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COMMUNICATION

Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes†

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In the dye-sensitized solar cells co-photosensitized with an alkoxy-silyl-anchor dye of ADEKA-1 and a carboxy-anchor organic dye of LEG4, LEG4 was revealed to work collaboratively by enhancing the electron injection from the light-excited dyes to the TiO2 electrodes, and the cells exhibited a high conversion efficiency over 14% under the one sun illumination.

Dye-sensitized solar cells (DSSCs), which are composed of mesoporous nanocrystalline-TiO2 thin layers modified by photosensitizing dyes as working electrodes, redox electrolytes and counter electrodes, have been actively investigated as the photovoltaic device in next generation of the alternative to conventional silicon-based inorganic solar cells (Fig. S1, ESI†), because of a potential low cost for the production, shorter energy and CO2 payback time, low toxicity of constituting elements and relatively high light-to-electric energy conversion efficiencies (η) especially under low-light intensity and scattered light conditions.1-4 In the DSSCs, η of 11-13% under the simulated sunlight at one sun have been reported up to now by the photosensitization using polypyridyl and porphyrin complexes of metals such as ruthenium or zinc and a few metal-free organic dyes with carboxy-anchor moieties for binding to the surface of the TiO2.1-9

Organosilicon compounds such as silanols and alkoxy-silanes have high bonding ability to metal-oxide surfaces by forming firm Si-O-metal bonds. With paying attention to the characteristics of silanols and alkoxy-silanes, we have focused on the development of photosensitizing dyes for DSSCs possessing silyl-anchor moieties,10-12 and recently we succeeded in achieving over 12% conversion efficiency in the cells by using a carbazole/alkyl-functionalized oligothiophene/alkoxy-silyl-anchor moiety type compound, ADEKA-1 (Fig. 1a), as the photosensitizer.13 Besides the high photovoltaic performance, the TiO2 photoelectrode sensitized with ADEKA-1 possesses much higher durability to solvents, e.g. nitrile, water and mixtures of them, and to surface modification using wet processes than those sensitized with carboxy-anchor dyes. The durability of the photoelectrode allows co-adsorption of another sensitizing dye to the electrode for producing a co-sensitization effect, and actually we succeeded in improving the η to 12.8% by means of the co-sensitization of ADEKA-1 and a silyl-anchor coumarin dye of SFD-5.14

For further improvement in the efficiency of ADEKA-1-sensitized DSSCs, we have expanded the study of co-sensitizers for the cells to widely developed carboxy-anchor dyes, which have been demonstrated to possess high sensitizing property as photosensitizers in DSSCs. In the investigation we found that the ADEKA-1-sensitized cells with the co-sensitizer of LEG415 (Fig. 1b) exhibited considerably higher photovoltaic performance by a collaborative sensitization of the dyes, and succeeded in achieving over 14% conversion efficiency in the cells. The efficiency shows the high potential of DSSCs as practical light-to-electric energy conversion device in the near future.

Fig. 1. Molecular structures of photosensitizing dyes: (a) silyl-anchor dye ADEKA-1 and (b) carboxy-anchor dye of LEG4.
As the co-sensitizers for the ADEKA-1-sensitized DSSCs, we selected the carboxy-anchor organic sensitizing dyes reported to have a high sensitizing property and an absorption band in the shorter wavelength region than ADEKA-1 of LEG4, D35, L0 and D131 (Figs. S2-S6 and Table S1, ESIF). To check the potential of those dyes as the co-sensitizer to ADEKA-1, we fabricated the cells sensitized by ADEKA-1 and by ADEKA-1 with the dyes using an electrolyte solution containing I$_2$/I$_3$-redox mediator (Cell-A; the fabrication procedures of the cells were described in ESIF). Among the cells, significant and the largest improvement in the incident monochromatic photon-to-current conversion efficiency (IPCE) was observed in the cell photosensitized by ADEKA-1 with LEG4 (Fig. 2a and Fig. S7 in ESIF). The cell exhibited much higher IPCE values close to 90% than those of the cells sensitized only by ADEKA-1 and only by LEG4 in all the visible region. The increment of the open-circuit photovoltage ($V_{oc}$) and the short-circuit photocurrent density ($J_{sc}$) from those of the cell sensitized by ADEKA-1 resulted from the improvement of the $\eta$ by a factor of 1.3 under the simulated sunlight at one sun (AM-1.5G, 100 mW cm$^{-2}$; Table S2, ESIF).

