Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 164 (2004) 67–73

Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Multi-colored dye-sensitized solar cells

Hideo Otaka, Michie Kira, Kentaro Yano, Shunichiro Ito,
Hirofumi Mitekura, Toshio Kawata, Fumio Matsui*

Hayashibara Biochemical Laboratories Inc., Tokyo Cooperative Research Center, 2-1-6 Kabukicho, Shinjuku-ku, Tokyo 160-0021, Japan

Received 15 July 2003; received in revised form 14 November 2003; accepted 16 November 2003

Abstract

Multi-colored solar cells sensitized with organic dyes were developed by optimizing electrolytes and counter electrodes to enhance the transparence of the both by reducing the concentration of iodine dissolved in the imidazolium-based electrolytes and by employing a platinum layer of a 0.5 nm thickness. The solar cells were assembled by using nano-crystalline TiO_2 electrodes adsorbing sensitizing dyes, an electrolyte consisting of a mixture of iodine and 1-butyl-3-methylimidazolium iodide in a 0.2:10 molar ratio and the counter platinum electrode to give cells bearing red, purple, blue, green and black colors. The multi-colored solar cells were connected in series to exhibit a 2.1% conversion efficiency under AM 1.5 (1 sun, $100\,mW\,cm^{-2}$) irradiation with a total semiconductor area of $25\,cm^2$.

Keywords: Dye-sensitization; Multi-colored solar cell; Titanium dioxide; Molten salt; Sensitizing dye

1. Introduction

Dye-sensitized solar cells using nano-crystalline TiO_2 electrodes have been investigated since the report by Grätzel and coworkers on attaining reasonable conversion efficiencies of high intensity solar light into electric power [1]. Enormous efforts have been concentrated on to improve the conversion efficiency [2–4], whereas the optimization of cell structures and the reliability of cell performances have been studied from a viewpoint of mass production. But practical uses seem to still remain much to be done. Sensitizing dyes for this type of cells include not only various kinds of metal complexes, but also multiple types of organic dyes to improve the conversion efficiency. Among organic dyes developed so far [5,6], it has been reported that a coumarin dye displays a 7.7% efficiency with an organic solvent electrolyte under AM 1.5 irradiation (1 sun, $100\,mW\,cm^{-2}$) [7]. On the other hand, the efficiency of silicon-based solar cells exceeds 20%, so that continuous efforts have been continued to fabricate the dye-sensitized solar cells which exhibit markedly enhanced conversion efficiency, excellent reliability and reasonable cost.

We report here the fabrication and performances of multi-colored solar cells by using appropriate combinations of organic dyes to display a decorative appearance, stressing on their inherent properties which exhibit multi-farious color tones. The major concern of this work is to optimize chemical structures and ingredients of electrolytes as well as to seek fabrication procedures of electrodes so as to approach to our final goal by which solar cells with a decorative effect are attained.

2. Experimental

2.1. Materials

The *cis*-dithiocyanato-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid)ruthenium(II) complex (N3) [2] was purchased from Kojima Kagaku Co. Ltd. The other non-metal sensitizing dyes shown in Fig. 1, 4-[3-(7-diethylamino-2-oxo-2H-chromen-3-yl)-2-methyl-3-oxo-propenyl]-benzoic acid (**1**), {3″-carboxymethyl-5-[2-(5-chloro-3-ethyl-3H-benzothiazol-2-ylidene)ethylidene]-3-ethyl-4,4′,4″-trioxo-2″-thioxo-[2,5′;2′,5″]terthiazolidin-3′-yl}-acetic acid (**2**), 2-[2-(3,3′-diethyl-4,4′-dioxo-2′-thioxo-[2,5′]bithiazolidinyliden-5-ylidene)ethylidene]-3-ethyl-2,3-dihydro-benzothiazole-5-carboxylic acid (**3**), and {5-[2-(5-chloro-3-ethyl-3H-benzothiazol-2-ylidene)-ethylidene]-3′-ethyl-4,4′-dioxo-2′-thioxo-[2,5′]bithiazolidinyliden-3-yl}acetate triethylammonium salt (**4**), were synthesized according to the procedures which are reported elsewhere. 1-Alkyl-3-methylimidazolium iodides as molten salts at room temperature [8,9] were pre-

---

[*] Corresponding author. Tel.: +81-3-5292-3129; fax: +81-3-5292-3129.
E-mail address: aaa80870@pop11.odn.ne.jp (F. Matsui).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2003.11.012

