



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 photovoltaic 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/cm², 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.

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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 photo-conversion 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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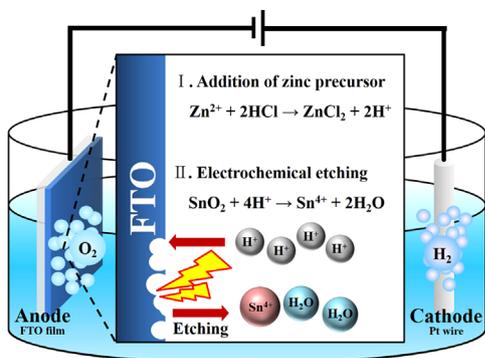


Fig. 1. Ideal schematic diagram of the electrochemical etching system.

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 ($\sim 8 \Omega/\square$, 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 ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 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 ($\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$, Solaronix) in ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 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 ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, Aldrich) in 2-propanol ($(\text{CH}_3)_2\text{CHOH}$, 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.

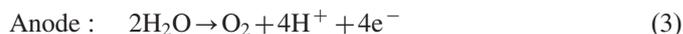
The morphological and topographical properties of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and atomic force microscopy (AFM, diDimension™ 3100), respectively. The structural changes of the samples were analyzed by X-ray diffraction (XRD, Rigaku 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 (Pecell Technologies, PEC-L01) equipped with a 150 W xenon arc lamp with a light intensity of $100 \text{ mA}/\text{cm}^2$.

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]:



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



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



Thus, H^+ formed by reaction (1) results in the etching of SnO_2 in the FTO films. The resulting Sn^{4+} then forms $\text{Sn}(\text{Cl})_6^{2-}$ 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

Cl_2 [12]. Therefore, the use of a zinc precursor can lead to the successful etching of the FTO films during the electrochemical etching process.

Fig. 2 shows top-view and cross-sectional SEM images that were obtained from the bare and surface-modified FTO films. The surface of the bare FTO films, as shown in Fig. 2(a), exhibits the pyramidal crystals that are continuously connected. On the other hand, it is noted that the surface-modified FTO films randomly formed pores with diameters

between ~ 48.16 and ~ 134.93 nm on the FTO surface, as shown in Fig. 2(b). This indicates that the electrochemical etching induces the surface modification of the FTO films, which increases the surface roughness of the FTO films. In the cross-section shown in Fig. 2(c) and (d), relatively different surface morphologies were observed between the bare and the surface-modified FTO films, which is in good agreement with the top-view SEM images. In addition, the average thicknesses of the samples are observed to be ~ 694.14 nm for the bare

