles, 1D and 2D nanostructures to 3D hierarchical structures [15–19]. However, for monolayer of TiO_2, it is very difficult to simultaneously increase surface area and light scattering for improved light harvesting efficiency while at the same time retain the excellent electron transport characteristic in the film for improved charge collection efficiency. To address this issue, one versatile strategy, that is to fabricate the layered-stacking (double-layered, tri-layered or even multi-layered) TiO_2 film on front substrates. For the prototyped double-layered TiO_2 film, it was designed with a transparent TiO_2 under layer of 12–14 μm and a scattering TiO_2 layer of 2–5 μm [20]. On the other hand, in the development of such full-fledged layered-stacking technique for film fabrication, different integration of purposely selected TiO_2 nanostructures with different shapes into multi-layered architectures have been attempted to accommodate all incompatible aforementioned key factors required to make highly efficient photovoltaic devices [21]. From another perspective, this LTFs technique also gives a great deal of flexibilities and possibilities in the film structure design and optimization, in which the multi-stack architectures with separated functional layer can confer a synergistic advantages of optimized surface area for sufficient dye adsorption, tailored optical properties for broadband light confinement and harvesting as well as engineered charge transfer characteristics for efficient charge collection [22].

Herein, we present a review of the recent progress and advances made in the development of LTFs on solar cell applications. The findings of structural and functional characteristics for double-layered, tri-layered or multi-layered TiO_2-based DSSCs are introduced and discussed in terms of tailored optical, electronic and photovoltaic performances of the films electrodes. Notably, special attention is devoted to covering the technological innovation of LTFs with multi-layered configuration as a mean of simultaneously balancing light harvesting and charge collection efficiencies of the films, which represent a considerable advancement in conventional double-layered TiO_2 film design. Finally, we conclude with our perspective on the future development of much more efficient LTFs based photovoltaics.

2. Double-layered TiO_2 structure

Successive stacking of TiO_2 films into a double layered structure has been regarded as the most general but ideal approach to construct the more efficient photoanode, owing to the synergistic advantages for both components. Herein, the prototype double layered TiO_2 photoanodes will be briefly reviewed in terms of component design as well as fabrication procedure, with special focus on the newly designed double-layered structure of prominent structure functionality and enhanced photovoltaic performance.

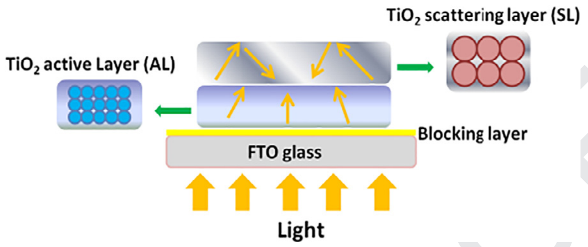

Fig. 1. Sketch of prototype TiO_2 double-layered film consisting of active layer (AL) plus scattering layer (SL).

2.1. *Prototype active layer (AL) plus scattering layer (SL) structure design*

Fig. 1 shows one of the simplest double layered TiO_2 film designs, in which a scattering layer (SL) was on top of a transparent TiO_2 active layer (AL). In general, for an AL, TiO_2 nanoparticles (NP) of size ~20 nm would be employed to attain sufficient dye uptakes; while for a SL, sub-micron/micron-sized particles or hollow spheres would be introduced to enhance the light scattering ability and thus boost the light harvesting at longer wavelengths ranged from 600–800 nm [20,23].

In general, double layered TiO_2 photoanodes can be produced by the most straightforward screen-printing method, which provides great flexibility to tune the thickness and component compositions of each layer in a convenient fashion. For application in solar cells, Park et al. first proposed the bifunctional nano-embossed TiO_2 hollow spheres as scattering layer for constructing double layered TiO_2 based photoanodes, and DSSCs based on a nanocrystalline (8 μm)/nano-embossed hollow spheres (7 μm) double-layered structure (Fig. 2a) yielded an impressive power conversion efficiency (PCE) of 10.3% (Fig. 2c), which greatly outperformed the nanocrystalline/CCIC based counterparts. The significantly enhanced photovoltaic performance can be attributed to the bifunctional properties of nano-embossed hollow spheres, which exhibited higher amount of dye adsorption and superior light scattering capability (Fig. 2b) [20]. Afterward, many different double layered TiO_2 films photoanodes with tunable components design have been widely reported.

Fig. 2(d–l) shows different types of representative TiO_2 AL/SL double-layered structures, including nanocrystalline TiO_2/mesoporous TiO_2 beads (Fig. 2d) [23,24], TiO_2 nanooctahedra/agglutinated mesoporous TiO_2 microspheres (Fig. 2e) [25], TiO_2 octahedrons (30 nm in diameter)/TiO_2 octahedrons (300 nm in diameter) (Fig. 2f) [26], TiO_2 nanospindles/TiO_2 nanospindles [27], P25/hollow spheres (Fig. 2g) [28,29], P25/shell-in-shell TiO_2 hollow spheres (Fig. 2h) [30], TiO_2 nanoparticles/quasi-inverse opal TiO_2 [31], TiO_2 nanoparticles/TiO_2 yolk-shell spheres (Fig. 2i) [32], P25/anatase TiO_2 mesocrystals with nearly 100% exposed (001) facet (Fig. 2j) [33], P25/layer-by-layer self-assembly hierarchical TiO_2 nanosheets (Fig. 2k) [34], and TiO_2 nanoparticles/rice-like brookite TiO_2 (Fig. 2l) [35]. All aforementioned double layered TiO_2 photoanode based DSSCs showcased markedly enhanced PCE as compared to their single layered counterparts. Encouragingly, DSSCs based on optimized double layered TiO_2 film (20 nm sized TiO_2 nanoparticles transparent layer plus 400 nm sized large particles scattering top layer), porphyrin-based sensitizer and cobalt redox couple electrolyte have up to date achieved the

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