# Improved performance of dye-sensitized solar cells with patterned fluorine-doped tin oxide electrodes

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## ARTICLE INFO

## ABSTRACT

Patterned fluorine-doped tin oxide electrodes for dye-sensitized solar cells were fabricated by a facile wet etching method. The pattern depth could be controlled by altering etching time. Most dye-sensitized solar cells with patterned fluorine-doped tin oxide electrodes exhibited larger photocurrents. The energy conversion efficiency gradually increased with increasing etching time and obtained a maximum of 7.71% when etching time was 240 s. Then it dropped abruptly if etching duration was more prolonged. An optimum pattern depth is required to achieve the highest performance. The improved performance could be mainly attributed to enhanced light harvesting and scattering due to larger amount of titanium dioxide nanoparticles filled in the circular pattern leading to more dye adsorption. The charge transfer impedance at the titanium dioxide/electrolyte interface also affected the performance of dye-sensitized solar cells. By appropriate etching for surface patterning of fluorine-doped tin oxide electrodes, the device performance had a 16% improvement, which was more efficient than merely adding layer of titanium dioxide nanoparticles on non-patterned fluorine-doped tin oxide.

## 1. Introduction

DSSC (dye-sensitized solar cell) has attracted considerable attention due to its facile and lower-cost manufacture processes in spite of the lower energy conversion efficiency ($\eta$) as compared to silicon- and CIGS (copper indium gallium selenide)- based thin film solar cells [1–4]. DSSC performance depends on some factors such as the size, morphology and film thickness of $TiO_2$ (titanium dioxide) nanostructures, the nature of dye, the composition of electrolyte, and the properties of TCO (transparent conducting oxide) electrode and CE (counter electrode), etc. FTO (Fluorine-doped tin oxide) on glass substrates is frequently employed in DSSCs as TCO electrode since it is electrically more stable than ITO (indium tin oxide) at high temperatures during the fabrication of DSSCs [5–8]. An effective FTO electrode for DSSCs should have high conductivity and low absorption of visible light. However, the decrease of resistivity is correlated with a decreased transmission. The interfacial properties and compatibility of FTO electrodes are also important since they determine the quality of contact between the deposited material and FTO.

Although intensive researches have been executed over the past decade, there has been no remarkable improvement in DSSC performance. The approaches developed to improve DSSC performance include uses of new dyes, new electrode materials, $TiO_2$ with different sizes and nanostructures, and modification of electrodes [9–17]. $TiO_2$ nanorods obtained from electrospun nanofibers were found to generate a highest $\eta$ of 4.56%. An adiabatic mechanism with strong electronic coupling efficiency of photoexcited electrons was suggested for the nanorods [14]. Flower-like ZnO with nanostructured petals was synthesized by hydrothermal process, and the highest $\eta$ obtained from the ZnO-based DSSCs was 3.60% [15]. Composite film consisting of multi-wall carbon nanotubes and polypyrrole was prepared by electropolymerization and served as the counter electrode for DSSCs. The enhanced $\eta$ of 7.42% comparable to those of Pt-based DSSCs was achieved [16]. The overall transmission of light was improved by implementing textured surfaces. According to the simulation on optical properties of FTO glass, pyramidal structures could produce increased transmission due to decrease in reflection [17].

As one of these efforts, FTO electrodes with line and space patterns were achieved by lithography coordinated with inductively coupled plasma reactive ion etching. The etching parameters, such as gas concentration and dc-bias voltage to the substrate, were tuning up to obtain better DSSC performance. It has been reported

that the sheet resistance ($R_s$) of FTO increased after the dry etching, indicating that the dry etching caused damage to FTO during etching process. The DSSCs with patterned FTO electrodes obtained by the dry etching showed an enhancement of η from 4.63% to 5.60% [18]. Nanopatterned periodic submicron nanostructures were created on FTO using nanoimprint lithography and reactive ion etching to obtain enhanced light scattering. Both short-circuit photocurrent density ($J_{sc}$) and open-circuit voltage ($V_{oc}$) were found to be higher for patterned electrodes, leading to improved performance as compared to unpatterned electrodes. However, the overall η was not higher than 3.5% [19]. The above-mentioned dry etching methods can also be applied to different TCOs such as zinc oxide, indium zinc oxide and aluminum doped zinc oxide.

In addition to dry etching, FTO could also be patterned by wet etching [20]. The DSSCs with patterned FTO electrodes obtained by wet etching had drastic decrease in performance and showed even lower η which was 1.99%–2.38%. However, there was no significant change in $V_{oc}$, and their performance was able to be maintained after long-term aging test. Compared with dry etching, the wet etching method is lower-cost, more facile and easier to be performed in laboratory. Moreover, it has the advantages of faster reaction rate and ease to obtain high aspect ratio, so the probable application of wet etching to DSSCs is still worthy to be studied because there seems to be lots of room for performance improvement especially when costly equipments are not available in laboratory. To the best of our knowledge, only very few researches regarding the application of etching technique to pattern FTO electrode have been reported [18–20]. A higher DSSC efficiency could be expectable after wet etching by referring to the results of patterned FTO obtained by dry etching. However, too complicated patterns are hard to be achieved by wet etching technique in laboratory. Thus a simple circular pattern was chosen to be the target pattern. Just as expected, higher DSSC performance was obtained by appropriate wet etching time to obtain an optimum depth of FTO pattern.

