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Effects of low pressure plasma treatments on DSSCs based on rutile TiO_2 array photoanodes

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ABSTRACT

In this paper, three types of low pressure plasma including hydrogen (HP), oxygen (OP) and nitrogen (NP) treatments have been utilized for the first time to improve DSSCs based on rutile TiO_2 array photoanodes. Their effects on the photoanodes and the cell performance have been systematically compared by characterizing the dye loading amount, flat-band potential, donor concentration, electron lifetime and the photovoltaic parameters. Experimental results show that all the three plasma treatments increase the dye loading owing to improved hydrophilicity or enhanced surface roughness. It is found that NP and OP treatments significantly increase the TiO_2 donor concentration and decrease trapping sites. By this way, the electron transport is enhanced and the electron recombination is effectively restrained. These comprehensive effects make NP and OP treatments beneficial for the overall performance, by which 13% and 5% increases in efficiency are achieved. However, HP treatment causes obvious reduction in the donor concentration and more severe electron recombination, which decreases the efficiency by about 15%.

1. Introduction

Since the first report in 1991 by Graetzel and coworkers [1], dye-sensitized solar cells (DSSCs) have been regarded as the promising alternative to traditional silicon based solar cells due to their low fabrication cost, facile assembly process and high light-to-electricity conversion efficiency [2–4]. Titania is now the most commonly used DSSC photoanode material as it owns physical and chemical stability under illumination in liquid electrolytes, as well as an appropriate band structure [5–7].

In recent years, one-dimensional titania materials such as nanorods [8–10], nanowires [11], nanotubes [12,13], become the focus for constructing DSSC photoanodes since they are expected to build up direct electron transport pathways. Generally, one-dimensional anatase electrodes can result in higher light-to-electricity conversion efficiencies than rutile. However, they are routinely fabricated on Ti substrate and need to be transferred to transparent FTO substrates before use. Otherwise, only back-illuminated cells with much lower efficiency can be assembled. In contrast, one-dimensional rutile DSSC can be fabricated much easily since rutile nanorod arrays can grow directly on FTO substrates by a facile hydrothermal process [14]. Furthermore, rutile has smaller bandgap (3.02 eV) and better light reflecting properties than anatase [15–17]. These combinative benefits arouse attention to rutile array as DSSC anode materials and many related studies have been reported [18–20].

In order to improve the photovoltaic performances of rutile array DSSCs, various post-treatment techniques have been developed. For example, Lv et al. [21] proposed a chemical etching method to reinforce the adhesion of rutile arrays onto FTO substrate and an efficiency of 5.94% was achieved. Wang et al. [22] found that $TiCl_4$ post-treatment on rutile array photoanodes could induce the formation of anatase nanoparticles, which could increase their surface area and dye loading abilities. Ling et al. [23] used hydrogenation post-treatments to increase the electron density in the rutile arrays and increased the efficiency from 0.28% to 0.45%.

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Recently, plasma surface treatments have been applied to enhance the performance of DSSCs. For instance, Kim et al. [24] applied H_2 plasma to treat anatase nanoparticles and improved electron lifetime in the cell. Wang et al. [25] tried O_2 plasma to treat anatase nanotube arrays and achieved an optimized cell efficiency of 7.37% in a back-illuminated cell. However, most of the studies have only tried one specific type of plasmas and there is still a lack of systematic comparison about photovoltaic performance after different types of plasma treatments, especially in one-dimensional rutile array electrodes.

In this paper, three types of low pressure plasma including hydrogen (marked as HP), oxygen (OP), and nitrogen (NP) have been used to treat rutile array photoanodes of DSSCs. By taking tests on Mott–Schottky (MS) plot, impedance electrochemical spectroscopy (EIS) and open-circuit voltage decay (OCVD), the effects of different plasma treatments on the electrode's flat-band potential, the electron transport and the electron recombination behavior are systematically investigated. Based on the above results, the effect of plasma treatments on the light-to-electricity conversion efficiency of DSSCs is finally discussed. It is expected that this paper can give an overall understanding of the plasma treatment effect on the electrochemical properties of TiO_2 and provide basis for the selection of appropriate plasma treatments for improving DSSCs.

2. Experiment

2.1. Fabrication of rutile array photoanode

The fabrication of the rutile array photoanode was modified from a literature procedure [21]. In brief, FTO substrates were ultrasonically rinsed in ethanol, deionized (DI) water, acetone and ethanol sequentially and further dried at 60 °C. 0.5 ml of titanium tetrabutoxide ($Ti(OBu)_4$) was added into 20 ml 1:1 hydrochloric acid, followed by 10 min of ultrasonication to obtain a transparent solution. Then four pieces of as-cleaned FTO substrate were set into a 40 ml Teflon autoclave vertically with a customized holder. A hydrothermal treatment process was carried out at 170 °C for 6 h, and thereafter the autoclave was cooled down to room temperature. After the samples were rinsed with DI water, it was further chemically etched by another hydrothermal process using hydrochloric acid (1:1, vol:vol) at 150 °C for 4 h. After rinsed with DI water for several times, the samples were calcined at 450 °C for 30 min.

