

Dye-sensitized solar cells with Pt- and TCO-free counter electrodes†

Kun Seok Lee,^a Hang Ken Lee,^b Dong Hwan Wang,^b Nam-Gyu Park,^a Jun Young Lee,^a
O Ok Park^b and Jong Hyeok Park^{*a}

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Here for the first time, we demonstrate novel DSSCs with a Pt- and TCO-free counter electrode, which have a highly conductive polymer exhibiting high catalytic ability and charge transport, and the photovoltaic performance increases as we increase the PEDOT film conductivity.

Dye-sensitized solar cells (DSSCs) with a mesoporous network of interconnected TiO₂ nanocrystals, promising sensitizers, novel electrolytes, and platinum (Pt) as a counter electrode are attracting widespread scientific and technological interest as a high-efficiency and low-cost alternative to conventional inorganic photovoltaic devices.^{1,2} Typically, counter electrodes in DSSCs have been prepared by Pt vacuum deposition or thermal annealing of a Pt precursor on a transparent conductive oxide (TCO) substrate to reduce the overpotential for reduction of I₃⁻ to I⁻ in redox electrolytes.³ Although Pt has a high conductivity, catalytic activity and stability, Pt is one of the most expensive components in DSSCs.⁴ Therefore, the development of finding alternative materials for the development of Pt-free DSSCs is expected to reduce the production cost for DSSCs.

As a Pt-free counter electrode, carbon-based materials, such as activated carbon, carbon nanotubes, graphite, and carbon black have been introduced as catalysts for DSSCs.^{5–10} Recently, Murakami *et al.* reported carbon black-based counter electrodes in DSSCs and a remarkable conversion efficiency of approximately 9% under 100 mW cm⁻² was achieved.¹⁰ However, to obtain a high-efficiency DSSC, the thickness of the counter electrode should be much greater than that of the Pt electrode. A second approach to a Pt-free counter electrode has used several conducting polymers to obtain a maximum conversion efficiency approximately 7.8% under 100 mW cm⁻².¹¹ A power conversion efficiency of 7.1% has been achieved with the microporous polyaniline counter electrode.¹² More recently, the Ahmad group reported 7.93% by using poly(3,4-alkylenedioxythiophene) PEDOT nanoporous layers prepared from electro-oxidative polymerization.¹³ Conducting polymers have the potential to replace the Pt counter electrode in DSSCs because of the high electrochemical activity. Until

now, PEDOT is of special interest due to its high conductivity, electrochemical stability, transparency, and catalytic ability.^{14–16} However, typical Pt-free counter electrode materials in DSSCs should be prepared on TCO substrates to have efficient charge transport. Given that the TCO is also expensive (about 60% of total cost), the development of a cost-effective counter electrode should simultaneously remove the use of Pt and TCO. Considering the literature published on alternative counter electrodes besides Pt, there has been no report on conducting polymers dually acting as the Pt and the TCO substrate.

To achieve a Pt- and TCO-free counter electrode, a highly conductive polymer exhibiting high catalytic ability was used to simultaneously act as a catalyst for I₃⁻ reduction and charge transport. Herein, we report the cell performances of DSSCs with several PEDOT-based materials, which were used as the counter electrode without TCO. By tuning the electric conductivity of the conducting polymer, the DSSCs without Pt and TCO in the counter electrode showed a comparable cell efficiency with cells using a Pt/FTO counter electrode.

PEDOT thin film with very high electrical conductivity was fabricated by a modified simple pre-solution/*in situ* polymerization method. In this process, the monomer solution was first prepared by dissolving 3,4-ethylenedioxythiophene (EDOT), poly(vinyl pyrrolidone) as a matrix polymer and pyridine as a retardant in 1-butanol or ethanol. An oxidant solution was separately prepared by dissolving ferric *p*-toluene sulfonate (FTS) in 1-butanol or ethanol. The monomer and oxidant solutions were then mixed together, followed by solution polymerization at a temperature ranging from 5 to 30 °C for 3 to 72 h. The pre-polymerized PEDOT solution was then coated onto a substrate to form a pre-polymerized PEDOT film. PEDOT film was obtained by post-polymerization at 70 °C for 20 min, followed by washing with methanol and drying, resulting in a film with a very high electrical conductivity and extraordinarily smooth surface. Electrical conductivity and root mean square surface roughness of the PEDOT film were as high as approximately 800 S cm⁻¹ and as low as 1.0 nm, respectively. PEDOT thin film with a thickness of approximately 60 nm showed a low surface resistivity of approximately 130 Ω/□ with 88% transmittance at 550 nm (see ESI†).

The electric conductivities of the PEDOT counter electrode used in Pt- and TCO-free DSSCs were controlled by adjusting the molar ratio of the monomer to the oxidant or to the retardant. A schematic diagram of the DSSC prepared with a Pt- and TCO-free counter electrode is shown in Fig. 1.

