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A novel bilayer photoanode made of carbon nanotubes incorporated TiO_2 nanorods and Mg^{2+} doped TiO_2 nanorods for flexible dye-sensitized solar cells

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ABSTRACT

TiO_2 nanorods (NRs), Mg^{2+} doped TiO_2 (Mg^{2+}/TiO_2) NRs, and carbon nanotubes incorporated TiO_2 (CNTs/TiO_2) NRs are fabricated from the corresponding electrospun nanofibers (NFs) by ultrasonic treatment, respectively. Then these NRs are made into various photoanodic films through electrospray deposition and hot-compression for flexible dye-sensitized solar cells (FDSSCs). The conversion efficiency of FDSSCs is improved with the CNTs incorporation or the Mg^{2+} ions doping of TiO_2. To further improve the properties of FDSSCs, various bilayer photoanodic films made of the smaller diameter NRs as under-layer and the larger diameter NRs as over-layer are prepared. Finally, a highest conversion efficiency of 3.9% is obtained using the bilayer NRs film composed of the smaller diameter CNTs/TiO_2 NRs and the larger diameter Mg^{2+}/TiO_2 NRs. This efficiency is much higher than that of the single-layer NRs film based FDSSCs. This may be attributed to the increased light harvesting resulting from the scattering layer of the larger diameter NRs and the faster electron transport due to the two-level energy steps of the bilayer NRs film.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted increasing interest as one of the most promising photovoltaic devices due to their easy manufacturing process and low cost [1–3]. Although higher than 14% conversion efficiency of DSSCs has been reported [4], the conversion efficiency of most DSSCs is still low. This is mainly due to the energy loss of the DSSCs in many ways. For instance, the recombination between the injected electrons and the oxidized dye or ions in the electrolyte could cause a great reduction of conversion efficiency [5]. The low-intensity back scattering of small TiO_2 nanoparticles (NPs) leads to the optical loss [6]. Therefore, many approaches have been explored to restrain electron recombination and increase light harvesting by optimizing TiO_2 photoanodic film.

Modification of TiO_2 is one of the promising methods. To date, the TiO_2 modified through surface post-treatment [7], coating treatment [8], incorporation with carbon nanomaterials [9] or noble metal nanoparticles (NPs) [10], or doping [11] have been proved to effectively accelerate electron flow, improve electron collection, and restrain electron recombination. Additionally, employment of TiO_2 nanostructures such as one-dimensional (1D) nanostructures (nanotubes, nanorods, nanowires, or nanofibers), nanotrees, and nanoforests with direct pathways for charges, less grain boundaries and less surface states instead of zero-dimensional (0D) NPs and always reduce the probability of electron recombination [12,13]. Moreover, inclusion of a light scattering layer is an effective approach to improve light harvesting [14]. Nevertheless, it should be noted that only one approach was used to optimize TiO_2 electrode in most of the reported studies. It would be of interest to ask if the conversion efficiency of DSSCs could be further improved when the above optimizing methods are used in combination. One promising method for integration of the various optimizing approaches is electrospinning. Specifically, the modification of 1D TiO_2 nanostructures can be easily achieved by electrospinning with a simple one-step approach. For example, Yang and Leung [15] reported that the multiwall carbon nanotubes (MWCNTs) incorporated TiO_2 nanorods (NRs) were prepared for glass-based DSSCs by electrospinning to improve electron transport and electron collection. As a result, a conversion efficiency of 10.24% was achieved in their work. Furthermore, electrospun TiO_2 nanostructures decorated by metal NPs [16], followed by surface post-treatment [17], and coated by metal oxide to form a core-sheath structure [18] have been reported. However, to the best of our knowledge, only a few papers concerning metal

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ions doped electrospun TiO_2 for DSSCs were reported, such as Nb doped TiO_2 NFs [19]. As it is known, metal ions such as W, Zn, Al, and Mg^{2+} doped TiO_2 NPs have been found to change the conduction band and surface states of TiO_2, suppressing electron recombination [11,19]. Among these metal ions, the TiO_2 doped by Mg^{2+} ions possessed higher conduction band edge than TiO_2, which greatly enhanced V_{oc} and thereby improved conversion efficiency [20,21]. We hypothesize that the Mg^{2+} ions doped electrospun TiO_2 with higher conduction band edge could improve the conversion efficiency of DSSCs when it served as photoanodic materials.

