Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Effective enhancement of the performance of black dye based dye-sensitized solar cells by metal-oxide surface modification of TiO_2 photoelectrode

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Experimental Section

Materials and General Measurements

Black dye was prepared according to the literature.[1] Titanium isopropoxide and deoxycholic acid (DCA) were purchased from Tokyo Chemical Industry Co. 1,2-Dimethyl-3-propylimidazolium iodide (DMPImI) was purchased from Shikoku Kasei. All solvents and reagents were of the highest quality available and were used as received.

The elemental analysis was carried out on a Perkin Elmer 2400II elemental analyzer using acetanilide as a standard material. ^{1}H NMR spectra were acquired on a Bruker BioSpin AVANCE 400M spectrometer, where chemical shifts in CD_3OD were referenced to internal standard tetramethylsilane. XPS spectra were obtained using a JEOL JPS-9010MC X-ray photoelectron spectrometer. TEM images were obtained using a Hitachi H-9500 transmission electron microscope.

Preparation of TiO_2 photoelectrodes and DSCs

TiO_2 pastes were prepared using titanium isopropoxide.[2] Nanocrystalline TiO_2 photoelectrodes were prepared by screen printing the TiO_2 paste on fluorine-doped SnO_2 conducting glasses (FTO, Nippon Sheet Glass Co., 10 Ω/square). TiO_2 thin films were composed of six layers (from the bottom to the third layer: 20 nm TiO_2 particles, the fourth and fifth layers: a 8:2 mixture of 20 nm and 100 nm particles, and the top layer: a 6:4 mixture of 20 nm and 100 nm particles, film thickness: approximately 35 μm).[3] TiO_2 photoelectrodes were calcinated at 520 °C after every layer was coated. Surface modification of TiO_2 photoelectrodes were carried out by immersing them into the solution of metal salt for 20 min under N_2 atmosphere, and then calcinated at 500 °C for 1 h. The active areas of these TiO_2 films were determined using a KEYENCE VHX-200 digital microscope. The TiO_2 photoelectrodes were immersed in 0.2 mM black dye 1-propanol solution[4] containing of 20 mM DCA for 18 h at room temperature to adsorb black dye onto the TiO_2 surface. Black dye was desorbed from the TiO_2 film by immersing in 0.05 M NaOH solution, and the amount of dye adsorption was estimated from the absorption spectrum of the resulting solution.

Photoelectrochemical measurements were performed in a two-electrode sandwich cell configuration composed of the dye-adsorbed TiO_2 photoelectrode, a platinum-sputtering counter electrode, a spacer film (50 μm), and an electrolyte solution (0.05 M I_2, 0.1 M LiI, 0.6 M DMPImI and 0.3 M *tert*-butylpyridine (TBP) in acetonitrile).

Photovoltaic measurements

The photocurrent-voltage (*I-V*) characteristics of the DSCs were measured on a Keithley 2400 source meter under irradiation of AM 1.5, 100 mW/cm^2 (1 sun) supplied by a solar simulator (Yamashita Denso, YSS-150A). The incident light intensity was calibrated with a grating spectroradiometer LS-100 (EKO Instruments) and Si photodiode (Bunkoh Keiki). The incident monochromatic photon-to-current conversion efficiency (IPCE) was measured on a PEC-S10 (Peccell Technologies). Electrochemical impedance spectroscopic (EIS) studies were conducted using an electrochemical interface SI 1287 (Solartron) and a frequency response analyzer 1255B (Solartron).

The open-circuit voltage decay (OCVD) measurements

The OCVD measurements were conducted to investigate the electron lifetimes in the TiO_2 photoelectrodes. In this measurement, decay of V_{oc} value was monitored after the irradiation for the cell was stopped. The electron lifetime was estimated from the fitting for the obtained decay curve of V_{oc}.[5,6]

In the case that estimated electron lifetime was relatively shorter, it suggests that backward electron transfer processes (electron transfer from the conduction band of TiO_2 to the oxidized form of dyes or to I_3^-) were facilitated. On the other hand, relatively longer electron lifetime suggests that such backward electron transfer processes were retarded.

