Electronic Supplementary Information

Fabrication of a dye-sensitized solar cell containing a Mg-doped TiO_2 electrode and a Br_3^-/Br^- redox mediator with a high open-circuit photovoltage of 1.21 V

Kenji Kakiage,[a,b] Toru Tokutome,[a] Shinji Iwamoto,[a,c] Toru Kyomen[a,c] and Minoru Hanaya*[a,c]

[a] *Department of Chemistry and Chemical Biology, Graduate School of Engineering, Gunma University, Tenjin-cho 1-5-1, Kiryu, Gunma 376-8515, Japan*

[b] *Human Resource Cultivation Center (HRCC), Gunma University, Tenjin-cho 1-5-1, Kiryu, Gunma 376-8515, Japan*

[c] *International Education and Research Center for Silicon Science (Silicon Center), Graduate School of Engineering, Gunma University, Tenjin-cho 1-5-1, Kiryu, Gunma 376-8515, Japan*

* Fax: +81-277-30-1360; Tel: +81-277-30-1360; E-mail: mhanaya@gunma-u.ac.jp

Experimental Section

Synthesis of Mg-doped TiO_2 powder

Nanoparticles of Mg-doped TiO_2 with a Mg/Ti atomic ratio of 0.1 were synthesized by the solvothermal method:[1] Titanium tetraisopropoxide (24.2 g), magnesium acetate tetrahydrate (1.83 g) and 1,4-butanediol (100 mL) were added to an autoclave. The atmosphere in the autoclave was replaced with N_2 gas, and then the assembly was heated at 300 °C for 2 h. After cooling, the solid product dispersed in the organic solvent was collected by a centrifugation, then washed in acetone and air-dried. The obtained powder was annealed in air at 450 °C for 30 min.

Preparation of Mg-doped TiO_2 and TiO_2 electrodes with SFD-5 dye

To prepare the working electrodes with thin layer of the Mg-doped TiO_2 for DSSCs, F-doped SnO_2 coated (FTO) glass plates (25 × 50 mm^2, 9-11 Ω $sq.^{-1}$; Asahi Glass) were used as the current collector. As a pre-treatment, the FTO glass plates were immersed into a 80 mM $TiCl_4$ aqueous solution at 75 °C for 1 h and washed with water and ethanol, and then calcined in air at 300 °C for 30 min.[2] On the $TiCl_4$-treated FTO glass plates, thin layer of the Mg-doped TiO_2 was coated by a screen-printing method using a paste prepared by mixing the synthesized Mg-doped TiO_2 powder, water, nitric acid and polyethylene glycol with homogenizers. The Mg-doped TiO_2 electrodes were then sintered in air at 490 °C for 1 h. The thickness of the porous layer of the Mg-doped TiO_2 was estimated to be ~3.5 μm by the FE-SEM observation of the cross section of the electrodes. An anatase-TiO_2 powder of AMT-600 (TAYCA Corporation: crystalline particle size ~ 30 nm) was used as a reference to the Mg-doped TiO_2, and the working electrode with the TiO_2 powder was prepared in the same way as the Mg-doped TiO_2 electrode. Adsorption of the photosensitizer of **SFD-5** on the electrodes was performed by immersing the electrodes in a toluene solution with 3.0×10^{-4} M **SFD-5** and 5.0×10^{-3} M coadsorbent of isooctyltriethoxysilane (Gelest, Inc.) at 60 °C for 10 h. Before the immersion, the electrodes were heated in air at 120 °C for 3 h and then cooled to 60 °C to eliminate adsorbed water on the Mg-doped TiO_2 and the TiO_2 electrodes for efficient dye adsorption.

