



# An integrative method to prepare low-platinum/fluorine doped tin oxide counter electrode for cost-effective dye-sensitized solar cells



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## ABSTRACT

Conventional pyrolytic platinum loaded on commercial F-doped tin oxide (Pt//cFTO) conductive glass as counter electrode (CE) is a crucial component of DSSCs. In this paper, an integrative method was used to prepare platinum loaded on in-house-made iFTO glass (Pt//iFTO) without cFTO glass and the newly synthesized Pt//iFTO electrodes were applied as CEs in the DSSCs. Compared with common Pt//cFTO electrode loading amount of Pt of 32.17  $\mu\text{g cm}^{-2}$  which shows an efficiency of 6.70% as a CE in DSSCs, Pt//iFTO electrode loading less amount of Pt of 13.01  $\mu\text{g cm}^{-2}$  still displays a slight higher cell efficiency of 6.77%. The integrative method requires simple equipment, easy operation, and discards the cFTO glass and significantly reduces costs. Meanwhile, Pt catalyst layer and iFTO substrate layer were formed at the same time in this method, saving a lot of thermal energy, which provides a new method for preparing electrodes needed high temperature post-processing.

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## 1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted extensive attention for 25 years as a promising renewable energy source, because of their easy fabrication, low-consumption, transparency and powerful harvesting efficiency (Kay and Grätzel, 1996; O'Regan and Grätzel, 1991). Generally, a typical DSSC has a sandwich-type structure consisting of a sensitizing dye adsorbed nanocrystalline TiO<sub>2</sub> anode, an electrolyte containing the iodide/triiodide (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) redox couple and a traditional platinized commercial fluorine-doped tin oxide counter electrode (Pt//cFTO CE) to collect electrons and catalyze the redox couple regeneration (Grätzel, 2001). Until now, the highest energy conversion efficiency of conventional DSSCs has been reported to reach 13% (Mathew et al., 2014). However, quite a few challenges remain to be addressed before its commercialization, including the photovoltaic performance, long-term stability and the fabricating cost.

For practical usage, further cost reduction is warranted in addition to the need for further increasing the efficiency. The issue has been attempted to be addressed by companies (Dürr et al., 2004; Han et al., 2004) and institutes research (Dai et al., 2005; Deb, 2005), and several strategies allowing for lowering the cost have been made. For instance, introducing conductive plastic substrates, based on polyethylene terephthalate (PET) or polyethylene naph-

thalate (PEN) films, to DSSCs can reduce the cost through mass production by roll-to-roll manufacturing system (Dürr et al., 2005; Lindström et al., 2001). Organic dyes may afford a cut in sensitizer cost (Horiuchi et al., 2004). The CE is an equally important component of the DSC. Apart from the conventional Pt//cFTO CE, conducting polymers including polypyrrole (Bu et al., 2013; Hwang et al., 2014; Lu et al., 2014), polyaniline (Lee et al., 2013), etc., and inorganic compounds such as metal nitrides (Jiang et al., 2009), sulfides (Sun et al., 2011; Wang et al., 2009), carbides (Jan et al., 2010; Wu et al., 2011) and oxides (Xia et al., 2010) etc., have already been applied as CEs in DSSCs. To date, almost all the efforts are committed to finding new materials to replace Pt catalyst and very few work is to elaborate novel methods and processes to lower the cost.

Usually, cFTO glass is an important part of a CE. However, it takes 30% of the total DSSC cost (Veerappan et al., 2011; Wang et al., 2012). Hence, reduction of, and preferably elimination of cFTO glass is the key to effectively cut cost. In this paper, we employed an integrative method for preparing of Pt loaded on in-house-made FTO electrodes (Pt//iFTO) as CEs and applied them to DSSCs devices. Compared to Pt//cFTO CE, the optimized Pt//iFTO electrode loading less Pt content even shows higher cell efficiency. Above all, this integrative technique discarding costly cFTO glass, makes the iFTO layer and Pt layer formed together during annealing. It saves much time and energy consumption, dramatically reduces the fabricating cost.

