Letters

Dye-sensitized nanocrystalline TiO$_2$ solar cells based on novel coumarin dyes

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Abstract

We have developed dye-sensitized nanocrystalline TiO$_2$ solar cells (DSSCs) based on novel coumarin-dye photosensitizers. The absorption spectra of these novel dyes are red-shifted remarkably in the visible region relative to the spectrum of C343, a conventional coumarin dye. Introduction of a methine unit (–CH=N–) connecting the cyano (–CN) and carboxyl (–COOH) groups into the coumarin framework expanded the π-conjugation in the dye and thus resulted in a wide absorption in the visible region. These novel dyes performed as efficient photosensitizers for DSSCs. A DSSC based on 2-cyano-5-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]anthracen-9-yl)-penta-2,4-dienoic acid (NKX-2311), produced a 6.0% solar energy-to-electricity conversion efficiency ($\eta)$, the highest performance among DSSCs based on organic-dye photosensitizers, under AM 1.5 irradiation (100 mW cm$^{-2}$) with a short-circuit current density ($J_{sc}$) of 14.0 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 0.60 V, and a fill factor of 0.71. Our results suggest that the structure of NKX-2311 whose carboxyl group is directly connected to the –CH=N– unit, is advantageous for effective electron injection from the dye into the conduction band of TiO$_2$. In addition, the cyano group, owing to its strong electron-withdrawing ability, might play an important role in electron injection in addition to a red shift in the absorption region. On a long-term stability test under continuous irradiation with white light (80 mW cm$^{-2}$),
stable performance was attained with a solar cell based on the NKX-2311 dye with a turnover number of $2.6 \times 10^7$ per one molecule.

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1. Introduction

Dye-sensitized solar-cells (DSSCs) based on nanocrystalline TiO$_2$ photoelectrode have been actively studied since Grätzel and co-workers reported high solar energy-to-electricity conversion efficiencies, $\eta$, of up to 10% with a DSSC based on a Ru-complex photosensitizer [1,2]. Several Ru complexes, e.g., cis-dithiocyanato bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) (the N3 dye) and trithiocyanato 4,4'4''-tricarboxy-2,2':6',2''-terpyridine ruthenium(II) (black dye), have been used in DSSCs as efficient photosensitizers [1–12].

Organic dyes such as 9-phenylxanthene dyes (e.g., rose bengal, fluorescein, and Rhodamine B) were also used as photosensitizers for DSSCs in early studies [13–16]. Recently, construction of nanocrystalline DSSCs based on organic-dye photosensitizers has been reported [17–23]. Organic dyes have several advantages as photosensitizers for DSSCs: (1) they have larger absorption coefficients (attributed to an intramolecular $\pi-\pi^*$ transition) than metal-complex photosensitizers (which are due to MLCT absorption), and these large coefficients lead to efficient light-harvesting properties; (2) the variety in their structures provides possibilities for molecular design, e.g., the introduction of substituents, and thus allows for easy control of their absorption spectra; (3) there are no concerns about resource limitations, because organic dyes do not contain noble metals such as ruthenium.

Coumarin dyes, e.g., coumarin 343 (C343, Fig. 1), are good organic-dye photosensitizers for injecting electrons efficiently into the conduction band of semiconductors. Ultrafast electron-injection times of $<200$ fs [24], $<20$ fs [25], and 125 fs [26] from C343 into the conduction band of TiO$_2$ have been observed. The $\eta$ for nanocrystalline DSSCs based on the C343 dye, however, are lower than the efficiencies of DSSCs based on Ru-complex photosensitizers, owing to a lack of absorption in the visible region. Therefore, the absorption spectra of organic dyes must be red-shifted for highly efficient solar-cell performance in terms of harvesting sunlight.

