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An achievement of over 12 percent efficiency in an organic dye-sensitized solar cell†

Kenji Kakiage,[ab] Yohei Aoyama,[a] Toru Yano,*[a] Takahiro Otsuka,[a] Toru Kyomen,[c] Masafumi Unno[c] and Minoru Hanaya*[c]

Dye-sensitized solar cells fabricated by using a novel metal-free alkoxysilyl carbazole as a sensitizing dye and a Co$^{3+/2+}$-complex redox electrolyte exhibited light-to-electric energy conversion efficiencies of over 12% with open-circuit photovoltages higher than 1 V by applying a hierarchical multi-capping treatment to the photoanode.

Dye-sensitized solar cells (DSSCs), composed of mesoporous nanocrystalline-TiO$_2$ films modified *via* sensitizing dyes as photoelectrodes, redox electrolytes and counter electrodes, have become a promising alternative photovoltaic technology of the next generation to conventional inorganic solar cells because of their ease of fabrication and potential low costs.[1–3] Towards the realization of higher photovoltaic performance and durability in DSSCs, the development of the sensitizing dyes is one of the most important approaches. However, the investigation of the sensitizing dyes has been mostly limited to those including carboxy groups as the anchor moiety for chemical bonding to the surface of the TiO$_2$ electrodes.[1–5]

Organosilicon compounds such as alkoxysilanes and silanols have high bonding ability to metal-oxide surfaces by forming firm Si–O–metal bonds,[6–9] and alkoxysilyl dyes have been demonstrated as potential materials for sensitizing dyes by a higher electron-transfer efficiency from the light-excited dye to the TiO$_2$ electrode through Si–O–Ti (titanosiloxane) bonds and a higher photovoltage of the cell than that using the carboxy analog.[10] Recently, metal-free MK dyes of carbazole/alkyl-functionalized oligothiophene/cyanoacrylic acid type compounds were reported by Koumura and Hara.[11–13] The DSSCs sensitized with those organic dyes were demonstrated

^{a} *Environmental & Energy Materials Laboratory, ADEKA CORPORATION,*
  7-2-35 Higashiogu, Arakawa, Tokyo 116-8554, Japan. E-mail: yanotoru@adeka.co.jp
^{b} *Human Resource Cultivation Center (HRCC), Gunma University, 1-5-1 Tenjin-cho,*
  Kiryu, Gunma 376-8515, Japan
^{c} *Division of Molecular Science, Faculty of Science and Technology, Gunma University,*
  1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan. E-mail: mhanaya@gunma-u.ac.jp
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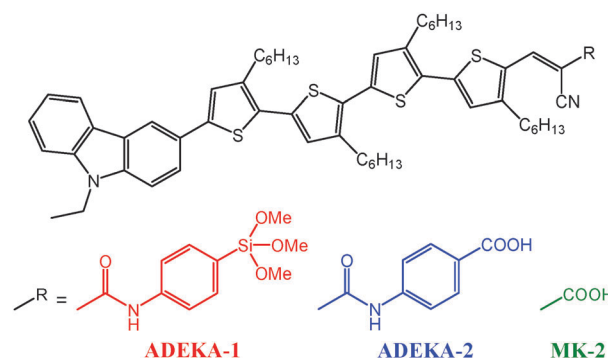 c4cc02192d

Fig. 1 Molecular structures of carbazole dyes with a trimethoxysilyl group (**ADEKA-1**) and with a carboxy group (**ADEKA-2** and **MK-2**) as the anchor moiety for chemical bonding to the surface of the TiO$_2$ electrodes.

to possess high photostability and showed relatively high light-to-electric energy conversion efficiencies (η) of about 8%,[11,12] and 9–10% efficiencies have been obtained by using a cobalt(III/II) tris(2,2′-bipyridine) complex ([Co(bpy)$_3$]$^{3+/2+}$) as the redox electrolyte in the cells.[13,14] By the application of anchoring with titanosiloxane bonds to this type of dyes and by employing Co$^{3+/2+}$-complex redox electrolytes, it would be possible to produce efficient DSSCs. In this work, therefore, we designed and synthesized an alkoxysilyl derivative of **MK-2**, **ADEKA-1** (Fig. 1), and succeeded in achieving the η value of 12.5% in a DSSC sensitized by the dye.

