Study of Pt nanoparticles with conductive PEDOT:PSS as an effective replacement for Pt counter-electrodes in DSSC.

Veeramol Vailikhit¹, Pojchamarn Kleebthong¹ and Kunlatida Suwannaput¹

ABSTRACT

The use of laboratory synthesised Pt nanoparticles, produced using two variations of the ethylene glycol reduction method, in combination with the conductive polymer PEDOT:PSS as counter-electrodes in dye sensitised solar cells (DSSC) was investigated. It was found that mixing nanoparticles with the polymer and spin-coating FTO glass in one step resulted in aggregation of the Pt particles and sinking of the particles in the polymer. This reduced the catalytic properties of Pt. However, coating the FTO glass in two steps with the polymer first and Pt nanoparticles on top resulted in an electrode with properties similar to a Pt only coated electrode.

Keywords: DSSC, PEDOT:PSS, Pt nanoparticles, counter-electrodes

Corresponding author; e-mail address: veeramol.v@ku.ac.th

¹Sustainable Chemistry Research Unit, Chemistry Department, Faculty of Liberal Arts and Science, Kasetsart University, Kamphaeng Saen Campus, Kamphaeng Saen, Nakhon Pathom 73140

¹หน่วยวิจัยเคมีแบบยั่งยืน โครงการจัดตั้งสายวิชเคมี คณะศิลปศาสตร์และวิทยาศาสตร์ มหาวิทยาลัยเกษตรศาสตร์ วิทยาเขตกำแพงแสน อ. กUALA,จ. นนทบุรี 73140

440
Introduction

In the field of renewable energy production, solar cells are seen as highly practical devices due to their relatively simple construction and direct conversion of sunlight energy to electrical energy. The traditional silicon based solar cells, however, are rather expensive to produce due to the need for highly refined silicon. Dye sensitised solar cells (DSSC) are considered to be a useful and cheaper alternative as they do not need high temperatures for fabrication, nor as highly refined materials (O’Regan et al., 1991).

DSSCs still require a few expensive materials in their construction, such as platinum, ruthenium-based dyes, and transparent conductive oxide glasses (fluorine-doped tin oxide, FTO, glass for example). Much research work is based on finding cheaper alternatives to these materials. This present work investigates the efficiency of DSSCs with the relatively expensive Pt on FTO glass counter-electrode replaced by Pt nanoparticles and a layer of conductive polymer, PEDOT:PSS (Chang et al., 2011).

Reported work has shown that the combination of Pt/PEDOT:PSS works as efficiently on bare glass as on FTO glass. This allows one expensive inorganic component to be replaced by cheaper organic polymer. However, in this current work, only FTO glass has been used for consistency. Rather, the focus of the work has been on synthesis of Pt nanoparticles and nanostructure by two different ethylene glycol reduction methods, and on how incorporation of Pt in the polymer affects the counter-electrode properties. It also looks at spin-coating the Pt onto a layer of polymer and its effects.

The electrical properties of the counter-electrodes alone and as part of an actual DSSC were determined. Also SEM was used to investigate the surface morphology of the electrodes.

Experimental

Materials and reagents

Chloroplatinic acids (H₂PtCl₆·6H₂O, 99.9% and 98.5%, Wako Pure Chemicals Industries) were used as the metal precursor for the synthesis of Pt nanoparticles in the poly(vinyl pyrrolidone) (PVP)-free polyol method and double layer Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS):Pt nanostructured platinum film. PEDOT: PSS aqueous solution (CLEVIOS P, 1.2-1.4 wt% dispersed in water) was obtained from Heraeus Clevios GmbH. Ethylene glycol (99.5%, Wako Pure Chemicals Industries) was used as a solvent and reducing agent.

Fluorine-doped tin oxide (FTO) conductive substrate (~20Ωcm², 1.8mm thick, Asahi), commercially available TiO₂ Japanese paste (PST-18NR, particle size ~20nm, Catalysts and
Chemicals Ind. Co. Ltd.), N719 dye (Solaronix SA), Pt paste (Platisol T/SP, Solaronix SA) and handmade iodolyte electrolyte were used to construct the dye-sensitised solar cell.

Sample preparation
Preparation of Pt nanoparticles and PEDOT:PSS with different loadings of Pt nanoparticles

At room temperature, 0.1g of H$_2$PtCl$_6$ was dissolved in 10ml MilliQ water in a glass vial. 5ml of ethylene glycol (EG) was added and the mixture immediately transferred to a round-bottom flask, pre-heated to 90°C and fitted with a cooling condenser, with vigorous stirring. The reduction reaction was allowed to proceed at this temperature for 4 hours, after which the solution was transferred to a rotary evaporator for 30 minutes at ~60°C to remove the water (Chang et al., 2011).