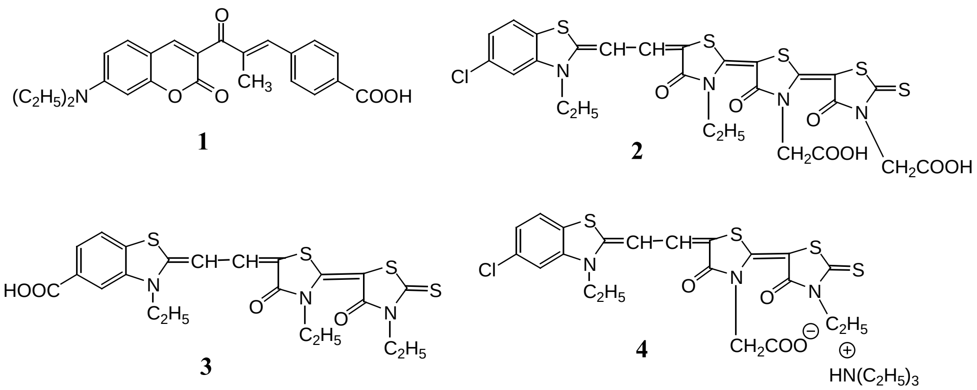

Fig. 1. Chemical structures of sensitizing dyes.

pared by the quaternization of 1-methylimidazole with the corresponding alkyl iodide (C_1–C_{10}) without solvent and purified by decantation with ether [10]. Nano-crystalline TiO_2 was prepared according to the general procedure [3].

2.2. Preparation of TiO_2 electrodes

A TiO_2 paste was prepared by mixing two types of TiO_2 nano-particles, of which diameters were 12 and 24 nm, respectively, with polyethyleneglycol (PEG) of a molecular weight of 20 000 as a binder with a proportion of 20 wt.% of the TiO_2. Subsequently, the paste was placed on an electroconductive glass substrate (Asahi TCO glass, fluorine-doped SnO_2 overlayer; thickness 1.8 mm) by means of screen printing technique or by using a bar coater, followed by sintering at 450 °C in air for 0.5 h to give a TiO_2 electrode with an effective area of 1.0 cm^2, and a TiO_2 film thickness of 5 ± 2 μm. An electroconductive glass substrate was coated optionally with TiO_2 by sputtering when was needed.

2.3. Preparation of counter electrode

A counter electrode was prepared by sputtering a thin platinum layer on an electroconductive glass substrate. Thickness of the platinum layer was controlled to be 100 nm to evaluate performances of a sensitizing dye, whereas 0.5 nm thick platinum layer was employed to fabricate cells which exhibit high transparence.

2.4. Electrolyte preparation

Two kinds of electrolytes consisting of acetonitrile and nonvolatile molten salts, respectively, were used in this study. The former was prepared by dissolving 45 mM of iodine, 30 mM of lithium iodide, 330 mM of 1,2-dimethyl-3-hexylimidazolium iodide and 100 mM of 4-*tert*-butylpyridine in acetonitrile according to the literature with a modification [3]. The latter was comprised of 1-alkyl-3-methylimidazolium iodide and iodine, whereas concentrations of iodine were less than 20 mol%.

2.5. Cell fabrication

Adsorption of a sensitizing dye on a TiO_2 surface was carried out by soaking a TiO_2 electrode in a methanol solution of the dye of which concentration was 3×10^{-4} M at room temperature for 12 h, followed by rinsing with methanol and drying. A photoelectrochemical cell was fabricated by using a dye-sensitized TiO_2 electrode, on which a drop of an iodine-based electrolyte was deposited in advance, and a platinum-coated conductive glass as a counter electrode, and they were glued with an epoxy adhesive. An effective area of the cell electrode was generally 1.0 cm^2 (1.0 cm × 1.0 cm). The cell gap was adjusted by using a spacer film of 50 μm thick. In the case of a molten salt electrolyte, the cell assembly was performed without a spacer.

