Conductive Polymer-based Mesoscopic Counterelectrodes for Plastic Dye-sensitized Solar Cells

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Semitransparent mesoporous counterelectrode was prepared on a plastic substrate by low-temperature coating of a viscous composite comprising nanocrystalline TiO_2 particles and PEDOT–PSS. The electrode shows high cathodic activity in a full-plastic dye-sensitized solar cell, yielding energy conversion efficiency of 4.38%.

Recent advancements of plastic electronics[1] are successfully absorbing the technology of printable materials to develop thin flexible and cost-effective devices. Dye-sensitized solar cells (DSCs)[2] is a strong candidate for a lightweight plastic power source, which can be manufactured by rapid printing processes under atmospheric pressure. We have been fabricating plastic DSCs using organic liquid electrolytes[3–5] and carbon-based solid conductive materials.[6–8] Key process is the low-temperature preparation of thin electrode materials on plastic substrates both for photoelectrode (anode) and counterelectrode (cathode). For the photoelectrode, we have shown that a mesoporous TiO_2 layer is prepared from a viscous binder-free TiO_2 paste that is capable of interparticle connection.[4,5] The counterelectrode requires a cathode catalyst for reduction of triiodide (I_3^-) to iodide (I^-). Platinum has been widely used for this purpose on glass and plastic substrates. On plastic substrates, however, Pt films can be only prepared by vacuum sputtering. This process and expensive source of Pt are serious drawback in cost-effective fabrication. Non-platinum methods for counterelectrode have so far been attempted by using carbon materials[9–13] and conductive polymer materials[14–16] including derivatives of poly(3,4-ethylenedioxythiophene). Using plastic substrates having hydrophobic surfaces, however, we found that these materials have difficulty in coating and lack in sufficient performance as the cathode of DSC. In this communication, we show a high-performance printable material suitable for assembling plastic cathode.

Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT–PSS) was used as an electroconductive and catalytic material for counterelectrode, an aqueous dispersion of which (polymer concentration 1.24%, Polysciences) was mixed with various metal oxide nanosized particle such as Al_2O_3, ZnO, and TiO_2. These particles were used to enhance the surface area of counterelectrode. Among them TiO_2 powder (particle size 50 nm, specific surface area 30–40 $m^2\,g^{-1}$) was found to be best in creating highest cathodic activity. In order to convert the PEDOT–PSS/TiO_2 dispersion to a paste form of printable viscosity, an alcoholic slurry of indium-tin-oxide (ITO, particle size 20 nm, 15 wt %, C. I. Kasei) was added to the dispersion at vol ratio 1:1 to form a composite paste (TiO_2•ITO/PEDOT–PSS). ITO-coated poly(ethylenenaphthalate) (ITO–PEN) (sheet resistance 13 ohm/square, thickness 200 μm, PECF-IP, Peccell Technologies) was used as a plastic substrate of counterelectrode, on which the mixture paste was coated by doctor blade or screen printing method followed by heat drying at 110 °C for 5 min. A reference PEDOT–PSS film was coated using an ethanol mixture of the PEDOT–PSS dispersion. Photoelectrode of dye-sensitized solar cell was also prepared on an ITO–PEN substrate by the previously reported method,[4,5] using a binder-free TiO_2 paste for low-temperature coating and a ruthenium complex dye (N719), *cis*-bis(thiocyanato-*N*)bis(4,4′-tetrabutylammonium hydrogen dicarboxylato-2,2′-bipyridine-κ^2N)ruthenium(II) as a sensitizer.

Electrochemical activities of the counterelectrodes for I_3^- reduction were evaluated by cyclic voltammetry in an electrolyte solution comprising 10 mM LiI, 1 mM I_2, and 0.1 M $LiClO_4$ in acetonitrile using an Ag/AgI reference electrode and a Pt counterelectrode. Photovoltaic performance of full-plastic DSCs (irradiation area 0.24 cm^2) was measured under AM 1.5, 100 $mW\,cm^{-2}$ irradiation with a solar simulator (PEC-L10, Peccell Technologies) using an electrolyte comprising 0.4 M LiI, 0.4 M tetrabutylammonium iodide (TBAI), 0.04 M I_2, 0.3 M *N*-methylbenzimidazole (NMB) in acetonitrile (AN)/3-methoxypropionitrile (MPN) (vol ratio 1:1).

TiO_2•ITO/PEDOT–PSS nanocomposite films coated on ITO–PEN are semitransparent, reflecting the optical nature of the nanoparticles (see Graphical Abstract). High adhesion strength was obtained on a hydrophobic surface of ITO–PEN. Figure 1 shows cross-sectional structure and surface morphology observed by scanning electron microscope (SEM). The nanocomposite film has macro- and mesoporous structures with high roughness factor (>1000) comparable with the TiO_2 photoelectrode. However, TiO_2-free PEDOT–PSS film lacks such porosity (figure not shown here). Thickness of the mesoscopic layer is around 10 μm.