Specific volumes of Pt nanoparticles dispersed in EG (0.125, 0.25, 0.5, 1.0 and 1.5ml) were added to 1ml PEDOT:PSS aqueous solution at room temperature. The compositions of the final solutions were adjusted by the addition of ethylene glycol or water to give a volume ratio of 2:1 for water to EG, and were then ultrasonicated for 10 minutes, giving 6.8%, 12.7%, 22.5%, 36.7% and 46.5% w/w Pt in PEDOT:PSS respectively. These mixtures had, respectively, 0.0628%, 0.126% w/v for the first two, and 0.251 w/v Pt in solution for the final three.

A plain PEDOT:PSS counter-electrode (without Pt) was prepared using the same procedure by the addition of 0.5ml ethylene glycol to 1ml PEDOT:PSS.

Preparation of double layer PEDOT:PSS-Pt nanostructured platinum film counter-electrode

PEDOT:PSS film on FTO glass was prepared by spin-coating the PEDOT:PSS aqueous solution at 4500rpm for 45 seconds and subsequently drying at 110°C for 30 minutes. For the Pt deposition, 0.02M H$_2$PtCl$_6$ solution was prepared by dissolving H$_2$PtCl$_6$ in EG with stirring for 5 minutes. A Pt film was deposited by dropping 50μl of this solution onto FTO glass on a hot plate at 180°C. After 5 minutes, the Pt film was cooled to room temperature in air and subsequently was rinsed with ethanol three times. Finally, the Pt film was dried at 60°C for 10 minutes before use as a counter electrode (Sun et al., 2010).

Preparation of Pt nanoparticle DSSC counter-electrodes

Various counter-electrodes were prepared by separately spin-coating on FTO glass at 4500 rpm: synthesised Pt nanoparticles, commercial Pt nanoparticles, commercially available PEDOT:PSS, and the prepared homogenous mixtures of 6.8%, 12.7%, 22.5%, 36.7% and 46.5% w/w Pt in PEDOT:PSS. All were sintered at 120°C in air for 20 minutes to remove residual solvents.
Preparation of DSSC photoanode

TiO$_2$ paste was coated onto a FTO glass using the *doctor-blading* technique. The coated TiO$_2$ was dried in air and then sintered at 450°C for 30 minutes in an electric furnace. The resulting area of the TiO$_2$ was 0.25 cm$^2$. The TiO$_2$ coated glass was immersed in an acetonitrile solution of N719 dye in a petri dish for at least 24 hours.

Characterisations

Transmission electron microscopy (TEM)

The size of the nanoparticles was examined using TEM. A drop of each solution was separately placed on a copper grid and allowed air-dry. The drop-coated grid was then analysed with a JEOL 3200FS TEM.

Surface characterisations: The size of the Pt nanoparticles was confirmed using TEM, while the morphology and dispersion of the Pt nanoparticles were determined using a Field Emission Scanning Electron Microscope (FE-SEM; JEOL Ltd., JSM-6700F).

Photovoltaic performance test of DSSC: Photovoltaic measurements were conducted under a commercial solar simulator (PES-L11, Peccell Technologies) equipped with a xenon lamp. The wavelength-integrated power density was calibrated at 1000 Wm$^{-2}$ by using a standard Si photodiode. The J-V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a digital multimeter (model 2400, Keithley).

Results and discussion

Preparation and surface characterisation of Pt nanoparticles

The Pt nanoparticles, prepared following the method described by Chang *et al.* (2010), but with the reduction reaction temperature fixed at 90°C, were approximately 5 nm in diameter as seen in TEM images. (Figure 1)

![Figure 1. TEM image of synthesised Pt nanoparticles in EG.](image-url)
These nanoparticles were successfully used to spin-coat FTO glass as seen in Figure 2. The surface of plain FTO glass (Figure 2a) consists of multiple crystallites which, in comparison, can be seen to be covered by a even distribution of individual Pt nanoparticles in Figure 2b. Figure 2c, however, shows that use of commercial Pt nanoparticles resulted in a coating of larger particles and aggregates of these particles.

**Figure 2.** FE-SEM image of (a) bare FTO glass, (b) synthesised and (c) commercial Pt nanoparticles, (d) PEDOT:PSS-6.8%Pt, (e) PEDOT:PSS-22.5%Pt, and (f) PEDOT:PSS.

