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High-efficiency dye-sensitized solar cell with a novel co-adsorbent†

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A new record efficiency (11.4%) of dye-sensitized solar cell was obtained by design and syntheses of donor–acceptor type co-adsorbents which effectively overcome the competitive light absorption by I^-/I_3^- , avoid dye aggregation, and reduce the charge recombination. This result was certified by a public research center (AIST).

Dye-sensitized solar cells (DSCs) are promising next-generation alternatives to conventional silicon-based photovoltaic devices owing to their low manufacturing cost and potentially high conversion efficiency.^{1,2} A typical DSC comprises a dye-sensitized nanocrystalline titanium dioxide (TiO_2) film deposited on a transparent conducting oxide (TCO) glass, a platinum (Pt) counter-electrode, and an electrolyte solution with a dissolved I^-/I_3^- ion redox couple. Until now, the certified champion efficiency of 11.1% was achieved,² which is lower than that achieved with bulk silicon solar cells. In the approach to new record efficiency, much effort has been carried out to solve the problems that limit improvement, such as (i) utilizing efficient single or multi-sensitizers with broad light absorption spectra that extend into the visible and infrared regions,^{3–8} (ii) utilizing an

alternative I^-/I_3^- redox couple to improve open circuit voltage (V_{OC}) and/or overcome the strong dip in the incident photon-to-electron conversion efficiency (IPCE) spectrum around 380 nm induced by the competitive light absorption of triiodide,^{9–11} (iii) utilizing co-adsorbents to avoid the competitive adsorption and aggregation among dyes that may induce unfavorable charge or energy transfer and quenching of photo-excited states,^{12–15} and (iv) utilizing additives to reduce the recombination of electrons in the TiO_2 film with I_3^- or other acceptor species.¹⁶ Unfortunately, in the past five years no efficiency has exceeded the certified highest value of 11.1%. In contrast, certified efficiencies of more than 10% reported until now have all involved the use of black dye alone and I^-/I_3^- redox couples.^{2,17–19} A feasible strategy for further improvement of the efficiency is therefore the development of new compounds that can be used as co-adsorbents in black dye based DSCs with advantageous characteristics for overcoming the aforementioned problems. The ideal candidate for a co-adsorbent should have three characteristics: (i) it should have a large molar extinction coefficient (ϵ) in the infrared region or around 400 nm to recover the dip in the IPCE spectra induced by I_3^- ; (ii) the structure of the molecule should be suitable for avoiding competitive adsorption among dyes while effectively suppressing the aggregation of dyes on the TiO_2 surface; and (iii) it should be able to reduce the recombination of electrons in the TiO_2 film with I_3^- and other acceptor species by the formation of a compacted molecule monolayer covering the bare TiO_2 surface.

In this work we successfully designed and synthesized two simple donor–acceptor type co-adsorbents, denoted as **Y1** and **Y2**, with intense absorption maxima between 350 nm and 400 nm. We used these co-adsorbents to improve the IPCE spectra by offsetting the competitive visible light absorption due to I_3^- . Moreover, we

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Broader context

The development of photovoltaic technology is expected to help solve problems related to energy shortages and environmental pollution caused by the use of fossil fuels. Dye-sensitized solar cells (DSCs) fabricated with low-cost are regarded as one of the most promising photovoltaic devices. However, the overall efficiency of I^-/I_3^- based DSCs has been limited because light harvesting is not fully achieved, and the photo-excited electrons always recombine with the acceptor species before the electrode collects them. Here, we show the design and synthesis of a small donor–acceptor type co-adsorbent, which can effectively increase the short circuit current by offsetting the competitive light absorption by I^-/I_3^- and improve the open circuit potential by introducing butyloxyl chains into the molecule to avoid dye aggregation and reduce the charge recombination. A certified new record efficiency of 11.4% was achieved by using the novel co-adsorbent. This work illustrates a new pathway to achieve highly efficient DSCs for practical applications.

introduced butyloxyl chains into the **Y1** molecule to adjust the distance between dyes in order to study the effect of the structure of co-adsorbents on cell performance.

