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Investigating the Effect of Substrate Photo-Electrode Based on Screen Method on Performance of Dye-Sensitized Solar Cells

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ABSTRACT

In this paper, we studied preparation of working films of dye-sensitized solar cells using screen printed method. The organic dye based on phenoltiazine with cyanoacrylic acid as the electron acceptor group was utilized as photosensitizer. Fluorine-doped thin oxide (FTO) coated glass is transparent and electrically conductive which is ideal for use in dye-sensitized solar cells. FTO glass was coated by screen printed method for investigating the effect of fabrication parameters. The influence of the squeegee printing angle of 37°, 55° and 65° on the dye-sensitized solar cells performance was investigated in order to assess changes in the status of the power conversion efficiency. The conversion efficiency for 37°, 55° and 65° were 2.71% and 1.96% and 1.58%, respectively. When using the FTO glass for working electrode preparation, a low squeegee angle gives a porous thick film, which is ideal for dye absorption. Prog. Color Colorants Coat. 11 (2018), 47-54© Institute for Color Science and Technology.

1. Introduction

In recent years, because of the depletion of fossil fuels and increased greenhouse gas emissions, that have resulted in the problem of global warming, the investigation and development of alternative renewable and environmentally friendly energy sources has become increasingly important [1]. In particular, solar energy has been acknowledged as a potential alternative energy resource [2]. Dye-sensitized solar cells convert sunlight directly into electricity [3]. Dye-sensitized solar cells (DSSCs) or Gratzel Cells have attracted great attentions, as they offer high energy conversion efficiencies due to their low cost and they are also environmentally friendly [4]. Although some modifications have been proposed, a DSSC typically has a sandwich structure: a dye-adsorbed porous TiO_2 film coated on the transparent-conductive- oxide (TCO) covered substrate as the working electrode, a catalytic/ conductive counter electrode and an electrolyte between two electrodes. When photons excite the TiO_2 absorbed dye molecules, the excited electrons inject into the conduction band of TiO_2 and

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the electrons are delivered to TCO through the networking of TiO_2 [5, 6]. The electrons are delivered to the counter electrode through the external loop, reducing the redox mediator in the electrolyte at the counter electrode. The reduced ion further regenerates the oxidized sensitizer and develops the complete electric loop [5, 7]. Doctor-blade technique is a customary and suitable for preparation of the photoelectrode but this method is commonly used for preparation of small area DSSC working electrodes in laboratories. For commercialization of solar cells, however, large-scale photoelectrode production method is required. One of the most reliable methods is screen printing technique [8, 9].

Tsoukleris et al. prepared nanocrystalline titanium dioxide thin films by screen printing in order to control and optimize the main step of the DSSCs fabrication process. Illumination of the cell under light power of 1000 Wm^{-2} produced a photovoltage of 820 mV and gave a photocurrent as high as 4.84 mA cm^{-2}. The fill factor of the cell was 0.47 and the energy-conversion efficiency was 1.87% [10]. Fan et al. studied the effects of the paste components on the properties of porous TiO_2 film electrodes prepared through screen-printing technique in order to efficiently control and optimize the main fabrication step of the dye-sensitized solar cells (DSSCs). The experimental results indicated that the microstructural characteristics of the printed films and the performance of the corresponding DSSCs are dependent on the paste compositions [11]. Hocevar et al. reported that a simple manufacturing process based on screen-printing is crucial for a successful commercialization of dye-sensitized solar cells (DSSCs). They developed the sol–gel based TiO_2 paste in such a way that solely a single step deposition is sufficient to realize a sponge-like structure of the layer assuring its high activity in DSSCs. The conversion efficiency of the PV mini-module with the active area of 75 cm^2 reaches 5.7% at STC [12]. Wang et al. prepared three kinds of paste by mixing TiO_2 with particle sizes of 23 and 100 nm in different proportions and screen-painted these pastes layer by layer on the conductive glass to prepare TiO_2 film [13].

In the present study, the influences of screen printing parameters on photovoltaic characteristics of the corresponding DSSCs are not fully understood. The effects of squeegee printing pressure (angle) and the screen types on the properties of working electrode and photovoltaic performance of the corresponding cells are investigated. The chemical structure of used organic dye is given in Figure 1.

2. Experimental

2.1. Materials and instrumentation

All compounds used in this study were of analytical grade unless otherwise stated. The synthesis route and full characterization of intermediates have been described previously [14, 15]. Transparent conducting oxide, FTO (F-doped SnO_2, DyeSol), TiO_2 pastes and scattering layer were purchased from Sharif Solar Co. The UV-visible spectrophotometry was performed using a Cecil 9200 double beam transmission spectrophotometer.