Generally, a light scattering layer is composed of the solid TiO_2 particles with large sizes [22]. Although such large particles increase light scattering, they obviously reduce the dye loading. While, the electrospun 1D nanostructures as scattering layer can improve light scattering ability and shorten the electron transport pathways simultaneously [23]. Therefore, the various modifications of electrospun TiO_2 are used in combination to optimize TiO_2 electrode to further increase the conversion efficiency of DSSCs. However, all the mentioned reports concerning the electrospun TiO_2 nanostructures with and without modification were associated with glass substrate based DSSCs. The rigidity and weight of glass substrates make the continuous manufacture of DSSCs a complicated and costly procedure thus limiting its applications [24,25]. Hence, the lightweight flexible dye sensitized solar cells (FDSSCs) have attracted much attention. It is noteworthy that continuous electrospun TiO_2 NFs are not suitable for FDSSCs as the TiO_2 NFs with large length-to-diameter ratio break easily under bending. In contrast, the TiO_2 NRs or NWs can promisingly overcome this drawback.

Among the numerous flexible substrates for FDSSCs, plastic substrates such as PET (polyethylene terephthalate) and PEN (polyethylene naphthalate) are widely used due to their low cost, high flexibility, high transparency, and the possibility of roll-to-roll manufacturing [26]. However, the conversion efficiency of FDSSCs based on the plastic substrates is quite low, as the flexible polymer substrates cannot withstand the high temperature over 450 °C sintering usually necessary to enhance the TiO_2 particle interconnection and remove the organic residues from the TiO_2 paste for the glass-based cells. Many approaches such as hydrothermal necking, chemical sintering, microwave sintering, UV irradiation, mechanical compression, and deposition have been explored for FDSSCs [26–28]. Among these methods, depositions (electrospray and electrophoretic deposition) are commonly used to fabricate a high quality TiO_2 film with binder-free TiO_2 pastes [28,29]. Besides, the compression method is considered to be a most efficient technique to fabricate FDSSCs with strong interconnections among TiO_2 nanostructures and strong binding force between photoanodic film and substrate [26,30–32]. Recently, Chen et al. fabricated a highly efficient plastic-based FDSSC using a combination method of the electrophoretic deposition process followed by compression treatment [29]. Accordingly, the electrospray and followed by compression treatment is a promising method to fabricated a highly efficient plastic-based FDSSC.

In this regard, we report here a combination approach to address the issues of FDSSCs. Specifically, we fabricate various single-layer NRs films and novel bilayer NRs films via a combined method of ultrasonic treatment, electrospray deposition, and hot-compression for FDSSCs. The performance of FDSSCs developed in our laboratory is investigated in detail.

