Recombination Reduction in Dye-Sensitized Solar Cells by Screen-Printed TiO_2 Underlayers *

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In dye-sensitized solar cells (DSSCs), the TiO_2 underlayer can block the electron recombination at the FTO (fluorine doped SnO_2) glass/electrolyte interface. This underlayer was traditionally prepared by spray-pyrolysis or spin coating. In this study, we develop an alternative method based on screen-printing. The quality of the screen-printed underlayers is characterized by SEM, XPS and the photoelectrochemistry measurements. The prepared underlayers are smooth and effective. The screen-printing technique is cheap and easy to handle and can produce films with different patterns. These advantages will facilitate applications of the screen-printed underlayer.

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The dye-sensitized solar cell (DSSC) is a new type of photoelectrochemical cell. It has received considerable attention over the past decade because of its high light-to-electricity conversion efficiency, relatively easy fabrication procedure and low production cost.[1−3] The DSSC consists of nanocrystalline porous TiO_2 coated on the FTO (fluorine doped SnO_2) glass as an anode, a monolayer of dye molecules adsorbed on the nanocrystalline TiO_2 surface, an electrolyte containing I_3^-/I redox coupler, and a platinum cathode. In this cell, the output photocurrent comes from the velocity difference between the electron injecting from dye to TiO_2 and the photoelectron recombination in the anode with I_3^- or oxidized dye. The lower the velocity of the photoelectron recombination, the better the photovoltaic performance of DSSC is. Thus the photoelectron recombination is one of the key factors to determine the DSSC performance.

The main recombination in DSSCs is that the photoelectrons in the anode recombine with the I_3^- ions in the electrolyte. For the porous nature of the nanocrystalline TiO_2 layer, the FTO glass cannot be separated from the electrolyte by the nanocrystalline TiO_2 layer. The connection between the FTO and the electrolyte is an important recombination route. To reduce this kind of recombination, separating the FTO from the electrolyte is needed. Normally a thin TiO_2 underlayer between the FTO and the nanocrystalline porous TiO_2 layer is used for this purpose.

In the solid electrolyte DSSCs this underlayer has been proven to be necessary.[4−6] Recently, many researcher have focused on the underlayer mechanism[6−8] and its effects on the photovoltaic performance[9−12] of the liquid electrolyte DSSCs. Some recent studies have revealed that adding a TiO_2 underlayer between the FTO glass and the TiO_2 nanocrystalline porous layer can improve the performance of the liquid electrolyte DSSCs.[10,12] Cameron and Peter suggested that much lower interchange current density of the TiO_2 underlayer/electrolyte interface than that of the FTO glass/electrolyte interface is the reason why the TiO_2 underlayer can reduce the back reaction at the FTO/electrolyte interface.[8] Therefore, it is obvious that high quality underlayers are useful to further improve the DSSC performance.

The underlayer should completely cover the FTO glass surface for the effective separation and it should be sufficiently thin for collecting electrons effectively. The coating cost must be low to hold the low cost of the DSSCs. There are several methods for preparing the TiO_2 underlayer: for example, spray-pyrolysis,[13] spin coating,[6] dip coating,[14] and sputtering.[15] In this study, we develop an alternative method based on screen-printing. In the DSSC fabrication, screen-printing is used to prepare a thick porous TiO_2 layer (several micrometres in thickness). To our knowledge, there have been no reports on using screen-printing to prepare thin TiO_2 underlayer (less than 100 nanometres in thickness). Producing a large-area DSSC needs preparation of the underlayers with a large area and different patterns. These are just the characteristics of the screen-printing technique. Thus this screen-

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printed underlayer method has the potential to be used in producing large DSSC modules.

The TiO_2 underlayer was obtained by the screen-printing method. Its paste was prepared as follows: 0.3 ml of tetra-isopropyl-orthotitanate and 0.7 g of ethyl cellulose were added into 16 mL of α-terpineol. Then the mixture was stirred at 50°C. After all of the solute dissolved, the paste was cooled down to room temperature. After screen-printed it on the cleaned FTO glass, the glass was dried at 70°C for 30 min and then was fired at 450°C for 30 min. The prepared thin TiO_2 underlayer was measured to be 30 nm thick by an atomic profiler (AMBLOS Technology XP-2).