Considering this point, we have designed and synthesized novel coumarin derivatives able to absorb in the visible range from 400 to 750 nm (Fig. 1). Introduction of the methine (–CH=–CH–) unit connecting the cyano (–CN) and carboxyl (–COOH) groups into the coumarin framework expanded the $\pi$-conjugation in the dye and resulted in wide absorption in the visible region. We were able to construct highly efficient DSSCs based on these new coumarin-dye photosensitizers. We reported that a 5.6% $\eta$ was attained under AM 1.5 (100 mW cm$^{-2}$) with a DSSC based on 2-cyano-5-(1,1,6,6-tetramethyl-10-
oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]anthracen-9-yl)-penta-
2,4-dienoic acid (NKX-2311) [27]. It has been suggested that owing to their
strong electron-withdrawing abilities, the carboxyl and cyano groups directly
connected to the –CH=CH– unit, play an important role in effective electron
injection into the conduction band of TiO2 in addition to red-shifting the absorption
region. In this paper, we report the details of the solar-cell performance of DSSCs
based on novel coumarin-dye photosensitizers. Our results strongly indicate
that the molecular design of organic-dye photosensitizers for DSSCs can be
successful and that the prospects for application of these photosensitizers in DSSCs
are promising.

2. Experimental section

2.1. Synthesis

2.1.1. 3-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-
benzo[de]anthracen-9-yl)-acrylic acid (NKX-2398)

A 40 ml of acetonitrile solution including 5 g of 1,1,6,6-tetramethyl-10-oxo-2,3,5,6-
tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]anthracene-9-carbaldehyde 1 (15 mmol)
and malonic acid (2.4 g, 23 mmol) was refluxed in the presence of 0.6 ml of piperidine
for 4 h. Recrystallization of resulting precipitates from chloroform afforded orange
red crystals of NKX-2398; m.p. 253–257°C. 1H NMR (DMF- d7): δ 1.26 (6H, s), 1.48
(6H, s), 1.72–1.78 (4H, m), 3.33 (2H, t), 3.40 (2H, t), 6.83 (2H, d), 7.40 (1H, s), 7.53
(1H, d), 8.17 (1H, s). HRMS–EI (m/z): [M]+ calcd for \(\text{C}_{22}\text{H}_{25}\text{NO}_{4}\), 367.1782; found, 367.1770 (100%); [M–\text{CH}_3]+ calcd for \(\text{C}_{21}\text{H}_{22}\text{NO}_2\), 352.1548; found, 352.1525 (46%).

2.1.2. 2-Cyano-3-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]anthracen-9-yl)-acrylic acid (NKX-2388)

A 32 ml of acetonitrile solution including 3.25g of 1 (10mmol) and cyanoacetic acid (1.28g, 15mmol) was refluxed in the presence of 0.4ml of piperidine for 4h. Recrystallization of resulting precipitates from acetonitrile in the presence of triethylamine afforded triethylammonium salt. The triethylammonium salt was recrystallized from chloroform in the presence of acetic acid, resulting in black purple crystals of NKX-2388; m.p. 300–303°C. 1H NMR (CDCl3): \(\delta\) 1.31 (6H, s), 1.54 (6H, s), 1.72–1.82 (4H, m), 3.27 (2H, t), 3.36 (2H, t), 7.19 (1H, s), 8.38 (1H, s), 8.75 (1H, s). MS–ESI (m/z): 391.1 (M–H)–, 783.2 (2M–H)–. HRMS–EI (m/z): [M–\text{CO}_2]+ calcd for \(\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2\), 348.1836; found, 348.1807 (100%); [M–\text{CO}_2–\text{CH}_3]+ calcd for \(\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2\), 333.1602; found, 333.1560 (74%).

2.1.3. 2-Cyano-5-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-oxa-3a-aza-benzo[de]anthracen-9-yl)-penta-2,4-dienoic acid (NKX-2311)

To a 120 ml of N,N-dimethylformamide (DMF) solution including 30g of 1 (0.092mol) and methyltriphenylphosphonium iodide (50g, 0.124mol) was added 25ml of 28% \(\text{CH}_3\text{ONa}\) solution at room temperature. The solution was allowed to stand for 2h at 60°C. After extraction by chloroform and evaporation of the solvent, 76g of oily product containing 1,1,6,6-tetramethyl-9-vinyl-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]anthracen-10-one 2, was obtained.

