Engineered platinum nanoparticles via pulse electrochemical deposition for bifacially transparent and efficient full-plastic dye-sensitized solar cells

Yu-Ting Huang 1, Hyeonseok Lee 1, Wen-Di Li **, Shien-Ping Feng 

Department of Mechanical Engineering, The University of Hong Kong, Pokfulam, Hong Kong

HIGHLIGHTS

- A highly transparent, flexible, and efficient PtNPs CE is developed via PED.
- The front & rear-side PCE of full-plastic DSSCs with PtNPs CE reached 5.72% and 5%.
- >80% of the PCE under 0.01sun, enlightening the potential to indoor application.

ABSTRACT

In this work, a highly transparent, flexible, and efficient Pt counter electrode (CE) via pulse-electrodeposition (PED) is developed for bifacial and flexible dye-sensitized solar cells (DSSCs). The CEs fabricated with Pt nanoparticles by PED technique (PED-PtNPs) is favourable for large-scale production and cost-effective process because the uniform distribution of PtNPs with the size less than 30 nm leads a high catalytic ability, high transmittance, and less Pt loading. The front-side and rear-side power conversion efficiency of full-plastic DSSCs with PED-PtNPs are 5.72% and 5%, respectively. This is 11–18% higher performance than those from the previously reported methods and ~90% of the PCE from front illumination is produced from rear illumination. Moreover, our full-plastic DSSCs produce >80% of the PCE under 1sun illumination regardless of illumination direction and reduction in illuminated light intensity, enlightening the potential to indoor application.

1. Introduction

The interest in the field of energy-harvesting systems from flexible solar cells have attracted substantial attention for a variety of applications. The great promising characteristics includes lightweight, bendability, and portability [1–5]. Plastic substrates based and flexible dye-sensitized solar cells (DSSCs) are considered promising since their architecture are simple, low-cost, suitable for large-scale production, and applicable as portable devices that can convert ambient energy to useable electrical power [1,6–8]. Considerable research have been carried out to improve the overall performance of flexible DSSCs but further research progresses are easily hindered by their intrinsic properties of plastic substrate such as incompatibility with high temperature process. Therefore, the power conversion efficiency (PCE) is generally lower than that of rigid DSSCs and challenging to obtain higher PCE [9,10]. One promising solution could be the bifacial DSSCs, which is conceived for utilizing the incident light from both front and rear illumination simultaneously, allowing more efficient light harvesting [11–14]. With the bifacial structure, DSSCs can also have wide-range applications in electricity-generation from abundant dim-light energy that provides the low levels of illumination compared with outdoor deployments [15–17].

In such device architecture, an efficiently transparent and plastic counter electrode (CE) is required to utilize the rear-side illumination and flexibility. In addition, the expensive Pt materials that conventionally used for CEs also become a hurdle for lowering production cost. Therefore, the development of low-cost, flexible, and transparent CEs for bifacial DSSCs is the key challenge for the commercial realization such as roll-to-roll process. The dominant material currently for platinizing on plastic conductive CE is indium tin oxide (ITO) coated poly(ethylene naphthalate) (PEN) or poly(ethylene terephthalate) (PET) substrates prepared by expensive vacuum processes such as sputtering [18,19] and atomic layer deposition [20]. In order to overcome the drawbacks,
alternative techniques have been developed by employing dipping [21], spray coating [22], electrochemical deposition [23–25], and chemical reduction [26]. One of the successful demonstration for the full plastic and flexible DSSCs was carried by using a two-step dip-coating process for depositing polyvinylpyrrolidone-capped Pt nanoparticles (PVP-nPt) on a plastic substrate, exhibiting 6% of PCE [27,28]. Most of these techniques are favourable to achieve low-cost process but limit the performance of bifacial DSSCs due to the unnecessary heavy loading of Pt on the entire substrate, causing an inevitable extra loading of expensive Pt material. Furthermore, the optical transmittance of substrate will be reduced for the heavy loaded Pt materials, leading to a poor efficiency through the rear CE side. In particular, even for the research done with PVP-nPt above, it shows 6% of high performance but only the front-side illumination was applicable and the loss of its light transmittance was approximately 10% [28]. Although recent efforts have been made on developing Pt-free CEs in DSSCs, their conductivity, catalytic activity, and chemical stability are still inferior compared to those of Pt [29–32]. In addition, the deposition of efficient PtNPs on plastic substrates was demonstrated via several different electrochemical deposition wave forms but the average particles sizes of Pt are still large to obtain high transparency [23–25,33–36].