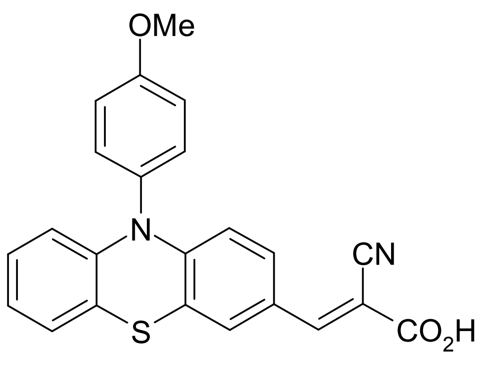

Figure 1: Chemical structure of organic dye.

2.2. Photoelectrode working electrode preparation

The TiO_2 working electrode was prepared using P200 paste. When preparing P25 pastes, the chemicals listed in Table 1 were sealed in a 250 mL milling jar together with 25 g zirconium milling balls with diameter of 2 cm. The chemicals were homogenized in a planetary ball mill rotating at 300 rpm for 2 h and the pastes were thereby obtained. The screen has an opening of 10 mm-10 mm and a thickness of 0.06 mm. A 708 rubber squeegee was used in the screen printing process. The influence of the squeegee printing angle on DSSC performance was tested using SP200 paste with the squeegee printing speed of 11 mm/s. The influence of the printing angle of 37°/55° and 65° on the dye-sensitized solar cells performance was investigated.

2.3. Dye-sensitized solar cells (DSSCs) assembly and photovoltaic characteristics of the resultant solar cells

The dye was adsorbed by dipping the coated glass in a 5×10^{-5} M ethanolic solution of the dye containing 7% 4-tert-butylpyridine and 50 mM 3α,7α-dihydroxy-5β-cholic acid (cheno) for several hours. The visible bands in the absorption spectrum of the dyes after adsorption on the nano TiO_2 film only appeared after the TiO_2 electrodes were dipped in the dye solution for at least 18 hr. The presence of 4-tert-butylpyridine and cheno is necessary to avoid surface aggregation of the sensitizer. Finally, the film was washed with an acetonitrile-ethanol 1:1 mixed solution. Acenonitrile-ethylene carbonate (v/v=1:4) containing tetrabutyl ammonium iodide (0.5 mol dm^{-3}) was used as the electrolyte. The dye-adsorbed TiO_2 electrode, the Pt counter electrode and the electrolyte solution were assembled into a sealed sandwich-type solar cell [16-19].

An action spectrum was measured under monochromatic light with a constant photon number (5×10^{15} photon cm^{-2} s^{-1}). J-V characteristics were measured under illumination with AM 1.5 simulated sun light (100 mW cm^{-2}) through a shading mast (5.0 mm×4 mm) by using a Bunko-Keiki CEP-2000 system.

3. Results and Discussion

Organic dyes based on indoline synthesized from phenothiazine in our group were used [14]. For this purpose, phenothiazine was reacted with various p-substituted bromobenzene in toluene in the presence of potassium tert-butoxide. The aldehyde components were prepared by a Vilsmeier reaction of N-substituents carbazole with phosphoryl chloride ($POCl_3$) in DMF Finally, aldehyde components were allowed to react separately with cyanoacetic acid in the presence of piperidine to give organic dye (Figure 1) [20, 21].

Table 1: The composition of the TiO_2 pastes [5].

components	quantity
Powder (g)	10.00
Ethyl cellulose (g)	0.60
Isopropyl alcohol (mL)	10.0
a-Terpineol (mL)	30.0
Titanium (IV) isopropoxide (g)	2.00
Triton X-100 (g)	1.00
PEG 20000 (g)	3.00
4-Hydroxybenzoic acid (g)	0.25
Paste viscosity (cps)	27,500

SEM images of SP200 films (5 nm) prepared at a squeegee printing velocity of 11 mm/s and a squeegee angle of 55° are shown in Figure 2. The typical thickness of the DSSC working electrode is 10–20 mm [22]. Therefore, while the working electrode prepared by the stencil screen needs one screen printing process to achieve the desired film thickness, the screen printing process has to be repeated several times to achieve the desired working electrode thickness when the stainless steel cloth screen is used [5]. The short-circuit current density J_{sc}, open-circuit voltage V_{oc}, and power conversion efficiency of solar cells with the multi-layer SP200 working electrode are shown in Table 2. The decreasing of V_{oc} is attributed to the fact that the electrons excited deeper in the working electrode have longer path to reach the front photoelectrode. The probability for the electron recombination increases, thus V_{oc} decreases with increasing the film thickness [5, 23].