The cyclic voltammograms of I⁻/I₃⁻ redox on the PEDOT-coated glass substrate and Pt-coated FTO substrate are shown in Fig. 2, illustrating that the PEDOT counter electrode exhibited nearly the similar peak positions, when compared

^a Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea. E-mail: luttis@skku.edu

^b Department of Chemical and Biomolecular Engineering (BK21 Graduate Program), Interdisciplinary Program for Polymers, Korea Advanced Institute of Science and Technology, 335 Gwahangno, Yuseong-gu, Daejeon 305-701, Republic of Korea

† Electronic supplementary information (ESI) available: Photograph of PEDOT coated plastic substrate, AFM image of the PEDOT surface, PEDOT film coated glass substrate with 800 S cm⁻¹ electric conductivity, and DSSC with counter electrode prepared from PEDOT coated glass substrate. See DOI: 10.1039/c0cc00432d

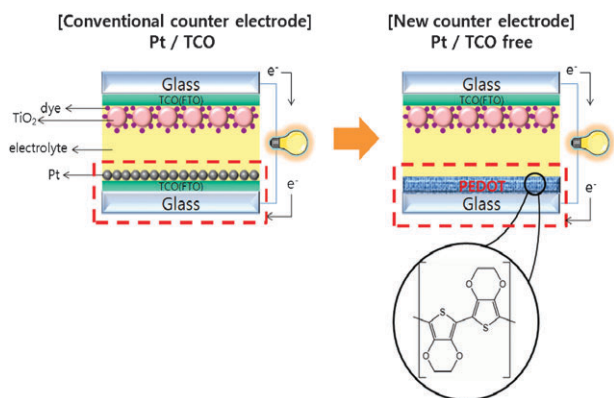


Fig. 1 Schematic diagram of DSSC with Pt- and TCO-free counter electrode.

to those of the Pt counter electrode. The reduction peak current densities of the PEDOT counter electrode were slightly greater than those of the Pt electrode. Therefore, the PEDOT counter electrode was more electrochemically active, which indicated a much faster reaction rate on PEDOT even though the PEDOT counter did not have a TCO substrate. A Pt- and TCO-free transparent DSSC unit cell can be prepared using a PEDOT counter electrode, as shown in Fig. S3 (ESI[†]).

The performance of such counter electrodes can be compared directly with a Pt counterpart by fixing other parameters, such as the TiO₂ layer, dye, electrolyte, and conditions of cell assembly, as shown in Fig. 3. Anatase TiO₂ nanoparticles were made *via* a sol-gel hydrolysis from autoclaving of titanium isopropoxide at 230 °C for 12 h in an acetic acid aqueous solution. Then, TiO₂ nanoparticles were dispersed in α -terpinol with ethyl cellulose as a binder. A 8 μm -thick single-layer TiO₂ film on FTO substrate was used as a photoanodes. After heat treatment at 500 °C for 30 min, the nanocrystalline TiO₂ electrodes were immersed in 50 mM N719 solution. Pt based counter electrodes were prepared by spin-coating an FTO glass with a H₂PtCl₆ and heating it at 400 °C for 15 min. The dye-adsorbed nanocrystalline TiO₂ electrode and Pt based or PEDOT based counter electrode were assembled into a sealed sandwich-type cell by heating

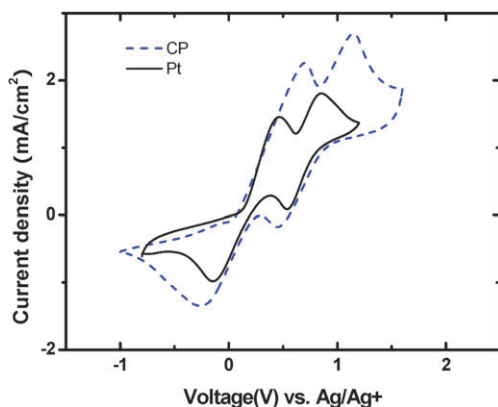


Fig. 2 Cyclic voltammograms of the CP (PEDOT film (800 S cm⁻¹)) on glass substrate and the Pt on FTO/glass substrate cycled in I⁻/I₃⁻ electrolyte (10 mM LiI + 1 mM I₂ + 0.1 M LiClO₄ + acetonitrile) at a scan rate of 100 mV s⁻¹.

