Highly Efficient Plastic Dye-sensitized Photoelectrodes Prepared by Low-temperature Binder-free Coating of Mesoscopic Titania Pastes

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Mesoporous TiO_2 layers were prepared on a plastic conductive electrode by low-temperature coating of a binder-free nanocrystalline TiO_2 paste capable of interparticle connection. Dye-sensitized solar cell with optimized TiO_2 particle size and electrolyte composition yielded a highest energy conversion efficiency of 6.4%.

The last decade has seen a tremendous number of studies on dye-sensitized solar cell (DSSC). R & Ds for industrialization are most active in this country as are reflected by numerous patent applications following the pioneering invention by the Grätzel's group.[1,2] Record power efficiency of DSSC exceeding 11%[3] has been achieved by high-temperature sintering of a nanocrystalline TiO_2 paste on a conductive glass. While competing in efficiency, superiority of DSSC over the existing Si-based photovoltaic cells is evident in its environmentally benign low-cost manufacture processes. DSSC is a sole utility-type photovoltaic cell manufactured in the ambient atmosphere. It enables a dramatic cost reduction, in particular, by realizing roll-to-roll printing process for electrode fabrication using flexible substrate. Further, lightweight flexible DSSC is highly useful not only for attachment on round surfaces but also for applications to ubiquitous powers. To this end, various methods have been invented previously to fabricate plastic DSSC, including mechanical compression[4] and low-temperature coating of TiO_2 particles.[5] Electrophoretic deposition of TiO_2 followed by chemical necking treatments was one of our solutions to low-temperature coating.[6–8] In this report, we show a single-step coating process by preparation of a binder-free mesoscopic TiO_2 paste.

Indium–tin–oxide (ITO)-coated polyethylene naphthalate (PEN) was selected as a low-cost transparent plastic electrode (thickness, 200 µm; sheet resistance, 13 Ω sq.$^{-1}$; transmittance, 80%). T_g of PEN, 121 °C, requires that electrode processing be made in a low-temperature range less than 150 °C. To realize a TiO_2 nanocrystalline paste that works without the sintering process, amply high viscosity should be attained without use of insulating binder materials, which remain in the dried film and blocks carrier transports between TiO_2 particles. Secondly, the paste should have high adhesion to the hydrophobic surface of ITO-coated PEN. Third, all liquid components of the paste should be finally evaporated at low temperatures (<150 °C). Finally, all components of the paste should be inert against corrosion of the ITO layer; acidic precursors for interparticle connection ($TiCl_4$, etc.) that react with ITO can not be applied. To fulfill the above requirements, TiO_2 nanoparticles (Showa Denko Co., rutile–anatase mixtures) of various average sizes of 30–150 nm were dispersed in a mixed solvent of water and *t*-butanol. Large TiO_2 particle (average size, 250 nm) was mixed to the nanoparticles to enhance light-harvesting effect by scattering. *t*-Butanol reduces the surface tension of the liquid paste to improve its adhesion to the hydrophobic ITO-PEN surface. An aqueous colloidal TiO_2 sol was added to the dispersion as an interparticle connection agent,[7] which contains brookite-type TiO_2 nanocrystals (size, 10–35 nm) at 20 wt % in a mixture of 25% aqueous hydrochloric acid (pH 2) and 75% ethanol. Viscosity of the resulted binder-free dispersion reached around 2000 mPa·s by adjusting the water content as 30 wt % vs. total weight. Doctor-blade coating of the binder-free TiO_2 paste on an ITO-PEN sheet followed by drying at 110–125 °C gave a mesoporous TiO_2 layer tightly attached to the ITO surface. The TiO_2-loaded ITO-PEN sheet showed high anti-exfoliation of TiO_2 against bending, showing antiscratching pencil hardness of more than H. Interparticle connection of TiO_2 is assumed to proceed by dehydration of hydrogen-bonded network of TiO_2 nanoparticles with surfaces covered with hydroxy groups (See Supporting Information[13]).