2.6. Physical measurements

Efficiencies for solar energy conversion were evaluated under illuminating cells with a solar simulator (Yamashita Denso, YSS-100A) as an AM 1.5 light source (1 sun, 100 $mW\,cm^{-2}$) and electrochemical analyzer (ALS Inc., Model 600A). Cell temperatures were kept at 25 °C during the illumination. Light intensity was calibrated by using a thermopile power meter (Anritsu, ML-9050A) and was controlled by neutral density (ND) filters. Spectral intensity distribution of the light was measured with a diode spectrometer (Ootsuka, MCPD-1000), whereas the incident photon-to-current conversion efficiency (IPCE) measurement was achieved at 25 °C which ranged from 375 to 900 nm at a 25 nm interval by using band-pass filters with a 5 nm half-width. Layer thickness of platinum on glass substrates was estimated by amount of sputtering platinum recorded on a quartz thickness monitor.

3. Results and discussion

3.1. Preparation of nano-crystalline TiO_2 paste

Since, the TiO_2 electrodes of our cell are made of mixtures of two types of nano-crystalline TiO_2 with average particle sizes of 12 nm (TiO_2-12) and 24 nm (TiO_2-24), respectively, cell performances were examined as a function of weight ratios of the two, which were suspended with PEG in aqueous acidic solutions to prepare the porous electrodes. Fig. 2 shows the results for cells activated by a molten salt electrolyte and dye **4**. It was found that there exist an optimum value at [TiO_2-12] : [TiO_2-24] = 4:6 for both short-circuit photocurrent density (J_{SC}) and light energy conversion efficiency (η). It is assumed, however, that the optimum ratio is altered by nature of the adsorbed sensitizing dyes, taking notice of the fact that a molecular size of a sensitizing dye is not negligible with respect to porosity sizes of the TiO_2 electrode, which are influenced not only by ratios of the two particles, but also by concentrations of PEG as a binder to ensure the high porosity conformation after baking which leads to sintering.

3.2. Prevention of the short-circuit on TiO_2 electrodes

Since, only minute light absorption is performed by monolayered dye molecules adsorbed on a flat surface, it is crucial to employ a substrate covered with a porous, nano-structured TiO_2 film which exhibits high surface roughness resulting in enhanced light absorption by adsorbing plenty amounts of dye molecules on the surface [2,3]. It was anticipated that performances of a cell assembled with this kind of a substrate deteriorate due to the short-circuit of a fluid electrolyte on a conductive glass substrate with highly porous TiO_2 electrode. In order to prevent the short-circuit, the conductive glass substrate was subjected to sputtering with TiO_2, followed by the fabrication of a TiO_2 electrode as described above. Fig. 3a shows the effect of the TiO_2 sputtering on photocurrent–voltage curves of cells assembled with a molten salt electrolyte and dye **4**. Compared to the cell with a TiO_2 electrode which was not sputtered (thickness = 0 nm), the cells with TiO_2 electrodes modified by sputtering TiO_2, which ranged from 10 to 30 nm, displayed a marked enhancement of open-circuit voltages (V_{OC}) and the fill factor (ff). Values of V_{OC} were 0.63 and 0.57 for 10–30 and 0 nm, respectively. Note that 10 nm in thickness is enough to attain the effect. As shown in Fig. 3b and c, the effect of the TiO_2 sputtering is more clearly observed when the light intensity is lowered at 1/10 and 1/100 sun, whereas the improvement of cell performance is not remarkable even in the same electrode when a solvent electrolyte was used.

3.3. Assembly of multi-colored solar cells

3.3.1. The optimization of electrolyte and counter electrode

Taking notice of the decorative effect of sensitizing dyes on solar cells, our primary attention was paid to reduce the color tone due to iodine dissolved in an electrolyte. Prior to optimizing iodine concentration, an examination was attempted on fluid electrolytes, because a solvent electrolyte consisting of acetonitrile has a serious drawback due to poor durability of cells coming from damage of a sealant by the solvent and the subsequent leakage of the electrolyte. Accordingly, we replaced the solvent electrolyte by molten salt electrolytes comprised solely of 1-alkyl-3-methylimidazolium iodide as a molten salt and iodine.