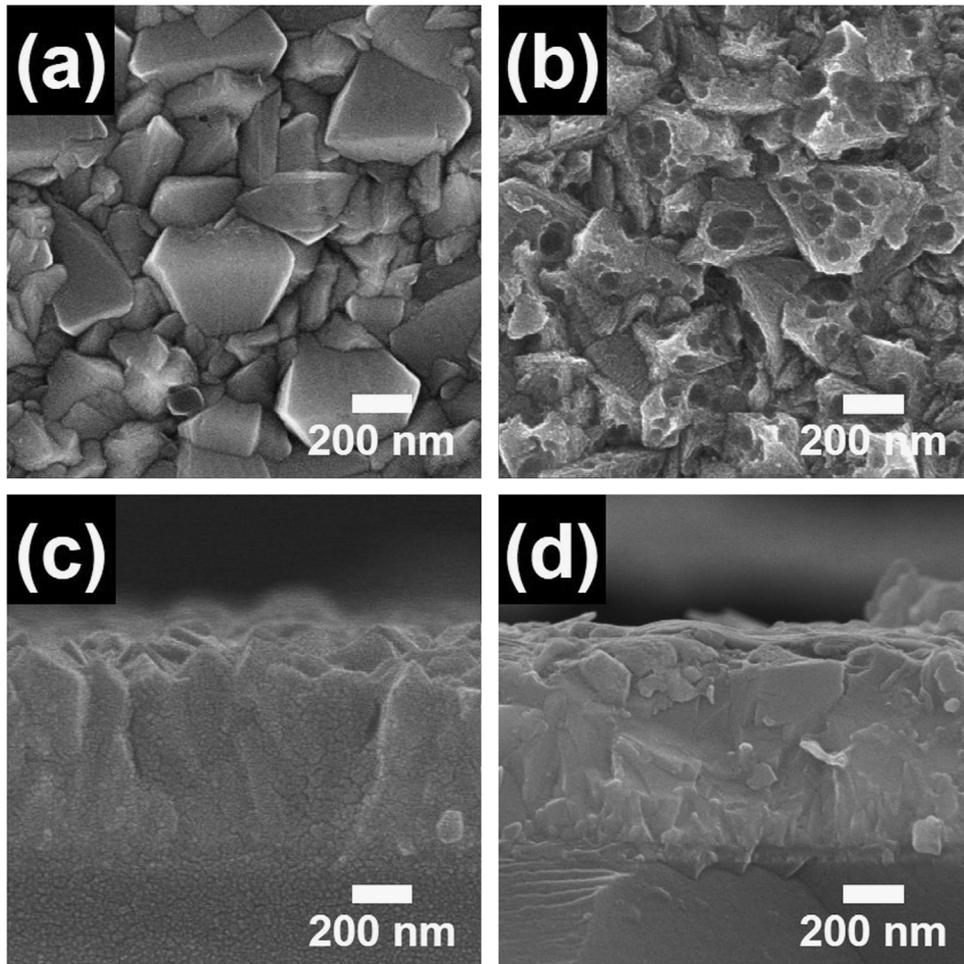


Fig. 2. Top-view (a) and (b) and cross-sectional FESEM images (c) and (d) of the bare FTO films and surface-modified FTO films.

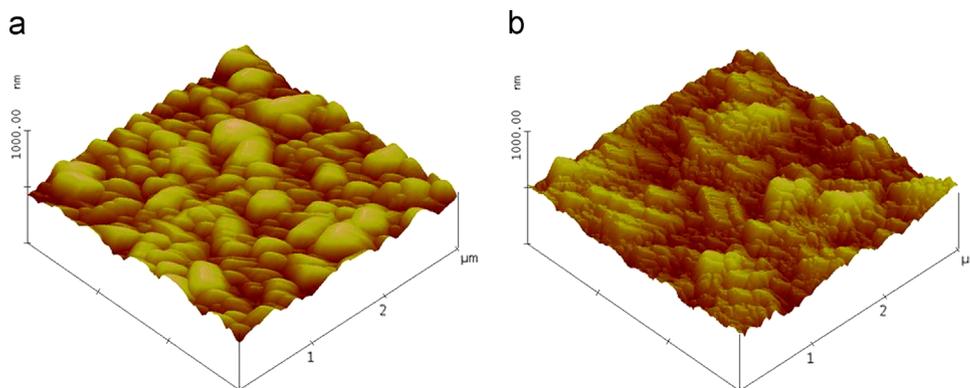


Fig. 3. AFM images obtained from the bare and surface-modified FTO films.

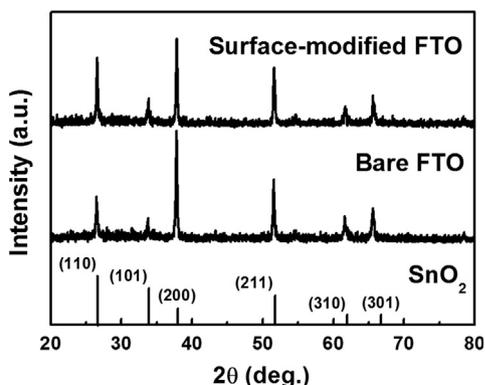


Fig. 4. XRD patterns of the FTO films before and after electrochemical etching.

FTO films and ~ 684.00 nm for the surface-modified FTO films. These results indicate that the surface modification of the two samples occurs only through electrochemical etching. Thus, the surface modification of the FTO films can improve the roughness of the FTO surface, which would affect the photovoltaic performance of the DSSCs [4].