The resulting 76g of oil was dissolved in 150 ml of DMF and then Vilsmeier reagent, which was prepared from 100 ml of DMF and 25 ml of phosphorus oxychloride, was added into the solution at 14–22°C and then kept for 1h (Vilsmeier–Haack reaction). After neutralization with 25% \(\text{NaOH}\) solution to pH 8, the product was extracted by chloroform. After evaporation of chloroform, 3-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]anthracen-9-yl)-propenal 3 was obtained. It was purified by column chromatography using silica gel and a chloroform–ethyl acetate mixed solvent as the eluting solution. 1H NMR (CDCl3): \(\delta\) 1.31 (6H, s), 1.56 (6H, s), 1.74–1.83 (4H, m), 3.27–3.40 (4H, m), 6.97 (1H, dd), 7.13 (1H, s), 7.46 (1H, d), 7.75 (1H, s), 9.63 (1H, d).

A 10 ml of acetonitrile solution including 1 g of 3 (2.8 mmol) and cyanoacetic acid (0.36g, 4.2 mmol) was refluxed in the presence of 0.1 ml of piperidine for 1h. The resulting precipitates were dissolved in DMF and bright purple crystals of NKX-2311 were obtained upon recrystallization by adding 2-propanol; m.p. 270–275°C. 1H NMR (CDCl3): \(\delta\) 1.31 (6H, s), 1.53 (6H, s), 1.74–1.85 (4H, m), 3.41–3.49 (4H, m), 7.47 (2H, m), 7.75 (1H, dd), 8.08 (1H, d), 8.22 (1H, s). HRMS–EI (m/z): [M]+ calcd for \(\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_4\), 418.1891; found, 418.1836 (6%); [M–\text{CO}_2]+ calcd for \(\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_2\), 374.1993; found, 374.1942 (100%).
2.1.4. 2-Cyano-7-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]anthracen-9-yl)-hepta-2,4,6-trienoic acid (NKX-2586)

To a 440 ml of DMF solution including 40 g of 1 (0.12 mol) and allyltriphenylphosphonium iodide (105.9 g, 0.24 mol) was added 18.4 g of 60% NaH (NaH, 0.47 mol) at 12–35°C. The solution was kept at room temperature for 30 min and then added into 4.8 l of H2O. The resulting precipitates were extracted with 1.9 l of ethyl acetate. After evaporation of ethyl acetate, 9-buta-1,3-dienyl-1,1,6,6-tetramethyl-2,3,5,6-tetrahydro-1H,4H-11-oxa-3a-aza-benzo[de]anthracen-10-one 5 was obtained.

5-(1,1,6,6-Tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]anthracen-9-yl)-penta-2,4-dienal 6 was prepared from 5 by Vilsmeyer–Haack reaction by a similar procedure as for 3. The obtained 6 was purified by column chromatography using silica gel and a toluene–ethyl acetate mixed solvent as the eluting solution: 1H NMR (CDCl3): δ 1.30 (6H, s), 1.56 (6H, s), 1.74–1.83 (4H, m), 3.25–3.71 (4H, m), 6.27 (1H, dd), 6.95 (1H, d), 7.09 (1H, s), 7.11–7.43 (2H, m), 7.63 (1H, s), 9.58 (1H, d).

A 10 ml of acetonitrile solution including 1 g of 6 (2.7 mmol) and cyanoacetic acid (0.34 g, 4 mmol) was refluxed in the presence of 0.08 ml of piperidine for 1 h. The resulting crystalline was dissolved in a chloroform (30 ml)–methanol (10 ml) mixed solvent. After evaporation of the solvent, green crystals of NKX-2586 were obtained; m.p. 272–274°C. 1H NMR (CDCl3): δ 1.30 (6H, s), 1.56 (6H, s), 1.71–1.81 (4H, m), 3.33–3.44 (4H, m), 6.71–6.80 (1H, m), 7.06 (1H, d), 7.40–7.56 (3H, m), 8.02 (1H, d), 8.14 (1H, s). HRMS–EI (m/z): [M]+ calcd for C27H28N2O4, 444.2047; found, 444.2017 (29%): [M–CO 2]+ calcd for C26H28N2O2, 400.2155; found, 400.2149 (100%).