Table S1. Solar cell performances of the black dye based DSCs with the TiO_2 photoelectrode modified by various kinds of metal oxide[a]

Precursor (0.1 M)	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	η (%)	Amount of dye adsorption ($\times 10^{-7}$ mol/cm^2)
none	20.82	0.703	0.711	10.42	1.5
$Mg(OC_2H_5)_2$	20.89	0.715	0.714	10.67	1.5
$MgCl_2$	20.14	0.710	0.719	10.28	1.6
$Al[OCH(CH_3)_2]_3$	17.68	0.739	0.738	9.65	1.1
$AlCl_3$	19.39	0.718	0.714	9.93	1.5
$Bi[OCOCH(C_2H_5)(C_5H_{11})]_3$	6.67	0.756	0.782	3.94	1.3
$BiCl_3$	12.77	0.708	0.814	7.36	1.0
YCl_3	18.65	0.731	0.706	9.61	1.7
$Zr(OH)_3(OCOCH_3)$	18.50	0.718	0.696	9.25	1.1
$Ca(OC_2H_5)_2$	14.26	0.742	0.760	8.04	1.4
$Nb[OCH(CH_3)_2]_5$	20.31	0.707	0.704	10.12	1.6

[a]The electrolyte was an acetonitrile solution containing of 0.05 M I_2, 0.1 M LiI, 0.6 M DMPImI, and 0.3 M TBP (TiO_2 films thickness: ca. 35 μm, active area: 0.26 cm^2). Irradiation was carried out by using the solar simulator (AM 1.5, 100 mW/cm^2).

Table S2. Solar cell performance of the DSC with black dye[a]

Cell number	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	η (%)
1	20.82	0.703	0.711	10.42
2	20.73	0.705	0.708	10.35
3	20.83	0.710	0.696	10.31
4	21.02	0.704	0.707	10.46
5	20.98	0.699	0.713	10.45
6	20.77	0.701	0.709	10.32

[a]The electrolyte was an acetonitrile solution containing of 0.05 M I_2, 0.1 M LiI, 0.6 M DMPImI, and 0.3 M TBP (TiO_2 films thickness: 35 μm, active area: 0.26 cm^2). Irradiation was carried out by using the solar simulator (AM 1.5, 100 mW/cm^2).

Table S3. Solar cell performance of the black dye based DSC with TiO_2 photoelectrode modified by MgO using different concentration of $Mg(OEt)_2$ solution[a]

Cell number	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	η (%)
0.01 M				
1	20.71	0.704	0.708	10.31
2	21.07	0.698	0.703	10.34
3	20.45	0.709	0.706	10.23
4	20.38	0.710	0.710	10.28
0.05 M				
1	20.75	0.713	0.715	10.59
2	21.05	0.702	0.714	10.63
3	21.04	0.712	0.708	10.61
4	19.97	0.724	0.732	10.58
0.10 M				
1	20.89	0.715	0.714	10.67
2	21.01	0.706	0.716	10.62
3	20.67	0.724	0.713	10.66
4	20.60	0.723	0.719	10.71
0.15 M				
1	20.43	0.727	0.724	10.75
2	20.41	0.721	0.729	10.74
3	20.87	0.726	0.708	10.73
4	20.02	0.733	0.734	10.77
0.20 M				
1	20.25	0.721	0.717	10.46
2	20.37	0.720	0.716	10.50
3	20.18	0.722	0.718	10.46
4	20.10	0.724	0.723	10.51

[a]The electrolyte was an acetonitrile solution containing of 0.05 M I_2, 0.1 M LiI, 0.6 M DMPImI, and 0.3 M TBP (TiO_2 films thickness: 35 μm, active area: 0.26 cm^2). Irradiation was carried out by using the solar simulator (AM 1.5, 100 mW/cm^2).

Table S4. Solar cell performance of the black dye based DSC with TiO_2 photoelectrode modified by MgO using different concentration of $MgCl_2$ solution[a]

Cell number	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	η (%)
0.01 M				
1	20.27	0.712	0.717	10.37
2	20.19	0.708	0.722	10.33
3	20.61	0.703	0.717	10.40
4	20.09	0.722	0.720	10.43
0.05 M				
1	20.21	0.711	0.713	10.24
2	20.53	0.703	0.707	10.21
3	20.50	0.700	0.710	10.20
4	20.18	0.721	0.704	10.25
0.10 M				
1	20.14	0.710	0.719	10.28
2	20.25	0.705	0.723	10.32
3	20.00	0.708	0.731	10.34
4	20.38	0.718	0.697	10.20

[a]The electrolyte was an acetonitrile solution containing of 0.05 M I_2, 0.1 M LiI, 0.6 M DMPImI, and 0.3 M TBP (TiO_2 films thickness: 35 μm, active area: 0.26 cm^2). Irradiation was carried out by using the solar simulator (AM 1.5, 100 mW/cm^2).