Although J_{sc} is smaller, the cell with a mono-layer TP200 working electrode shows higher conversion efficiency than the cell with a four-layer SP200 working electrode. This is due to the fact that the four-layer working electrode structure experiences four printing–drying–sintering cycles. The inter-layer resistance was produced between each printing–drying–sintering cycle, causing a low fill factor and hence a low cell conversion efficiency. Nevertheless, the tandem design may be adapted to the multi-layer working electrode [5, 24]. We selected 3 layer for investigating the effect of screen printing angle.

Table 2: photovoltaic properties of mono and multi-layer working electrodes.

Layer	V_{oc} (V)	J (mAcm^{-2})	FF	η (%)
1	0.64	5.16	0.55	1.82
2	0.60	5.48	0.56	1.84
3	0.58	8.17	0.57	2.71
4	0.55	9.04	0.55	2.74

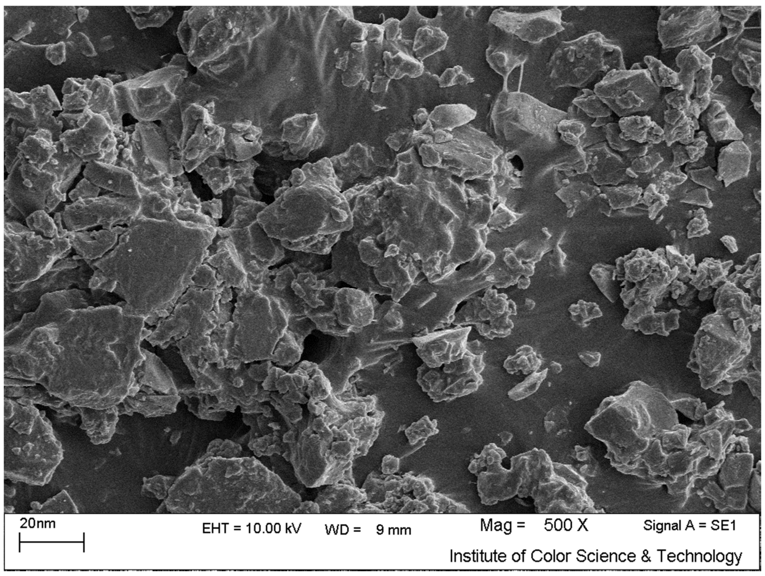

Figure 2: SEM images of SP200 films prepared at squeegee angle of 55°.

The wavelength of maximum absorption (λ_{max}) and the molar extinction coefficients (ε_{max}) for the organic dye in acetonitrile were 434 nm and 22760 $M^{-1}cm^{-1}$, respectively. The wavelength of maximum absorption of the corresponding dyes adsorbed on the TiO_2 film is listed in Table 3. The absorption peaks at around 434 nm for organic dye can be assigned to an intra-molecular charge transfer between the donor and acceptor groups [25], providing an efficient charge-separation for the excited state. Upon dye adsorption on to a photo-anode surface (TiO_2), the wavelength of maximum absorption is bathochromically shifted by 19, 17, 15 and 18 for 1, 2, 3 and 4 layer, respectively, as compared to the corresponding spectra in solution, implying that dyes adsorbed on to the TiO_2 surface contain partial J-type aggregates [26-28]. The molar extinction coefficients of organic dye in acetonitrile indicate that this dye has good light harvesting abilities [29]. The UV-Vis absorption of dye adsorption on to a photo-anode surface is depicted in Figure 3.

Dye-sensitized solar cells (DSSCs) were constructed and compared in order to clarify the relationships between the sensitizing behavior of organic dye molecules at different printing angles. A typical photocurrent–photovoltage (J–V) curve for dye-sensitized solar cells based on organic dye is depicted in Figure 4. The detailed photovoltaic parameters are also summarized in Table 4. The solar energy to electricity conversion efficiency (η) of the DSSCs is calculated from short circuit current (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (FF), and the intensity of the incident light (P_{in}) [29-31].

Table 3: Absorption properties of dyes adsorbed on the TiO_2 film.