The TiO_2-coated ITO-PEN was dye-sensitized by Ru bipyridyl complex dyes, N719 or N712, which bear two and four tetrabutylammonium (TBA) groups, respectively, as the counter cation of carboxy group.[9] The photoelectrode was combined with a platinum-coated glass counter electrode by insertion of an organic electrolyte comprising 0.4 M LiI, 0.4 M tetrabutylammonium iodide (TBAI), 0.04 M I_2, 0.3 M *N*-methylbenzimidazole (NMB) in a mixture of acetonitrile (AN) and 3-methoxypropionitrile (MPN) (vol ratio 1:1), denoted as electrolyte A, to construct a mask-attached cell with 0.24-cm^2 irradiation area. Photocurrent (*I*)–voltage (*V*) characteristics were measured with solar simulator (Peccell Technologies, L11) at room temperature (See Supporting Information[13]).

The TiO_2 layer was first optimized regarding the thickness and the average size of TiO_2 nanoparticle for maximizing photovoltaic performance. Short-circuit photocurrent density (J_{sc}) of the N719-sensitized electrode increased with increased thickness and showed saturation at TiO_2 loadings of 18–20 g m^{-2} corresponding to layer thicknesses of 11.5–12.5 µm. Energy-conversion efficiency (η) did not simply follow the photocurrent increase but was affected by light intensity. It gave a maximum at 18–20 g m^{-2} TiO_2 for low irradiance, 12.2 mW cm^{-2} (1/8 sun) but showed a saturation at lower TiO_2 loadings of

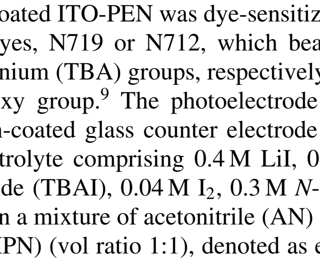

Figure 1. Effect of the average particle size of TiO_2 on short-circuit photocurrent density (solid line) and the amount of adsorbed dye molecules (dashed line).

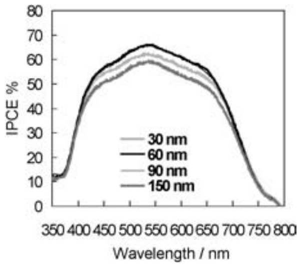

Figure 2. IPCE action spectra of N719-sensitized TiO_2/ITO-PEN electrodes of different TiO_2 average particle sizes.

13–18 $g\,cm^{-2}$ for high irradiance, 100 $mW\,cm^{-2}$ (1 sun) (See Supporting Information[13]). Overall efficiency is apparently affected by fill factor (*FF*), which decreases with increased photocurrent (high irradiance) at thick layers. With TiO_2 loadings of 18 $g\,cm^{-2}$, average size of nanoparticle was optimized. Figure 1 shows the size dependence of the N719-sensitized photocurrent in comparison with the amount of dye adsorbed on the TiO_2 layer. While the amount of dye simply decreases with increased particle size, photocurrent showed a peak at around 60 nm. In the present nonsintering coating, a desirable porosity for the electrolyte diffusion in the mesoscopic layer is formed by 60-nm particles, which is larger than 20–25 nm normally used for sintering method[10] where pores are created by burning of polymer binder materials. Incident photon to current conversion efficiency (IPCE) was also maximized with the 60-nm TiO_2 layer as compared in Figure 2. The IPCE action spectrum exhibits a sharp cutoff in the ultraviolet region less than 400 nm, which is due to optical absorption by PEN and is effectively protecting dye from excitation of TiO_2 (<390 nm).

Composition of the electrolyte solution was modified in order to improve efficiency for high and low irradiances. The solvent AN/MPN of electrolyte A was replaced with pure MPN in electrolyte B. In the place of NMB in electrolyte B, *tert*-butylpyridine (TBP) was added in electrolyte C. NMB and TBP are known to increase open-circuit voltage (V_{oc}) by shifting the surface potential of TiO_2.[11] The electrolytes A–C were applied to the electrodes sensitized by N719 and N712, respectively. *I–V* characteristics were measured under high and low irradiances at least three times for each condition to take an average. Table 1 summarizes the results for both dyes. For N719, both electrolytes A and B using NMB yield larger photocurrent than the TBP-based electrolyte C for 1 sun. Electrolyte A containing AN yielded highest efficiency due to improved *FF*. At 1/8 sun, however, electrolytes B and C using pure MPN gave higher efficiency due to improved V_{oc}. N719 gave maximal efficiencies of 5.5% (1 sun) and 6.0% (1/8 sun). Similar behavior occurred for N712-sensitized cells, which reached higher efficiency than N719 owing to an increased in V_{oc}, which is attributed to the effect of TBA cations. Figure 3 compares the top *I–V* performances obtained by the N719- and N712-sensitized plastic electrodes. Best efficiencies achieved with N712 are 5.8% (1 sun) and 6.4% (1/8 sun).