In the cell photosensitized by ADEKA-1 with LEG4, in which the relative amount of the dyes adsorbed on the TiO$_2$ electrode was estimated to be 1.0 : 0.25 for ADEKA-1 : LEG4, the improvement of IPCE values from those of the ADEKA-1-sensitized cell was observed not only in the light-absorption wavelength region of LEG4 but also in the longer wavelength region where the light absorption by LEG4 was absent (Fig. S8, ESIF), differently from the other co-sensitized cells. In order to clarify the origin of the peculiar and large improvement in the IPCE by the co-sensitization with LEG4, we examined DFT calculations of the dyes (Figs. S9, S10 and Tables S3, S4 in ESIF). The light-to-electric energy conversion in DSSCs proceeds through the electron injection from the LUMO of the light-excited dye to the conduction band of TiO$_2$. In ADEKA-1 the alkoxyxysil-anchored moiety links to the chromophore (carbazole/alkyl-functionalized oligothiophene moiety) via the phenyl-amide moiety, and the LUMO has a small electron distribution around the siyl-anchor moiety. On the other hand, the LUMO of LEG4 has a large electron distribution around the carboxy-anchor moiety and thus LEG4 is expected to have a higher electron injection efficiency from the LUMO to the TiO$_2$ conduction band than ADEKA-1 (Fig. S5, ESIF). When comparing the energy levels of LUMOs of the dyes, only LEG4 has lower LUMO than that of ADEKA-1 differently from other dyes of D35, L0 and D131 (Fig. S6, ESIF), an emission analyses by the use of the Al$_2$O$_3$ porous film modified by ADEKA-1 with LEG4 showed that the emission from ADEKA-1 was quenched almost completely by the existence of LEG4 as the co-adsorbent (Fig. S11, ESIF). From the MO properties and the result of the emission analyses, the large improvement of the photovoltaic performance in the cell photosensitized by ADEKA-1 with LEG4 is considered to be brought by the collaborative sensitization of the dyes through an electron injection enhancement effect due to the existence of the LEG4 molecules near the ADEKA-1 molecules on the TiO$_2$ electrode and the electron transfers from the light-excited ADEKA-1 to the co-adsorbent of LEG4 and immediate electron injection occurs from the LEG4 to the conduction band of TiO$_2$ with much higher efficiency than the direct electron injection from the light-excited ADEKA-1 (Fig. 2b). Internal quantum efficiency (IQE) measurements revealed a considerably high electron injection efficiency in the cell photosensitized by ADEKA-1 with LEG4, and the maximum IQE was evaluated to be 99±2% (Fig. S12, ESIF). The increment of $V_{oc}$ (Table S2, ESIF), the decrease of the dark-current (Fig. S13, ESIF) and the elongation of the electron lifetime in the TiO$_2$ conduction band estimated from the transient open-circuit voltage decays (Fig. S14, ESIF) observed in the co-sensitization with LEG4 indicate that the

![Fig. 2](a) IPCE spectra of the cells photosensitized by ADEKA-1, by LEG4 and by ADEKA-1 with LEG4 (Cell-A) and (b) schematic drawing of the charge separation processes for the TiO$_2$ electrode sensitized collaboratively by ADEKA-1 and LEG4.
adsorbed LEG4 on the TiO2 electrode works also as the suppressor for preventing the back electron transfer from the TiO2 electrode to the electrolyte by covering the naked surface of the TiO2 electrode with its plural alkyl-chain substituents.15-18 By using the I3-/I− redox electrolyte solution with an experimentally optimized composition, the cell photosensitized collaboratively by ADEKA-1 and LEG4 (Cell-B; the fabrication procedures of the cell were described in ESIT) exhibited the η of 11.2% under the AM-1.5G one sun illumination (Entry 1 in Table 1).

The maximum photovoltage (Vmax) obtained in the DSSC is attributed to the energy gap between the quasi-Fermi level of the TiO2 [approximately the energy level of the conduction-band edge (EC,cb)] and the redox potential of the electrolyte, and the increment of the efficiency of DSSCs is possible by the increment of the photovoltage with using the electrolyte having more positive (lower) redox potential than the I3-/I− redox.14,7,9,11,13-15 The redox potential of a cobalt(III/II) tris(1,10-phenanthroline) complex ([Co(phen)]33+/2+) is lower than that of the I3-/I− redox by ca. 0.2 V,19 and the values of the HOMO levels of ADEKA-1 and LEG4 are still more positive than the redox potential of the cobalt(III/II) complex (Fig. S15, ESIT), which provides the thermodynamic driving force for the dye regeneration reaction by the electron transfer from the Co3+/2+ electrolyte to the oxidized dye.13-15 Thus we employed [Co(phen)]33+/2+ as the redox electrolyte to the co-sensitized cell by ADEKA-1 and LEG4 for further improvement of the η of the cells.