MgO surface modification and acetic acid treatment of electrodes

The Mg-doped TiO_2 electrode before the dye adsorption was immersed into a 0.05 M 2-propanol solution of $Mg(OC_2H_5)_2$ at 25 °C for 1 h, rinsed in ethanol, and then calcined in air at 490 °C for 1 h as the MgO surface modification.[3] After the adsorption of the dye, **SFD-5**, the electrode was immersed in a 0.01 M toluene solution of CH_3COOH at 25 °C for 10 min, and washed in toluene, acetonitrile and methanol as the acetic acid treatment.[4]

Photovoltaic measurements

Photovoltaic measurements were performed for the electrochemical cells of an open sandwich type. A Pt-sputtered FTO glass plate was employed as the counter electrode and three electrolyte solutions, electrolyte A-C, were used as the electrolyte. The **SFD-5**-adsorbed Mg-doped TiO_2 electrode or the **SFD-5**-adsorbed TiO_2 electrode, the counter electrode and a polyethylene film spacer of 30 μm thick were assembled, and one of the electrolyte solutions was injected into the space between the electrodes.

The photovoltaic performances of the cells were assessed from the *I-V* properties of the cells measured with a solar simulator of OTENTO-SUN III (Bunkoh-Keiki) and a source meter of R6240A (Advantest). The aperture area of the cells was maintained at 0.25 cm^2 in a square shape using a shading mask and the *I-V* properties were measured under AM-1.5G one sun illumination conditions (100 mW cm^{-2}) at 25 ± 2 °C. The power of the solar-simulated light was calibrated by using a reference Si photodiode. *I-V* curves were obtained by applying an external bias to the cells and measuring the generated photocurrent with the source meter. A voltage step and a delay time for photocurrent measurements were set to be 5 mV and 80 ms, respectively.

Results

Mg-doped TiO_2

The synthesized Mg-doped TiO_2 powder was confirmed to possess anatase structure by X-ray diffraction analysis, and the crystalline particle size of the Mg-doped TiO_2 was estimated to be ~25 nm from the diffraction peak width by using Scherrer's formula.[5] The band gap of the Mg-doped TiO_2 was evaluated to be 3.3 eV by the tauc plot of the UV-visible diffuse reflectance spectrum.[6]

Sensitizing dye (SFD-5)

The maximum molar absorption coefficient of **SFD-5** was evaluated to be 58,400 $dm^3\ mol^{-1}\ cm^{-1}$ at λ_{max} = 440 nm in acetonitrile solution. The oxidation potential (E_{ox} ≈ HOMO level) of **SFD-5** was determined to be 1.15 V vs. SCE by the cyclic voltammetry, and the excited-state oxidation potential (E_{ox}^* ≈ LUMO level) was evaluated to be -1.51 V vs. SCE from the E_{ox} value and the zeroth-zeroth energy ($E_{0\text{-}0}$ = 2.66 eV) based on the absorption and fluorescence spectra in the solution.[7] UV-visible absorption and fluorescence spectra of **SFD-5** in acetonitrile solution are shown in Figure S1.

I-V properties of the cells

I-V properties of cell 1-5 observed under the illumination of the simulated sunlight (AM-1.5G, 100 mW cm^{-2}) are shown in Figure S2.

