Highly efficient plastic substrate dye-sensitized solar cells using a compression method for preparation of TiO_2 photoelectrodes

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The efficiency of a plastic-substrate dye-sensitized solar cell was much improved by a new method consisting of a press method without heat treatment, light confinement effect of TiO_2 film and water-based TiO_2 paste; this device shows the highest light-to-electrical energy conversion efficiency based on plastic-substrate dye-sensitized solar cells, 7.4% under 100 mW cm^{-2} (1 sun) AM1.5 illumination.

Dye-sensitized solar cells (DSCs)[1] are presently under intense investigation in many laboratories, because of their high efficiency (~11%) and the potential for low-cost production.[2] In particular, a DSC using a flexible, thin and lightweight conducting plastic film is presently receiving much attention because of its potential for commercial applications. However, one of the problems with plastic-substrate DSCs is that they have a lower efficiency than that of glass-substrate DSCs, due to the thermal instability of the plastic substrates at the higher sintering temperature (450–550 °C) of the TiO_2 photoelectrode. Therefore, many companies and academic institutions have been engaged in research and development to find a solution to this problem.[3–11] Hagfeldt and co-workers introduced the compression method for low-temperature preparation of nanostructured TiO_2 films.[3–5] Using films prepared by this method, they achieved an efficiency of 5.5%[5] under 10 mW cm^{-2} (0.1 sun) irradiation; however, under 1 sun illumination, the efficiency decreased to 3%.[4] Dürr *et al.* subsequently developed the lift-off process.[6] In this process, the TiO_2 layer was first applied to a thin gold layer on a glass substrate. After sintering, the TiO_2 layer was removed from the glass by dissolving the gold layer. The TiO_2 layer was then transferred onto an ITO-coated PET film by application of high pressure. By this process, Dürr *et al.* achieved an efficiency of 5.8% under 100 mW cm^{-2} (1 sun). However, this efficiency is still low for commercial use. After many studies using the compression method, we have achieved an efficiency of 7.4% under 1 sun irradiation. In the present paper, we discuss our process for improving the efficiency of plastic-substrate DSCs.

The TiO_2 paste used was composed of a mixture of TiO_2 powder and ethanol at a concentration of 20 wt%. Photoelectrodes were made as follows: first, the TiO_2 paste was applied onto an ITO-PEN film (13 Ω $\square^{-1}$) by doctor-blade coating. After air drying, heat (150 °C, 10 min) or pressure (100 MPa)[12] treatment, or both were applied. The coated and treated film was then dipped into an ethanol solution of a Ru complex dye N719, the bis(tetrabutylammonium) salt of *cis*-diisothiocyanatobis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II), which had been synthesized according to the literature.[13] The area of the TiO_2 photoelectrode was about 0.25 cm^2 and its thickness ranged from 4 to 8 μm. The area of the photoelectrode was measured with a digital micrometer VHX-200 (Keyence) using an objective micrometer ruler as a reference. The film thickness was monitored with a surface texture-measuring instrument SURFCOM1400D (Tokyo Seimitsu). As an electrolyte, a mixture of I_2 (0.05 M), LiI (0.1 M), 1,2-dimethyl-3-propylimidazolium iodide (0.6 M) and 4-*tert*-butylpyridine (0.5 M) in dehydrated acetonitrile was used. The sandwich-type solar cell was assembled by placing a Pt-sputtered ITO-PEN film (counter electrode) on the dye-loaded TiO_2 photoelectrode in contact with an electrolyte. The photocurrent–voltage (*I–V*) characteristics of the DSCs were measured on a Keithley 2400 source meter under irradiation AM1.5, 100 mW cm^{-2} (1 sun) supplied by a solar simulator (Peccell Technologies). The incident light intensity was calibrated with a grating spectroradiometer LS-100 (EKO Instruments) and a Si photodiode (Bunkoh–Keiki).

It is known that the light-confined effect of TiO_2 photoelectrodes composed of an optimum mixture of nanosized TiO_2 particles and large-size light scattering TiO_2 particles is very effective for increasing the solar cell efficiency of a glass-substrate DSC to more than 10%.[14,15] Therefore, we applied this technique to plastic-substrate DSCs. TiO_2 powders with various particle sizes were prepared by hydrolysis of $Ti(OCH(CH_3)_2)_4$ following the autoclave treatment.[14] The average particle sizes of three different TiO_2 powders were 20, 50 and 100 nm in diameter as obtained by X-ray diffraction. Using these three TiO_2 powders, three different TiO_2 pastes were prepared[16] (Table 1). These pastes consisted of only TiO_2 particles and ethanol solvent, and did not include any binder materials. The N paste was composed of only 20 nm diameter TiO_2 particles. The M′ paste was composed of a mixture of 20 and 50 nm diameter TiO_2 particles with a weight ratio of 7 to 3. The M paste was composed of a mixture of 20 and 100 nm diameter TiO_2 particles with a weight ratio of 7 to 3. The applied

Table 1 Effect of the light confined effect on solar cell performance

TiO_2 paste	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	η (%)	t^a/μm	$10^8\Gamma^b$/mol cm^{-2}
P25[c]	7.2	0.79	0.74	4.2	4	3.4
N	6.4	0.76	0.69	3.3	4	2.9
M′	8.9	0.77	0.67	4.5	4	3.0
M	11.2	0.75	0.67	5.6	7	4.6

[a] Film thickness. [b] Dye attached on TiO_2. [c] Provided from Nihon Aerosil.