2.2. Preparation of dye-sensitized TiO2 thin films

TiO2 nanoparticles were prepared by the method reported by Grätzel and co-workers [11,28]. An organic paste containing TiO2 nanoparticles, a binder, and a solvent was printed on a glass plate coated with transparent conducting oxide (TCO, F-doped SnO2, Nippon Sheet Glass Co., 8–10 Ω/sq, transparency 80%) by means of a screen printing machine (Mitani Densi, MEC-2400). After sintering at 500°C under air for 1 h, a TiO2 thin-film electrode was obtained. Detailed procedure for preparing the organic paste have been reported in a previous paper [19]. After the film preparation, a 50 mM aqueous solution of TiCl4 (Wako Chemical) was dropped onto the TiO2 films and kept at 25°C for more than 18 h [2]. After TiCl4 treatment, the films were calcined at 450°C for 30 min in air. The thickness of the TiO2 thin films, measured by an Alpha-Step 300 profiler (Tencor Instruments), was ca. 13 μm.

Coumarin dyes (0.3 mM) were dissolved in dehydrated ethanol (Kanto Chemical) or a 50:50 solution of tert-butanol (Kanto) and acetonitrile (Kanto, dehydrated for organic synthesis). These solvents were used as obtained from the suppliers without further purification. The TiO2 thin films were immersed into the dye solution and then kept at 25°C for more than 12 h so that the dye could be adsorbed onto the surface of the TiO2 electrodes.
2.3. Characterization of the dyes

$^1$H NMR spectra of the coumarin dyes were recorded with a JEOL JNM-AL300 spectrometer. High-resolution mass spectra (HRMS) and electrospray ionization mass spectra were obtained with a Hitachi M-80 B spectrometer and a Micromass Quattro II mass spectrometer, respectively. The absorption spectra of the dyes in solution and adsorbed on TiO$_2$ films were measured with a Shimadzu UV-3101PC. The amount of the dye adsorbed on the TiO$_2$ surface was estimated spectroscopically after the dye had been desorbed in a 1.0 mM solution of NaOH in ethanol–H$_2$O (50:50). FT-IR absorption spectra were measured with a Perkin Elmer Spectrum One spectrometer in trancparency mode with an ATR system equipped with a ZnSe prism. The oxidation and reduction potentials of the dyes in DMF solution were measured in a normal one-compartment cell with a glassy carbon working electrode, a Pt counter electrode, and a Ag/AgCl reference electrode in a saturated KCl solution. The measurements were performed with a Yanaco polarographic analyzer P-3000. Thermogravimetric (TG) analysis of the dyes was performed with a Rigaku, TG8120 analyzer.

2.4. Photovoltaic measurements of the solar cells

The electrochemical cell (two-electrode type) used for photovoltaic measurements consisted of a dye-sensitized semiconductor electrode, a counter electrode, a polyethylene film spacer (25µm thick), and an organic electrolyte. The counter electrode was a Pt film sputtered on a TCO-coated glass plate by means of a sputtering system (Eiko engineering, IB-5). The apparent surface area of the TiO$_2$ film electrode measured with a microscope (Nikon, model C-PS) was 0.245–0.26cm$^2$ (ca. 0.5cm x 0.5cm).

The electrolyte consisted of 0.6M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPImI), 0.1M LiI, and 0.05M I$_2$ in methoxyacetonitrile (MAN) with and without 0.5M 4-tert-butylpyridine (TBP). Reagent-grade LiI (Wako) and I$_2$ (Wako) were used for the electrolyte. TBP (Aldrich) and MAN (Aldrich and Tokyo Kasei) were distilled before use. DMPImI was synthesized from 1,2-dimethylimidazolium (Tokyo Kasei) and n-propyl iodide (Tokyo Kasei), as reported by Bonhôte et al [29].