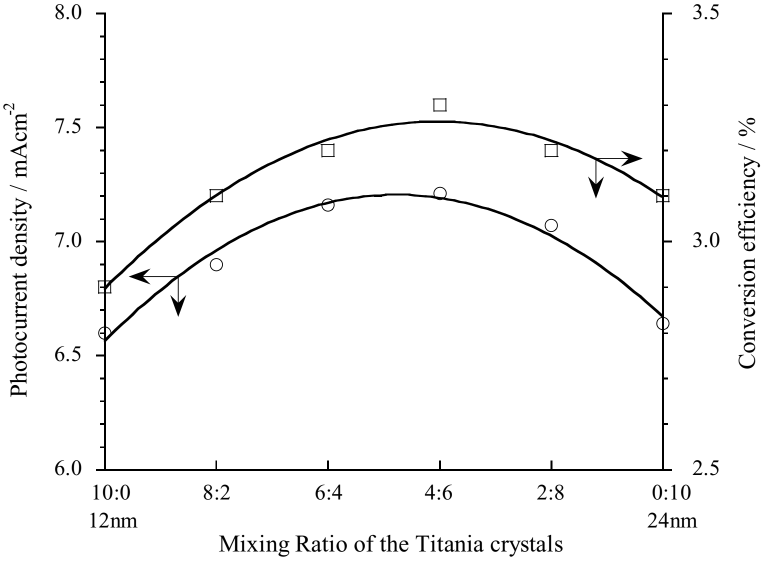

Fig. 2. Short-circuit photocurrent density (J_{SC}) and solar energy conversion efficiency (η) as a function of mixing weight ratios of two types of TiO_2 particles of 12 and 24 nm in diameter, respectively.

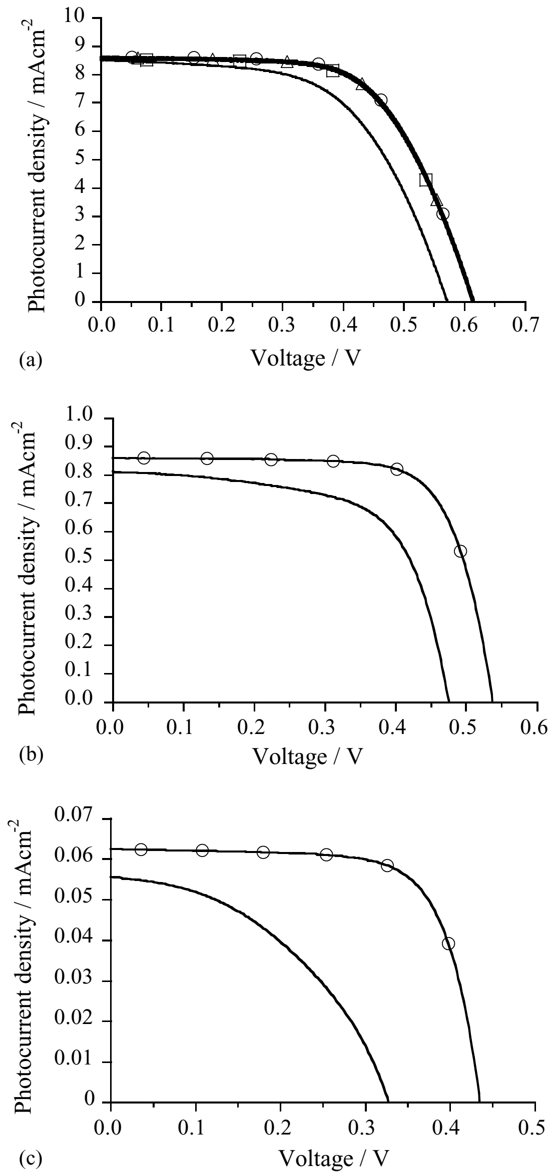

Fig. 3. Photocurrent–voltage curves of dye **4**-sensitized solar cells assembled with porous TiO_2 electrodes coated with and without sputtered TiO_2 layers: (a) under 1 sun; (b) under 1/10 sun; (c) under 1/100 sun irradiation. The thickness of sputtered TiO_2 layers are 0 nm (continuous line), 10 nm (open circles), 20 nm (open triangles) and 30 nm (open squares).