Donor- π -acceptor (D- π -A) type compounds are particularly attractive because it is possible to readily tune their highest occupied molecular orbital (HOMO) levels, lowest unoccupied molecular orbital (LUMO) levels, and other properties through a systematic variation of the donor and acceptor units. We herein developed simple and small D- π -A structure molecules, **Y1** and **Y2** (Fig. 1a). The structural design of these molecules includes three key features: (i) butyloxyl-substituted phenyl as an electron-donating unit, thiophene as a π -spacer, and a cyanoacetic acid group as an acceptor and anchor, the result being a **Y1** molecule with a strong absorption around 400 nm that could compensate for the short wavelength dip in the IPCE spectrum; (ii) a fluorine-substituted phenylene as a weak donor was used in molecule **Y2** to hypsochromically shift the absorption peak to a wavelength region similar to that of I_3^- ; (iii) two butyloxyl groups were added in **Y1** to avoid dye aggregation; and (iv) the molecular sizes of both **Y1** and **Y2** are smaller than the black dye molecule and it makes them suitable for compact monolayer formation through covering the bare TiO_2 surface during the dye uptake process. For these reasons molecules **Y1** and **Y2** were suitable as co-adsorbents for the black dye.

The co-adsorbents **Y1** and **Y2** showed strong absorptions near 390 nm and 360 nm, respectively (Fig. 1b). We assigned these absorptions to the intramolecular charge transfer between the donors and the acceptors in the co-adsorbents. **Y2** with a substituted fluorine showed the same absorption peak as I_3^- , whereas the absorption peak of **Y1** with a substituted butyloxyl shifted to 390 nm because of the electron-donating properties of the butyloxyl groups. The peak molar extinction coefficients (ϵ) of **Y1** and **Y2** were $3.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $3.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, which are much higher than those

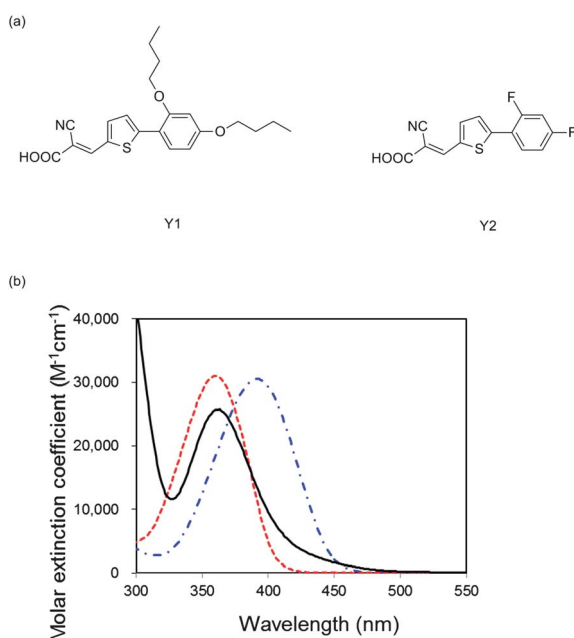


Fig. 1 Properties of co-adsorbents. (a) The chemical structure of co-adsorbents. (b) UV-visible absorption spectra of co-adsorbent **Y1** (dashed-dotted line), **Y2** (dashed line) and triiodide (solid line) in ethanol solutions.

of black dye ($\epsilon = 1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and I_3^- ($\epsilon = 2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) at this wavelength. Comparison to the molar extinction coefficients of I_3^- , **Y1** and **Y2** showed much higher light harvesting ability in this region. Hence we expected the loss of the light absorption by I_3^- to be suppressed by the use of co-adsorbent **Y1** or **Y2**.

Recovering the dip in the black dye based IPCE spectra near 400 nm due to the competitive absorption of light by I_3^- required that the co-adsorbents could easily inject electrons from the co-adsorbents into the TiO_2 film. The higher LUMO levels of **Y1** (-2.96 eV) and **Y2** (-2.80 eV) compared to the TiO_2 conduction band edge (-4.2 eV) facilitated the injection of electrons from the co-adsorbents to the TiO_2 film. The lower HOMO levels of **Y1** (-5.82 eV) and **Y2** (-6.00 eV) compared to the redox potential of I^-/I_3^- (-5.1 eV) facilitated electron transfer from I^- to the co-adsorbents.