To date, different PV cells, such as DSSCs, organic photovoltaic solar cells, and amorphous silicon solar cells have been tested as dim-light energy harvesters with artificial light at intensities expected of indoor conditions, which is a factor of ~10^4 less light intensity levels than the 100 mW/cm^2 intensity of 1-sun illumination, making indoor applications challenging [6,7,37]. Among these harvesters, DSSCs present a higher power outputs because the photo-excited response by complex dye such as ruthenium based N719 and N3 is more suitable in absorbing indoor light such as fluorescent, incandescent, and LED lights that extend in the wavelength lower than 800 nm.

In this paper, we experimentally demonstrate and characterize low cost and full-plastic solar cells with transparent PtNPs CEs via the pulse electrochemical deposition (PED). This facile, scalable, and solution-based process enables the deposition of PtNPs to be tuned by the waveform on both rigid and plastic substrates without considerably reducing its optical transparency. By integrating the CEs with the liquid electrolyte and dye-sensitized TiO_2 photoanodes, the resultant device can generate electricity from both illumination directions, front and rear illumination, efficiently. The fabricated flexible and bifacial DSSCs exhibited remarkable PCEs of 5.72% from front-side illumination and ~90% of that PCE is produced from rear-illumination (5.00% of PCE), which is among the highest ratio in published literature, to our knowledge. In addition, the PCE of the DSSCs is kept >80% of that at 1 sun in both illumination directions and under reduced light intensity.

2. Experimental

2.1. Deposition of Pt-NPs

ITO glass (20 Ω/□, 1.1 mm, University Wafer) and FTO glass (8.3 Ω/□, 3.1 mm, Nippon Sheet Glass) was immersed in 4% glass substrate cleaner (PK-LCG545, Parker Corp.) for 30 min, using sonication to clean the surface followed by deionized water to rinse. The ITO-PEN (125 μm, ≈13 Ω/□) was first cleaned using acetone under sonication for 10 min and then subjected to UV ozone treatment. The Pt-NPs substrates were stacked face-to-face and sealed with a 30 μm-thick thermal-plastic Surlyn spacer (SX170-25, Solakor). A proper amount of liquid electrolyte for ITO-PEN anode that contains 0.4 M TBAI (tetrabutylammonium iodide, Sigma), 0.3 M NMB (N-methylbenzimidazole, Sigma), 0.4 M I_3 (Iodine, Sigma), and 0.04 M I_2/I_3 (iodine, Sigma) in mixture of ACN (Acetonitrile) and 3-MPN (3-methoxypropionitrile, Sigma) (1:1, v/v) was separately injected into the gap between the two electrodes.

2.2. DSSCs assembly

The ITO-PEN (125 μm, ≈13 Ω/sq, transmittance > 80%) was first cleaned as above mentioned and then subjected to UV ozone treatment to increase the wettability and to improve the adhesion between low-temperature TiO_2 paste and substrate. The mesoporous and binder-free TiO_2 containing particle size 50 nm and 400 nm was then coated on ITO-PEN by doctor-blade method to reach TiO_2 thickness of 7 μm. The wet film was followed by drying process at 70 °C to improve particles necking. In order to further eliminate water, the film was then heated at 120–150 °C. The TiO_2-coated film was sensitized by Ru complex dye, N719 (dyesol) ethanol solution at room temperature in a 0.4 mM dye solution for 4 h to complete the dye impregnation. The effective area of the TiO_2 photoanode was 0.23 cm^2. The dye-adsorbed photoanode and the Pt-NPs substrates were stacked face-to-face and sealed with a 30 μm-thick thermal-plastic Surlyn spacer (SX170-25, Solakor). A proper amount of liquid electrolyte for ITO-PEN anode that contains 0.4 M TBAI (tetrabutylammonium iodide, Sigma), 0.3 M NMB (N-methylbenzimidazole, Sigma), 0.4 M I_3 (Iodine, Acros), and 0.04 M I_2/I_3 (iodine, Sigma) in mixture of ACN (Acetonitrile) and 3-MPN (3-methoxypropionitrile, Sigma) (1:1, v/v) was separately injected into the gap between the two electrodes.