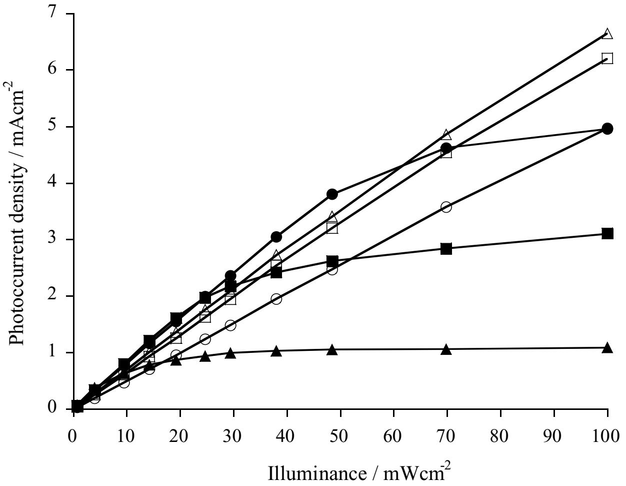

Fig. 4. Short-circuit photocurrent density (J_{SC}) of dye **4**-sensitized solar cells assembled with molten salt electrolytes as a function of illuminance. The electrolytes consist of iodine and 1-hexyl-3-methylimidazolium iodide in mixing molar ratios of 0:10 (filled triangles), 0.1:10 (filled squares), 0.2:10 (filled circles), 0.5:10 (open triangles), 1:10 (open squares) and 2:10 (open circles).

Figs. 4 and 5a show performances of cells sensitized with dye **4**, which clearly explain the effect of concentration of iodine doped in 1-hexyl-3-methylimidazolium iodide (C6ImI) as a representative molten salt. As seen in Fig. 4, the short-circuit photocurrent densities (J_{SC}) as a function of illuminance increase with the increment of iodine concentrations up to a mixing molar ratio of I_2:C6ImI = 0.5:10 at an illuminance of 100 mW cm^{-2} corresponding to 1 sun, followed by a gradual decline at larger iodine concentrations, except in the case of I_2:C6ImI=0.2:10, where the largest J_{SC} values are observed at lower illuminances and reduced at higher illuminances. Fig. 5a shows solar energy conversion efficiency (η) as a function of illuminance at various concentrations of iodine. The results show that there are optimum η values at the smaller mixing ratios, followed by gradual decreases with an increase in illuminance, whereas this kind of η decline becomes insensitive to illuminance when the ratio is larger than 0.5:10. Note that the largest J_{SC} and η in a wide range of illuminance are obtainable at I_2:C6ImI = 0.2:10.

The structural effect of the molten imidazolium salts with different alkyl chain lengths from methyl (C_1) to decyl (C_{10}) on cell performances was systematically investigated to optimize the composition of molten salt electrolyte. Fig. 5b shows η values as a function of an illuminance for solar cells assembled by using the imidazolium salts doped with iodine at I_2:CnImI = 0.2:10, on the basis of the results described just above. The results show that the alkyl chain length influences η values drastically and regularly. For instance, η increases as the increment of the chain length at an illuminance of 10 mW cm^{-2}, except for the longest C_{10}, whereas the chain length giving the maximum η values becomes shorter when illuminances increase. It is noteworthy that η is scarcely affected by the illuminance in the imidazolium salts substituted with shorter alkyl chains (C_1–C_4). In particular, 1-butyl-3-methylimidazolium iodide (C4ImI) gives rise to constant η values at a high level in a wide range of illuminance and to the largest one at 1 sun. As suggested in [11], it is likely that the results are related with viscosity of the imidazolium salts, which increases with increase of the alkyl chain length. On the basis of all of the results, the electrolyte comprised of iodine and C4ImI at a 0.2:10 ratio was used for the following experiments.

Concerning a counter electrode, the effect of thickness of platinum layers sputtered on conductive glass substrates was determined for cells assembled by using a solvent