The photovoltaic performance of the solar cells based on coumarin dyes was measured with a source meter (Keithley, model 2400, or Advantest, R6246). We employed an AM1.5 solar simulator (Wacom, WXS-80C-3 with a 300-W Xe lamp or Yamashita Denso Co., YSS-150A with a 1000-W Xe lamp) as the light source. The incident light intensity was calibrated with a standard solar cell for amorphous silicon solar cell produced by Japan Quality Assurance Organization. Action spectra of the monochromatic incident photon-to-current conversion efficiencies (IPCEs) for the solar cells were measured with a CEP-99W system (Bunkoh-keiki Co., Ltd.).
3. Results and discussion

3.1. Synthesis

A typical novel coumarin dye, NKX-2311, was synthesized as outlined in Scheme 1. Compound 3 was prepared from 1 by a Wittig reaction and then a subsequent Vilsmeier–Haack reaction. NKX-2311 was synthesized from 3 and cyanoacetic acid in an acetonitrile solution with piperidine under reflux condition for 1 h. The precipitated NKX-2311 was dissolved in DMF, and a bright purple crystalline compound was obtained upon recrystallization.

3.2. Absorption properties of coumarin dyes

Fig. 2 shows the absorption spectra of a conventional coumarin dye, C343, and novel coumarin dye (NKX-2398, 2388, 2311, and 2586) in ethanol. All absorption peaks for the novel coumarin dyes are shifted toward the longer-wavelength region relative to the peak for C343. The absorption peak for NKX-2398 (451 nm), which has a methine unit and carboxyl group on the coumarin framework, is slightly red-shifted compared to the peak for C343 (442 nm). Adding a cyano group (–C≡N) to NKX-2398, giving NKX-2388, caused a further red shift, to 493 nm. For dyes with a cyanoacetic acid unit (=C–C≡N–COOH) connected directly to the methine chain, the absorption spectra were considerably red-shifted by the extension of the methine chain (NKX-2388, 2311, and 2586). These results obviously indicate that connecting the cyanoacetic acid moiety, to the coumarin framework, via a methine chain leads to a considerable red shift in the absorption properties of the dyes, a shift that is desirable for harvesting light from the solar spectrum. The absorption spectrum of NKX-2311 shows a long tail spreading out to 750 nm (ε ca. 100), which suggests the possibility of converting 400–750-nm visible light to current using this dye. The molar absorption coefficients, ε, at the peak for these dyes range from...
44,200 to 59,100 M\(^{-1}\) cm\(^{-1}\) (M: mol cm\(^{-3}\)). The amount of coumarin dye adsorbed on a 10-μm TiO\(_2\) film was ca. 1 \times 10^{-7} \text{ mol cm}^{-2}, which is similar to that for the N3 dye [2] and results in sufficient light-harvesting property of the film.

### 3.3. Photovoltaic performance of DSSCs based on coumarin dyes

Action spectra of monochromatic IPCEs for DSSCs composed of a nanocrystalline TiO\(_2\) electrode, novel coumarin dyes, and an iodine redox electrolyte are shown in Fig. 3. The IPCEs are represented by the following equation:

\[
\text{IPCE} (\%) = \frac{1240 \text{ [eV nm]} \times J_{\text{ph}} \text{ [mA cm}^{-2}\text{]} \times 100}{\lambda \text{ [nm]} \times \Phi \text{ [mW cm}^{-2}\text{]}}
\]