with a hot melt of polymer film (Surllyn, Dupont 1702). A drop of the electrolyte solution was introduced into a hole drilled in the counter electrode of the assembled cell, followed by sealing the holes using microcover glass and Surllyn. The electrolyte was composed of 0.6 M butylmethylimidazolium iodide, 0.03 M I₂, 0.1 M guanidinium thiocyanate, and 0.5 M 4-*tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (v/v, 85:15). The *J-V* curves were measured at AM 1.5 illumination using a Keithley 2400 source measure unit. A 1000 W xenon lamp (Oriel, 91193) served as the light source and its intensity was calibrated using a Si reference cell (Fraunhofer ISE, certificate no. C-ISE269). The photocurrent (*J*) and photovoltage (*V*) of the DSSC were measured with an active area of $\sim 0.2 \text{ cm}^2$ using simulated solar light at AM 1.5. The *J-V* characteristics of the devices with Pt-coated, TCO counter electrodes and two different PEDOT-based counter electrodes with different conductivities are shown in Fig. 3. At 1 sun illumination, the Pt DSSC exhibited a *J*_{sc} of 12.0 mA cm⁻², a *V*_{oc} of 0.72 V, a fill factor (FF) of 0.68, and an overall conversion efficiency of 5.88%. However, the performances of the DSSCs based on the PEDOT counter electrode were strongly dependent on the electric conductivity of the film. The DSSC with a PEDOT (800 S cm⁻¹) counter electrode had the highest fill factor of 0.60 and a *J*_{sc} of 11.6 mA cm⁻², a *V*_{oc} of 0.73 V, and a conversion efficiency of 5.08%, which is comparable to using the Pt/TCO electrode. The *J-V* characteristics of the device with PEDOT coated FTO substrate was also shown in Fig. S4.[†]

Fig. 4 presents the IPCE spectra of the DSSCs with a Pt/TCO or PEDOT counter electrode. The IPCE spectra were measured as a function of wavelength from 300 nm to 800 nm using a specially designed IPCE system (PV Measurements, Inc.) for DSSCs. The introduction of PEDOT only on the glass substrate based counter electrodes exhibited comparable quantum efficiency over the whole spectral range of incident light. Fig. 5 shows the impedance spectra for the DSSCs with different counter electrodes. The spectra were measured using an impedance analyzer (Zahner IM6). The main difference was ohmic resistance of the dye-sensitized solar cells representing electron transport processes with a very short time constant. With increasing electrical conductivity, the value decreased gradually; however, the DSSC with the 800 S cm⁻¹ PEDOT

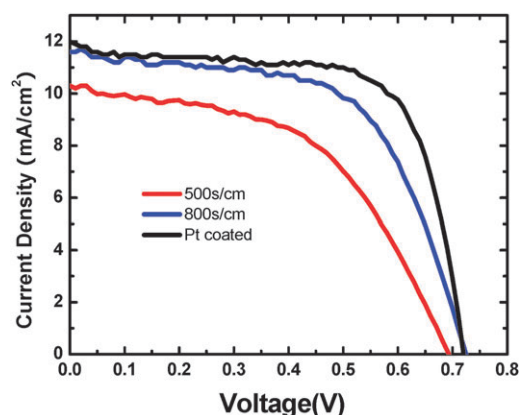


Fig. 3 Current density–voltage characteristics of DSSCs with various counter electrodes.

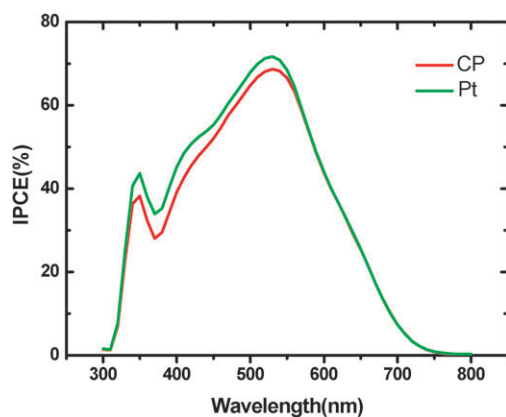


Fig. 4 IPCE spectra of DSSCs with different counter electrodes (the CP (PEDOT film (800 S cm^{-1})) on glass substrate and the Pt on FTO/glass substrate).

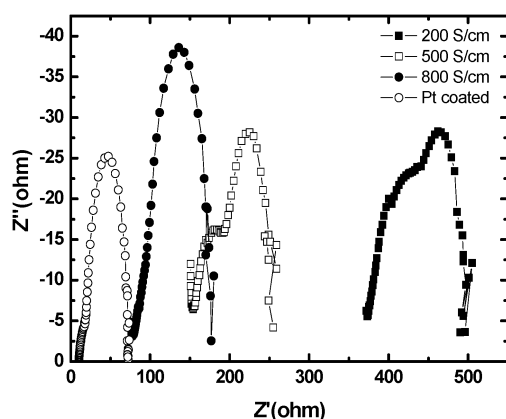


Fig. 5 Nyquist plots of DSSCs with different counter electrodes from the impedance measurement.

counter electrode still had a much higher ohmic resistance. Nevertheless, the DSSC with an 800 S cm^{-1} PEDOT counter electrode showed similar cell performance to the Pt/TCO cell due to a small cell area of approximately 0.2 cm^2 .

Highly conductive PEDOT films were synthesized on a glass substrate by a modified simple pre-solution/*in situ* polymerization method. Only films without TCO were used as a counter electrode in the fabrication of DSSCs, resulting in a power conversion efficiency of 5.08% when a DSSC with a Pt/FTO counter electrode was 5.88%. The obtained efficiency

was the first report to date using only a conducting polymer as a counter electrode. Therefore, if the electric conductivity of the PEDOT film can be further increased, the performance of a PEDOT-only counter electrode can be improved, which eliminates the utility of Pt and TCO.

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