Electronic Supplementary Information (ESI) for

Promotion of strongly anchored dyes on the surface of titania by tetraethyl orthosilicate treatment for enhanced solar cell performance

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Fig. S2 Full range ATR-FTIR spectra of (a) TiO₂ films immobilized with Z907 sensitizing dye alone and Z907/TEOS.

An ATR-FTIR spectrum of TEOS was measured using a JASCO FT/IR-4200 spectrometer with ATR PRO450-S accessory and ZnSe crystal. The spectra of the stained TiO_2 surface was scanned from 4000 to 400 cm⁻¹ at a resolution of 2 cm⁻¹ with 64 scans. No ATR correction has been applied to the data.

Table S1 Absolute values of ATR-FTIR peak intensity of CH_2 and COO^{-} on Z907 immobilized TiO₂ films before or after TEOS treatment and relative ratio of CH_2 to COO^{-} .

	Dye and coadsorbent	COO ⁻ intensity	CH ₂ intensity	[COO ⁻]/[CH ₂]
Device-Z	Z907 only	0.96	1.97	0.49
Device-ZT	Z907+TEOS	0.94	0.99	0.94

In order to gain more information on the strong anchoring dye of the TEOS treated TiO₂ films, we used ATR-FTIR spectroscopy. Table S1 lists the absolute peak intensity of CH₂ and COO⁻ in Z907 dyed photoanodes before or after TEOS treatment and the relative ratio of CH₂ to COO⁻ After the co-adsorbing process, the CH₂ peak intensity dramatically decreases by about 50% (0.50 = (1.97-0.99)/1.97), indicating the amount of Z907 loading considerably decreases by the same degree. Meanwhile, the peak intensity of COO⁻, showing an anchoring bond between Z907 dye and TiO₂ film, slightly decrease by about 4% (4 = (0.96-0.94)/0.96). Values of [COO⁻]/[CH₂] of device-Z and device-ZT are 0.49 and 0.94, respectively. This implies that about the dyes form two carboxylates, i.e. strong anchoring bond. Considering that CH₂ of TEOS ethoxy chains is attributed to some part of CH₂ intensity value (0.99), it indicates that TEOS treatment helps promote the conversion of weakly anchored dyes into strongly anchored dyes.



Fig. S3 Representative normalized ATR-FTIR spectra of TiO₂ films immobilized with N719 sensitizing dye alone and N719/TEOS.



Fig. S4 Schematic diagram showing the surface structure of TEOS forming a polymer layer on a hydrophilic N719 modified TiO₂ surface

Table S2 J-V characteristics^a for all devices under AM 1.5 irradiation and the relative dye load^b for N719/TiO₂ films.

	Dye and coadsorbent	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF (%)	η (%)	Relative dye load
Device-N	N719 only	12.9 ± 0.3	753 ± 2	65.5 ± 0.9	6.3 ± 0.0	1.00
Device-NT	N719 + TEOS	10.7 ± 0.1	734 ± 1	70.8 ± 0.1	5.6 ± 0.0	0.68

^a Values obtained represent the average over 2 devices for each experiment. The cell active areas were 0.27 cm².

 b By subtracting the absorbance of the 5.5 μ m thick transparent TiO₂ electrode, values for the dye loading amount of both device-N and device-NT were estimated. Then the dye loading of the modified cells was determined from the absorption difference of the dipping solution before and after co-adsorbent treatment at 518 nm.

To compare the effect of TEOS treatment for the amphiphilic dye-Z907-system with that of the less hydrophilic dye-N719-system, photovoltaic performances of the DSSCs in N719 system were measured under both 1 sun illumination (AM 1.5G, 100 mW/cm²), as summarized in Table S2. Unlike the effect of TEOS treatment in Z907 system, TEOS treatment with N719 did not show any improvement in the cell performance, because the amount of the strongly anchored N719 was not increased even after the TEOS treatment (see Fig. S3). This is due to the fact that the N719 dyed film did not provide a hydrophobic surface to repel water molecules, whereas it was observed that the TEOS treatment with Z907 enhanced the photocurrent density and the conversion efficiency. Since the N719 coated film does not provide a hydrophobic surface but instead a hydrophilic surface, the absorbed water molecules act as silanization-catalysts on the TiO₂ surface, thereby yielding unwanted polymerization of the siloxane co-adsorbent onto the interface (Fig. S4). This implies, in the case of hydrophilic N719 dyed TiO₂ surface, that the TEOS cannot be employed as an equilibrium shifting agent, unlike the Z907 system. Thus, this is indicative that when a hydrophobic dye such as Z907 is used the TEOS (an equilibrium shifting agent) treatment is effective and also the strongly anchored dyes may become dominant and consequently help increase J_{sc} due to the rise in the charge injection efficiency.



Fig. S5 Variation of DSSC performances as a function of time for Device-ZT.



Fig. S6 Photoinduced charge density as a function of open-circuit voltage.

As proposed by Frank et al.,¹ the photoinduced charge density at open-circuit is calculated based on the IMVS results. ¹ S. Y. Huang, G. Schlichthörl, A. J. Nozik, M. Grätzel, A. J. Frank, *J. Phys. Chem. B*, 1997, **101**, 2576.



Fig. S7 Typical electrochemical impedance spectra of device-Z and device-ZT in the form of (a) Nyquist plots and (b) Bode plots. The spectra were measured at an external potential of -0.75 V in the dark

In the following impedance spectra (Fig. S7), electron lifetime, τ_n , is equal to $R_{ct} \times C_{\mu}$ or $1/(2\pi f_{min})$ as obtained by Nyquist and Bode plots, respectively, where R_{ct} and C_{μ} are recombination resistance and chemical capacitance in the second semicircle of the Nyquist plots and f_{min} is the frequency of the mid-frequency peak of the Bode plots. The τ_n values of Devices-Z and -ZT are 0.022 and 0.013, representing that device-Z has a little longer electron lifetime relative to device-ZT.

	Dye and coadsorbent	Device no.	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF (%)	η (%)
Device-Z	Z907	1	9.8	728	0.71	5.1
		2	8.9	744	0.71	4.7
		3	9.3	733	0.72	4.9
		4	9.3	718	0.71	4.8
Device-ZT	Z907 + TEOS	1	11.0	722	0.69	5.5
		2	11.1	729	0.69	5.6
		3	11.1	717	0.69	5.5
		4	10.9	742	0.70	5.7
^{<i>a</i>} The cell active are	eas were 0.27 cm^2 .					

Table S3 Reproducible J-V characteristics^a of Device-Z and Device-ZT evaluated using each 4 devices under AM 1.5 irradiation.



Fig. S8 Reproducible J-V curves of Device-Z and Device-ZT evaluated using each 4 devices under AM 1.5 irradiation.



Fig. S9 Photovoltaic parameters of devices treated with different TEOS concentrations for 4 days evaluated under AM 1.5 irradiation.



Fig. S10 Photovoltaic parameters of devices treated using 300 mM TEOS solution with time evaluated under AM 1.5 irradiation.

Note that high TEOS treatment concentration, here 300 mM led to slightly enhanced overall power conversion efficiency (Fig. S9). On the basis of 300 mM TEOS concentration, we varied the treatment time and obtained negligible differences in the photovoltaic performances (Fig. S10).

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Fig. S11 Short-circuit current density varying light intensity.

Linear relation of short-circuit current density with light intensity under different light irradiation is of indicative that electrolyte diffusion especially at TiO_2 nanopore is not limited, *i.e.* TiO_2 pore is not clogged after the TEOS treatment.