UV Light-assisted Chemical Vapor Deposition of TiO_2 for Efficiency Development at Dye-sensitized Mesoporous Layers on Plastic Film Electrodes

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Chemical vapor deposition of TiO_2 combined with UV light irradiation at nanocrystalline TiO_2 particle layers coated on plastic film electrodes (ITO-PET) drastically enhanced dye-sensitized photocurrent and improved photovoltage up to 750 mV, achieving energy conversion efficiency of 3.8%.

Low temperature preparation of mesoporous semiconductor film is essential for devising plastic film-based dye-sensitized solar cells (DSSCs), which are a recent highlight in application of the DSSC technology. The main subject in film preparation is to improve conversion efficiency which is much lower than those attained by high temperature sintering (<450 °C) method (8–10%).[1–3] Pichot et al. have studied binder-free coating of nanocrystalline particles, showing low conversion efficiency due to lack of inter-particle binding (i.e., necking) for mesoporous structures.[4] Various methods have been applied to preparation of TiO_2 mesoporous films at temperatures below 150 °C that allows for use of plastic supports such as polyethylene terephthalate (PET). Hagfeldt et al. showed that a film made by compression of nanocrystalline TiO_2 on glass substrate realizes efficiency up to 3% under irradiation of $100\,\mathrm{mW\,cm^{-2}}$.[5] Hydrothermal synthesis of TiO_2 has been studied by Yin et al.[6] and Zhang et al.,[7,8] which was proved to be useful for constructing plastic-based DSSCs of efficiency up to 3.3%.[8] These efficiencies are however still low compared to the state-of-the-art Si-based thin film solar cells.[9] We have studied efficiency improvement of electrophoretically-deposited mesoporous TiO_2 films on SnO_2 glass electrode.[10] Aim of the present study is to extend our method to use of conductive plastic electrode and to elicit highest efficiency from binder-free TiO_2 coatings by means of chemical vapor deposition and UV light irradiation for surface treatments as chemical necking treatments.

TiO_2 particle, F-5, was supplied from Showa Titanium Co. Ltd., which is anatase-rich (70%) nanocrystalline particle with an average size of 20–30 nm. Indium tin oxide-coated polyethylene terephthalate (ITO-PET) film (125 μm thick, transmittance of 76–78%, surface resistance of 8–12 Ω/□) was provided by Tobi Co. Ltd., and was used as transparent conductive plastic electrode. Binder-free TiO_2 nanoparticle layers were formed on the ITO-PET electrode by electrophoretic deposition method.[10] A homogeneous dispersion of F-5 in *tert*-butyl alcohol and acetonitrile (95:5) mixture (40 g/L) sandwiched between the ITO-PET electrode and conductive SnO_2 glass counter electrode and a DC field of −200 V/cm was applied to the ITO-PET electrode for 30 s. The F-5 nanoparticles were totally deposited on the ITO surface with uniform thickness of 10 μm. After drying, the deposited layer gave a high porosity of 80% and, on microscopic observation, the film surface exhibited a crackle-rich structure characteristic to electrophoretic deposition. In an attempt to improve photoelectric property, the deposited layer was subjected to chemical vapor deposition (CVD) and/or UV light irradiation treatments. The CVD treatment was performed by exposure of the layer to gaseous $[(CH_3)_2CHO]_4Ti$ at 80 °C in a closed chamber, bare ITO surfaces being covered by masking tape for protection. For UV treatment, TiO_2 layers were exposed to 254-nm light supplied by a 13-W low-pressure mercury lamp (Nippo SGL-400T4U) at 110 °C, where bare ITO surfaces were again protected with an aluminum foil. Shortly afterwards, the post-treated TiO_2 layer on ITO-PET film was dye-sensitized by adsorption of Ru complex dye (Solaronix), *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II)bis-tetrabutylammonium, by dipping the film in a 0.3 mM ($\mathrm{M} = \mathrm{mol\,dm^{-3}}$) solution of the dye in mixed solvent of acetonitrile:ethanol:*tert*-butyl alcohol (2:1:1) at 40 °C for 1 h. The dye-adsorbed TiO_2–ITO-PET film was combined with a platinum-deposited SnO_2 glass counter electrode by insertion of a porous polyethylene film (thickness 7 μm, porosity 39%) as a separator to prevent short circuit. Electrolyte solution comprised a mixture of 0.05 M I_2, 0.1 M LiI, 0.5 M 4-*tert*-butylpyridine, and 0.6 M 1,2-dimethyl-3-propylimidazolium iodide in methoxyacetonitrile, which was injected between both electrodes separated by 25 μm. Photocurrent-voltage characteristics were measured on a Keithley 2400 source meter in combination with a 300-W xenon arc lamp solar simulator attached with AM 1.5 filters.Three independent processes were examined in which CVD treatment alone (CVD), UV irradiation alone (UV), and a combined process of CVD treatment followed by UV irradiation (CVD/UV), respectively, were applied to the electrophoretically deposited TiO_2 layers. On illumination of $85\,\mathrm{mW\,cm^{-2}}$, virgin TiO_2 layer without the treatments yielded a short circuit photocurrent density (Jsc) of $2.9–3.3\,\mathrm{mA\,cm^{-2}}$, as a minimal level of Jsc before chemical necking treatments, which was increased by the above processes. Figure 1 exhibits Jsc of TiO_2-coated ITO-PET electrodes treated by CVD, UV, and CVD/UV processes, respectively, in function of the time of treatment. In the combined CVD/UV process, all the samples underwent UV irradiation for 20 min following the CVD treatment. The result shows that all processes are effective to increase dye-sensitized current. In particular, large enhancement of photocurrent occurred with combined CVD/UV treatment, in which Jsc was twice increased from initial value of nontreated TiO_2 layer. Although both of CVD and UV processes increased Jsc, origin of these effects is assumed to be quite different. TiO_2 formation by CVD is a well-established reaction.[11] In CVD, gaseous precursor is introduced between existing particles to form TiO_2,[12] developing a necking structure that promotes interparticle electron conduction. UV irradiation, however, is regarded nothing to do with chemical necking as far as UV is solely employed. It can be understood that the some impurities of insulation adsorbed on TiO_2