(1)
where $J_{\text{ph}}$ is the short-circuit photocurrent density for monochromatic irradiation and $\lambda$ and $\Phi$ are the wavelength and the intensity, respectively, of the monochromatic light. As we have seen, the IPCE spectra of DSSCs based on novel coumarin dyes are remarkably red-shifted compared to the spectrum of C343. The onset of the IPCE spectrum of a DSSC based on NKX-2311 is 750 nm, and high IPCE performance (>70%) was observed in the range from 460 to 600 nm, with a maximum value of 80% at 470 nm (Fig. 3). When the reflection and absorption losses in the TCO substrate are considered, the net photon-to-current conversion efficiency in this range is higher than 90%, which is very efficient solar-cell performance. We have succeeded in the most red shift in the absorption spectrum of NKX-2586 by expansion of the methine unit of NKX-2311, as shown in Fig. 2. Therefore, it is prospective that a DSSC based on NKX-2586 shows the highest solar-cell performance in terms of light harvesting and thus the highest photocurrent. In fact, the onset of the IPCE spectrum for a DSSC based on NKX-2586 was the most red-shifted, reaching 800 nm. Its IPCEs are, however, lower than the value for NKX-2311 (ex. the maximum is 63% at 460 nm), whereas the reduction potential (i.e., LUMO level) of NKX-2586 differs little from that of NKX-2311. Then we employed a co-adsorbate, deoxycholic acid, as employed in the previous study [30], the IPCE performance of the DSSC based on NKX-2586 was improved. It was suggested that aggregates of NKX-2586 form on the TiO$_2$ surface and thus decrease electron-injection yield owing to intermolecular energy transfer.

Table 1 shows the photovoltaic performance of DSSCs based on coumarin dyes under AM 1.5 irradiation (100 mW cm$^{-2}$) using an electrolyte of 0.6 M DMPImI–0.1 M LiI–0.05 M I$_2$ in MAN (without TBP), where $J_{\text{sc}}$ is the short-circuit photocurrent density under irradiation, $V_{\text{oc}}$ is the open-circuit voltage, and ff represents the fill factor. As shown in Table 1, the $J_{\text{sc}}$ values for all the DSSCs based on the novel coumarin dyes were higher than the value for the DSSC based on C343; these higher values are reflected in their improved IPCEs. The $J_{\text{sc}}$ values for the DSSCs based on NKX-2311 and 2586 reached 15 mA cm$^{-2}$, and a 5.2% $\eta$ for a DSSC based on NKX-2311 was attained ($J_{\text{sc}} = 15.2$ mA cm$^{-2}$, $V_{\text{oc}} = 0.55$ V, and $\text{ff}=0.62$). So far, however, no DSSC based on NKX-2586 has exhibited higher photovoltaic performance than the DSSC based on NKX-2311. This is mainly due to

<table>
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<th>Dye</th>
<th>$J_{\text{sc}}$ (mA cm$^{-2}$)</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>ff</th>
<th>$\eta$ (%)</th>
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<td>0.56</td>
<td>0.9</td>
</tr>
<tr>
<td>NKX-2398</td>
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<td>0.51</td>
<td>0.60</td>
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<td>0.50</td>
<td>0.64</td>
<td>4.1</td>
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<tr>
<td>NKX-2311</td>
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<td>0.55</td>
<td>0.62</td>
<td>5.2</td>
</tr>
<tr>
<td>NKX-2586</td>
<td>15.1</td>
<td>0.47</td>
<td>0.50</td>
<td>3.5</td>
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Table 1: Photovoltaic performance of coumarin dye-sensitized nanocrystalline TiO$_2$ solar cells

Conditions: Irradiated light, AM 1.5 (100 mW cm$^{-2}$); photoelectrode, TiO$_2$ (13 $\mu$m thickness and 0.25 cm$^2$); electrolyte, 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide—0.1 M, LiI—0.05 M I$_2$ in methoxyacetone-nitrile.
the lower $V_{oc}$ and $ff$ values for the DSSC based on NKX-2586. The $V_{oc}$ and $ff$ values of the solar cell must be improved if highly efficient photovoltaic performance is to be achieved.

At the present stage, the maximum 6.0% $\eta$, the highest efficiency so far among DSSCs based on organic dyes, was achieved by optimization under AM 1.5 with a DSSC based on NKX-2311 ($J_{sc} = 14.0$ mA cm$^{-2}$, $V_{oc} = 0.60$ V, and $ff = 0.71$), as shown in Fig. 4. This result indicates that the prospects for using organic-dye photosensitizers in DSSCs are promising.