The addition of PEDOT:PSS appears to have caused the Pt nanoparticles to aggregate, as seen in Figures 2d and 2e with 6.8% and 22.5% Pt w/w respectively. The aggregation of particles is particular prevalent at the higher Pt concentration. Figure 2f shows PEDPT:PSS only coating for comparison, and the universal coverage of the FTO glass by polymer strands can be seen. These images suggest that adding PEDOT:PSS to the Pt nanoparticles is causing them to aggregate and be covered in polymer. In essence, the polymer is causing the Pt to ‘sink’ below the observed surface.
DSSC performance

The use of the various counter-electrodes in actual DSSCs allowed the measurement of photovoltaic performance. From Table 1, it can be seen that the plain PEDOT:PSS electrode had a low fill factor, FF = 0.48 and lowest solar energy conversion efficiency, $\eta = 4.0\%$.

The FF is a comparison of the measured maximum power output of a DSSC versus its ideal maximum, and only considers the electrical properties of the cell. The ideal maximum power is determined from the open circuit voltage and short circuit current, both of which are the maximum possible values for voltage and current respectively for any electrical cell. However, connecting a cell to any useful load will always result in lower values of each due to internal resistance loses in the cell. As such, the FF is expected to decrease with increased overpotential $\Delta E$ and with increased electrical resistance of the electrode system itself. The overall conversion efficiency, $\eta$, is affected by the FF, but also considers photon capture and energy transfer to electron transport through the cell.

Adding Pt nanoparticles to the PEDOT:PSS increases the FF and generally increases the efficiency of reaction and electron transfer. The overall energy conversion efficiency also increases. With 46.5% w/w Pt added, the electrodes approach the efficiency of Pt only electrodes.

The Pt nanoparticle and double-layer electrodes show the importance of Pt being present on the surface and in direct contact with the electrolyte for efficient electron transfer as they have the highest FF and $\eta$.

<table>
<thead>
<tr>
<th>Counter electrode</th>
<th>Jsc (mA)</th>
<th>Voc (mA)</th>
<th>FF</th>
<th>$\eta%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial Pt Paste</td>
<td>12.0</td>
<td>0.760</td>
<td>0.607</td>
<td>5.56</td>
</tr>
<tr>
<td>Synthesised Pt nanoparticles</td>
<td>11.9</td>
<td>0.799</td>
<td>0.634</td>
<td>6.01</td>
</tr>
<tr>
<td>Doublelayer PEDOT:PSS-Pt</td>
<td>11.1</td>
<td>0.724</td>
<td>0.663</td>
<td>5.33</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>11.0</td>
<td>0.762</td>
<td>0.476</td>
<td>4.00</td>
</tr>
<tr>
<td>PEDOT:PSS - 6.8%Pt</td>
<td>11.9</td>
<td>0.791</td>
<td>0.446</td>
<td>4.20</td>
</tr>
<tr>
<td>PEDOT:PSS - 12.7%Pt</td>
<td>13.9</td>
<td>0.758</td>
<td>0.427</td>
<td>4.49</td>
</tr>
<tr>
<td>PEDOT:PSS - 22.5%Pt</td>
<td>12.4</td>
<td>0.789</td>
<td>0.458</td>
<td>4.46</td>
</tr>
<tr>
<td>PEDOT:PSS - 36.7%Pt</td>
<td>13.3</td>
<td>0.772</td>
<td>0.508</td>
<td>5.20</td>
</tr>
<tr>
<td>PEDOT:PSS - 46.5%Pt</td>
<td>11.6</td>
<td>0.796</td>
<td>0.592</td>
<td>5.49</td>
</tr>
</tbody>
</table>
Conclusion

It was found that using Pt nanoparticles and conductive PEDOT:PSS polymer can produce counter-electrodes with efficiencies approaching that of Pt-only on FTO glass. However, the Pt nanoparticles tended to sink into the polymer and aggregate on its surface, hindering the reduction reactions and decreasing efficiency.

In contrast, producing Pt nanostructure with a simplified synthesis procedure and spin-coating onto bare PEDOT:PSS produced counter-electrodes that had similar efficiencies to Pt on FTO glass. Also, the PEDOT:PSS does not require the FTO as the polymer is conductive and can carry the necessary electrical charges.

Acknowledgements

The authors would like to thank The Institute of Molecular Science (IMS), Japan and Research Promotion and Technology Transfer Center, Faculty of Liberal Arts and Science, Kasetsart University for financial support. Prof. Koichiro Mitsuke is also thanked for his supervision. Also, I would like to thank Wilhelm J. Holzschuh from the English Department, Faculty of Liberal Arts and Science, Kasetsart University for his assistance in preparing this manuscript.

References

