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Enhancing dye-sensitized solar cell efficiency by anode surface treatments

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ABSTRACT

In this study, titanium substrates treated with HF solution and KOH solution sequentially forming micro- and nano-structures were used for the fabrication of flexible dye-sensitized solar cells (DSSCs). After wet etching treatments, the titanium substrates were then exposed to the O_2 plasma treatment and further immersed in titanium tetrachloride ($TiCl_4$) solution. The process conditions for producing a very thin TiO_2 blocking layer were studied, in order to avoid solar cell current leakage for increasing the solar cell efficiency. Subsequently, TiO_2 nanoparticles were spin-coated on Ti substrates with varied thickness. The dye-sensitized solar cells on the titanium substrates were subjected to simulate AM 1.5 G irradiation of 100 mW/cm^2 using backside illumination mode. Surface treatments of Ti substrate and TiO_2 anode were found to play a significant role in improving the efficiency of DSSC. The efficiencies of the backside illumination solar cells were raised from 4.6% to 7.8% by integrating these surface treatments.

1. Introduction

Significant progress has been recently achieved in developing dye-sensitized solar cells (DSSCs) with low cost and eco-friendly characteristics and high solar-power efficiencies (~15%) [1]. However, a typical DSSC is restricted by the heavy, rigid, and fragile transparent conductive oxide glass as the photoanode. Hence, flexible and lightweight substrates such as metal foil and plastics are required for roll to roll mass production, which can broaden the applications of DSSC. Nevertheless, the necking between TiO_2 nanoparticles remain poor by heating them up to 150 °C, an upper temperature limit for the plastic substrate to be thermally stable, resulting in low solar cell efficiency [2]. So many research groups have proposed the usage of metal substrates, in particular titanium (Ti) substrate, as the anode. Ti substrate is a good alternative to the plastic substrate due to its low sheet resistance, good flexibility, and superior corrosion resistance [3,4]. Grätzel et al. [5] reported highly efficient (7.2%) flexible DSSCs using a Ti foil substrate.

Aiming at improving the cell performance, previous researchers have proposed several one-dimension (1D) TiO_2 nanostructures to replace TiO_2 nanoparticles [6–8]. Those 1D nanostructures can transfer electrons faster from dye molecules to the substrate for raising the collection efficiency. But, 1D TiO_2 nanostructures are not so densely packed leading to less dye adsorption. Wang et al. introduced nanotube morphology in conjunction with oxygen plasma, which compensated for less internal surface area and dye adsorption, and achieved a high power conversion efficiency (PCE) of 7.37% [9]. In addition, some other researchers investigated the effect of the underlayers between Ti substrate and TiO_2 film to enhance the electrical contact and suppress the dark current. For example, Yun et al. reported that the roughened substrates increased the PCE of DSSC on a stainless substrate from 4.3% to 5.7% [10]. Lee et al. revealed a PCE of 6.75% by introducing a sponge-like TiO_2 interfacial layer [11]. Tsai et al. obtained a high PCE of 7.1% by introducing an underlayer of TiO_2 network nanosheet [12]. Besides, some researchers sputtered Ti, Ni, Cu, and Al on the fluorine-doped tin oxide (FTO) to form a blocking layer and prevented the current leakage due to the recombination of electrons in FTO with I_3^- in electrolyte [13,14].

Consequently, this study proposes various surface-treatment methods including $TiCl_4$ pre-treatments [5,15] and post-treatments [16–18], micro-nanostructures made by HF-KOH etching, and oxygen plasma pre-treatment. These surface treatments may act as the connection layer, the light scattering layer, and the blocking layer. This study further explores the effects of TiO_2 thickness and the O_2 plasma exposure time on the cell efficiency. After integrating these treatments using the optimized conditions, the PCE of the DSSC is dramatically improved.

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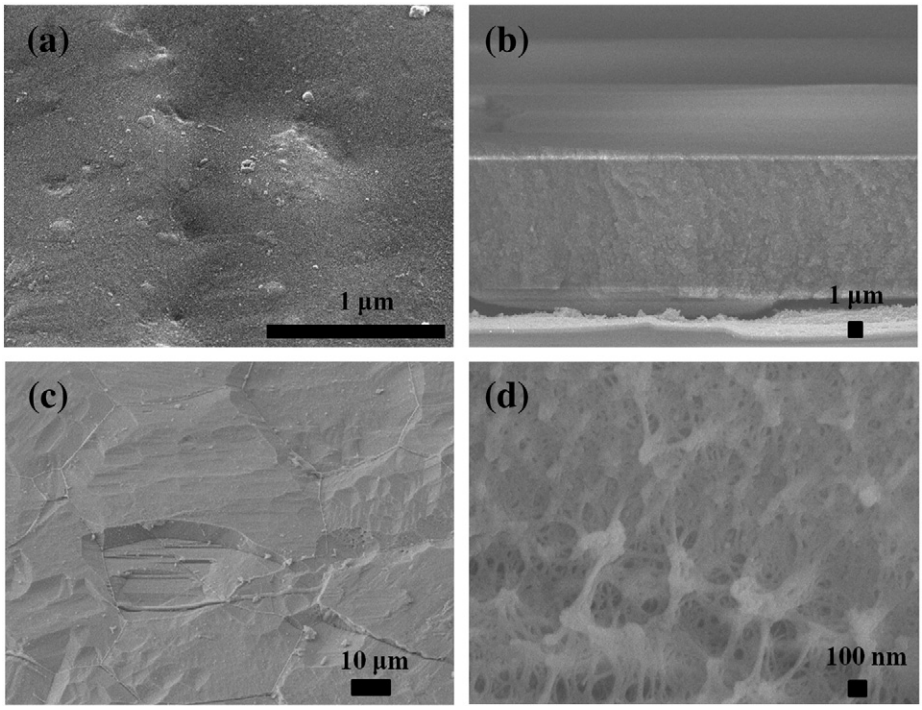