Surface patterning slightly increases the surface area of FTO electrode and makes better contact between FTO and $TiO_2$ nanoparticles. By this way, more $TiO_2$ nanoparticles fill the pattern and result in more dye adsorption. Even though increase of $TiO_2$ layer on non-patterned FTO electrode also increases dye adsorption, patterned FTO makes more compact filling and stacking of $TiO_2$ nanoparticles and is thereby considered to be a preferable way to improve light harvesting and scattering. The equipments for lithography and dry etching are relatively costly compared with those of wet etching. Herein we demonstrate a facile and inexpensive approach for surface patterning of FTO. Dye adsorption increased with increasing pattern depth of FTO electrode. An optimum depth was obtained by controlling the time of wet etching. Enhanced light harvesting and scattering were resulted from more filling of $TiO_2$ nanoparticles, leading to the achievement of a highest η of 7.71%, which was around 16% higher than that of the standard DSSC with non-patterned FTO electrode and also much superior than the η values of the DSSCs with patterned FTO obtained by any etching methods ever reported before [18–20].

## 2. Experimental

### 2.1. Surface patterning of FTO

Commercially available FTO conductive glasses were used to form patterned FTO electrodes. The FTO conductive glasses were firstly cleaned with detergent, rinsed twice with de-ionized water, followed by ultrasonication in acetone and isopropyl alcohol baths sequentially, and finally dried with nitrogen gas flow. Anti-corrosion polyimide (PI) adhesive tape was stuck on the surface

of clean FTO conductive glasses to protect the part without pattern from being etched. 0.05 M Zinc (Zn) powder in 1 M HCl (hydrogen chloride) aqueous solution was used as the etching solution to form required patterns [21]. The pattern on FTO conductive glass was a circle with an area of 0.1963 $cm^2$. Various pattern depths were achieved by different etching times (60 s, 90 s, 120 s, 150 s, 180 s, 210 s, 240 s, 270 s and 300 s). The PI tape was removed after the wet etching process was accomplished. The effective region of DSSCs was of a square shape with an area of 0.75 × 0.75 $cm^2$, and the circular pattern was located in the middle of the square. Pattern depth increased with increasing etching time. FTO was almost thoroughly etched away when etching time was 300 s. All pattern depths and profiles were examined by the surfcoder (ET-3000, Kosaka Laboratory Ltd.). The total FTO thickness on glass substrate was approximate to 550 nm. The $R_s$ of FTO electrodes was measured by the four-point probe method.

### 2.2. Preparation of $TiO_2$ electrode and dye adsorption

Before patterned FTO conductive glasses could be used as the substrates for fabrication of DSSCs, they were treated again by the same cleaning processes as described above. The nanoporous $TiO_2$ electrode was composed of three-layer $TiO_2$ nanoparticles. The diameter of the nanoparticles is 13 nm in the first two layers (Ti-Nanoxide T/SP, Solaronix) and 400 nm in the uppermost layer (Ti-Nanoxide R/SP, Solaronix). The nanoparticles of each layer were spread on FTO substrates by doctor blade method, followed by air-drying at room temperature and baking at 100 °C respectively for 2 h, and then calcination at 500 °C for 60 min. The three-layer nanoporous $TiO_2$ electrodes with an effective area of 0.75 × 0.75 $cm^2$ were used for dye adsorption. After being taken out from the furnace, they were immersed in 0.3 mM dye solution (N719 in *t*-butanol/acetonitrile (1:1, v/v)) immediately for 24 h. After being drawn out from dye solution and rinsed with acetonitrile, the dye-anchored $TiO_2$ electrodes were blow-dried with nitrogen gas and ready for use as photoelectrodes in the fabrication of DSSCs. Dye desorption was carried out by soaking the dye-anchored $TiO_2$ photoelectrodes in 0.1 M NaOH aqueous solutions. The amounts of dye adsorbed on $TiO_2$ covered on patterned FTO electrodes with various pattern depths were compared by the absorption spectra obtained from a UV–Vis spectrophotometer equipped with an integrating sphere setup (U-3900H, Hitachi).

### 2.3. Preparation of Pt counter electrode

The FTO conductive glass for preparation of Pt CE was also cleaned by same processes as described above to obtain clean FTO substrate. The deposition of Pt was executed by an ion sputter coater with a deposition rate of 0.75 Å $s^{-1}$ and a sputtering time of 40 s in vacuum to form uniform Pt ultra-thin film on clean non-patterned FTO substrate [22]. After the sputtering deposition of Pt, calcination was performed on the Pt CE at 500 °C for 60 min. When cooling down to room temperature, the Pt CE was immediately used for the fabrication of DSSCs.

### 2.4. Fabrication and characterization of DSSCs

The DSSCs were of the sandwich type consisting of a dye-anchored $TiO_2$ electrode, a PI spacer and a sputter-deposited Pt CE. The electrolyte solution was prepared from 0.5 M LiI, 0.05 M $I_2$, 0.5 M TBP (*tert*-butylpyridine) and 0.5 M MPII (1-methyl-3-propylimidazolium iodide) in acetonitrile and injected into the narrow space between two electrodes by a microsyringe. The photovoltaic characterizations of DSSCs were accomplished by a solar simulator (SS50ABA, Photoemission Tech. Inc.) under AM 1.5