Efficient Nonsintering Type Dye-sensitized Photocells Based on Electrophoretically Deposited TiO_2 Layers

Tsutomu Miyasaka,* Yujiro Kijitori, Takurou N. Murakami, Mitsuhiro Kimura,† and Sadao Uegusa†
Graduate school of Material Science, Toin University of Yokohama, 1614 Kurogane-cho, Aoba, Yokohama, 225-8502
†*School of Information Technology and Electronics, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa 259-1292*

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A non-sintering method for preparing nanoporous semiconductor layers for dye-sensitized photocells was developed in which TiO_2 particles were electrophoretically deposited on an electrode and post-treated by chemical vapor deposition of Ti alkoxide and microwave irradiation. The method provides photocells with energy conversion efficiency up to 4.1% under irradiation of AM1.5 light (100 mW/cm^2).

After the pioneering work of Grätzel and coworkers,[1] technologies of dye-sensitized solar cells (DSCs) have stimulated a number of studies on efficiency and stability improvements of the cell.[2,3] Recent advancements in this field are solidification of the cell[4–6] and nonsintering methods[7–12] for fabrication of plastic photocells; both are key technologies for DSCs to compete with silicon-based solar cells. Use of commercially available low-cost plastic films such as PET is in most case limited to a temperature range of $<150\,^{\circ}$C. In this respect, low-temperature processing of semiconductor layers has been studied by means of electrochemical deposition method,[7,8] electrophoretic deposition,[9] binder-free coating,[10] hydrothermal synthesis,[11] and mechanical pressing technique.[12] Among them, relatively high power conversion efficiency of 3% and 2.3% (under incident power of 100 mW/cm^2) for glass-based cells and plastic cells, respectively, has been obtained by the mechanical compression of TiO_2 layers. Electrophoretic technique enables formation of binder-free semiconductor coating and could yield about 1.4% (efficiency calculated from reported parameters)[9] after postannealing of the layer at 350–500 °C. We report in this communication our attempt to improve the efficiency of electrophoretically deposited TiO_2 layer by combining chemical and thermal post-treatments that can be applied to plastic cells.

Commercially available TiO_2 nanoparticle powers, P-25 of Degussa and F-5 of Showa Denko Co., both of anatase-rich crystalline particles with different crystal shapes (average size, 20–30 nm), were used for film formation. The powders were suspended in a dry mixed solvent of *tert*-butanol and acetonitrile (volume ratios from 1/0 to 1/1) at concentration of 20 to 30 mg/mL without the addition of stabilizer (organic polymer, etc.). A layer of the suspension, 0.3 mm thick, was sandwiched between two flat electrodes, one of which is to be used as a dye-sensitized working electrode. The electrode is either F-doped SnO_2 transparent conductive glass or ITO-coated PET (polyethylene terephthalate) plastic film of substantially equal resistance of 7–9 $\Omega/\square$. For electrophoretic deposition, DC electric field of -200 V/cm was applied to the working electrode for 0.5 to 1 min by using a voltage generator Advantest TR6142. This resulted in formation of porous TiO_2 layer of uniform thickness. The TiO_2 surface density (g/m^2) was controlled by the concentration of the suspension. The electrodeposited TiO_2 layer was subjected to post chemical treatments; the layer was exposed to gaseous phase of $Ti(OC_3H_7)_4$ at 80 °C for 2 to 20 min to undergo chemical vapor deposition (CVD) of the alkoxide, followed by exposure to ultraviolet light (254 nm, 8 W) for 20 min. The TiO_2-bearing electrode thus completed was dried at 90 °C and was subjected to dye adsorption in a 3×10^{-4} mol/L solution of Ru complex dye (Ru535 bisTBA supplied from Solaronix SA) in a mixture of acetonitrile : *tert*-butanol : ethanol (2 : 1 : 1). For comparative experiments, the above deposited layer and a TiO_2 layer prepared by coating of a binder (polyethylene glycol)-containing TiO_2 paste were sintered at 550 °C for 30 min (for case of F/SnO_2 electrode only). For these sintered layers, no additional chemical treatments were applied for maximizing the efficiency.

Dye-sensitized electrodes were combined with a Pt counter-electrode (vacuum-deposited Pt layer on conductive F/SnO_2 glass electrode) by inserting a 25 μm-thick layer of methoxyacetonitrile-based electrolyte containing 0.1 M LiI, 0.05 M I_2, 0.5 M *tert*-butylpyridine, and 0.6 M dimethylpropylimidazolium iodide (1 M = 1 mol/L). Photocurrent-voltage characteristics were measured on a Keithley 2400 source meter under simulated solar irradiation of 100 mW/cm^2 supplied by a 300 W xenon arc lamp (Perkin Elmer) combined with a AM1.5 G filter (Optical Coatings Japan). Incident energy was monitored with a black body-based power meter, Melles Griot 13 PEM 001.

The TiO_2 particles exhibited positive ζ potentials (260 mV for F-5) in butanol, indicating that electrophoresis should occur to negatively biased electrode. Uniform TiO_2 layers of good adherence (6–12 g/m^2, thickness of 7–13 μm) were formed on the both surfaces of F/SnO_2 glass and ITO-PET plastic film. Particularly the TiO_2-bearing ITO-PET showed mechanical stability against bending of the film up to a curvature of 0.2 mm^{-1} (diameter of 10 mm). The amount of TiO_2 deposited per area showed a linear relationship to TiO_2 concentration of the suspension. Optimal conditions for homogeneous deposition were found not only in the particle concentration but also in the amplitude of DC field and in adjustment of electrode-electrode distance.