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## 2. Experimental section

### 2.1. Preparation of Pt//iFTO and Pt//cFTO electrodes

All of the following reagents used if no special instructions are of analytical grade and from Sinopharm Chemical Reagent Co., Ltd. The F:SnO<sub>2</sub> precursor was prepared according to a previous literature (Samad et al., 2011). Briefly, 6 g of SnCl<sub>4</sub>·5H<sub>2</sub>O was dissolved in 60 mL of absolute ethanol in a sealed round-bottomed flask, stirred for 5 h until all the tin chloride pentahydrate completely dissolved. The NH<sub>4</sub>F solution was prepared by dissolving 1.2 g of NH<sub>4</sub>F in 2.4 mL of distilled water. Then the tin chloride pentahydrate solution was heated to 40 °C and NH<sub>4</sub>F solution was added using a syringe. The mixture solution was stirred overnight standby. The Pt electrodes were prepared as follows: The clean bare glass (25 mm × 25 mm × 1 mm in size) was slowly warmed to 450 °C and kept for several minutes, then the above F:SnO<sub>2</sub> precursor and 1% H<sub>2</sub>PtCl<sub>6</sub>/2-propanol solution were successively sprayed onto bare glass using a nozzle of mini air compressor [0.1 Mpa], respectively. The nozzle was at a distance of about 10 cm from the bare glass. The spraying times of F:SnO<sub>2</sub> precursor was controlled at 30–60 times, and the spraying times of 1% H<sub>2</sub>PtCl<sub>6</sub>/2-propanol solution was controlled at 2–4 times. Adjacent spraying time should be intervals of 10 s. Then the glass substrates were kept at 450 °C for 30 min. After cooling down to room temperature, the as-prepared electrodes was obtained. The preparation parameters of different electrodes are shown in Table 1. In contrast, the traditional Pt//cFTO electrode was prepared by spin-coating 2% H<sub>2</sub>PtCl<sub>6</sub>/2-propanol solution on cFTO conductive glass and subsequently sintering at 450 °C for 30 min. Both the integrative method to prepare Pt//iFTO electrode and the traditional procedure to prepare Pt//cFTO electrode were shown in Fig. 1. And the mini air compressor used in the experiment was shown in the inset graph in Fig. 1.

### 2.2. Preparation of TiO<sub>2</sub> photoanodes and cell fabrications

The mesoporous TiO<sub>2</sub> paste was prepared followed a previously described method (Wang et al., 2003) except that autoclaving was conducted at 200 °C instead of 250 °C. An 8 μm thick layer of as-prepared 20-nm-sized TiO<sub>2</sub> nanoparticle layer was loaded on cFTO glass by doctor-blading technique. The films were dried in the air for 15 min, then calcined at 450 °C for 30 min and cooling down to room temperature, the obtained layer was further coated with a 2 μm thick scattering layer of 200-nm-sized TiO<sub>2</sub>, followed by second annealing at 450 °C for 30 min. After cooling down to 80 °C, the TiO<sub>2</sub> films were immersed into a solution of 0.3 mM of N719 dye [bis(tetrabutylammonium)cis-(diisothiocyanato)bis(2,2'-bipyridyl)-4,4' dicarboxylato] ruthenium (II), (Solaronix, Switzerland) in a mixture of acetonitrile and tertiary butyl alcohol (volume ratio is 1:1), and maintained at room temperature for 18 h to complete the sensitizer uptake. The dye-sensitized electrodes were then washed with ethanol to remove unanchored dye before use.

**Table 1**  
The preparation parameters of different Pt electrodes by integrative method.

Electrodes	Spraying times of H <sub>2</sub> PtCl <sub>6</sub> solution/times	Spraying times of F:SnO <sub>2</sub> solution/times
(2,30)Pt//iFTO	2	30
(2,45)Pt//iFTO	2	45
(2,60)Pt//iFTO	2	60
(4,30)Pt//iFTO	4	30
(4,45)Pt//iFTO	4	45
(4,60)Pt//iFTO	4	60

The DSCs were fabricated with a photoanode, a CE, and an electrolyte containing 0.1 M LiI (AR, Aladdin), 0.05 M I<sub>2</sub> (AR, TCI Shanghai), 0.5 M *tert*-4-butylpyridine (AR, TCI Shanghai) and 0.3 M 1-propyl-3-methylimidazoleiodine in 3-methoxy-propionitrile/acetonitrile (volume ratio is 1:1).