ADEKA-1 and **ADEKA-2**, which is a benzoic-acid derivative of **ADEKA-1** synthesized as a reference dye, exhibited similar UV-visible absorption spectra to **MK-2** in toluene solutions; their major absorption bands assignable to the π–π* transition were observed in the visible region between 400 and 600 nm (Fig. S1, ESI†). The maximum molar absorption coefficients (ε_{max}) at λ_{max} were evaluated to be 43 200 (498 nm), 42 700 (504 nm) and 37 400 (489 nm) for **ADEKA-1**, **ADEKA-2** and **MK-2**, respectively. Slight red shifts of λ_{max} and increments of ε_{max} in **ADEKA-1** and **ADEKA-2** compared with **MK-2** are considered to be due to the introduction of the phenylamide moieties. The oxidation potentials (E_{ox}: approximately the energy levels of HOMO) of these dyes were determined by means of
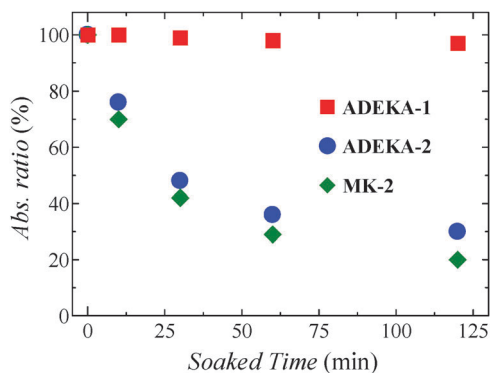
Fig. 2 Changes of the absorbances due to the carbazole dyes (**ADEKA-1**, **ADEKA-2** and **MK-2**) adsorbed on the TiO_2 electrodes with the soaked time into 3-methoxypropionitrile–water (1:1 in volume) at 85 °C in the dark.

cyclic voltammetry (Fig. S2, ESI†). **ADEKA-1** and **ADEKA-2** introduced phenyl-amide moieties showed more positive E_{ox} of 0.99 V and 1.01 V vs. NHE, respectively, compared to that of **MK-2** (0.95 V). The values of E_{ox} are more positive than that of the redox potential of 0.56 V vs. NHE in $[Co(bpy)_3]^{3+/2+}$,[15] thus providing thermodynamic driving forces for the dye regeneration reactions by the electron transfer from the $[Co(bpy)_3]^{3+/2+}$ redox.

The adsorptions of carboxy dyes such as **ADEKA-2** and **MK-2** on the TiO_2 electrodes are understood to proceed from the formation of ester-like and/or bridging linkages between the carboxy groups and the hydroxy groups on the surface of the TiO_2 electrode.[3,11] On the other hand, **ADEKA-1**, which has a trimethoxysilyl group as the anchor moiety to the TiO_2 electrode, is considered to adsorb on the electrode with the formation of three titanosiloxane (Si–O–Ti) bonds (Fig. S3, ESI†).[7,9,10] To examine the durability of the linkages between the dyes and the TiO_2 electrodes, we soaked the dye-adsorbed TiO_2 electrodes into a mixed solvent of 3-methoxy-propionitrile and water (1:1 in volume) at 85 °C in the dark and traced the time dependence of the light absorption due to the dyes on the TiO_2 electrodes (Fig. 2, Fig. S4 and S5, ESI†). As shown in Fig. 2, although 70–80% of adsorbed dye molecules were observed to eliminate from the electrodes after 120 min soaking in the cases of **ADEKA-2** and **MK-2**, more than 95% of **ADEKA-1** molecules were confirmed to be on the TiO_2 electrode. These results evidence the robustness of the linkage by the titanosiloxane bonds.

The photovoltaic properties of the cells fabricated using the three carbazole dyes as sensitizers are listed in Table 1. The photovoltaic parameters, short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (FF) and η, were assessed from the photocurrent–voltage (I–V) curves under the simulated AM-1.5G solar irradiation with the intensity of 100 mW cm^{-2} (Fig. S6, ESI†). Entries 1–3 are the cells using the $[Co(bpy)_3]^{3+/2+}$ redox electrolyte. Among the cells, the **ADEKA-1**-sensitized cell exhibited slightly higher J_{sc} and V_{oc} values than the cells sensitized by the carboxy dyes of **ADEKA-2** and **MK-2**, and a higher η over 10% was evaluated than those for the cells with **ADEKA-2** and **MK-2**. The higher η is considered to be mainly due to the higher V_{oc} caused by the linkage of the dye by the titano-siloxane bonds on the surface of the TiO_2 electrode (Fig. S3, ESI†).[10]