Photovoltaic characteristics of the above nonsintered TiO_2 layers were assessed with the F/SnO_2 glass-based photocells. On illumination of 100 mW/cm^2 light, electrophoretically deposited, virgin film of P-25 without post-treatments yielded J_{sc} (photocurrent density) = 4.2 mA/cm^2 and η (conversion efficiency) = 2.0, which was one third the efficiency, 6.0%, obtained with a TiO_2 film that underwent 550 °C annealing of the same film. The sintered TiO_2 film made from binder-containing TiO_2 paste as a conventional reference yielded a higher efficiency (>6.5%). Although the efficiency of the virgin film is not of satisfactory level, post-treatments of the film by CVD and UV light irradiation

proved to greatly improve the photoelectric performance. The results of I–V characteristics are shown in Figure 1 in comparison with those of nontreated (virgin) film and sintered film. The post-treatment improved J_{sc} by 30 to 80%, depending on the particle and CVD conditions, from the level of virgin film. The conversion efficiency by the CVD treatment reached 3.7%, which is more than half that of the photocell made by high-temperature sintering.

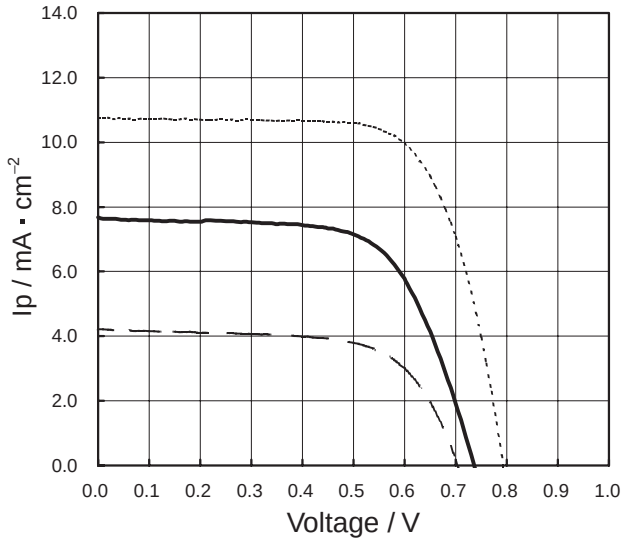

Figure 1. Photocurrent-voltage (Ip-V) characteristics of dye-sensitized photocells (F/SnO_2 glass-based photocells). – –: electrodeposited TiO_2 (P-25) film without post-treatments ($\eta = 2.0\%$), —: film with CVD + UV treatment ($\eta = 3.7\%$), - - - -: reference film after sintering at 550 °C for 30 min ($\eta = 6.0\%$).

Table 1 summarizes the I–V performance of the photocells of the present method and reference photocells made by sintering method. Comparing the efficiency parameters, what is essentially inferior to the sintering-type cells is J_{sc}. There occurred relatively small loss in V_{oc} and fill factors by displacing the sintered films with the nonsintered films. The lowering of J_{sc} must be due to a lack of interparticle connection for efficient electron migration, which is shown by the fact that J_{sc} recovers to a maximum level by additional 550 °C annealing. To reinforce the interparticle electron conduction, we attempted local heating of the deposited layer by applying microwave irradiation. The TiO_2 layer was exposed for 2–5 min to 2.45 GHz microwave of a commercial 550 W microwave oven (Sharp PE-T12). This treatment proved to increase J_{sc} for maximizing the efficiency. We could finally obtain conversion efficiencies of 4.1% for P-25 layer (9–12 g/m^2) and 3.4% for F-5 TiO_2 layer (6–8 g/m^2) that exceed the previously reported efficiencies of nonsintered type cells.[6,9,10,12]

Plastic photocells based on the above method yielded an efficiency level of 2.3–3.0% by applying the microwave treatment. For the low efficiency compared to the F/SnO_2 glass-based photocells, we suspect the presence of a large current loss due to a back electron transfer at the ITO-TiO_2 interface.

Table 1. Photoelectric performances of dye-sensitized photocells[a]

TiO_2 preparation	J_{sc}/Acm^{-2}	V_{oc}/V	*FF*	η/%
P-25 ED only	4.2	0.70	0.66	2.0
ED + CVD	7.7	0.74	0.65	3.7
ED + MW	9.0	0.73	0.62	4.1
Sintering	10.8	0.79	0.70	6.0
F-5 ED only	4.8	0.79	0.64	2.5
ED + CVD	6.2	0.80	0.66	3.2
ED + MW	5.6	0.78	0.66	2.9
ED + CVD + MW	7.1	0.76	0.63	3.4
Sintering	10.3	0.79	0.60	4.9

[a]F/SnO_2 glass-based photocells. Notation; ED: electrodeposition, CVD: chemical vapor deposition of $Ti(OC_3H_7)_4$ followed by UV irradiation, MW: microwave irradiation, sinter: 550 °C sintering of electrodeposited layer as a reference preparation (see text). Amount of TiO_2 deposited; P-25: 9–12 g/m^2, F-5: 6–8 g/m^2.

With omission of the high-temperature sintering process, our method enables completion of electrode making in considerably short time and thus minimizes the risk of environmental load. In this respect, we are now focusing on developing low-cost materials and processes for manufacturing all-plastic type photocells.

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