Figure 2 compares cyclic voltammograms (CV) for I^-/I_3^- redox reaction on counterelectrode catalytic films for a plain PEDOT–PSS film, an ITO/PEDOT–PSS composite film, and a TiO_2•ITO/PEDOT–PSS composite film in which TiO_2 content is 4 wt %. Peak separation between the oxidation wave ($3I^- \rightarrow I_3^- + 2e^-$) and the reduction wave ($I_3^- + 2e^- \rightarrow 3I^-$), as a sign of overpotential (η), indicates that the plain

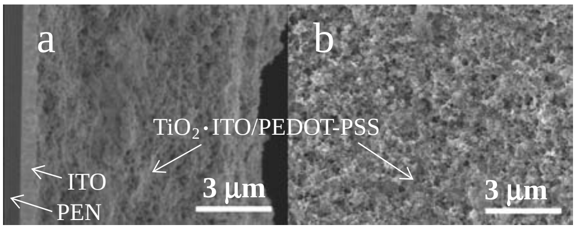

Figure 1. SEM observation for the TiO_2•ITO/PEDOT–PSS nanocomposite film; (a) cross section, (b) surface.

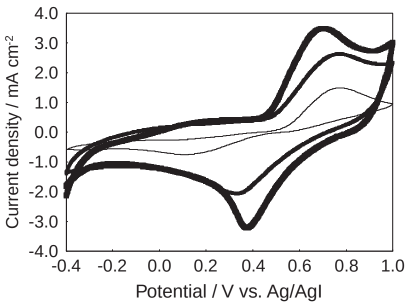

Figure 2. Cyclic voltammograms for I^-/I_3^- redox reactions on various counterelectrode films. Scan rate, 100 mV s^{-1}. Thin line, PEDOT–PSS film; medium line, ITO/PEDOT–PSS film; bold line, TiO_2•ITO/PEDOT–PSS film.

PEDOT–PSS film has a high η while the TiO_2•ITO/PEDOT–PSS composite film yields a low η and highest reaction rate (current density). TiO_2-free ITO/PEDOT–PSS composite film is less active than the TiO_2-added composite film. Optimization of the paste composition showed that TiO_2 content of more than 6 wt % tends to deteriorate CV performance owing to a loss in the function of PEDOT–PSS as catalyst and conductor. 4 wt % TiO_2 proved to give a best cathodic activity, which is a result of enhanced surface area and catalytic/conductive function of PEDOT–PSS in the optimized paste composition. More quantitative analysis for the reaction activity at the cathode interface based on the Tafel plot (not shown here) also supports the above results.

Charge-transfer resistance for the interface of electrolyte and the composite film, measured by an AC impedance analyzer, showed that the interfacial resistance tends to be minimized at a TiO_2 loading amount of around 15 g m^{-2} for the TiO_2•ITO/PEDOT–PSS film (4 wt % TiO_2). With this condition the composite film shows an interfacial resistance close to that of a sputtered Pt coated on a glass electrode. There is, however, a gap in the DC resistance due to the substrate sheet resistance, which is higher for ITO than for metallic Pt surface.

Figure 3 exhibits photocurrent density–voltage (*I*–*V*) curves of DSCs with different films on ITO–PEN counterelectrodes. Apparently ITO–PEN itself does lack the cathodic activity for I_3^- reduction. The PEDOT–PSS film coated on ITO–PEN is still insufficient to enhance *I*–*V* performance of the cell yielding small short-circuit photocurrent density (J_{sc}). Fairly high performance was obtained with ITO/PEDOT–PSS and TiO_2•ITO/PEDOT–PSS films, both having porous surfaces. Replacement of TiO_2 with Al_2O_3 and ZnO particles could give performance better than the nonporous electrodes but did not exceed the TiO_2-based sample. We consider that the TiO_2 surface best interacts with PEDOT–PSS for forming a polymer-coated mosoporous structure. Energy conversion efficiency of a full-plastic cell using the ITO–PEN counterelectrode coated with TiO_2•ITO/PEDOT–PSS reached 4.38%, which approaches the level of a cell using a sputtered Pt-coated FTO (F-doped SnO_2) glass electrode, 5.41%. J_{sc} with the composite plastic electrode is 8% lower than that with Pt glass electrode. This decrease in J_{sc} mainly involves the influence of the high sheet resistance of ITO as well as of the effect of light reflection that exists at the Pt-coated surface.

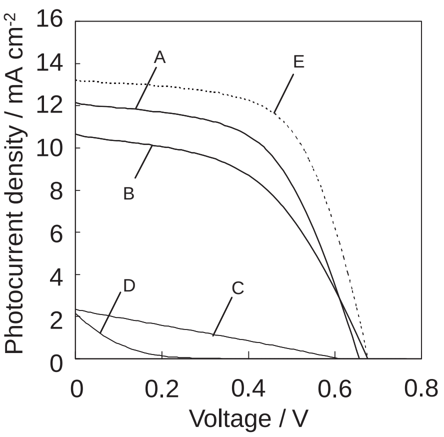

Figure 3. *I*–*V* curves for dye-sensitized plastic photocells using various counterelectrode materials coated on ITO–PEN plastic substrate. (A) TiO_2•ITO/PEDOT–PSS film, (B) ITO/PEDOT–PSS film, (C) PEDOT–PSS film, (D) None (ITO–PEN substrate), (E) Sputtered Pt film on FTO-glass as a reference. Electrolyte composition, 0.4 M LiI, 0.4 M TBAI, 0.04 M I_2, 0.3 M NMB in AN/MPN (vol ratio 1:1).

Using the present counterelectrode composite, full-plastic flexible DSCs can be fabricated by low-cost printing processes both for photo- and counterelectrodes. The composite film coated on ITO–PEN exhibited high adhesion stability against mechanical scratching and bending and high stability as plastic DSC electrode against light and heat.

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