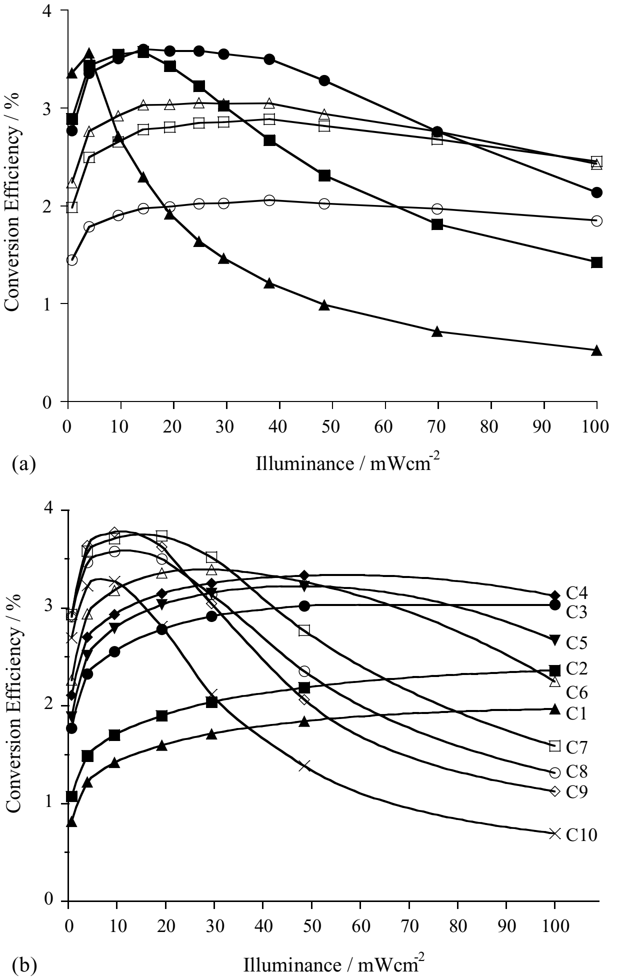

Fig. 5. Solar energy conversion efficiencies (η) of dye **4**-sensitized solar cells assembled with molten salt electrolytes as a function of illuminance: (a) the electrolytes consist of iodine and 1-hexyl-3-methylimidazolium iodide in mixing molar ratios of 0:10 (filled triangles), 0.1:10 (filled squares), 0.2:10 (filled circles), 0.5:10 (open triangles), 1:10 (open squares) and 2:10 (open circles); (b) the electrolytes consist of imidazolium iodides substituted with various alkyl chain lengths as a function of illuminance. The molar ratio of iodine and imidazolium iodide was fixed at 0.2:10.

electrolyte and the ruthenium complex N3, and the results are shown in Fig. 6. Values of ff at platinum thickness of 0, 0.5 and 100 nm were 0.07, 0.66 and 0.72, respectively. It should be stressed that photocurrent–voltage curves are scarcely influenced by the platinum thickness in the range from 0.5 to 100 nm so that even 0.5 nm thickness is workable, increasing ff of the cells. The results are of great significance for the present purpose in assembling multi-colored solar cells, since a transmittance of a platinum electrode of 0.5 nm thickness in a visible wavelength region exceeds about 80% so that the electrode essentially becomes transparent.

3.3.2. *Fabrication of colorful cells*

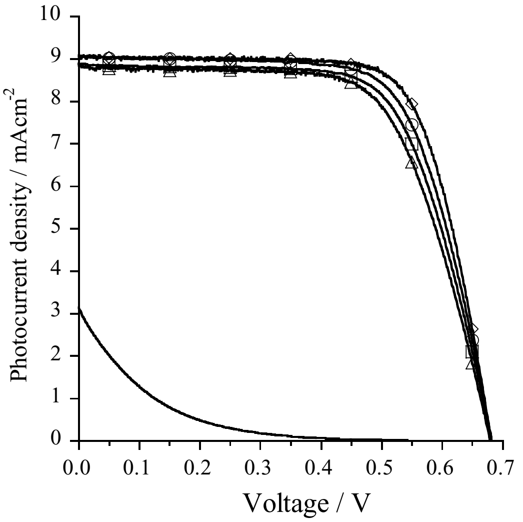

Fig. 6. Thickness effect of platinum layers sputtered on glass substrates as counter electrodes on photocurrent–voltage curves of solar cells under AM 1.5 (1 sun, $100\,\mathrm{mW\,cm^{-2}}$). The thickness of sputtered platinum layers are 0 nm (continuous line), 0.5 nm (open triangles), 10 nm (open squares), 40 nm (open circles) and 100 nm (open diamonds).

Taking multi-farious color tones of these dyes into account, the dye-sensitized solar cells can bear decorative appearances. In this context, based on the results for minimizing the amount of iodine and preparing a transparent platinum electrode we could assemble colorful solar cells by the combinations of dyes shown in Fig. 1 and their mixtures. Whereas, the coumarin dye **1** is yellow, three merocyanines **2**–**4** are blue, red and purple, respectively. Green color is obtained by mixing **1** and **2**, and a mixture of **1**–**3** is black by subtraction of colors. Fig. 7 shows action spectra of IPCE for cells based on the yellow, blue, red, purple, green and black sensitizing dyes. Green and black cells, giving high efficiencies shown in Fig. 7, were obtained by optimizing mixing ratios of the corresponding dyes. The optimum molar ratios to give green and black layers were **1**:***2*** = 8:2 and