2. Experimental

2.1. Preparation of the photoanodic films

According to our previous work [32], the preparation process of the photoanodic film involves the three stages: the synthesis of NFs, the fabrication of NRs, and the formation of NRs film. Typically, as shown in Fig. 1, TiO_2 NFs, Mg^{2+} doped TiO_2 NFs (Mg^{2+}/TiO_2 NFs), and CNTs incorporated TiO_2 NFs (CNTs/TiO_2 NFs) with smaller diameters and larger diameters were synthesized by electrospinning, respectively. It is well established that the diameter of the electrospun NFs strongly depends on the electrospinning processing parameters such as the concentration of polymer in solution, flow rate, and intensity of electric field. For a given electrode separation distance, the increase of the concentration of polymer in solution or the flow rate always leads to the diameter of electrospun NFs increasing. By contrast, the increase of the applied voltage can decrease the diameter of electrospun NFs. Accordingly, the concentration of PVAc, the flow rates, and the electric voltages for the smaller diameters and larger diameters NFs were respectively 12 wt% and 15 wt%, 0.6 mL/h and 0.9 mL/h, 25 kV and 16 kV with the same collector distance of 12 cm. Specifically, the precursor electrospinning solution of TiO_2 NFs with smaller diameters is made of 0.5 g of polyvinyl acetate (PVAc, Mw = 500,000, Aldrich), 1.0 g of titanium (IV) isopropoxide (TiP, 97%, Aldrich), and 0.5 mL of acetic acid and 4 mL *N*,*N*-dimethyl formamide (DMF, 99.5%, Aladdin). For smaller diameter Mg^{2+}/TiO_2 NFs, a small amount of $Mg(NO_3)_2{\cdot}H_2O$ with the Mg/Ti mole ratio of 3% were dissolved in the precursor solution of TiO_2. Likewise, a small amount of MWCNTs (the average diameter of about 15 nm) with the mass ratio of MWCNTs/TiO_2 of 0.3 wt% were added into the precursor solution of TiO_2 and then ultrasonically treated for 2 h to disperse MWCNTs. The larger diameter TiO_2 NFs were fabricated from a solution of 0.68 g of PVAc, 1.36 g of TiP, 0.5 mL of acetic acid and 4 mL DMF with a flow rate of 0.9 mL/h and a voltage of 16 kV. The Mg/Ti mole ratio and the mass ratio of MWCNTs/TiO_2 were also 3% and 0.3% for the larger diameter Mg^{2+}/TiO_2 NFs and CNTs/TiO_2 NFs, respectively. After electrospinning, the PVAc/TiP NFs, PVAc/TiP/$Mg(NO_3)_2$ NFs, and PVAc/TiP/MWCNTs NFs with smaller and larger diameters were obtained, respectively. Subsequently, all the as-spun NFs were calcined in a muffle furnace at 450 °C for 1 h to achieve the corresponding TiO_2 NFs, Mg^{2+}/TiO_2 NFs, and CNTs/TiO_2 NFs.

Secondly, these NFs were converted into short NRs through ultrasonic treatment. The ratio is 0.1 g NFs per 1 mL ethanol. The time of ultrasonic treatment of the smaller and larger diameter NFs were respectively 30 min and 20 min to control the lengths of NRs.

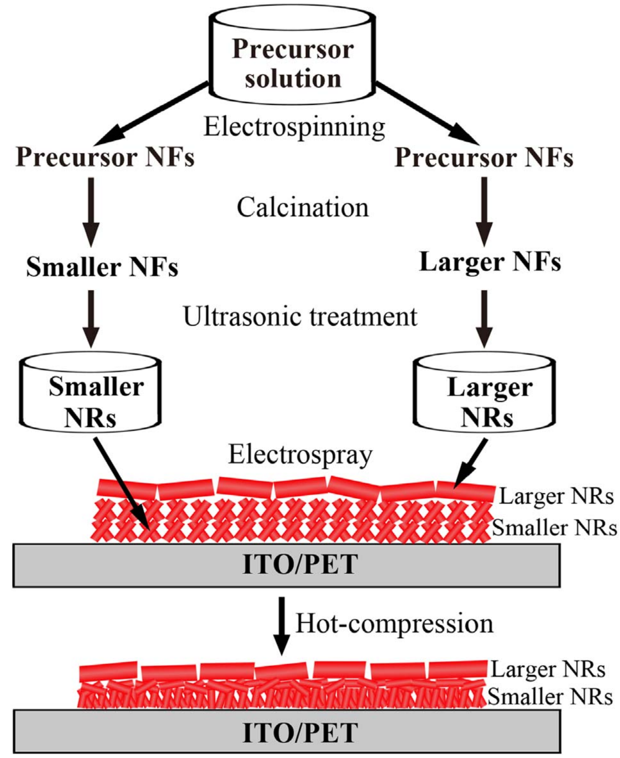

Fig. 1. Schematic diagram of fabrication procedure for the bilayer NRs photoanodic film.