The cell with only black dye had a broad IPCE spectrum extending across the whole visible range and into the near-IR region as far as 950 nm and displayed the highest IPCE value (81%) in the wavelength range from 600 to 700 nm (Fig. 2), suggesting that electrons are efficiently collected in the cell which is well fabricated. As mentioned above, the decrease of the IPCE to 43% in the wavelength range 350–450 nm was due to competitive light absorption between I_3^- and the black dye. Addition of **Y1** restored the dip in the IPCE spectrum more efficiently than **Y2**, which is in agreement with the IPCE spectra of devices with **Y1** and **Y2** alone respectively (Fig. S1†). This fact indicated that the co-adsorbents had adsorbed onto the TiO_2 surface with efficient electron injection. Addition of co-adsorbent **Y1** for the cell with black dye enhanced the platform of the IPCE over a large spectral region at wavelengths from 300 nm to 700 nm. This result was consistent with the absorption spectrum of **Y1**. However, in the cell with co-adsorbent **Y2**, the enhancement occurred only in a narrow range of wavelength from 350 nm to 420 nm. We attributed this difference in the effects of co-adsorbents **Y1** and **Y2** to their different light-harvesting properties. In contrast, in the spectral region from 700 to 900 nm, the IPCE spectrum of the black dye did not change after addition of the co-adsorbents. This result indicated that the co-adsorbents competitively adsorbed and/or interacted with the black dye to a negligible extent. These results suggest that it is possible to achieve a high IPCE in the visible and infrared wavelength region by developing suitable co-adsorbents with strong light absorption.

Addition of co-adsorbent **Y1** effectively improved the conversion efficiency (η) of the DSC up to 11.3% with a J_{SC} of 20.88 mA cm^{-2} and V_{OC} of 0.743 V (Table 1). Compared to the cell sensitized by

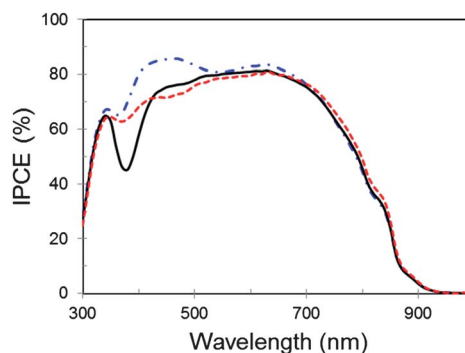


Fig. 2 Incident photon-to-electron conversion efficiency (IPCE) spectra. IPCE spectra of DSCs with co-adsorbent **Y1** (dashed-dotted line), with co-adsorbent **Y2** (dashed line) and without co-adsorbent (solid line).

Table 1 The current–voltage performance data^a of DSCs sensitized by black dye without co-adsorbent, with co-adsorbent **Y1** or **Y2** measured under one sun simulated sunlight (air mass 1.5)

Sample	$J_{SC}/\text{mA cm}^{-2}$	V_{OC}/mV	FF	η (%)
Black dye	20.45 ± 0.06	727 ± 2	0.720 ± 0.002	10.70 ± 0.02
Black dye + Y1	20.88 ± 0.07	743 ± 4	0.727 ± 0.002	11.28 ± 0.06
Black dye+ Y2	20.60 ± 0.06	706 ± 6	0.706 ± 0.006	10.28 ± 0.13

^a The standard deviation is calculated based on 4 samples and measured twice for the same cell composition and fabrication procedure.

black dye alone, addition of the co-adsorbents increased the J_{SC} value corresponding to the IPCE spectra. Interestingly, there was about a 20 mV enhancement of the V_{OC} in the cell with co-adsorbent **Y1** compared to the cell with black dye only, whereas in the case of addition of **Y2**, the V_{OC} is decreased.