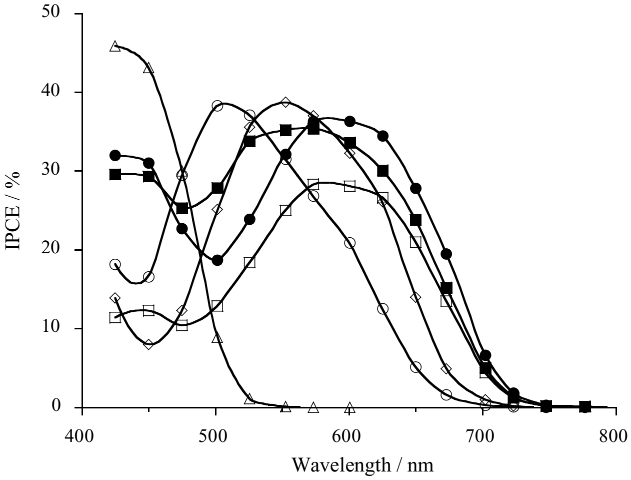

Fig. 7. IPCE spectra of TiO_2 electrodes sensitized by dye **1** (open triangles), **2** (open squares), **3** (open circles), **4** (open diamonds), a mixture of **1** and **2** (filled circles) and a mixture of **1**–**3** (filled squares).

Table 1
Characteristics of colored solar cells[a]

Sample	I_{SC}[b] (mA)	J_{SC}[c] (mA cm^{-2})	V_{OC}[d] (V)	P_{max}[e] (mW)	ff[f]	η[g] (%)
Red	25.1	5.03	0.596	9.54	0.64	1.9
Purple	35.4	7.08	0.619	13.6	0.62	2.7
Blue	21.1	4.22	0.588	7.99	0.64	1.6
Green	30.4	6.09	0.589	11.1	0.62	2.2
Black	30.8	6.16	0.586	10.9	0.60	2.2
TiO_2 electrode side[h]	27.9	5.58	3.03	53.3	0.63	2.1
Counter electrode side[h]	13.2	2.64	2.93	24.5	0.63	1.0

[a] Under irradiation of AM 1.5, 100 mW cm^{-2}.
[b] Short-circuit photocurrent.
[c] Short-circuit photocurrent density.
[d] Open-circuit voltage.
[e] Maximum output power.
[f] Fill factor.
[g] Solar energy conversion efficiency.
[h] Solar cell fabricated by connecting five colored cells with an electrode area of 5 cm^2 in series.

1:**2**:**3** = 6:4:1, respectively, so that TiO_2 electrodes were immersed in methanol solutions of these mixtures for the dye adsorption. The green and black cells with a semiconductor electrode area of 1 cm^2 gave higher η values of 2.5 and 2.8%, respectively, under 1 sun when compared with 1.0, 1.8 and 2.7% for **1**–**3**, respectively.

Fig. 8 shows the photocurrent–voltage curves of individual cells with an electrode area of 5 cm^2 (5 cm × 1 cm) under 1 sun to visualize dependence of cell performances on the dyes. Table 1 summarizes properties of the cells including short-circuit photocurrent (I_{SC}), J_{SC}, V_{OC}, ff, maximum output power (P_{max}) and η, displaying differences in the characteristics of the cells. Values of J_{SC} lie in the range of 4.2–7.1 mA cm^{-2}, whereas V_{OC} and ff values are slightly different among the cells in the range of about 0.59–0.62 V and 0.60–0.64. Values of η are in the range of 1.6–2.7%.

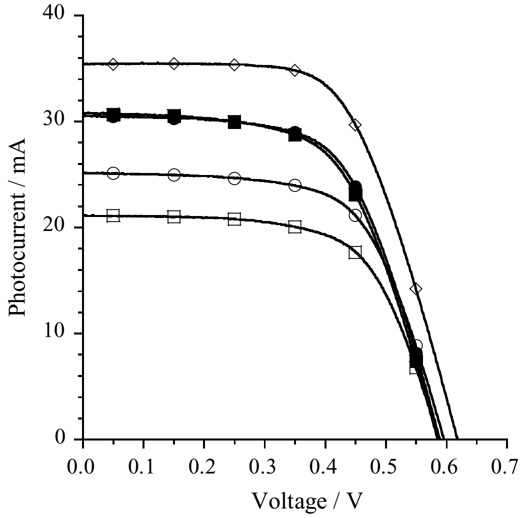

Fig. 8. Photocurrent–voltage curves of solar cells with a TiO_2 electrode area of 5 cm^2 exhibiting red (open circles), purple (open diamonds), blue (open squares), green (filled circles) and black (filled squares) colors under AM 1.5 (1 sun, 100 mW cm^{-2}).