2.3. Electrochemical and DSSC characterization

The morphologies of samples were characterized by a field-emission scanning electron microscope (Hitachi S-4800, Japan). Optical transmission spectra was measured by a UV–Vis spectrometer (PerkinElmer Lambda 25, USA). For electrochemical durability evaluation, cyclic voltammetry (CV) was conducted with PtNPs CEs (1.0 cm^2), Pt wire (F1403, 0.3 mm), and Pt plate (1 cm^2) served as working electrode, reference electrode and counter electrode, respectively. The electrolyte for CV test contained 50 mM LiI, 10 mM I_2, and 500 mM LiClO_4 in 3-MPN. The scan rate of the CV test was 5 mV/s. The Pt-loading-dependent catalytic activity toward tri-iodide reduction were measured by electrochemical impedance spectroscopy (EIS, Autolab PGSTAT320 N) with frequencies ranging from between 10^{-1}–10^{4} Hz with 10 mV amplitude in a symmetric cell. The photocurrent-voltage (J-V) curves of DSSCs were recorded with a computer-controlled digital source meter (Keithley 2400) under a standard solar simulator (Peccell, PEC-L01) of 1 sun illumination (AM 1.5G, 100 mWcm^{-2}) and different light intensities.

3. Result and discussion

3.1. Characterization of optimized PED Pt-NPs CE

For the realization of flexible and bifacial DSSCs, the device is required to be fabricated on flexible and transparent substrates such as ITO-PEN and ITO-PET for both dye-adsorbed TiO_2 photoanode and Pt CE. Here, Pt-coated CEs are prepared from a commercial and highly transparent ITO-PEN (sheet resistance = 12 Ω/□) via PED method. The potential is applied in pulse waveform during PED, which is being switched between the onset-potential (E_1) and a higher over-potential (E_2) as described in the inset of Fig. 1b. Fig. 1c shows the surface morphologies of Pt-deposited CEs via PED on various substrates. The deposited PtNPs were uniformly distributed on the substrates with average diameter of less than 30 nm regardless of the kind of substrates. No significant decrease in the transmittance at the selected wavelength of 550 nm until first 100 cycles of PED, the transmittance decreases as more than 100 PED cycles are carried out. This is influenced by the amount of Pt NPs loaded on the substrates since less number of PED cycles deposits widely dispersed and less loaded Pt NPs on the substrate.
than that of FTO or ITO glasses, respectively. ITO-PEN shows even higher or comparable transmittance at the visible to the near-infrared (400 nm).

Although ITO-PEN show relatively narrower range of wavelength for the transmittance owing to the optical property of the substrates themselves, the narrower range of wavelength would not be essential factor for limiting the performance of the solar cells because the dye sensitizer in DSSCs largely absorbs the wavelengths of light ranging from the visible to the near-infrared (400 nm–800 nm). Moreover, Pt-coated ITO-PEN shows even higher or comparable transmittance at >400 nm than that of FTO or ITO glasses, respectively.

The electro-catalytic activity toward \( \text{I}_3^- / \text{I}_2 \) redox reaction of PtNP CEs through PED was investigated by both CV scan and EIS measurement. The pair of anodic and cathodic peaks current density from CV scan is the reaction of interest and used to evaluate the electrochemical properties in range of –0.4 V–0.4 V versus the Ag/AgCl reference electrode, as shown in Fig. 2a. The higher the peak current value, more active surface area of PtNPs clusters formed during PED. In this view, it is expected that ITO-PEN sample possess relatively more active surface area than ITO-glass but less than FTO-glass samples. EIS measurements were further executed to evaluate the performance of the PtNPs CE using a symmetric cell. Nyquist plots shown in Fig. 2b represent the interfacial processes with three distinguishable impedance features. From high to low frequency, the three impedance features represent series resistance (Rs), charge transfer resistance (Rct), and Nernst diffusion resistance (Rd), respectively. The corresponding equivalent circuit is present in the inset of Fig. 2b and the best-fit values are summarized in Table 1. The Rs is mainly related to the intrinsic conductivity of substrate, which results in 9.92 Ω cm², 21.83 Ω cm², and 20.45 Ω cm² for FTO-glass, ITO-glass, and ITO-PEN, respectively. At the optimized loading, Rct of FTO-glass (11.33 Ω cm²) and ITO-PEN (17.88 Ω cm²) exhibited lower value compared to that of ITO-glass (59.74 Ω cm²). This corresponds well to the results from CV in Fig. 2a, supporting that electrochemical properties are dependent on the Pt loading and/or the density of Pt films. The characteristic frequency (ω) reflected from Rct, indicating the improved electro-catalytic activity is further manifested by a comparable ω in FTO-glass (1.4 kHz) and ITO-PEN (0.7 kHz). Furthermore, Fig. 2c shows the decreasing Rct with increasing number of PED cycles. Increase in PED cycles leads a significant decrease of Rct from 36.3 Ω cm² (50 cycles) to 2.8 Ω cm² (300 cycles). In contrast to this, loaded charge through the Pt CEs shows opposite trend to Rct. The charges increase as the PED cycles increase. This means the charges can be easily transferred through the CE/electrolyte interface as the PtNPs are coated with more PED cycles. This is also related to the finding above that higher number of PED cycles makes larger amount of Pt particles to be deposited and provide more surface area of the Pt CEs, resulting in higher electrochemical performance. Moreover, the performance of Pt-deposited through PED is stable for more than 150 CV cycles as shown in Fig. 2d. Therefore, 100 cycles of PED process on ITO-PEN is most suitable for making highly transparent, flexible, and efficient Pt NP CEs because the CEs possess minimum Rct without any reduction in transmittance and this is advantageous in bifacial system for maximum use of light energy.