The V_{OC} value of a DSC is related to the energy level of the TiO_2 conduction band (E_{CB}) and the conduction band electron density (n) in the TiO_2 film. The V_{OC} can be described as follows:

$$V_{OC} = \frac{k_B T}{q} \ln\left(\frac{n}{n_0}\right) \quad (1)$$

where k_B is the Boltzmann constant, T is the temperature (K), q is the elementary charge, and n_0 can be estimated under vacuum conditions as follows:

$$n_0 = N_C \exp\left(\frac{E_{CB} - E_{redox}}{k_B T}\right) \quad (2)$$

where N_C is the density of conduction band states and E_{redox} is the potential of redox species (I^-/I_3^-). From eqn (1) and (2) we can deduce that a shift of E_{CB} or change of the electron lifetime (τ) in TiO_2 will influence the V_{OC} because the electron density is correlated with the electron lifetime. To understand the different effects of the co-adsorbents on the V_{OC} , we measured E_{CB} with the charge extraction method (CEM)²⁰ (shown as Fig. S2 in the ESI†). We found that E_{CB} was not affected by **Y1** and **Y2**. Therefore we should attribute the different effects of **Y1** and **Y2** on V_{OC} to the influence of electron lifetime, which is related to the charge recombination process. We derived the electron lifetime τ as a function of the electron density (Fig. 3) with the use of intensity-modulated photovoltage spectroscopy (IMVS).²¹ The electron lifetime decreased with

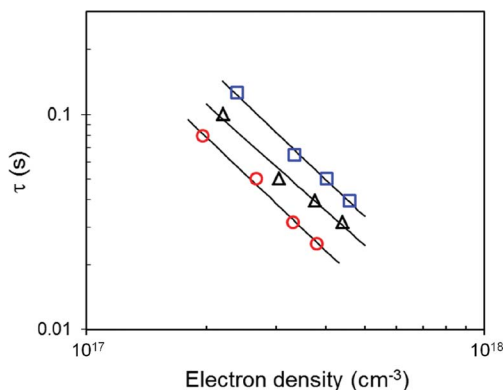


Fig. 3 Lifetime (τ) of electrons *versus* electron density. The τ in DSCs sensitized by black dye with co-adsorbent **Y1** (open squares), without co-adsorbent (open triangles) and with co-adsorbent **Y2** (open circles) were derived by using intensity-modulated photovoltage spectroscopy.

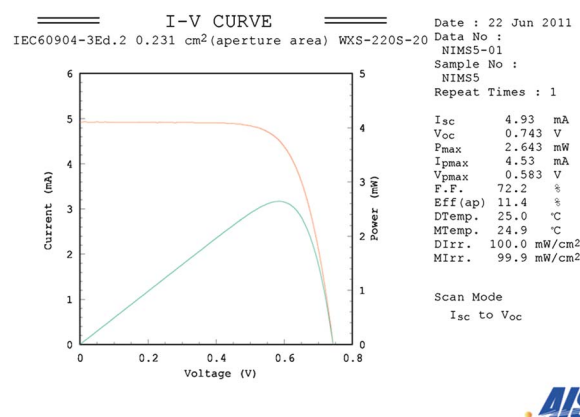


Fig. 4 Current–voltage characteristics of DSC with black dye and co-adsorbent **Y1**. Results were measured at 25 °C with an aperture area of 0.231 cm² by using a black metal mask and an irradiance of 100.0 mW cm⁻². Short circuit current density $J_{SC} = 21.3 \text{ mA cm}^{-2}$; open circuit voltage $V_{OC} = 743 \text{ mV}$; fill factor $FF = 72.2\%$; and efficiency = 11.4%. The upper line and lower line indicate current and power, respectively. This measurement was independently carried out by the Research Center for Photovoltaics, AIST.

increasing electron density in a manner consistent with a power law relationship. At a certain charge density, the electron lifetime was larger in the cell with co-adsorbent **Y1** than in the cell without co-adsorbent and in the cell with co-adsorbent **Y2**. This result suggested that adsorption of **Y1** onto the free area of the TiO_2 surface exposed to the redox electrolyte had resulted in the formation of a compacted monolayer that could effectively suppress the recombination of electrons in the TiO_2 film with I_3^- , with a resultant improvement of the V_{OC} . This result also revealed that butyloxyl chains in the molecular structure of the co-adsorbent played an important role in improving the V_{OC} . The successful exploitation of co-adsorbent **Y1** provided us with a new direction for developing novel materials that can increase not only the V_{OC} but also the IPCE in the IR wavelength region to further enhance solar cell efficiency.