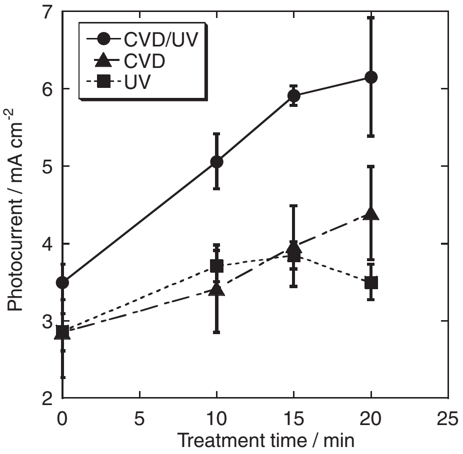

Figure 1. Short-circuit photocurrent densities (Jsc) of dye-sensitized TiO_2–ITO-PET electrodes as a function of the time of post-treatment processes. - - -■- - -, UV irradiation; -—▲-—, CVD treatment; —●—, CVD/UV treatment (with UV irradiation fixed as 20 min). Error bars are based on variation coefficients of at least four experiments.

surfaces were decomposed by UV irradiation and photocatalytic reaction of TiO_2.[13] In Figure 1, the Jsc increase by CVD/UV process exceeds the sum of increments by CVD and UV processes. This indicates that UV irradiation participates in the chemical process of CVD necking, i.e., photochemical and photocatalytic decomposition of alkoxide on TiO_2.

Figure 2 shows dependence of open circuit voltage (Voc) on treating time of individual processes. The Voc increased with CVD/UV and CVD treatments up to 10 min and remained constant afterwards, while little increase occurred with UV process alone.[14] It is to be noted that the Voc increase as much as 70 mV in CVD/UV process is significantly large and the maximum Voc obtained of 740–750 mV is a level comparable with that obtainable with dye-sensitized sintered TiO_2 electrodes of highest efficiency (10%).[1–3] Results of Jsc and Voc behavior (Figures 1 and 2) demonstrates that UV irradiation activates the CVD necking reaction that improves both of Jsc and Voc. Accordingly, UV irradiation in the absence of the precursor of CVD must have a small effect in Jsc enhancement.

The photocurrent density-voltage behavior of dye-sensitized plastic electrodes with binder-free TiO_2 layers treated by CVD, UV, and CVD/UV treatments and that of nontreated electrode are compared in Figure 3. The electrode fabricated by the CVD/UV treatment yielded 3.8% (Jsc $= 7.0\,\mathrm{mA\,cm^{-2}}$, Voc $=$ 750 mV, fill factor (FF) $=$ 0.61) under irradiation of $85\,\mathrm{mW\,cm^{-2}}$. Corresponding values achieved by CVD treatment only was 2.7% (Jsc $= 5.2\,\mathrm{mA\,cm^{-2}}$, Voc $= 720$ mV, FF $= 0.61$). The results are well-improved from 1.6% efficiency of a nontreated TiO_2 layer. Remarkably high standard of Voc achieved by the CVD/UV treatment contributes itself to high conversion efficiency of the cell.

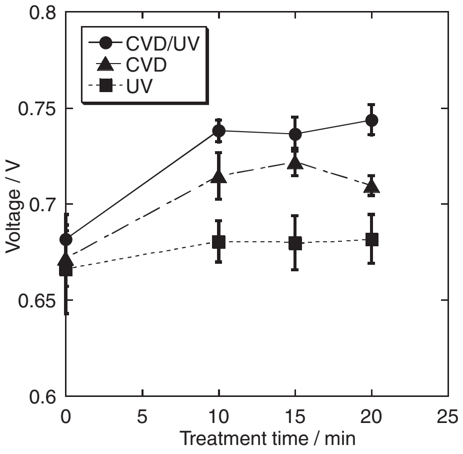

Figure 2. Open-circuit voltage (Voc) of dye-sensitized TiO_2–ITO-PET electrodes as a function of the time of post-treatment processes. Denotation of symbols are the same as in Figure 1.

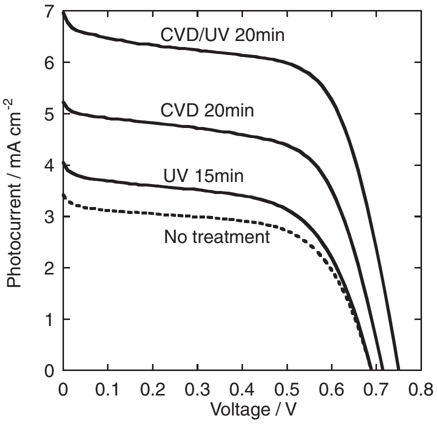

Figure 3. Photocurrent density-voltage characteristics for DSSCs based on dye-sensitized TiO_2–ITO-PET electrodes with and without the post treatments of TiO_2 layers.

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References and Notes

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