In order to further investigate the surface roughness of the samples, AFM analyses were carried out. Fig. 3(a) and (b) shows 3-dimensional AFM images of the FTO films before and after electrochemical etching. The measured root-mean square roughness (R_{ms}) and height roughness (R_a) are ~ 33.07 nm and ~ 27.40 nm, respectively, for the bare FTO films and ~ 41.43 nm and ~ 33.31 nm, respectively, for the surface-modified FTO films. It is noted that the FTO surface displays a considerably rough morphology because of the holes that are formed as a result of the SnO_2 that is dissolved during the electrochemical etching.

Fig. 4 shows XRD patterns of the bare and surface-modified FTO films. In case of both the samples, diffraction peaks are observed at 26.58° , 33.86° , 37.94° , 51.76° , 61.87° , and 65.95° that correspond to the (110), (101), (200), (211), (310), and (301) planes of the SnO_2 phases, which have a cassiterite tetragonal structure (space group $P4_2/mnm$ [136], JCPDS card no. 211250). The peak position of the FTO films corresponds to the left-shifted values in 2θ from that of the bare SnO_2 . Based on Bragg's equation ($n\lambda = 2d \sin\theta$), this result can be induced by the substitution of two F^- sites for one O^{2-} site because the ion radius (1.33 \AA) of F^- is slightly bigger than that (1.32 \AA) of O^{2-} , which is one reason for the excellent electrical properties of the FTO films [13,14]. Therefore, the SEM, AFM, and XRD results indicate that the FTO films are successfully surface-modified using electrochemical etching.

To investigate the electrical and optical properties of the surface-modified FTO films, we carried out Hall-effect measurements and UV–vis spectroscopy. Table 1 summarizes the electrical and optical properties of the bare and surface-modified FTO films. The carrier concentration and Hall mobility are $\sim 2.34 \times 10^{20} \text{ cm}^{-3}$ and $\sim 53.80 \text{ cm}^2/\text{Vs}$, respectively, for the bare FTO films and $\sim 2.26 \times 10^{20} \text{ cm}^{-3}$ and $\sim 51.87 \text{ cm}^2/\text{Vs}$, respectively, for the surface-modified FTO films. That is, the carrier concentration and Hall mobility of the surface-modified FTO films are slightly lower than those of the

bare FTO films due to the surface modification by electrochemical etching. Based on these results, the resistivity (ρ) can be calculated by the following equation [15,17]:

$$\rho = 1/(Ne\mu)$$

where N , e , and μ are the carrier concentration, electron charge ($1.60 \times 10^{-19} \text{ C}$), and Hall mobility, respectively. Therefore, the calculated resistivity is $\sim 4.95 \times 10^{-4} \Omega \text{ cm}$ for the bare FTO films and $\sim 5.30 \times 10^{-4} \Omega \text{ cm}$ for the surface-modified FTO films. The sheet resistance, which can be calculated by the resistivity/thickness, is $\sim 7.14 \Omega/\square$ for the bare FTO films and $\sim 7.75 \Omega/\square$ for the surface-modified FTO films. These results indicate that the sheet resistances of the FTO films exhibit similar values before and after electrochemical etching. For the optical properties of the bare and surface-modified FTO films, the average transmittance and haze in the range from 400 to 800 nm are observed to be $\sim 81.90\%$ and 8.50% , respectively, for the bare FTO films and $\sim 81.57\%$ and 12.40% , respectively, for the surface-modified FTO films. The transmittance between the two samples is almost the same. Interestingly, the haze value of the surface-modified FTO films is dramatically increased when compared to that of the bare FTO films. This result can be explained by the increased surface roughness of the FTO films after electrochemical etching, which can enhance light trapping by effectively scattering the incident light into the DSSCs. In general, the haze value is a ratio of the diffusively transmitted light to the total transmitted light at a specific wavelength, which can be calculated using the following equation [16,17]:

$$\text{Haze} = (T_{\text{total}} - T_{\text{direct}})/T_{\text{total}} \times 100\%$$

where T_{total} and T_{direct} are the total transmittance and direct transmittance, respectively. This factor is directly related to the optical scattering capability of the TCEs [18]. Therefore, the increased surface roughness of the FTO films after electrochemical etching can cause an enhancement in light scattering, which is a very useful strategy to improve the performance of DSSCs.

