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High-stability Ti^{4+} precursor for the TiO_2 compact layer of dye-sensitized solar cells

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ABSTRACT

A compact layer (blocking layer) can effectively block the direct contact between the fluorine-doped tin oxide (FTO) glass substrate and electrolyte in dye-sensitized solar cells (DSSCs). The $TiCl_4$ hydrolysis has been widely adopted for preparing the TiO_2 compact layer (H-TiO_2). However, the $TiCl_4$ aqueous solution is unstable for its high reactivity. To improve the chemical stability of $TiCl_4$ aqueous solution, the Ti^{4+} is encapsulated by the polymer, polyethyleneimine (PEI). Experimentals show that the Ti-PEI precursor solution can maintain their initial performances for several months. The resulting TiO_2 film (P-TiO_2) grown by the Ti-PEI precursor is dense, smooth and uniform without any visible and detectable cracks or voids. The P-TiO_2 compact layer is even denser than the H-TiO_2 compact layer, suggesting reducing the electron recombination and prolonging the electron lifetime in dye-sensitized solar cells. Indeed, the electron lifetime of the DSSC based on the P-TiO_2 is 13.15 ms, which is longer than the 10.83 ms based on H-TiO_2. Meanwhile, the power conversion efficiency of the DSSC based on P-TiO_2 compact film is about 12.5% higher than that based on H-TiO_2. Therefore, this encapsulation technology can not only improve the stability of the metal ions solution but also meet a large-scale fabrication demand of the TiO_2 compact layer in future DSSCs.

1. Introduction

Since O'Regan and Grätzel first developed the dye-sensitized solar cell (DSSC) in 1991, it has attracted a great deal of attention for its high power conversion efficiency [1–4]. A conventional DSSC consists of a work electrode, a counter electrode, an electrolyte, etc. The work electrode is fabricated by pasting nanoporous TiO_2 on fluorine-doped tin oxide (FTO) glass substrate and absorbing dye molecules at the TiO_2 surface. In recent researches [5,6], the work electrode has received considerable concerns as it excites dye molecules and generates electrons under the illumination. The electrons need to pass two interfaces of a DSSC: dye/TiO_2 and TiO_2/FTO, and then collecting on the FTO. Simultaneously, the electrons will recombine with the I_3^- from the electrolyte at the TiO_2/FTO interface, which will lead to the loss of photo current [7]. Thus, the TiO_2/FTO interface is essential to improve the photovoltaic performance. Inserting a compact layer between the FTO and nanoporous TiO_2 film is one of the effective methods to block the contact between the electrolyte and FTO. The compact layer also called as blocking layer, which can effectively reduce electrons recombination and guarantee a longer lifetime, resulting an increased density of short current (J_{sc}). The importance of a blocking layer has been studied, meanwhile, some materials for blocking layer have been proposed [8–11]. Until now, TiO_2 [12–14], ZnO [15,16], Nb_2O_5 [17], SnO_2 [18], MgO [19], $CaCO_3$ [20] and $BaCO_3$ [21] have been used as a blocking layer. Among them, TiO_2 has been proved theoretically and practically effective to block the recombination. Hence a large quality of methods have been used to deposit the TiO_2 blocking layer, such as sputtering [22], screen-printing [23], atomic layer deposition (ALD) [24], hydrolysis, spray pyrolysis [25], etc. While the $TiCl_4$ hydrolysis has been widely adopted in labs for preparing the TiO_2 compact layer [26,27], called H-TiO_2. However, there are some disadvantages due to the instability of $TiCl_4$ with ambient environment: releasing the harmful hydrochloric acid for reacting with H_2O in air and difficulty to keep the precursor for a long time [28]. Hence, it is a necessity to improve the chemical stability of the Ti^{4+} precursor for preparing the TiO_2 compact layer.

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The well-known way to improve the chemical stability is encapsulation or passivation technology [29]. In this paper, we develop an approach to enhance the chemical stability of metal Ti ions by encapsulation technology, which is called polymer-assisted deposition (PAD). It utilizes that the metal ions combined with the polymer, polyethyleneimine (PEI), to gain the stable Ti ion in the precursor solution. Theoretically, the simplest view of the metal polymer encapsulation is the formation of coordination bond or static electricity between the lone pairs on the nitrogen atoms and the metal ions. The polymer combining with the metal ions serves to encapsulate the metal ions to prevent chemical reaction. It deserves to be mentioned that PEI with the high molecular weights helps to removal of the unbounded metal ions by filtering through an Amicon ultrafiltration unit. Thereby, the obtained precursor is stabilization and homogeneity at a molecular level. The PAD method has successfully applied to prepare the films, such as single element materials [30], metal oxides [31], metal nitrides [32], and metal carbides [33]. Here, this method is employed to prepare the TiO_2 compact layer in dye-sensitized solar cells, called P-TiO_2 compact layer. The Ti^{4+} is encapsulated by the PEI which can keep stability for several months. After spin-coating the precursor solution on the substrate and annealing in air, the resulting film is dense and uniform. Due to the high quality of the P-TiO_2 compact layer, the dye-sensitized solar cells based on the P-TiO_2 show the excellent photovoltaic performance, even better than that based on the H-TiO_2. Therefore, it is a promising approach for improving the stability of the ion solution and preparing high-quality film.