According to the literature,[16] anodes of DSSCs were fabricated by screen-printing the P25 paste onto the cleaned FTO glass and FTO glass pre-coated with screen-printed TiO_2 underlayer respectively. Then the anodes were fired at 450°C for 30 min. The thickness of the nanocrystalline TiO_2 layer was about 10 μm. After being heated at 120°C for 30 min, the anodes were immersed in the 3 mM N3 dye ($RuL_2(NCS)_2{\cdot}2H_2O$, L = 2,2′-bipyridyl-4,4′-dicarboxylic acid) in anhydrous ethanol solution for 15 h. Then the anodes were washed with anhydrous ethanol and dried under vacuum. The cathode of the DSSC was the FTO glass coated with a layer of sputtered Pt. The electrolyte was composed of 0.6 M methylhexylimidazolium iodide, 0.05 M iodine, 0.1 M LiI, and 0.5 M tert-butylpyridine in 3-methoxypropionitrile.

The underlayer's morphology and composition were characterized by SEM and XPS. The SEM images were obtained by an XL30 S-FEG scanning electron microscope. The XPS spectra was performed on an MKII XPS spectrometer.

Two photoelectrochemistry measurements were used for evaluated the functions of the underlayer. A solar light simulator (Oriel, 91192) was used to give an illumination of 100 mW/cm^2 (AM 1.5) on the surface of the solar cells. The incident light intensity was measured with a radiant power/energy meter (Oriel, 70260) before each experiment. The photovoltaic performance measurements under these conditions were recorded by the potentiostat (Princeton Applied Research, Model 263A). The photovoltage decay measurements were carried out according to the literature.[17] After the cell was illuminated to a steady voltage by the solar light simulator (Oriel, 91192), the light was turned off by a shutter. Then the voltage decay of the cell was recorded by the potentiostat (Princeton Applied Research, Model 263A).

Figures 1(a) and 1(b) present the SEM images of the FTO glass without screen-printed TiO_2 underlayer and the FTO glass with screen-printed TiO_2 underlayer, respectively. In Fig. 1(a), we can find that the FTO layer is composed of F-doped SnO_2 crystalline particles which are about 200 nm. In Fig. 1(b), the underlayer has completely covered the FTO surface and the FTO surface has been smoothed.

Figure 2 shows the XPS spectra of this underlayer on the FTO glass. In Fig. 2, the peaks are assigned to Ti and O, and [O]/[Ti]=1.93. Thus the underlayer should be TiO_2. Because no Sn and F peaks have been detected, the TiO_2 underlayer has completely covered the FTO glass.

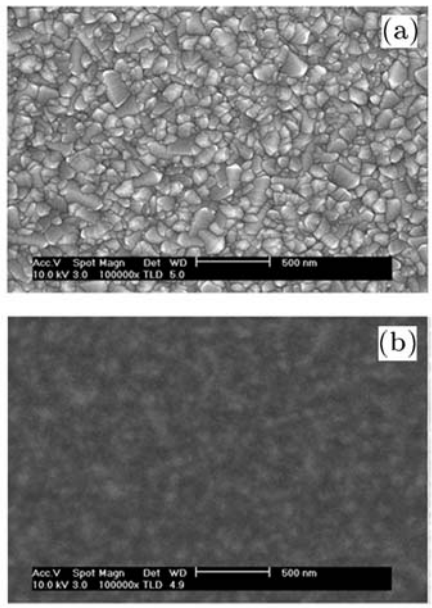

Fig. 1. SEM images of the FTO glass surface: (a) without screen-printed TiO_2 underlayer, (b) with screen-printed TiO_2 underlayer.

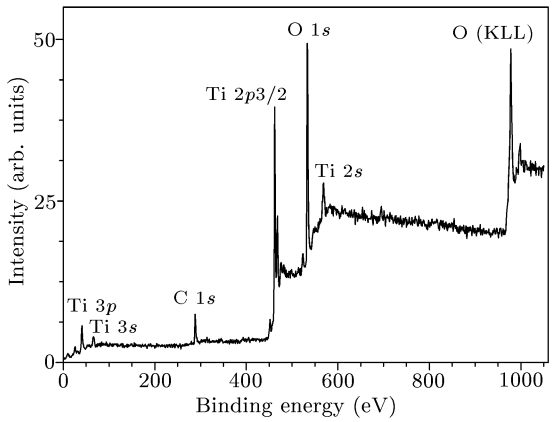

Fig. 2. XPS spectra of the TiO_2 underlayer on the FTO glass.