Layer	λ_{max} (nm)	△λ
1	434	19
2	438	17
3	456	15
4	455	18

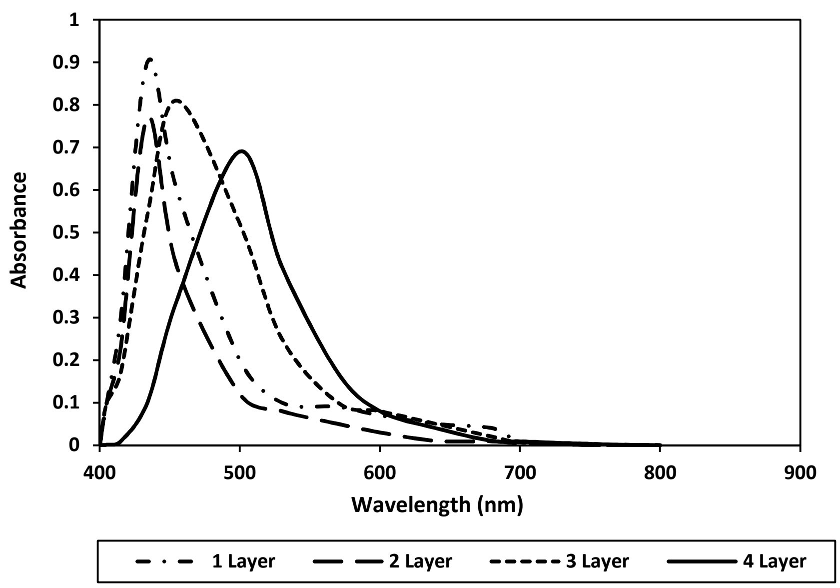

Figure 3: UV-Vis absorption of dye adsorption on to a photo-anode surface.

Table 4: Photovoltaic performance of DSSCs.

angle	V_{OC} (V)	J_{SC} (mA.cm^{-2})	FF	η (%)
37	0.58	8.17	0.57	2.71
55	0.55	6.15	0.58	1.96
65	0.52	5.17	0.59	1.58

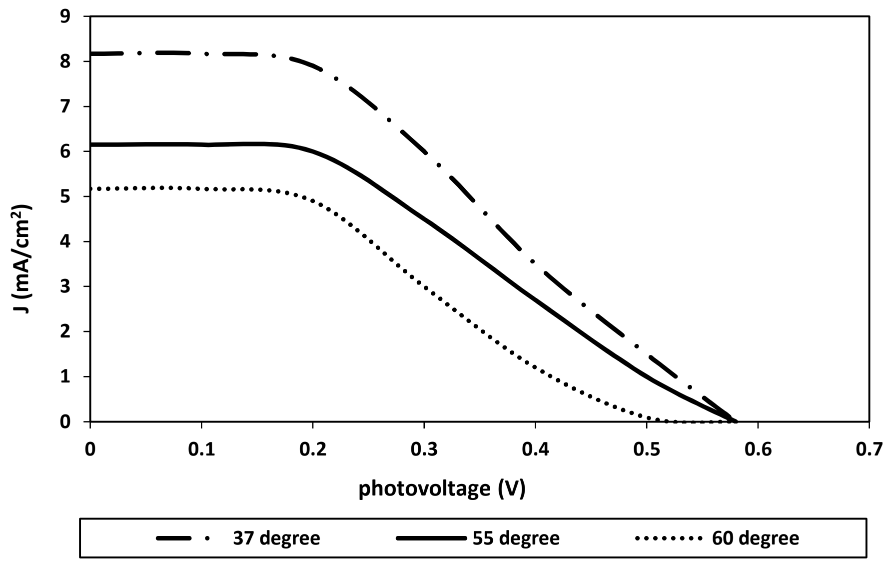

Figure 4: Current density-voltage characteristics for different angle.

According to the results shown in Table 4, under the standard global AM 1.5 solar condition, the conversion efficiencies of dye-sensitized solar cells based on indoline dye with printing angles of 37°, 55° and 60° are 2.71%, 1.96% and 1.58%, respectively. When the squeegee angle is 60°, the pressure acting on the squeegee is low [5]. The amount of the paste passing through the screen openings is limited. So, the removal of the screen after printing significantly affects the internal structure of the film, similar to film peeling mechanism [5, 32, 33]. The internal structure of the film influences the path of the excited electrons to the front transparent conductive oxide (TCO) contact. Due to the uncontrollable screen peeling mechanism, V_{oc} does not monotonically decrease with the increasing of the film thickness when the squeegee angle is as high as 60°.

4. Conclusions

The influence of the screen printing parameters on physical properties of working electrode films and photovoltaic characteristics of corresponding solar cells are studied. Since the same rubber squeegee had been used, a higher squeegee printing angle implies a smaller squeegee pressure acting on the screen. The organic dye based on phenoltiazine with cyanoacrylic acid as the electron acceptor group was utilized as photosensitizer. When using the FTO glass, a low squeegee angle and 11 mm/s speed gives a porous thick film, which is ideal for dye absorption. With a squeegee printing speed of 11 mm/s and a squeegee angle of 37°, a three-layer working electrode prepared using the stainless steel cloth screen gives a cell with the conversion efficiency of 2.71%. Spectrophotometric study of coated organic dyes on TiO_2 films showed that working electrode containing 4 layers showed bathochromic shifts compared to the working electrodes containing fewer layers. In all cases, the absorption maxima of organic dye applied on the surface of a TiO_2 film gave a bathochromic effect compared to the corresponding dye spectra in solution.

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