3.4. Mechanism of photon-to-current conversion in the DSSC based on NKX-2311

Fig. 5 shows a typical energy diagram for a DSSC based on a nanocrystalline TiO$_2$ electrode, NKX-2311 as photosensitizer, and the I$^-$/I$_3^-$ redox electrolyte. The HOMO and LUMO levels of the dye correspond to the oxidation and reduction potentials of the dye, respectively. The energy levels of the free dye might differ from the levels for the dye adsorbed on the TiO$_2$ surface. The following primary steps are involved in the conversion of photons to current. NKX-2311 adsorbed on the TiO$_2$ surface absorbs the incident photon flux and is then excited from the ground state to the excited state owing to the intramolecular $\pi-\pi^*$ transition. The electron of the excited state is immediately injected into the conduction band of the TiO$_2$ electrode before it is deactivated by emission and subsequent formation of the oxidized dye (i.e., the dye cation). Injected electrons in the conduction band of TiO$_2$ are
transported toward the back contact (TCO) and consequently reach the counter electrode through the external load and wiring. The oxidized dyes accept electrons from the $I^-/I_3^-$ redox mediator, regenerating the ground state of the dye, and $I^-/I_3^-$ is oxidized to $I^-$. The oxidized redox mediator, $I_3^-$, is rereduced to $I^-$ at the counter electrode. Overall, electric power is generated without permanent chemical transformation.

3.5. Effect of 4-tert-butylpyridine on cell performance

To achieve efficiencies higher than 5%, the $V_{oc}$ of the solar cell must be improved. Rereduction of $I_3^-$ by the injected electrons on TiO$_2$ (i.e., dark current) is one of the loss channels that diminishes solar-cell performance, especially $V_{oc}$ (Fig. 5). To improve the $V_{oc}$ values for DSSCs based on the N3 dye, researchers have added TBP to the electrolyte and have employed a TBP-treated TiO$_2$ photoelectrode, which resulted in a $V_{oc}$ higher than 0.7 V [2,10,28,31]. This improved $V_{oc}$ value is attributed to suppression of dark current owing to the blocking effect of TBP on the TiO$_2$ surface [2] and a negative shift of the conduction band level of TiO$_2$ due to TBP’s basicity. In addition, Greijer et al. have reported that TBP forms several complexes with $I_3^-$, and these complexes decreases the concentration of $I_3^-$ at the TiO$_2$ surface and consequently improve $V_{oc}$ [32].

The $V_{oc}$ values for DSSCs based on coumarin dyes were relative low (0.41–0.55 V), as shown in Table 1. Therefore, we investigated the effect of adding TBP to the
electrolyte on the photovoltaic performance of a DSSC based on NKX-2311. Current–voltage curves are shown in Fig. 6. The electrolyte was 0.6M DMPImI–0.1M LiI–0.05M I2 in a MAN solution with and without 0.5M TBP. The $V_{oc}$ of a DSSC based on NKX-2311 increased from 0.55 to 0.62V when TBP was added to the electrolyte. The onset of the current–voltage curve in the dark for the solar cell was shifted positively by the addition of TBP, which suggests that TBP suppressed the dark current on the TiO2 surface. However, the $J_{sc}$ decreased from 13.5 to 9.7mA cm$^{-2}$ when TBP was added. We attribute this decrease to a negative shift in the conduction band of TiO2, which leads to suppression of effective electron injection from NKX-2311 to TiO2. Consequently, we were unable to use TBP to improve the $Z$ for a DSSC based on NKX-2311.

