Supplementary Information

Improvement of Mass Transport of [Co(bpy)₃]^{II/III} Redox Couple by Controlling

Nanostructure of TiO₂ Film in Dye-Sensitized Solar Cell

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Fig. S1 Porosity and pore size of the TiO₂ films prepared from different EC contents.

Table S1 Pore volume, pore size, bulk volume and porosity of the TiO_2 films for the different ratio of ethyl cellulose (EC) to TiO_2 .

EC:TiO ₂ = x :1 Porosity & Pore Volume	0.2	0.3	0.4	0.5
Pore Volume, V _{pore} (cm ³ /g)	0.282585	0.300717	0.323529	0.368937
Pore Size (nm)	18.1379	19.4666	21.3761	23.9156
Bulk Volume, $V_{\text{bulk}} (\text{cm}^3/\text{g}) = V_{\text{pore}} + V_{\text{TiO2}}{}^a$	0.539324	0.557456	0.580268	0.625676
Porosity, $\phi = V_{\text{pore}} / V_{\text{bulk}}$	0.52396	0.53944	0.55755	0.58966

^{*a*}V_{TiO2} was calculated using anatase TiO₂ density of 3.895 g/cm³.



Fig. S2 (a) Energetic diagram for a mesoporous TiO_2 film sensitized with MK-2 employing $[Co(bpy)_3]^{II/III}$ redox electrolyte, (b) chemical structure of $[Co(bpy)_3]^{II/III}$ and (c) chemical structure of MK-2 dye.



Fig. S3 Regeneration efficiency vs light intensity for different porosity, where TiO_2 film thickness was 3 μ m.

Materials and methods

The cobalt complex, $[Co(bpy)_3](PF_6)_2$, and its oxidized form (Co^{III}) were prepared according to the reported procedure.¹ A mixture of $CoCl_2 \cdot 6H_2O$ (1.0 g, 4.12 mmol, 98% Aldrich) and 2,2'-bipyridyl (2.2 g, 13.94 mmol, >99% Aldrich) were dissolved in methanol (100 mL) and refluxed for 2 h. After the resulting solution was cooled to room temperature, ammonium hexafluorophosphate (3.4 g, 20.86 mmol, 99.99% Aldrich) was more added to the reaction mixture. The precipitate was filtrated and the residue was dried under vacuum to obtain $[Co(bpy)_3](PF_6)_2$ (3.1 g, 92% yield) as yellow solid. Additional oxidation of $[Co(bpy)_3](PF_6)_2$ (500 mg, 0.612 mmol) was carried out by using NOBF₄ (107 mg, 0.916 mmol, 95% Aldrich) in acetonitrile (15 mL) at room temperature for 0.5 h. After removed solvent under reduced pressure, the residue was dissolved in acetonitrile (5 mL) and NH₄PF₆ (502 mg, 3.08 mmol, 99.99% Aldrich) was more added to the solution. The precipitate of $[Co(bpy)_3](PF_6)_3$ (530 mg) was filtrated, dried under vacuum and used without further purification.

MK-2 dye, 2-Cyano-3-[5^{'''}-(9-ethyl-9H-carbazol-3-yl)-3',3^{''},3^{'''},4-tetran-hexyl-[2,2',5',2'',5'',2''']-quarter thiophen-5-yl] acrylic acid (95%, Aldrich), was purchased and dissolved in toluene to prepare 0.3 mM MK-2 dye solution. Anatase TiO₂ nanoparticles were synthesized by acetic acid catalyzed hydrolysis of titanium isopropoxide (97%, Aldrich), followed by autoclaving at 230 °C for 12 h.² Aqueous solvent in the autoclaved TiO₂ colloid solution was replaced by ethanol for preparation of non-aqueous TiO₂ paste. Ethyl cellulose (Aldrich), lauric acid (Fluka), and terpineol (Aldrich) were added into the ethanol solution of the TiO₂ particles, and then ethanol was removed from the solution using a rotary evaporator to obtain viscous pastes. For homogeneous mixing, the paste was further treated with a three-roll mill. The nominal composition of TiO₂/terpineol/ethylcellulose/lauric acid was 1/4/x/0.1 (x = 0.2, 0.3, 0.4 and 0.5).

FTO glasses (Pilkington, TEC-8, 8 Ω /sq) were cleaned in an ultrasonic bath containing ethanol for 10 min. To make a compact TiO₂ blocking layer, the cleaned FTO glasses were coated with 0.1 M Ti(IV) bis(ethyl acetoacetato)-diisopropoxide (Aldrich) in 1-butanol (Aldrich) solution by the spin-coating method, which was heated at 500 °C for 15 min. On the compact TiO₂ blocking layer, the nanocrystalline TiO₂ paste was deposited using a doctorblade method, followed by annealing at 550 °C for 1 h to obtain mesoporous TiO₂ film. Porosity and pore size of the mesoporous TiO₂ film were controlled by changing the ethyl cellulose content. Sintered TiO₂ films were trimmed with an area of ca. 0.45 cm^2 and immersed in the 0.3 mM MK-2 dye solution at room temperature for overnight. The composition of electrolyte was 0.22 M [Co(bpy)₃](PF₆)₂, 0.033 M [Co(bpy)₃](PF₆)₂, 0.1 M LiClO₄ and 0.2 M 4-tert-butylpyridine in acetonitrile. Pt counter electrodes was prepared with a droplet of 10 µL of 0.7 mM H₂PtCl₆·6H₂O in 2-propanol on the FTO glass and heated at 400 °C for 20 min. The MK-2 sensitized TiO₂ film and the Pt-treated counter electrode were sealed with 60 µm-thick Surlyn (Solaronix). The active area was measured by a digital camera (DCMe 500) and analyzed by an image analysis program (Leopard 2009). The thickness could be measured by alpha-step IQ surface profile (KLA Tencor). Adsorbed dve on TiO₂ film was desorbed in 0.1 M NaOH solution containing toluene and ethanol (toluene:ethanol = 1:1 v/v) for one day.

Measurements

The absorbance of desorbed solution was measured by a UV-vis spectrophotometer (Agilent 8453) in the wavelength range of 300-800 nm. Photocurrent and voltage were measured by a solar simulator (Oriel Sol 3A class AAA) equipped with 450 W xenon lamp (Newport 6279NS) and a Keithley 2400 source meter. The NREL-calibrated Si solar cell with KG-2 filter was used to adjust light intensity into one sun illumination (100 mW/cm²). Light

intensity was varied by introducing a neutral mesh. A black aperture mask was attached during photocurrent and voltage measurement.

The pore volume (V_{pore}) and pore size of TiO₂ films were measured by Brunauer-Emmett-Teller (BET) analyzer (Micromertics Instrument Corp. ASAP 2020). The porosity (ϕ) was obtained from the fraction of the pore volume (V_{pore}) over the total bulk volume (V_{bulk}) of mesoporous TiO₂ film.

Transient photocurrent was measured under modulated light intensity using a solar simulator (Oriel Sol 3A class AAA) equipped with 450 W xenon lamp (Newport 6279NS) at a short-circuit condition with time.^{1(b), 4}

References

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