The maximum photovoltage (V_{max}) obtained in the DSSC is attributed to the energy gap between the quasi-Fermi level [approximately the energy level of the conduction-band edge ($E_{C.B.}$)] of the TiO_2 [−0.5 V vs. NHE for anatase[2,3]] and the redox potential of the electrolyte. To obtain an even higher photovoltage and to improve the η value further in the cells, therefore, we employed a cobalt(III/II) tris(5-chloro-1,10-phenanthroline) complex ($[Co(Cl-phen)_3]^{3+/2+}$) as the redox electrolyte, which has a higher redox potential of 0.72 V vs. NHE than $[Co(bpy)_3]^{3+/2+}$.[15] By using the $[Co(Cl-phen)_3]^{3+/2+}$ redox electrolyte in the **ADEKA-1**-sensitized cell (entry 4), the V_{oc} value was increased to 0.897 V from that in the cell with the $[Co(bpy)_3]^{3+/2+}$ redox electrolyte of 0.848 V. The η was actually improved by an increment of the V_{oc} value, although the J_{sc} value decreased slightly by a sluggish diffusion of $[Co(Cl-phen)_3]^{3+/2+}$ compared to $[Co(bpy)_3]^{3+/2+}$ due to the bulki-ness.[15–17] On the other hand, a significant lowering of η was observed in the **MK-2**-sensitized cell using the $[Co(Cl-phen)_3]^{3+/2+}$ redox electro-lyte (entry 5). An energy gap between the E_{ox} of **MK-2** and the redox potential of $[Co(Cl-phen)_3]^{3+/2+}$ was estimated to be 0.23 eV, which is smaller than 0.27 eV for **ADEKA-1**. The low η value observed is considered to be the result of the lack of the thermodynamic driving force for the dye regeneration reaction, which proceeds through the electron transfer from the Co^{2+} complex to the dye in the oxidized state, by the small energy gap.[15–18]

The V_{oc} value in the **ADEKA-1**-sensitized cell was increased by using $[Co(Cl-phen)_3]^{3+/2+}$ redox instead of $[Co(bpy)_3]^{3+/2+}$. However the increment and the observed V_{oc} were much lower than the expected value from the estimated V_{max} of the cells, which are 1.22 V and 1.06 V in the cases of $[Co(Cl-phen)_3]^{3+/2+}$ and $[Co(bpy)_3]^{3+/2+}$,

Table 1 Photovoltaic parameters of the cells sensitized by the carbazole dyes (**ADEKA-1**, **ADEKA-2** and **MK-2**) using the cobalt complexes ($[Co(bpy)_3]^{3+/2+}$ and $[Co(Cl-phen)_3]^{3+/2+}$) as the redox electrolytes under the illumination of the simulated sunlight (AM-1.5G, 100 mW cm^{-2})

Entry	Dye	Redox/electrolyte[a]	Capping[b]	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
1	**ADEKA-1**	$[Co(bpy)_3]^{3+/2+}$/A	Single	16.1	0.848	0.762	10.4
2	**ADEKA-2**	$[Co(bpy)_3]^{3+/2+}$/A	Single	15.1	0.821	0.752	9.32
3	**MK-2**	$[Co(bpy)_3]^{3+/2+}$/A	Single	15.8	0.814	0.753	9.68
4	**ADEKA-1**	$[Co(Cl-phen)_3]^{3+/2+}$/A	Single	15.6	0.897	0.764	10.7
5	**MK-2**	$[Co(Cl-phen)_3]^{3+/2+}$/A	Single	8.8	0.811	0.752	5.37
6	**ADEKA-1**	$[Co(Cl-phen)_3]^{3+/2+}$/A	Multi	15.8	0.958	0.748	11.3
7	**ADEKA-1**	$[Co(Cl-phen)_3]^{3+/2+}$/B	Multi	14.9	1.034	0.777	12.0
8[c]	**ADEKA-1**	$[Co(Cl-phen)_3]^{3+/2+}$/B	Multi	15.6[d]	1.036[d]	0.774[d]	12.5[d]

[a] Electrolyte A: 0.25 M Co^{2+} + 0.035 M Co^{3+} + 0.10 M $LiClO_4$ + 0.50 M TBP in acetonitrile, electrolyte B: 0.25 M $[Co(Cl-phen)_3]^{2+}$ + 0.035 M $[Co(Cl-phen)_3]^{3+}$ + 0.07 M $LiClO_4$ + 0.02 M $NaClO_4$ + 0.03 M TBAPF + 0.01 M TBPPF + 0.01 M HMImPF + 0.30 M TBP + 0.10 M TMSP + 0.10 M MP in acetonitrile. [b] Single: the single-capping with heptanoic acid, multi: the hierarchical multi-capping. [c] The results for the cell attached with an antireflection film on the surface of the photoanode. [d] The value is the average of the results of the three cells examined (Table S2, ESI).