3.6. Stability of NKX-2311 and cell performance

For successful commercialization of DSSCs, the cell and module must have long-term stability. The long-term stability of DSSCs is currently being investigated at some institutions for commercial applications [33,34]. For example, 7000 h of cell stability, which corresponds to 6 years of outdoor use, has been obtained under 1000 W cm$^{-2}$ light with a UV cut-off filter [33]. In addition, a long-term stability of more than 10,000 h has also been accomplished with a small cell under in the absence of UV light at 17°C at 2.5 sun using an electrolyte of 0.5 M LiI, 0.05 M I2, and 0.3 M TBP in methoxypropionitrile solution [34]. An organic dye, merocyanine, also gave good stability in a sealed cell under continuous AM 1.5 irradiation with a $\lambda<420$ nm cut-off filter, although organic dyes are generally considered to be unstable compared to dyes based on metal complexes. We attained a stability of ca. 1500 h, corresponding to a turnover number of $1.6 \times 10^{6}$ [23]. We have investigated the cell
stability of a DSSC based on coumarin dye NKX-2311 under AM 1.5 irradiation with a UV cut-off filter (ca. 80 mW cm\(^{-2}\)) at 20°C; a turnover number of \(2.6 \times 10^7\) for NKX-2311 was attained for 1800 h of continuous irradiation. Good cell stability was also observed at 40°C. These results strongly indicate that the DSSC based on NKX-2311 shows sufficient physical and chemical stability during the illumination period. Nevertheless, stability tests at higher temperatures and humidities must be carried out before this system can be made practical for outdoor applications.

When the dye was damaged by high temperatures involved in the sealing procedure, the color of the dye on the TiO\(_2\) surface changed gradually from deep purple to yellow or green, and a 50% decrease in the \(J_{sc}\) for the solar cell was observed at 500 h of AM 1.5 irradiation. Therefore, thermal stability of NKX-2311 has been investigated by means of TG analysis under a N\(_2\) atmosphere. A 10% drop in mass was observed at around 230°C. In the FT-IR absorption spectrum, the disappearance of the absorption peak at 1675 cm\(^{-1}\) (attributed to the \(\text{C}═\text{O}\) stretching vibration of the carboxylate) after thermal treatment of NKX-2311 at 240°C for 30 min under a N\(_2\) atmosphere indicate that thermal decomposition of NKX-2311 is due to decarboxylation and that the decomposition begins at around 230°C. It has been reported that decarboxylation of the N3 dye occurs at temperatures higher than 290°C under N\(_2\) and higher than 260°C in air [35]. No change in the absorption peak due to the \(\text{C}≡\text{N}\) stretching vibration (2200 cm\(^{-1}\)) was observed after treatment at 240°C. We conclude that NKX-2311 has good thermal stability for use at relative low temperatures. However, the photothermal stability of the dye during irradiation must be investigated in further detail.

4. Conclusions

Introduction of the \(-\text{CH}═\text{CH}−\) unit connecting both cyano (\(-\text{C}≡\text{N}\)) and carboxyl (\(-\text{COOH}\)) groups into the coumarin framework expanded the \(\pi\)-conjugation in the dye and resulted in wide absorption in the visible region (NKX-2388, 2311, and 2586). These dyes performed as efficient photosensitizers for DSSCs. A DSSC based on NKX-2311 produced a 6.0% \(\eta\), the highest performance among DSSCs based on organic-dye photosensitizers, under AM 1.5 irradiation (100 mW cm\(^{-2}\), \(J_{sc} = 14.0\) mA cm\(^{-2}\), \(V_{oc} = 0.60\) V, and \(\text{ff} = 0.71\)). The onset of the IPCE spectrum for a DSSC based on NKX-2311 was 750 nm, and IPCEs higher than 70% were observed in the range from 460 to 600 nm. An IPCE spectrum for a DSSC based on NKX-2586 was expanded to 850 nm, but the maximum IPCE was low (63% at 460 nm) compared to the maxima for other DSSCs. The presence of TBP in the electrolyte improved the voltage of the DSSC based on NKX-2311. Stable solar-cell performance of a DSSC based on NKX-2311 was obtained in a long-term stability test under continuous irradiation (80 mW cm\(^{-2}\)) with a turnover number of \(2.6 \times 10^7\) per one molecule. Our results strongly support the prospects for successful application of DSSCs based on organic-dye photosensitizers and indicate the importance of molecular structure design for tuning photosensitizers to produce highly efficient DSSCs.
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