Finally, the Research Center for Photovoltaics, the National Institute of Advanced Industrial Science and Technology (AIST, Japan), independently certified the current–voltage characteristics. We achieved an overall conversion efficiency of 11.4% (Fig. 4), which is a new record efficiency confirmed by a public test center.

Conclusions

We succeeded in designing and synthesizing two small, simple donor–acceptor type co-adsorbents. The novel co-adsorbent **Y1** distinguished itself by integration of three advantages into one small and

simple molecule: offsetting the competitive visible light absorption due to I_3^- , adjusting the distance between dyes to avoid aggregation, and reducing the recombination of electrons in the TiO_2 film. The distinct properties of co-adsorbent **Y1** enabled DSCs sensitized with black dye to perform with high efficiency. Both J_{SC} and V_{OC} values were simultaneously higher in the cell with co-adsorbent **Y1**. A public research center (AIST) certified the cell's efficiency to be 11.4%, a new DSC efficiency record. These results emphasize the importance of the strategy that integrates multiple functions into one co-adsorbent to improve the device performance and will facilitate further improvement of efficient DSCs through the enhancement of the IPCE in the IR wavelength region.

Experimental

All reagents were purchased from Sigma-Aldrich and Alfa Aesar. The 1H NMR and ^{13}C NMR spectra of solutions in $CDCl_3$ and DMSO were recorded on 300 and 500 MHz NMR spectrometers. Chemical shifts were referenced relative to tetramethylsilane. Mass spectra were recorded on a Shimadzu Biotech MALDI-MS mass spectrometer. Absorption spectra were recorded on a Shimadzu model 3100 UV-Vis-NIR spectrophotometer.

Nanocrystalline TiO_2 films were prepared by using a variation of a reported method.²² TCO sheet glass electrodes (Nippon Sheet Glass Co., Japan) with a sheet resistance of 8–10 Ωm^{-2} and an optical transmission of greater than 80% in the visible range were used. The TiO_2 thin films of approximately 25 μm thickness (area: 0.25 cm^2) were deposited onto the conducting glass by screen-printing. The films were then sintered at 500 $^\circ\text{C}$ for 1 hour. The thickness of films was measured with a Surfcom 1400A surface profiler (Tokyo Seimitsu Co. Ltd.). The films were further treated with 0.1 M HCl aqueous solutions before examination.²³ The dye solution is a mixture of black dye [tri(thiocyanato)(4,4',4''-tricarboxy-2,2':6',2''-terpyridine) ruthenium(II)] and co-adsorbent **Y1** or **Y2** in 0.2 mM respectively with addition of deoxycholic acid at a concentration of 20 mM. To be specific, the cell performance is optimum when the molar ratio of black dye to **Y1** or **Y2** was 1 : 1. The TiO_2 films were immersed in the above solutions and then kept at 25 $^\circ\text{C}$ for 30 hours. The dye-deposited TiO_2 film and a platinum-coated conducting glass were separated by a Surlyn spacer (40 μm thick) and sealed by heating the polymer frame. An electrolyte consisting of a solution of 0.6 M dimethylpropyl-imidazolium iodide, 0.05 M I_2 , 0.1 M LiI and 0.4 M *tert*-butylpyridine in acetonitrile was used in all the cells.

The current–voltage characteristics were measured using a black metal mask with an aperture area of 0.231 cm^2 under standard air mass 1.5 sunlight (100 mW cm^{-2} , WXS-155S-10: Wacom Denso Co. Japan).²⁴ Monochromatic incident photon-to-current conversion efficiency spectra were measured with a monochromatic incident light of 1×10^{16} photons cm^{-2} in director current mode (CEP-2000BX, Bunko-Keiki). The electrochemical impedance spectra were obtained under one sun illumination with a potentiostat (Solartron1287) equipped with a frequency response analyzer (Solartron1255B) under a frequency ranging from 10^{-1} to 10^6 Hz. The photoemission yield curves were measured with a Riken Keiki Co. Ltd. model AC-3

photoelectron spectrometer surface analyzer under atmosphere with a 0.2 ml min^{-1} N_2 flow.

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