Fig. 1. (a) Top-view SEM image of untreated Ti substrate, (b) cross-section image of a 11.7 μm TiO_2 film deposited on the untreated Ti substrate, and (c, d) top-view images of Ti substrates treated sequentially with HF and KOH.

2. Experimental details

2.1. Ti substrate surface treatment

Commercial Ti foil substrates (0.1 mm thickness, 99.9% purity, E-light Technology Inc., Taiwan) were etched by 1.8 wt.% HF for 2 min, followed by 3 M KOH at room temperature for 1 h. The substrates were then cleaned subsequently with de-ionized water, acetone, isopropanol and dried with N_2. Next, the cleaned substrates were exposed to O_2 plasma at 30 W of power for various times. Chemical treatment was further performed by soaking the Ti foils in 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min. Prior to immersing the treated foils in dye solvent, $TiCl_4$ treatment was repeated again at the same condition.

2.2. Preparation of a TiO_2 film photoanode

The following steps were used to prepare TiO_2 colloidal solution: (1) mix 6 g of TiO_2, Degussa P25 powder, with 10 g of de-ionized water and stir the solution for 1 h with magnet. (2) Add 100 μl of Triton X-100 (Panreac) and 200 μl of acetyl acetone (Alfa Aesar) to TiO_2 colloidal solution, stir it for 1 h, in order to disperse the solution; and (3) put the solution in an ultrasonic bath at a constant temperature until the solution was uniformly mixed. Then, the solution was spread onto Ti foil by spin coating with a TiO_2 photoelectrode active area of 0.16 cm^2 (0.4 × 0.4 cm^2). The sample was sintered at 450 °C for 30 min to remove excess solvent and dispersant in the film and to create good necking between TiO_2 particles. After being cooled to 80 °C, the TiO_2 electrode was immersed in a 0.5 mM N719 dye dissolved in the mixture of acetonitrile and *tert*-butyl alcohol (volume ratio: 1:1) and kept at room temperature for 24 h.

Table 1
Photovoltaic performance of DSSCs using smooth and micro-/nano-structured Ti foil as photoanode followed by spin coating with TiO_2 nanoparticles for different times.

Spin coating time	TiO_2 thickness (μm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
Smooth Ti foil					
1	5.5	0.79	7.55	0.7	4.2 ± 0.05
2	11.4	0.78	7.94	0.74	4.6 ± 0.02
2[a]	–	0.79	8.64	0.73	5.0 ± 0.04
3	17	0.76	7.4	0.75	4.2 ± 0.03
Micro-nanostructures Ti foil					
1	5.5	0.81	8.34	0.69	4.7 ± 0.03
2	11.4	0.76	10.1	0.71	5.4 ± 0.04
2[(a)]	–	0.78	10.57	0.71	5.9 ± 0.05
3	17	0.74	9.98	0.67	4.9 ± 0.02

[a] $TiCl_4$ post-treatment.

2.3. Fabrication and characterization of the DSSCs

The indium tin oxide/poly(ethylene terephthalate) (Peccell Technology Inc., Japan) counter electrode was coated with a layer of platinum by sputtering at a current of 40 mA for 20 s. The photoelectrode was assembled with the counter electrode separated by 60 μm thick hot-melt spacers (SX1170-60, Solaronix). Then, the electrolyte, consisting of 0.1 M guanidinium thiocyanate, 0.03 M I_2, 0.6 M 1-butyl-3-methyl imidazolium iodide and 0.5 M 4-tert-butylpyridine in a mixture of acetonitrile and valeronitrile (volume ratio: 85:15), was injected into the solar cell. The photocurrent-voltage (I–V) characteristics of the DSSCs were measured using a solar simulator (Newport, Oriel class A, 91160A) under an irradiation of AM 1.5, 100 mW/cm^2. The surface morphology was characterized by scanning electron microscopy (SEM, JEOL JSM-6700F) using 10 kV accelerating voltage. The IPCE spectra were measured by using the monochromatic light from a specially designed system made of a xenon lamp, a monochromator, and filters. A time-of-flight secondary ion mass spectrometry (TOF-SIMS, Cameca IMS-6f) with Cs^+ ion gun operated at 15,385 eV was used for the O element depth profile analysis of the Ti substrate surface with and without the oxygen plasma treatment. The Ti substrate surface with and without the oxygen plasma treatment was also characterized by