Table S5. Solar cell performance of the black dye based DSC with TiO_2 photoelectrode modified by Al_2O_3 using different concentration of $Al(OiPr)_3$ solution[a]

Cell number	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	η (%)
0.01 M				
1	20.41	0.729	0.722	10.75
2	21.46	0.732	0.723	10.82
3	20.37	0.724	0.719	10.62
4	20.39	0.731	0.725	10.81
0.03 M				
1	19.54	0.731	0.728	10.41
2	19.66	0.731	0.731	10.49
3	19.73	0.730	0.725	10.44
4	19.25	0.732	0.730	10.29
0.05 M				
1	19.11	0.739	0.735	10.39
2	19.07	0.737	0.737	10.36
3	19.16	0.741	0.734	10.42
0.10 M				
1	17.68	0.739	0.738	9.65
2	17.56	0.738	0.739	9.57
3	17.74	0.740	0.742	9.74
4	17.75	0.739	0.734	9.63

[a]The electrolyte was an acetonitrile solution containing of 0.05 M I_2, 0.1 M LiI, 0.6 M DMPImI, and 0.3 M TBP (TiO_2 films thickness: 35 μm, active area: 0.26 cm^2). Irradiation was carried out by using the solar simulator (AM 1.5, 100 mW/cm^2).

Table S6. Solar cell performance of the black dye based DSC with TiO_2 photoelectrode modified by Al_2O_3 using different concentration of $AlCl_3$ solution[a]

Cell number	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	η (%)
0.01 M				
1	20.45	0.715	0.703	10.28
2	20.70	0.712	0.695	10.23
3	20.05	0.721	0.700	10.14
4	20.27	0.717	0.710	10.33
0.05 M				
1	20.35	0.714	0.708	10.30
2	20.41	0.719	0.707	10.38
3	20.21	0.713	0.708	10.22
3	20.44	0.709	0.710	10.29
0.10 M				
1	19.39	0.718	0.714	9.93
2	18.82	0.729	0.724	9.94
3	20.02	0.714	0.704	10.06
4	19.38	0.715	0.713	9.89

[a]The electrolyte was an acetonitrile solution containing of 0.05 M I_2, 0.1 M LiI, 0.6 M DMPImI, and 0.3 M TBP (TiO_2 films thickness: 35 μm, active area: 0.26 cm^2). Irradiation was carried out by using the solar simulator (AM 1.5, 100 mW/cm^2).

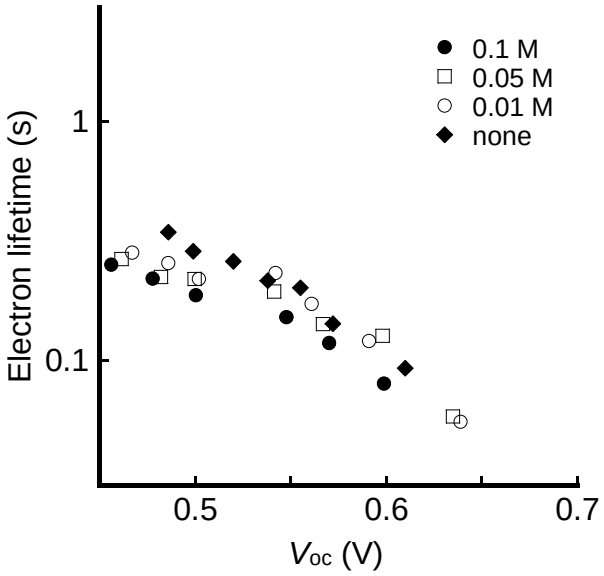

Figure S1. Electron lifetimes as a function of V_{oc} for the DSCs with MgO modified TiO_2 photoelectrode using $MgCl_2$ as a precursor.

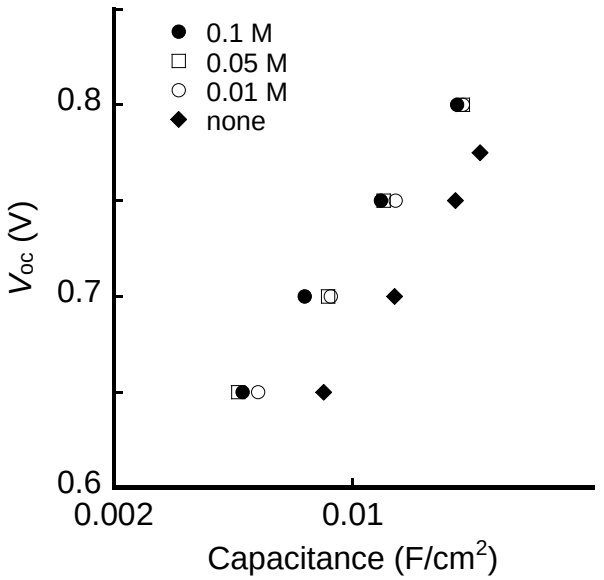

Figure S2. V_{oc} as a function of capacitance for the DSCs with MgO modified TiO_2 photoelectrode using $MgCl_2$ as a precursor.