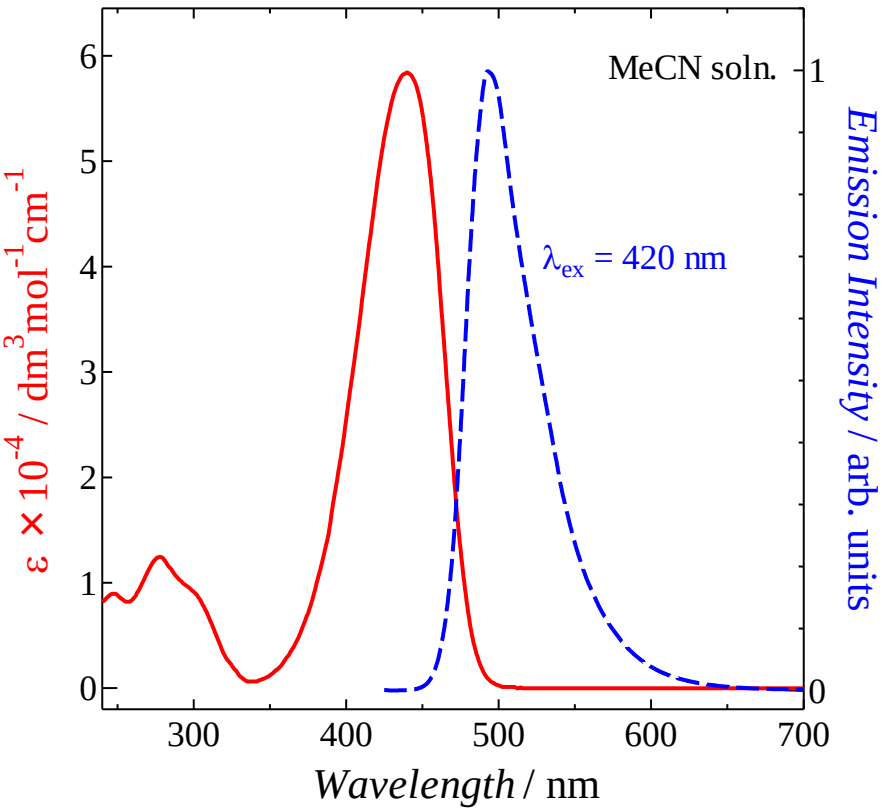

Figure S1 UV-visible absorption and fluorescence spectra of **SFD-5** in acetonitrile solution; solid line represents the result for absorption and broken line for fluorescence. The fluorescence spectrum was obtained by the excitation at 420 nm.

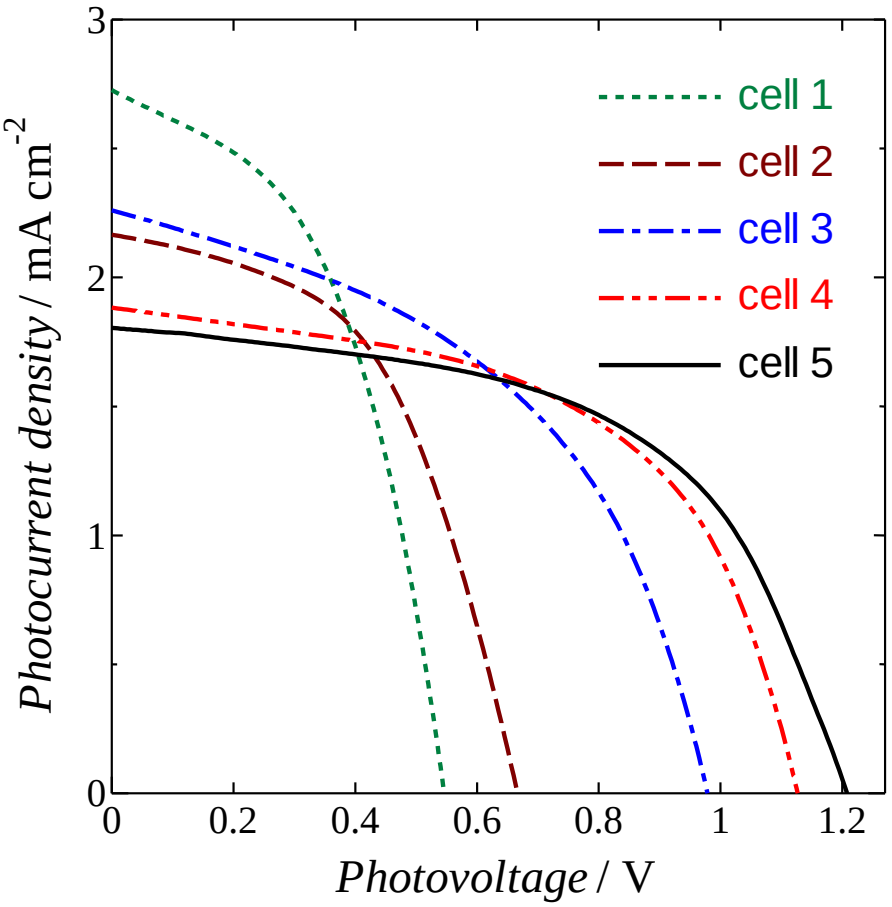

Figure S2 *I-V* properties of the cells using **SFD-5** as a photosensitizing dye (cell 1-5) under the illumination of the simulated sunlight (AM-1.5G, 100 mW cm^{-2}); dotted line represents the result for cell 1, broken line for cell 2, chain line for cell 3, two-dot chain line for cell 4, and solid line for cell 5.

References

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