### 2.3. Characterization

X-ray diffraction (XRD) measurements were carried out on a D8 advance X-ray diffractometer (Bruker Corp., Germany). Surface morphology of the samples was observed by using JEOL JSM-6700F field emission scanning electron microscope (FESEM) at an acceleration voltage of 15 kV. The existence of platinum was examined by the X-ray photoelectric spectroscopy (ESCALAB 250Xi, Thermo Fisher Inc., USA). Platinum was dissolved off the platinized electrodes by aqua regia, and its content was determined by atomic emission spectroscopy with an axial view inductively coupled plasma spectrometer (AES-ICP). The electrochemical impedance spectroscopy (EIS) measures were conducted in the dark at room temperature using a computer-controlled electrochemical station (CHI 604D, Shanghai), with a frequency range of 10<sup>-1</sup>–10<sup>5</sup> Hz, AC amplitude of 5 mV, and bias of -0.7 V. The symmetrical dummy cells were scanned from 0.1 Hz to 10<sup>5</sup> Hz at -0.7 V bias potential. The results were analyzed with an equivalent circuit model for interpreting the characteristics of the DSSCs and spectra were fitted using Z-view software. Cyclic voltammetry (CV) was performed in a three-electrode system in an acetonitrile solution containing 0.1 M LiClO<sub>4</sub>, 10 mM LiI, 1 mM I<sub>2</sub> at a scan rate of 50 mV s<sup>-1</sup>, with a CE of Pt wire, an Ag/AgCl reference electrode and as-prepared CEs as the working electrode. The four-point probe method (Four Probes Tech, Guangzhou) was used to measure the sheet resistance of the iFTO glass.

## 3. Results and discussion

### 3.1. X-ray diffraction and X-ray photoelectric spectroscopy analysis

Fig. 2a shows the XRD patterns of the F:SnO<sub>2</sub> powder peeled off iFTO glass. The peaks appearing at 26.6°, 33.8°, 37.9° and 51.70° are attributed to the (110), (101), (200) and (211) planes of SnO<sub>2</sub> (Ravichandran et al., 2010) according to the JCPDS Card No. 41-1445. The strong and sharp peak arising at 26.6° indicates that SnO<sub>2</sub> particle has high crystallinity and the preferred orientation is along the (110) plane. The fluorine phase was not visible in the diffractogram and it was assumed to be overlapped with the SnO<sub>2</sub> peaks (Zhang et al., 2010). This is reasonable considering that the fluorine doping level is relatively small for the system. However, the existence of fluorine was successfully determined by using XPS characterization analysis.

Fig. 2b shows the wide-scan spectra of as-prepared Pt//iFTO electrode. Besides C 1s, O 1s and Sn 3d peaks, Pt 4f and F 2s peaks can also be observed. No other elemental peaks were observed, indicating the sample was pure. Fluorine element is detected, verifying that F doped SnO<sub>2</sub> is successfully synthesized. In the Fig. 2c, two peaks of Sn 3d<sub>5/2</sub> and Sn 3d<sub>3/2</sub> at the position of 486.7 eV and 495.2 eV are consistent with the binding energy of SnO<sub>2</sub>, the binding energy of 487.7 eV is attributed to Sn–F bond. In the spectra of Pt 4f region (Fig. 2d), it has well separated spin-orbit components. The peaks appearing at 71.2 eV and 74.5 eV are corresponding to Pt 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub> of metal Pt separately. And the Δ value is 3.3 eV which is pretty close to that of metal Pt (Δ<sub>metal</sub> = 3.35 eV). The peaks attributed to Pt(+4) which should be located at 75–76 eV are not observed, indicating that H<sub>2</sub>PtCl<sub>6</sub> are completely pyrolysis into Pt(0). In brief, Pt(0) was undoubtedly coated on iFTO glass.

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