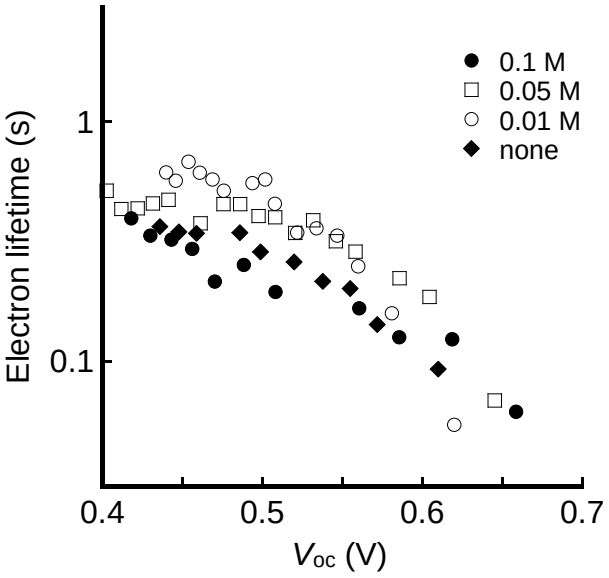

Figure S3. Electron lifetimes as a function of V_{oc} for the DSCs with Al_2O_3 modified TiO_2 photoelectrode using $AlCl_3$ as a precursor.

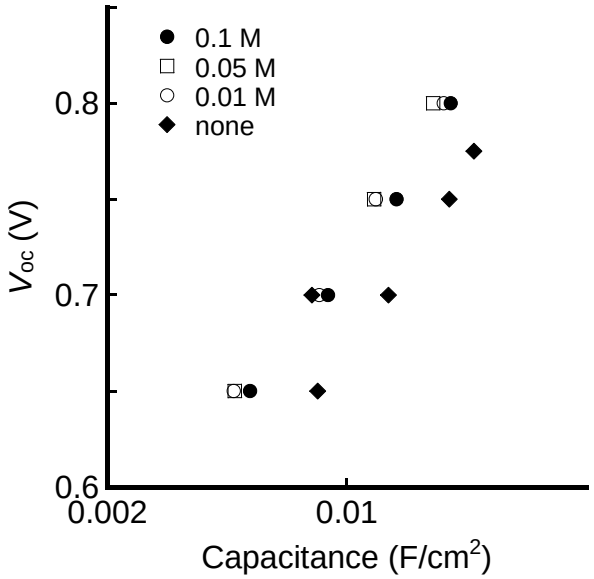

Figure S4. V_{oc} as a function of capacitance for the DSCs with Al_2O_3 modified TiO_2 photoelectrode using $AlCl_3$ as a precursor.

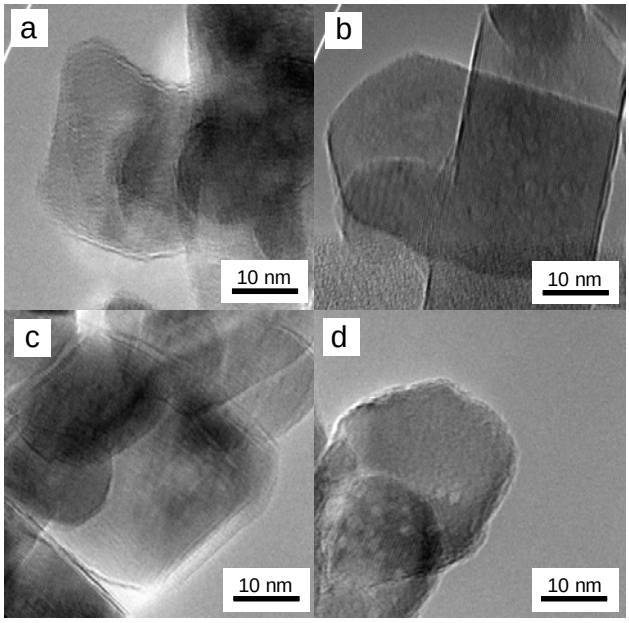

Figure S5. TEM images of TiO_2 nanoparticles treated with $Mg(OEt)_2$ (a), $MgCl_2$ (b), $Al(OiPr)_3$ (c), and $AlCl_3$ (d), respectively. The MgO or Al_2O_3 thin overlayer was formed in the case for (a) and (c).

References

(1) M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphyry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Grätzel, *J. Am. Chem. Soc.*, **2001**, *123*, 1613-1624.

(2) M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.*, **1993**, *115*, 6382-6390.

(3) Z.-S. Wang, T. Yamaguchi, H. Sugihara, H. Arakawa, *Langmuir*, **2005**, *21*, 4272-4276.

(4) H. Ozawa, M. Awa, T. Ono, H. Arakawa, *Chem.-Asian J.*, **2012**, *7*, 156-162.

(5) A. Zaban, M. Greenshtein, J. Bisquert, *Chem. Phys. Chem.*, **2003**, *4*, 859-864.

(6) J. Bisquert, A. Zaban, M. Greenshtein, I. Mora-Seró, *J. Am. Chem. Soc.*, **2004**, *126*, 13550-13559.