

Fast and economic preparation of Pt-based counter electrode for highly efficient dye-sensitized solar cell

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Dye-sensitized solar cell (DSSC) has been caught world-wide attention for its high energy conversion efficiency and potential low cost production. In particular, DSSC fabricated on plastic substrate having the possibility of roll-to-roll, large scale production of light-weight photovoltaic is even more attractive.

To fabricate a DSSC on plastic substrate like ITO-PET or ITO-PEN, it is apparent that process temperature involved has to be below 150°C due to the limitation of PET or PEN. To solve this, we have successfully developed a binder-free TiO₂ paste as well as relevant low temperature coating process to prepare mesoporous TiO₂ film on ITO-PEN[1-3]. Meanwhile, we have also developed a platinum/titanium bilayer on ITO-PEN by vacuum sputtering and found the surface platinum is far important than inner one, suggesting the platinum loading can be tiny if it is deposited on the right position[4].

The chief technical goal of DSSC technology is to manufacture it at low cost process while keep it efficient on photon to electron conversion rate. Vacuum deposition is known to energy-consumptive with low-throughput and is difficult to apply for large scale production. Therefore to develop a highly catalytic, low platinum loading counter electrode on plastic substrate with fast and cheap process is urgent.

We previously studied the utilization of polymer-protected platinum nanocluster (nPt) on rigid substrate and its application on high efficient DSSC[5-7]. According to our finding, protecting polymers surrounding nPt has no harm on the tri-iodide reduction but the surfactant between nPt and FTO glass creates noticeable barrier on electron transfer, resulting in large series and charge transfer resistance found on electrochemical impedance spectroscopy (EIS). It is also found the surfactant can be efficiently removed by a post heat treatment after nPt coating; however, the temperature we used is 270°C, which is still too high for any kind of plastic substrate. In this study, we found a novel method to remove the notorious surfactant layer by exposing plastic nPt counter electrode under ozone environment at room temperature.

Poly(N-vinyl-2-pyrrolidone) (PVP, MW8000, Aldrich) was chosen as the protecting agent for nPt. The "two-step dip coating" process was utilized to prepare PVP-nPt counter electrode and is simply described as follow: ITO-PEN film (13ohm/sq, 200 μm) was cleaned by acetone and then immersed into 4% surfactant (OM Group) for 5 min at 60°C followed by immersing in PVP-nPt ink for 5 min at 40°C. After PVP-nPt is coated, the film was rinsed with deionized water, and dried in open air. Finally the so-prepared PVP-nPt on ITO-PEN film was exposed under ozone atmosphere for several minutes to finish the whole process. Fig. 1 cartooned the whole process with relevant operation parameters.

EIS was used to examine the electrochemical catalytic performance of PVP-nPt on ITO-PEN for tri-iodide reduction. Symmetric cell comprised of one piece

of PVP-nPt on FTO glass and one piece of PVP-nPt on ITO-PEN as the electrodes with a 25 μm hot-melt film (Surlyn, Dupont) as separator. The reason for use glass/plastic combination is to ensure the satisfying sealing so that the data acquired is stable and reliable. Since EIS result is mathematically deductible, it is easy to separate individual contribution of the electrodes. The glass/plastic configuration provides another advantage for comparison catalytic effect of PVP-nPt on glass or on plastic substrate.

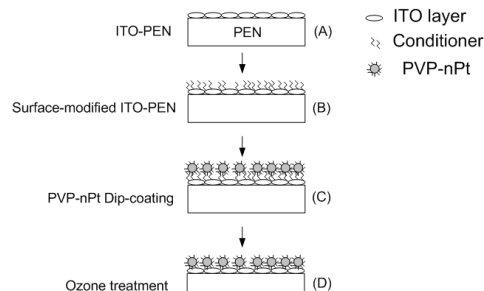


Fig. 1 Process flowchart of PVP-nPt on ITO-PEN, whole process is taken place at room temperature.

Fig2. is the Nyquist plot of PVP-nPt on FTO/ITOPEN cell with and without ozone treatment, the equivalent circuit under this cell configuration is also showed. From Fig.2, it is obviously the charge transfer resistance; R_{CT} of tri-iodide reduction is significantly reduced from 26 ohm-cm² to 2 ohm-cm² after 10 minutes ozone treatment, approaching the performance on the PVP-nPt/FTO with 350°C heat treatment. The result implies that ozone treatment may have same effect on removing ultra-thin surfactant layer, which is found to obstruct charges transport from substrate to Pt clusters.

In addition to EIS analysis, surface morphology and the performance of DSSC employed with this novel plastic counter electrode are also discussed and demonstrated.

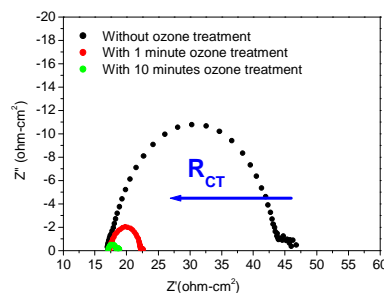


Fig 2. Nyquist plot on PVP-nPt-FTO/electrolyte/PVP-nPt-ITO cell with and without ozone treatment; electrolyte contains 1.0 M 1,3-dimethylimidazolium iodide (DMII), 0.03M iodine, 0.1M guanidinium thiocyanate and 0.5M *tert*-butylpyridine in a mixture of valeronitrile/ acetonitrile (15:85 v/v).

1. T. Miyasaka, *J. Phys. Chem. Lett.*, 2, 262-269(2011).
2. M. Ikegami, J. Suzuki, K. Teshima, M. Kawaraya, and T. Miyasaka, *Solar Ener. Mater. Solar Cells*, 93, 836-839(2009).
3. T. Miyasaka, M. Ikegami, and Y. Kijitori, *J. Electrochem. Soc.*, 154, A455-A461 (2007).
4. M. Ikegami, K. Teshima, K. Miyoshi, T. Miyasaka, T.C. Wei, C.C. Wan, and Y.Y. Wang, *Appl. Phys. Lett.*, 90, 153122-153124 (2007).
5. T.C. Wei*, Y.Y. Wang & C.C. Wan, *Appl. Phys. Lett.* 88, 103122 (2006)
6. Tzu-Chien Wei*, Chi-Chao Wan, Yung-Yun Wang, Chih-ming Chen and Han-sheng Shiu, *J. Phys. Chem. C*, 111, 4847(2007)

7. Jo-Lin Lan, Chi-Chao Wan, Tzu-Chien Wei, Wen-Chi Hsu, Ya-Huei Chang, *Prog. Photovolt: Res. Appl.* (2011), available online.