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Surface modification of fluorine-doped tin oxide films using electrochemical etching for dye-sensitized solar cells

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Abstract

We modified the surface of fluorine-doped tin oxide (FTO) films using electrochemical etching in order to improve the photovoltiac performance of dye-sensitized solar cells (DSSCs). For the electrochemical etching, a mixture of HCl and zinc precursor was used as the electrolyte, which generated the H^+ needed for activating the SnO_2 etching reaction. This led to the formation of surface-modified FTO films that resulted in an increase in surface roughness and a high level of haze without changing the sheet resistance and optical transmittance of the FTO films. The open circuit voltage, fill factor, and short-circuit current density of the DSSCs assembled using the surface-modified FTO films were 0.73 V, 60.53%, and 15.67 mA/cm^2, respectively. The surface-modified FTO films created using electrochemical etching showed an improved photoconversion efficiency (~6.95%) when compared to bare FTO films (~6.33%). This improvement in performance was caused by an improved ability to trap light by increasing haze, which resulted in an enhancement in the surface roughness of the FTO films.

Keywords: A. Films; B. Surfaces; E. Electrodes; Dye-sensitized solar cells; Fluorine-doped tin oxide (FTO)

1. Introduction

Dye-sensitized solar cells (DSSCs) have received considerable attention as an attractive candidate to replace conventional crystalline solar cells due to their low fabrication cost, simple cell structure, flexibility, and the diversity of their applications [1–3]. In general, DSSCs consist of a transparent conducting electrode (TCE), a working electrode with absorbed dyes, a Pt counter electrode, and a liquid electrolyte containing I^-/I^{3-} [1]. In particular, TCEs that have a low resistivity ($<10^{-4}\ \Omega$ cm) and high optical transparency ($>80\%$) in the visible range are used as the optical window. TCEs play an important role in determining the amount of light that is entering the device and in transferring the electrons to the external circuit [4]. Among the various TCE materials that are available (i.e., fluorine-doped tin oxide (FTO), tin-doped indium oxide (ITO), and aluminium-doped zinc oxide (AZO)), FTO is the most promising TCE material for DSSCs because it has advantages such as thermal stability, chemical inertness, a relatively low cost, and excellent mechanical hardness [4,5]. Hence, a number of studies have investigated FTO films in order to improve the photovoltaic performance of DSSCs. In addition to basic studies aimed at lowering resistivity and attaining a high optical transparency, the surface modification of FTO films is an important parameter that can enhance the photovoltaic performance of DSSCs. For example, Kong et al. carried out the surface modification of FTO films using lithography and inductively coupled plasma etching, which exhibited a photo-conversion efficiency of 5.60% [6]. Wang et al. fabricated a nanopatterned FTO electrode using nanoimprint lithography and reactive ion etching. DSSCs fabricated with this nanopatterned FTO electrode exhibited higher photoconversion efficiency (~3.50%) than those fabricated with unpatterned FTO (~2.38%) [7]. Therefore, the surface modification of FTO films can enhance photovoltaic performance due to increased light trapping by scattering and reflecting the incident light at different angles, which is an important strategy

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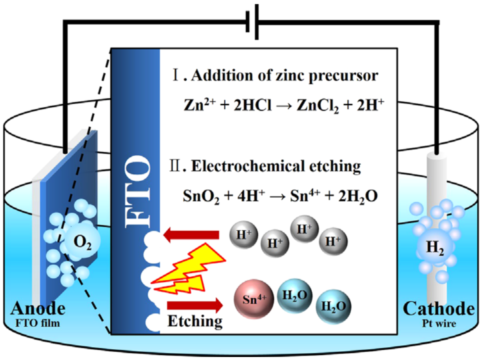

Fig. 1. Ideal schematic diagram of the electrochemical etching system.

used to obtain highly efficient photovoltaic devices [1]. However, in spite of the development of various etching techniques, the surface modification of FTO films using electrochemical etching has not yet been developed.

In this study, we prepared surface-modified FTO films using an electrochemical etching technique and demonstrated their photovoltaic properties for DSSCs. In particular, an electrochemical etching technique was chosen because of its advantages such as its high throughput, low processing cost, and simple procedure [8].