### 3.2. Photovoltaic performance of bifacial DSSCs using PED Pt-NPs CEs

PtNPs CEs through 100 PED cycles were prepared for the fabrication of DSSCs. Current density-voltage (J-V) characteristic of the DSSCs was firstly tested using standard TiO2 photoanode fabricated on FTO glasses with FTO-glass, ITO-glass, and ITO-PEN CEs. Fig. 3 and Table 2 represent...
the J-V curves of these DSSCs compared by light illumination from both sides. Under front (rear) illumination, DSSCs with PtNPs-FTO glass exhibited a \( J_{sc} \) of 17.65 (13.32) mA cm\(^{-2}\), a \( V_{oc} \) of 0.74 (0.74) V, and a FF of 64 (67) %, resulting in a PCE of 8.32 (6.52) %. DSSCs with PtNPs-ITO glass exhibited a \( J_{sc} \) of 17.32 (13.03) mA cm\(^{-2}\), a \( V_{oc} \) of 0.74 (0.74) V, and a FF of 56 (66) %, resulting in a PCE of 7.32 (6.37) %. DSSCs with PtNPs-ITO PEN exhibited a \( J_{sc} \) of 17.24 (13.74) mA cm\(^{-2}\), a \( V_{oc} \) of 0.72 (0.73) V, and a FF of 60 (68) %, resulting in a PCE of 7.62 (6.83) %. The performance itself of the DSSCs with Pt-coated ITO-PEN CEs is comparable to those incorporating other CEs. In addition, the conversion efficiency from rear illumination was achieved more than 90% of the conversion efficiency from front illumination, indicating this is highly efficient bifacial structure. This is attributed to the combination of the excellent transmittance and moderate level of electrochemical performance by Pt-coated ITO PEN CEs.

Fully flexible and bifacial DSSCs were demonstrated using ITO-PEN for both CE and photoanode, schematic diagram as shown in Fig. 4. As a comparison, a solution-based process of PVP-PtNPs-coated ITO-PEN CE was fabricated, which the substrate was fully covered with particles due to non-selectable deposition. Under front (rear) illumination, the device with PED PtNPs CE exhibited a \( J_{sc} \) of 11.31 (9.56) mA cm\(^{-2}\), a \( V_{oc} \) of 0.74 (0.74) V, and a FF of 60 (68) %, resulting in a PCE of 7.32 (6.37) %.

**Table 1**

<table>
<thead>
<tr>
<th>Dummy cell</th>
<th>Sheet Resistance (( \Omega/\square ))</th>
<th>( R_s(\Omega) )</th>
<th>( R_{ct}(\Omega) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtNPs-FTO glass</td>
<td>8.36</td>
<td>9.92</td>
<td>11.33</td>
</tr>
<tr>
<td>PtNPs-ITO glass</td>
<td>17.56</td>
<td>21.83</td>
<td>59.74</td>
</tr>
<tr>
<td>PtNPs-ITO PEN</td>
<td>14.13</td>
<td>20.45</td>
<td>17.88</td>
</tr>
</tbody>
</table>

**Fig. 2.** Electrochemical characterization of Pt-NPs cathode (a) Cyclic Voltammograms plots for various PtNPs-coated CEs (b) Nyquist plot for different substrates. The inset shows the equivalent circuit of dummy cell (c) Varied \( R_{ct} \) by the number of electro-deposition cycles (d) Cyclic Voltammograms plots for durability test from 10 to 150 cycles.

**Fig. 3.** J-V curves for the front and rear side illumination. All TiO\(_2\) photoanodes were prepared through standard process on FTO glasses.
of 0.72 (0.72) V, and a FF of 70 (73) %, resulting in a PCE of 5.72 (5.00) %, which is clearly improved from that of 5.08 (4.02) % PCE as achieved on the DSSC with PVP-PtNPs-coated ITO-PEN CE (Summarized in Table 3). This achievement is the best performance reported up to now in the flexible and bifacial structure of DSSCs. Moreover, The PCE from rear illumination of the full-plastic DSSCs in Fig. 4 a also reached to ~90% of the PCE from front illumination while the DSSCs with PVP-PtNPs-ITO-PEN show <80% of PCE from rear illumination.