2. Experimental details

2.1. Materials

Titanium tetrachloride ($TiCl_4$, Aldrich), polyethyleneimine (PEI, Aldrich), chloroplatinic acid (H_2PtCl_6, Aldrich), ethylenediamine tetraacetic acid (EDTA, Aldrich), peroxide (H_2O_2, 40% in water), ammonium hydroxide ($NH_3{\cdot}H_2O$), acetone and ethanol were purchased without further purification. The water was purified to 18 MΩ cm using a Milli-Q water treatment system. The 20 nm-sized mesoporous and 200 nm-diameter light-scattering TiO_2 colloidal was from HeptaChroma Solar Tech Co. The FTO (≤14 Ω/sq) was from Pilkington. The electrolyte consisted of 3-methoxypropionitrile (MPN, Merck), 1,2-dimethyl-3-propylimidazolium iodide (DMPII, Merck), lithium iodide (LiI, Alfa), Iodine (I2, Fluka) and 4-tert-butylpyridine (TBP, Fluka). Z907 dye [RuLL′ (NCS)2](L = 2,2′-bipyridyl-4,4′-dicarboxylic acid; L′ = 4,4′-dinonyl-2,2′-bipyridine) was from Solaronix.

2.2. The precursor preparation of P-TiO_2 compact layer

The precursor for the growth of P-TiO_2 films was prepared as the following steps. Firstly, 4 g polyethyleneimine (PEI) and 4 g ethylene-diamine-tetraacetic acid (EDTA) were added to 30 ml water and stirred vigorously for a while until the PEI dissolved completely. Secondly, mixing 5.0 g of 30% H_2O_2 with water before 2.5 g of $TiCl_4$ was slowly added to the mixture. Thirdly, the mixture solution was added to the PEI solution by small aliquots and maintained the pH of the PEI solution at about 7.5 by $NH_3{\cdot}H_2O$. This process was repeated until the mixture solution appears a precipitate. Fourthly, the solution was subjected to an Amicon ultrafiltrations unit including an ultrafiltration membrane under 60 psi argon pressure. The Amicon ultrafiltrations unit is designed to pass materials which have a molecular weight of less than about 10,000 g/mol while reserving the desired materials. The solution was diluted several times and the concentration of the solution of the final solution is analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, PerkinElmer Optima 8000).

2.3. Compact layer preparation

The FTO(≤14 Ω/sq) glasses have been unltrasonic bath in water, acetone and ethanol for 15 min, respectively. The Ti-PEI precursor was spin-coated on the cleaned FTO glass and heated on the hot plane at 500 °C for 30 min to obtain the P-TiO_2 compact layer, for comparison, the H-TiO_2 compact layer was prepared by depositing in 40 mM $TiCl_4$ aqueous solution at 70 °C on the cleaned FTO glass, then annealed on the hot plane at 500 °C for 30 min.

2.4. Dye-sensitized solar cells fabrication

The absorbed layer and the scattered reflection layer were prepared on the FTO substrate with compact layer by using a previously reported method [34]. Afterward, the obtained TiO_2 electrode was immersed in 0.5 mM ethanol solution of Z907 dyes [RuLL′ (NCS)2](L = 2,2′-bipyridyl-4,4′-dicarboxylic acid; L′ = 4,4′-dinonyl-2,2′-bipyridine) at room temperature for 24 h. The Pt counter electrode was prepared by dropped H_2PtCl_6 in ethanol on another cleaned FTO substrate, followed by drying and annealing at 400 °C for 15 min in air. The dye-sensitized solar cells were fabricated by sandwiching electrolytes between an obtained TiO_2 electrode and a Pt counter electrode via vacuum back filling.

2.5. Characterization

The crystallographic orientation of the films was characterized by X-ray diffraction (XRD) (Riguku D/MAX-2000PC). The thermal analysis of the precursor was carried out using thermogravimetric analysis (TGA) (SII Nano Technology, TG/DTA7300). The surface morphology of the films and the cross-section of the films were analyzed by field-emission scanning electron microscopy (FESEM) (HTTACHI SU-8010). The *J–V* curves ware tested by keithley 2400 source meter under air mass (AM) 1.5G solar irradiation at 100 mW cm^{-2} (Newport, Class AAA solar simulator, 94023A-U). The IPCE was characterized by EQE/IQE Measurement System (Newport, IQE-AC-XEN-EXT1). The electrochemical impedance spectra (EIS) were tested by electrochemical workstation (CHI600E), which was carried out under dark illumination at bias voltage of −0.7 V.

3. Results and discussion

3.1. Stability of Ti^{4+} precursor

Fig. 1 shows the photographs of Ti-PEI precursor by PAD and 40 mM $TiCl_4$ aqueous solution. In each photograph, the right bottle is filled with Ti-PEI precursor by PAD, and the left bottle is filled with 40 mM $TiCl_4$ aqueous solution. From the photographs, the color of the Ti-PEI precursor solution has not distinct difference for half a month, while the fresh 40 mM $TiCl_4$ aqueous solution become sturbidity after five days later, and the solution becomes milky-white after half a month later, even for a longer time the precipitate will arise on the bottle of the solution. As the previous reported [35], the $TiCl_4$ aqueous solution is hydrolyzed to TiO_2 or $Ti(OH)_4$. Meanwhile, we also have confirmed the unstability of the 40 mM $TiCl_4$ aqueous solution by Tyndall effect [36–40] as shown in Fig. S1. There is not an obvious track at the fresh stage of the 40 mM $TiCl_4$ aqueous solution, which indicates its solution nature, however, there is a clear track in the solution after five days because of the laser beam light scattering by its colloidal nature. Therefore, the Ti-PEI precursor solution has a better stability because Ti^{4+} is encapsulated to