In the fabrication of the cells using the cobalt(III/II) complex redox electrolytes (Cell-B), compositions of the electrolyte solutions as to the ratio of Co3+/Co3+, the kind of the counter anion of the cobalt(III/II) complex and the electrolyte additives were optimized experimentally according to the literatures7,13,14,20,21 with using a platinum-deposited F-doped SnO2 (FTO)-coated glass plate as the counter electrode. The cell using the electrolyte solution with the optimized composition exhibited the high Voc above 1 V and the η was improved to 13.8% under the AM-1.5G one sun illumination (Entry 2 in Table 1) as was expected from the more positive redox potential of [Co(phen)]33+/2+. However, the decrease of the Jsc was also observed in the cell from that in the cell with the I3-/I− redox electrolyte solution. In order to recover the Jsc, we employed graphene nanoplatelets (GNP) as the material for the counter electrode and composed the counter electrode on a FTO-coated glass plate with a structure of FTO/Au/GNP, because the counter electrode has been reported to produce higher Jsc and a fill factor (FF) in the photocurrent-voltage property than the usually applied platinum electrodes.8,22,23 Figure 3 shows an example of the J-V curve under the AM-1.5G one sun illumination (100 mW cm−2) and the IPCE spectrum of the cell co-sensitized by ADEKA-1 and LEG4. The photovoltaic parameters assessed as the averaged values from the J-V curves of the separately prepared four cells are listed in Table 1 as Entry 3 (Table S5, ESIT). The Jsc was improved actually in the cell from 17.8 to 18.3 ± 0.1 mA cm−2 by using the FTO/Au/GNP counter electrode and the maximum value in the IPCE spectrum was reached up to 91%, resulting in the η of 14.3% with Voc above 1 V. The better photovoltaic performance in the lower light intensity is a characteristic of DSSCs. That is also in the present cell and the cell exhibited the η close to 15% under the simulated sunlight with 50 mW cm−2 intensity (Entry 4 in Table 1 and Figs. S16, S17 in ESIT).

**Table 1 Photovoltaic parameters of the cells sensitized collaboratively by ADEKA-1 and LEG4 (Cell-B) under the illuminations of the simulated sunlight (AM-1.5G)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Electrolyte : Redox</th>
<th>Counter Electrode</th>
<th>Light Intensity</th>
<th>Jsc (mA cm−2)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A : I3−/I−</td>
<td>FTO/Pl</td>
<td>100 mW cm−2</td>
<td>19.11</td>
<td>0.783</td>
<td>0.748</td>
<td>11.2</td>
</tr>
<tr>
<td>2</td>
<td>F : [Co(phen)]33+/2+</td>
<td>FTO/Pl</td>
<td>100 mW cm−2</td>
<td>17.77</td>
<td>1.018</td>
<td>0.765</td>
<td>13.8</td>
</tr>
<tr>
<td>3</td>
<td>F : [Co(phen)]33+/2+</td>
<td>FTO/Au/GNP</td>
<td>100 mW cm−2</td>
<td>18.27</td>
<td>1.014</td>
<td>0.771</td>
<td>14.3</td>
</tr>
<tr>
<td>4</td>
<td>F : [Co(phen)]33+/2+</td>
<td>FTO/Au/GNP</td>
<td>50 mW cm−2</td>
<td>9.55</td>
<td>0.994</td>
<td>0.776</td>
<td>14.7</td>
</tr>
</tbody>
</table>

Photovoltaic parameters of the cells sensitized collaboratively by ADEKA-1 and LEG4 with the efficiency over 14% (Entry 3a in Table S5, ESIT) under the illumination of the simulated sunlight (AM-1.5G, 100 mW cm−2). Inset shows the IPCE spectrum of the cell.

![Fig. 3](https://example.com/figure3.png)
In conclusion, a carboxy-anchor organic dye of LEG4 was revealed to work effectively as the collaborative sensitizer to the silyl-anchor dye of ADEKA-1 in DSSCs, and we succeeded in obtaining the high IPCE up to 91%, Voc above 1 V and 14.3% conversion efficiency in the cell with the optimized cobalt(III/II) complex redox electrolyte solution and the GNP counter electrode. The result is attributed basically to the strong adsorption property of ADEKA-1 to the TiO2 electrode and shows the validity of silyl-anchor dyes as the photosensitizers for DSSCs. The observation over 14% conversion efficiency in the DSSC indicates a high potential of DSSCs as a light-to-electric energy conversion device. The collaborative sensitization by plural organic dyes including silyl-anchor dyes, which would bring a further improvement to DSSCs in their photovoltaic performance, are considered as a promising way to produce practical DSSCs.

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Notes and references