2. Materials and methods

For electrochemical etching, bare FTO films (~8 Ω/□, Pilkington) were prepared by ultrasonic cleaning in acetone, methanol, ethanol, and de-ionized (DI) water. The electrochemical etching was carried out using a potentiostat/galvanostat (Gamry instruments, Reference 600™) with a two-electrode setup consisting of the FTO films as the anode and a Pt wire as the cathode. The electrolyte was prepared by dissolving 0.03 M zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, DUCKSAN) in a 2 M hydrochloric acid (HCl, SAMCHUN) solution. The electrochemical etching process was carried out at room temperature and the voltage and activation time were 0.03 V and 600 s, respectively. The distance between the FTO films and the Pt wire was fixed at ~3 cm, and the resultant samples were then washed with DI water. In order to measure the photovoltaic performance, the bare and surface-modified FTO films were used as current collectors in the working electrode of the DSSCs. To fabricate the working electrode, a TiO_2 paste was prepared by grinding a mixture of P25 (DEGUSSA), hydroxypropyl cellulose (HPC, $M_w = \sim 80{,}000$ g/mol, Aldrich), acetylacetone (Aldrich), and DI water. After uniformly mixing the above-mentioned paste, it was coated on the bare and surface-modified FTO films, which was annealed at 500 °C for 1 h. The as-prepared samples were immersed into 0.5 mM N719 ($Ru(dcbpy)_2(NCS)_2$, Solaronix) in ethanol (CH_3CH_2OH, Aldrich) for 24 h in order to absorb the dye molecules. For the counter electrode, a Pt solution was prepared by dissolving chloroplatinic acid hydrate ($H_2PtCl \cdot xH_2O$, Aldrich) in 2-propanol ($(CH_3)_2CHOH$, Aldrich), which was spin-coated onto the bare FTO films at 2000 rpm for 30 s and then annealed at 450 °C for 0.5 h. Finally, a 0.6 M BMII (1-Butyl-3-methylimidazolium iodide) iodine-based solution was injected into the gap between the working electrode and the counter electrode in an assembled cell as the electrolyte.

The morphological and topographical properties of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and atomic force microscopy (AFM, diDimension™ 3100), respectively. The structural changes of the samples were analyzed by X-ray diffraction (XRD, Rigaku D/MAX2500V). The electrical and optical properties of the samples were measured using a Hall-effect measurement (Ecopia, HMS-3000) and ultraviolet–visible (UV–vis) spectroscopy (Perkin-Elmer, Lambda-35), respectively. The photovoltaic performance of the DSSCs was investigated using a solar simulator (Peccell Technologies, PEC-L01) equipped with a 150 W xenon arc lamp with a light intensity of 100 mA/cm^2.

3. Results and discussion

In order to obtain the surface-modified FTO films, we employed an electrochemical etching technique. Fig. 1 shows the electrochemical etching system, which consists of the FTO films as the anode, Pt wire as the cathode, and 2 M HCl as the electrolyte. The surface modification of the FTO films occurs because of two primary reactions during the electrochemical etching process: (1) the formation of H^+ by Zn^{2+} and (2) the etching of SnO_2 by the H^+ that is formed. In particular, the addition of zinc acetate dihydrate in the HCl electrolyte is an important factor that is needed for the success of the surface modification of the FTO films. Specifically, the H^+, which is the main source for etching activation, could be formed from Zn^{2+} in HCl solution as follows [9]:

$$Zn^{2+} + 2HCl \rightarrow ZnCl_2 + 2H^+ \tag{1}$$

Once the electrochemical etching process begins, H_2 and O_2 gases are generated by reduction and oxidization reactions at the anode and cathode, respectively [10,11]:

$$\text{Cathode}: \quad 2H^+ + 2e^- \rightarrow H_2 \tag{2}$$

$$\text{Anode}: \quad 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{3}$$

At the anode, the main reactions for FTO etching that may occur are as follows [11]:

$$SnO_2 + 4H^+ \rightarrow Sn^{4+} + 2H_2O \tag{4}$$

$$Sn^{4+} + 6Cl^- \rightarrow Sn(Cl)_6^{2-} \tag{5}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{6}$$

Thus, H^+ formed by reaction (1) results in the etching of SnO_2 in the FTO films. The resulting Sn^{4+} then forms $Sn(Cl)_6^{2-}$ through reaction (5), which can accelerate the etching of SnO_2 that occurs by reaction (4) [11,12]. In addition, the Cl^- that is formed may be oxidized to form