Table 1. *I–V* characteristics for N719-sensitized and N712-sensitized TiO_2 ITO-PEN plastic electrodes measured with different electrolyte compositions A–C (see the compositions at the foot of table)

N719	Electrolyte[a]	$TiO_2/g\,m^{-2}$	$J_{sc}/mA\,cm^{-2}$	V_{oc}/V	*FF*	$\eta/\%$
1[b]	A	18	12.7 ± 0.3	0.70 ± 0.01	0.62 ± 0.01	5.5 ± 0.1
	B	19	12.6 ± 0.3	0.69 ± 0.01	0.55 ± 0.01	4.8 ± 0.1
	C	19	12.0 ± 0.2	0.70 ± 0.01	0.55 ± 0.02	4.6 ± 0.2
2[c]	A	18	1.68 ± 0.04	0.62 ± 0.01	0.67 ± 0.01	5.7 ± 0.1
	B	19	1.70 ± 0.03	0.63 ± 0.01	0.68 ± 0.01	6.0 ± 0.1
	C	19	1.65 ± 0.03	0.64 ± 0.01	0.67 ± 0.01	5.8 ± 0.2

N712	Electrolyte[a]	$TiO_2/g\,m^{-2}$	$J_{sc}/mA\,cm^{-2}$	V_{oc}/V	*FF*	$\eta/\%$
1[b]	A	17	12.0 ± 0.3	0.75 ± 0.01	0.65 ± 0.01	5.8 ± 0.1
	B	17	11.9 ± 0.1	0.75 ± 0.01	0.59 ± 0.02	5.2 ± 0.2
2[c]	A	17	1.59 ± 0.03	0.66 ± 0.01	0.71 ± 0.01	6.1 ± 0.1
	B	17	1.56 ± 0.03	0.70 ± 0.01	0.72 ± 0.01	6.4 ± 0.1

[a] A: LiI (0.4 M), TBAI (0.4 M), I_2 (0.04 M), NMB (0.3 M) in AN/MPN (1:1), B: LiI (0.4 M), TBAI (0.4 M), I_2 (0.04 M), NMB (0.3 M) in MPN, C: LiI (0.4 M), TBAI (0.4 M), I_2 (0.04 M), TBP (0.3 M) in MPN. [b] Irradiance: 100 $mW\,cm^{-2}$ (1 sun). [c] Irradiance: 12.2 $mW\,cm^{-2}$ (1/8 sun).

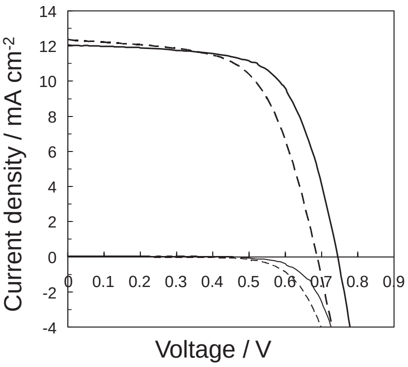

Figure 3. *I–V* characteristics for photocurrent under 1 sun irradiance (upper) and dark current (lower) for N712-sensitized (solid lines) and N719-sensitized (dashed lines) plastic electrodes obtained with electrolyte composition A (see, Table 1).

High efficiency of the plastic electrode is backed by high porosity, about 60%, of the present binder-free coating without undergoing mechanical compression that can destruct pores.[4] Recently, use of stainless steel has been attempted as a flexible alternative to the plastic electrode,[12] which, however, undergoes corrosion with the iodine-based electrolyte. We are conducting further improvements of the ITO surface to reinforce the mechanical connection at the ITO–TiO_2 interface.

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13 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/index.html.

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