respectively (Fig. S7, ESI†). The reason for the lower V_{oc} in comparison with the V_{max} is believed to be because the cells employing $Co^{3+/2+}$-complex redox electrolytes with more positive redox potentials are exposed to the faster recombination reaction, that is, the undesirable electron transfer from the TiO_2 electrode to the electrolyte, and the reaction can be suppressed by restricting the contact of the Co^{3+} complex to the naked surface of the TiO_2 electrode between the adsorbed sensitizing dye molecules.[16–22] Therefore, we examined a hierarchical multi-capping treatment of the **ADEKA-1**-adsorbed TiO_2 electrode using eight molecules with various alkyl-chain lengths and with three kinds of anchor moieties, *i.e.* carboxy, phosphonic and silyl groups (Fig. S8, ESI†). In the treatment, we performed the capping by larger agents, which need larger space for the adsorption, to smaller ones, which need only small space, and tried to form an 'alkyl-thicket' structure on the surface of the TiO_2 electrode between the adsorbed sensitizing dye molecules for an effective passivation of the electrode (Fig. S9, ESI†). The hierarchical multi-capping treatment worked properly in the **ADEKA-1**-sensitized cell with the $[Co(Cl\text{-}phen)_3]^{3+/2+}$ redox electrolyte, and the V_{oc} value was improved from 0.897 V to 0.958 V resulting in a higher conversion efficiency of 11.3% (entry 6; Table S1, ESI†).

In DSSCs, photovoltaic performances are well known to be affected by the compositions of the electrolyte solutions.[23–25] This was also true in the **ADEKA-1**-sensitized cell, and the η value was improved up to 12.0% with the V_{oc} of over 1 V by using an experimentally optimized electrolyte (entry 7; Fig. S10, ESI†). In order to harvest the incident light more efficiently, we finally attached an antireflection film to the cell in entry 7 (entry 8). The I–V curve and incident monochromatic photon-to-current conversion efficiency (IPCE) spectrum of the cell are shown in Fig. 3. A maximum IPCE value was reached to 85%, and we succeeded in obtaining an η value of 12.5%. This efficiency is the highest among those reported so far for DSSCs with organic dyes.[2–4,14,22,26] Such a high photovoltaic performance of the cell is based on the high stability of titanosiloxane bonds formed between **ADEKA-1** and the surface of the TiO_2 electrodes. The stability allowed the formation of

the 'alkyl-thicket' structure on the TiO_2 electrode by using the hierarchical multi-capping treatment.

The achievement of the η value of 12.5% under the one sun condition in the cell with the metal-free dye of **ADEKA-1** as a single sensitizer indicates the high potential of organic dyes with organosilicon tethers for binding the metal oxides as the photosensitizers for DSSCs, and the present results provide a fertile base for further improving the photovoltaic performance of DSSCs. The combination of the co-sensitization using plural sensitizing dyes with organosilyl anchor moieties and the hierarchical multi-capping in the cells with $Co^{3+/2+}$-complex redox electrolytes is one of the approaches for achieving a higher efficiency of over 13%, and such a challenge is currently underway in our group.

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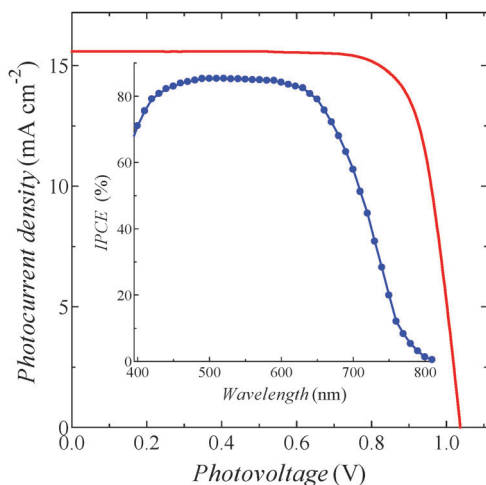26 M. Zhang, Y. Wang, M. Xu, W. Ma, R. Li and P. Wang, *Energy Environ. Sci.*, 2013, **6**, 2944.

Fig. 3 Typical I–V properties of the **ADEKA-1**-sensitized solar cell with the highest efficiency of 12.5% (entry 8 in Table 1) under the simulated one sun irradiation (AM-1.5G, 100 mW cm^{-2}). Inset shows the IPCE spectrum of the cell.