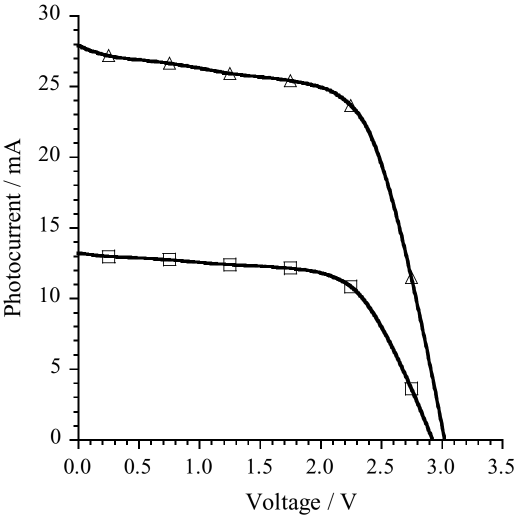

Fig. 9. Photocurrent–voltage curves of solar cells of a total electrode area of 25 cm^2 fabricated by connecting five colored cells in series under AM 1.5 (1 sun, 100 mW cm^{-2}) from TiO_2 electrode side (open triangles) and counter electrode side (open squares).

Subsequently, the cells exhibiting five colors were connected in series with each other to obtain photocurrent–voltage curves under 1 sun, as shown in Fig. 9. As listed in Table 1, a V_{OC} value is 3.03 V, being in line with the sum of V_{OC} values of the component cells. Values of I_{SC}, J_{SC} and η are 27.9, 5.6 mA cm^{-2} and 2.1%, respectively, demonstrating that all of the values are not far from the average of each cell. Note here that it is possible to gain η of 1.0% under illumination of the cells from their rear side of the counter electrode coated with a highly transparent platinum layer.

4. Conclusion

Aiming at developing dye-sensitized solar cells which display a multi-colored decorative effect, systematic studies have been made on TiO_2 electrodes, counter electrodes and electrolytes. Porous TiO_2 electrodes were prepared from a 4:6 mixture of TiO_2 particles of 12 and 24 nm sizes, respectively, as the optimum composition, whereas a counter electrode was fabricated by coating a conductive glass substrate with a ultra-thin platinum layer of 0.5 nm to ensure reasonable cell performances together with high transmittance in a visible light region. The *N*-alkyl chain length of imidazolium iodides as molten salts and mixing molar ratios of iodine and the imidazolium in electrolytes play a crucial role in assembling solar cells, and optimum results were obtainable by using a 0.2:10 mixture of iodine and 1-butyl-3-methylimidazolium iodide.

Solar cells sensitized with a coumarin and merocyanines and their mixtures display multi-farious colors including red, purple, blue, green and black in appearance because of the minimized iodine concentration and of a highly transparent platinum electrode. They exhibit moderate cell performances such as V_{OC} of about 0.6 V and η of 1.6–2.7%. When these cells are connected in series, V_{OC} equals to the sum of those of five cells, whereas η is an averaged value of those of every cell. Accordingly, these types of solar cells are of a practical value for devices performing light energy conversion and displaying decorative appearance characterized by their multiple colors.

References

[1] B. O'Regan, M. Grätzel, Nature 353 (1991) 737.

[2] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphrybaker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382.

[3] C.J. Brabé, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Grätzel, J. Am. Ceram. Soc. 80 (1997) 3157.

[4] K. Sayama, H. Sugihara, H. Arakawa, Chem. Mater. 10 (1998) 3825.

[5] S. Ferrere, B.A. Gregg, N. J. Chem. 26 (2002) 1155.

[6] Z.S. Wang, F.Y. Li, C.H. Huang, L. Wang, M. Wei, L.P. Jin, N.Q. Li, J. Phys. Chem. B 104 (2000) 9676.

[7] K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, N. J. Chem. 27 (2003) 783.

[8] N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhôte, H. Pettersson, A. Azam, M. Grätzel, J. Electrochem. Soc. 143 (1996) 3099.

[9] H. Matsumoto, T. Matsuda, T. Tsuda, R. Hagiwara, Y. Ito, Y. Miyazaki, Chem. Lett. (2001) 26.

[10] P. Bonhôte, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Inorg. Chem. 35 (1996) 1168.

[11] W. Kubo, T. Kitamura, K. Hanabusa, S. Yanagida, Chem. Commun. (2002) 374.