Fig. 5 shows the photocurrent–voltage (J – V) curves of the DSSCs that were assembled using the bare and surface-modified FTO films as the current collector for the working electrode. The photoconversion efficiency (PCE, η) of the DSSCs can be calculated from the equation given below [18]:

$$\eta(\%) = (J_{sc} \times V_{oc} \times ff)/(I_{max} \times V_{max})$$

where J_{sc} , V_{oc} , ff , I_{max} , and V_{max} are the short-circuit current density, open-circuit voltage, fill factor, maximum power current, and maximum power voltage, respectively. The measured photovoltaic parameters for all of the samples are summarized in Table 2. It is noted that the V_{oc} and ff values of the two samples are nearly identical, which is caused by the similar construction, including the TiO_2 , Pt, and electrolyte as well as the FTO films having similar sheet resistances [1,18]. On the other hand, the J_{sc} value of the surface-modified FTO films ($\sim 15.67 \text{ mA}/\text{cm}^2$) is higher than that of the bare FTO films ($\sim 14.62 \text{ mA}/\text{cm}^2$). This is due to enhanced light trapping by the surface modification of the FTO films. As a result, the

Table 1

List of electrical and optical properties obtained from the bare and the surface-modified FTO films.

Samples	Carrier concentration (cm^{-3})	Hall mobility ($\text{cm}^2/(\text{Vs})$)	Resistivity ($\Omega \text{ cm}$)	Sheet resistance (Ω/\square)	Transmittance (%)	Haze (%)
Bare FTO	2.34×10^{20}	53.80	4.95×10^{-4}	7.14	81.90	8.50
Surface-modified FTO	2.26×10^{20}	51.87	5.30×10^{-4}	7.75	81.57	12.40

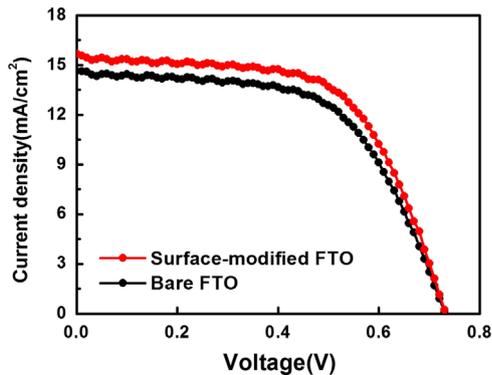


Fig. 5. Photocurrent–voltage curves of the DSSCs assembled using the bare FTO films and surface-modified FTO films.

Table 2

Summary of the photovoltaic performance for the DSSCs assembled using the bare and surface-modified FTO films.

Samples	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	η (%)
Bare FTO	0.73	14.62	59.15	6.33
Surface-modified FTO	0.73	15.67	60.53	6.95

photoconversion efficiency of the DSSCs assembled with the surface-modified FTO films ($\sim 6.95\%$) exhibited superior performance compared to that of the DSSCs assembled with bare FTO films ($\sim 6.33\%$). This performance improvement can be attributed to an increased J_{sc} due to the enhanced light trapping that was induced by the high haze value of the FTO films obtained after electrochemical etching. Moreover, the introduction of the surface-modified FTO films, which have a high haze value, can cause the effective scattering of the incident light, enhancing light trapping in the DSSCs [1]. As a result, this phenomenon can lead to the improvement of J_{sc} and allow for the achievement of high-performance DSSCs.

4. Conclusions

The surface-modified FTO films were prepared using an electrochemical etching technique. For electrochemical etching, the zinc precursor was used as an important source of etching activation. In particular, while their sheet resistances and average optical transmittances were almost the same, the surface-modified FTO films exhibited an enhanced haze value compared to the bare FTO films. This phenomenon can increase the light trapping by effectively scattering the incident light in the DSSCs. Therefore, DSSCs assembled with the surface-modified FTO films showed higher J_{sc} ($\sim 15.67 \text{ mA}/$

cm^2) and higher PCE ($\sim 6.95\%$) compared to DSSCs assembled with the bare FTO films. Thus, surface-modified FTO films prepared using electrochemical etching can be used as a current collector for the fabrication of high-performance DSSCs.

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