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Table 2 Dye-sensitized solar cell performances with different photoelectrode preparation methods

Method	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	η (%)	t^a/μm	$10^8\Gamma^b$/mol cm^{-2}
1	4.4	0.78	0.61	2.1	6	5.4
2	9.1	0.76	0.64	4.4	5	4.9
3	10.4	0.79	0.74	6.0	6	5.8
4	11.2	0.75	0.67	5.6	7	4.6
5	10.4	0.76	0.68	5.3	5	4.2

[a] Film thickness. [b] Dye attached on TiO_2.

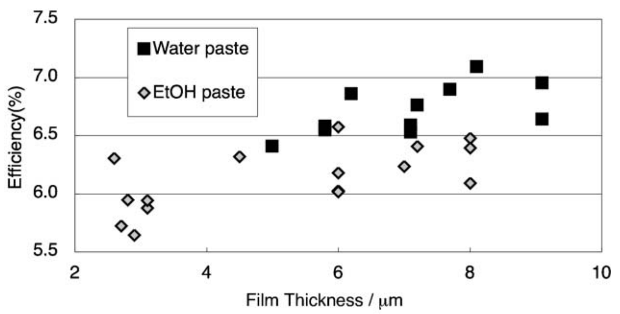

Fig. 1 Relation between efficiency and thickness of TiO_2(M) film prepared from using water paste (TiO_2, 10 wt%) and EtOH paste (TiO_2, 20 wt%).

pressure was 100 MPa; heat treatment at 150 °C for 10 min was conducted after applying the pressure. The solar cell efficiency and the photocurrent were much improved, from 3 to 5.6%, and from 6.4 to 11.2 mA cm^{-2}, respectively, by using mixed pastes such as the M′ and M pastes. This demonstrates that the light-confinement effect is very useful for improving efficiency in plastic-substrate cells as well as in glass-substrate cells.

To understand the role of heat treatment in the compression method, we applied five photoelectrode construction methods after coating the ITO-PEN films with M paste (Table 2). In method 1, we used drying at room temperature only; in method 2, heating at 150 °C for 10 min; in method 3, applying 100 MPa pressure without heating; in method 4, heating after applying pressure; and in method 5, heating before applying pressure under the same conditions. In methods 4 and 5 (heat treatment before and after applying pressure) little change in efficiency was observed: The performance of the solar cells was η = 5.3–5.6%. However, the efficiency was improved in method 3 (without heat treatment) to η = 6.0%. It is clear that the fill factor (FF) was much improved. After the heat treatment, we observed that the conducting plastic film was warped more than before, suggesting that heat treatment might decrease the adhesive force between the TiO_2 nanoparticles and the conducting plastic substrate. Therefore, we decided that heat treatment is not essential to the compression method.

We speculated that the organic solvent in the TiO_2 paste might influence the stability of the conducting plastic substrate. Therefore, TiO_2 paste using only water solvent was prepared by replacing ethanol solvent with water in the preparation procedure of TiO_2 paste (TiO_2, 10 wt%) and its performance was tested (Fig. 1). The performance of a solar cell with 8 μm thickness of photoelectrode, prepared from TiO_2-water paste, was improved to η = 7.1%, J_{sc} = 12.4 mA cm^{-2}, V_{oc} = 0.75 V and FF = 0.76. On the other hand, a solar cell prepared from the TiO_2 paste using

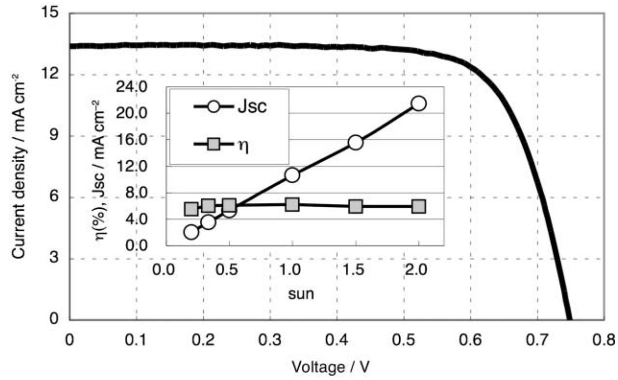

Fig. 2 Photocurrent–voltage curve of the optimized plastic based DSC. Solar energy to electricity conversion efficiency (η) = 7.4% with J_{sc} = 13.4 mA cm^{-2}, V_{oc} = 0.75 V and FF = 0.74. Cell area = 0.256 cm^2, Light intensity = 100 mW cm^{-2} (1 sun). The inset shows the dependence of J_{sc} and η on light intensity from 0.2 to 2 sun.

ethanol solvent with 8 μm thickness TiO_2 photoelectrode showed a performance of η = 6.5%, J_{sc} = 11.6 mA cm^{-2}, V_{oc} = 0.76 V and FF = 0.73. This demonstrates clearly that a water paste is better than an organic paste for making a plastic-substrate DSC.

Furthermore, UV–O_3 treatment of the ITO-PEN film before TiO_2 paste application slightly improved the cell efficiency. By this method, we could reliably prepare plastic-based DSCs having an efficiency of 7.4% (1 sun) (Fig. 2). Moreover, these cells show linearity of the J_{sc} *vs.* light intensity from 0.2 to 2 sun, showing that TiO_2 films made by this compression method have sufficient conductivity between the film and the conducting substrate.

In conclusion, the solar cell performance of a plastic-substrate DSC was much improved by this new method, which combines a compression method (without heat treatment) with the light-confining effect of a TiO_2-water paste. Enhancement of the cell area and long-term stability tests are in progress.

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