The applicability as indoor application was examined for the flexible and bifacial DSSCs through PED as shown in Fig. 5. The bifacial DSSCs were measured in the range of different light intensity illumination (1sun to 0.01sun) under both front and rear and the photovoltaic parameters were presented in normalized form. The photocurrent density is decreased with the decrease in light intensity owing to the proportionality of the photocurrent on the light intensity, but the conversion efficiency is kept almost constant. The DSSCs produced >80% of the PCE at 1 sun from all lower intensities than 1 sun and from bifacial illuminations. This is because the DSSCs can sustain Voc and FF with lower intensity of light owing to excellent PtNPs CEs through PED. This suggests the DSSCs through PED can be a promising candidate for indoor application under lower light intensity.

4. Conclusions

In summary, a highly flexible and transparent CE was fabricated by a facile control and low-cost PED method for bifacial and flexible DSSCs. This PtNPs decorated CEs via PED provide the remarkable advantages such as superior optoelectronic performances and high electro-catalytic activity for triiodide reduction. Further, by minimizing the loading of PtNPs to avoid the wastage of expensive PtNPs, synergetic advantages of PtNPs CEs enable superior performance for bifacial DSSCs. The fabricated flexible and bifacial DSSCs employing TiO2-ITO-PEN as photoanode and the PtNPs ITO-PEN as a CE exhibited remarkable PCEs of 5.72% (front-side illumination) and 5.00% (rear-side illumination). The front-to-rear PCE ratio of our bifacial DSSC approaches ~90%, which is among the highest performance in published literature. The performance of this bifacial DSSCs measured in the range of different light intensity illumination (1sun to 0.01sun) sustained Voc and FF with lower intensity of light, producing >80% of the PCE at 1 sun from all lower intensities than 1 sun and from bifacial illuminations. These auspicious results show the great potential of this excellent PtNPs ITO-PEN CEs through PED for easy scaling up, commercialization in low cost, and efficient indoor application of flexible DSSCs.

Table 2
Photovoltaic performance of DSSCs using rigid TiO2-FTO as photoanode.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Illumination</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2-FTO/PtNPs-FTO</td>
<td>Front</td>
<td>17.65</td>
<td>0.73</td>
<td>0.64</td>
<td>8.32</td>
</tr>
<tr>
<td>glass</td>
<td>Back</td>
<td>13.32</td>
<td>0.74</td>
<td>0.67</td>
<td>6.52</td>
</tr>
<tr>
<td>TiO2-FTO/PtNPs-ITO</td>
<td>Front</td>
<td>17.32</td>
<td>0.74</td>
<td>0.56</td>
<td>7.32</td>
</tr>
<tr>
<td>glass</td>
<td>Back</td>
<td>13.03</td>
<td>0.74</td>
<td>0.66</td>
<td>6.57</td>
</tr>
<tr>
<td>TiO2-FTO/PtNPs-ITO</td>
<td>Front</td>
<td>17.24</td>
<td>0.72</td>
<td>0.60</td>
<td>7.62</td>
</tr>
<tr>
<td>PEN</td>
<td>Back</td>
<td>13.74</td>
<td>0.73</td>
<td>0.68</td>
<td>6.83</td>
</tr>
</tbody>
</table>

Table 3
Photovoltaic performance of full-plastic DSSCs.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Illumination</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2-FTO-PEN/PtNPs-ITO</td>
<td>Front</td>
<td>11.31</td>
<td>0.72</td>
<td>0.70</td>
<td>5.72</td>
</tr>
<tr>
<td>ITO-PEN</td>
<td>Back</td>
<td>9.56</td>
<td>0.72</td>
<td>0.73</td>
<td>5.00</td>
</tr>
<tr>
<td>TiO2-FTO-PEN/PVP-PtNPs-ITO</td>
<td>Front</td>
<td>10.09</td>
<td>0.71</td>
<td>0.71</td>
<td>5.08</td>
</tr>
<tr>
<td>ITO-PEN</td>
<td>Back</td>
<td>7.89</td>
<td>0.71</td>
<td>0.72</td>
<td>4.02</td>
</tr>
</tbody>
</table>

Fig. 4. (a) J-V curves for the front and rear side illumination for full plastic DSSCs incorporating PtNP-coated ITO PEN CEs. (b) Large area of flexible DSSC.

Fig. 5. Photovoltaic performance of full-plastic DSSCs with PtNPs-coated CEs at different levels of light-intensity Illumination: (a) Jsc, (b) Voc, (c) FF, and (d) PCE.
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Conflicts of interest

No conflict of interest was reported by the authors.

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