2.2. Plasma surface treatment

As-fabricated photoanodes were subjected to a low pressure plasma treatment. Under 140 W RF power, one of the three process gas (hydrogen, oxygen, nitrogen) was introduced at a constant working pressure. All plasma treatments were taken for 10 min (See photographs in SI).

2.3. Assembly of DSSCs

The photoanodes were immersed for 24 h in 0.3 mM N719 (Di-tetrabutylammonium *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II)) dye solution in acetonitrile/tert-butanol (1:1, vol:vol) mixed solvent. The electrode was then rinsed with acetonitrile and dried. Then one drop of electrolyte, composed of 0.1 M lithium iodide (LiI), 0.6 M tetrabutylammonium iodide (TBAI), 0.05 M iodine (I_2), and 0.5 M 4-tert-butylpyridine dissolved in acetonitrile, was deposited onto the electrode. A sputtered platinum FTO counter electrode was clipped on to form a photovoltaic cell for further characterization.

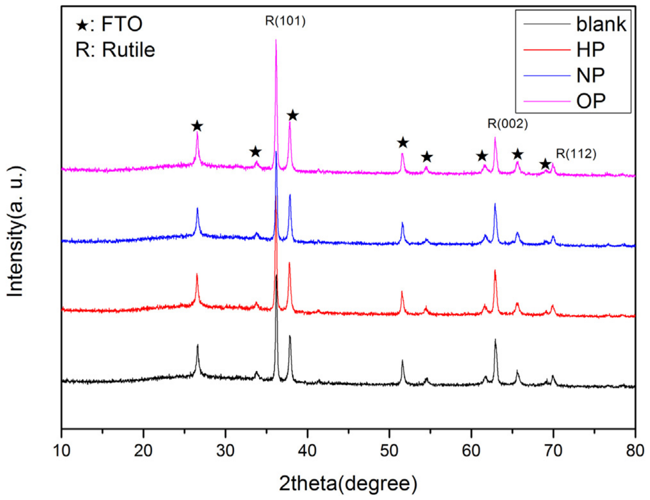

Fig. 1. XRD patterns of plasma treated rutile nanorod arrays.

2.4. Characterizations of samples

Compositions of the samples were investigated by X-ray diffraction (XRD, D/max 2550 V, Rigaku Tokyo) and Raman spectroscopy (DXR Raman Microscope with an excitation length of 532 nm, Thermo Fisher). The morphology was characterized with field emission electron microscope (FESEM, Hitachi S4800). Water contact angle (WCA) was measured by automatic contact angle meter (Model SL200B, China) to characterize the surface hydrophilicity. X-ray photoelectron spectroscopy (XPS) analysis was conducted using Al Kα (ESCAlab250, Thermo Fisher Scientific). Electrochemical impedance spectroscopy (EIS) measurements were carried out on a CHI 660D electrochemical workstation and further fitted by Z-view software. The Mott–Schottky (MS) plot measurement was performed by a potentiodynamic impedance spectroscopy applying a tri-electrode system on CHI 660D. The dark currents were characterized by taking linear sweep voltammetry (LSV) measurements with an applied bias set from 0 to 1.1 V. The electron lifetime determined by open-circuit voltage decay (OCVD) measurements was recorded on Solartron 1400A analytical center with a potentiostat. The photocurrent–voltage (*I*–*V*) curves were recorded using Keithley 2400 meter under simulated AM1.5G solar irradiation (100 mW/cm^2).

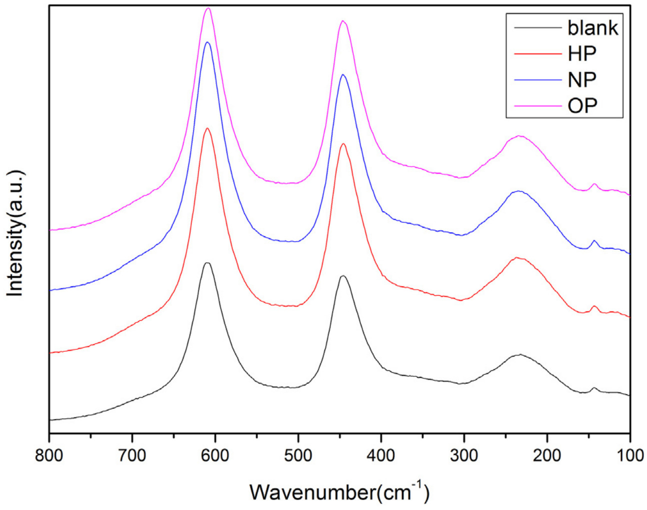

Fig. 2. Raman spectra of plasma treated rutile nanorod arrays.