Figure 3 depicts the photovoltage decay of DSSCs with and without the TiO_2 underlayer. Zaban *et al.* proposed that the velocity of photovoltage decay is inversely in proportion to the lifetime of the photoelectron in the DSSC, and the lifetime of the photo-

electron is inversely in proportion to the velocity of recombination.[17] Thus the recombination velocity of photoelectron should be in proportion to the velocity of photovoltage decay. In Fig. 3, the photovoltage decay velocity of the DSSC with this underlayer is much lower than that of the DSSC without this underlayer. This phenomenon implies that the screen-printed underlayer is effective and the recombination has been reduced.

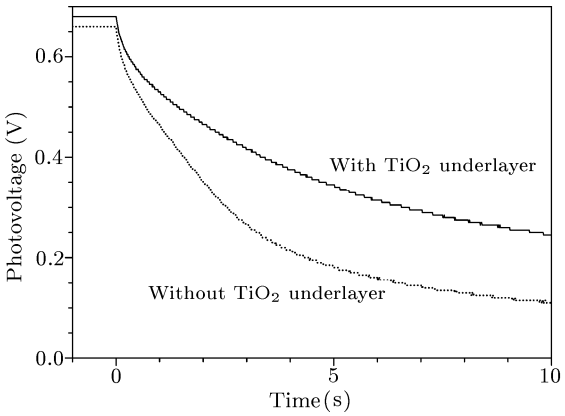

Fig. 3. Photovoltage decay of the DSSCs with the TiO_2 underlayers (solid line) and without the TiO_2 underlayers (dotted line).

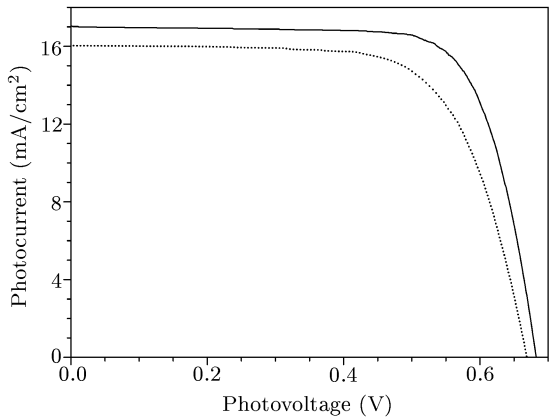

Fig. 4. Photovoltaic performance of the DSSCs with TiO_2 underlayer (solid line, the open circuit voltage U_{oc} = 684 mV, the short circuit current I_{sc} = 16.9 mA/cm^2, fill factor 0.74, photo-electrical *efficiency* 8.5%) and without TiO_2 underlayer (dotted line, U_{oc} = 669 mV, I_{sc} = 16.0 mA/cm^2, fill factor 0.69, *efficiency* 7.4%). The active area of the cells is 0.15 cm^2.

We measured the photovoltaic performance of the DSSCs with and without this underlayer. As shown in Fig. 4, the screen-printed underlayer can improve the open circuit voltage, short circuit current and fillfactor simultaneously. Thus, the photoelectrical conversion efficiency can be increased from 7.4% to 8.5%. Ito *et al.*[10] and Hore and Kern[12] reported that underlayers prepared by the spray-pyrolysis method has similar effects, indicating that the present screen-printing is as effective as spray-pyrolysis for preparing underlayers.

The increase of the DSSC photovoltaic performance can be explained by the DSSC model that we developed in the previous study.[18] In that model, reducing the recombination at FTO/electrolyte interface will increase the shunt resistance, which implies internal leakage of electrons from the FTO to the electrolyte, and the high shunt resistance leads to the high fillfactor, high short circuit photocurrent and high open circuit photovoltage.

In conclusion, we have developed an alternative method based on screen-printing to prepare TiO_2 underlayer for DSSCs. This method can prepare complete and smooth TiO_2 nanometre thin film on FTO glass. The prepared underlayer can effectively block the recombination at the FTO glass/electrolyte interface and dramatically improve the photovoltaic performance of DSSCs. Since the screen-printing technique can prepare a TiO_2 underlayer with a large area and different patterns, the screen-printed underlayer will have the potential applications in industry.

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