Supplementary Material (ESI) for *PCCP*

Electronic Supplementary Information

Zinc-doping in TiO_2 films to enhance electron transport in dye-sensitized solar cells under low-intensity illumination

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Elemental analysis with energy-dispersive X-ray spectroscopy (EDS): The EDS spectrum recorded from a Zn-doped TiO_2 film (TZ04) shows the Zn and Ti elements at a Zn/Ti atomic ratio of 0.4 at%, indicating that Zn element was doped into the TiO_2 nanoparticles.

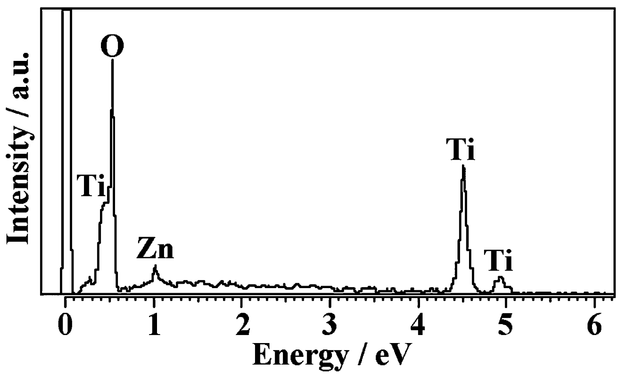

Fig. S1 The element spectrum of a Zn-doped TiO_2 film (TZ04) obtained by EDS attached to SEM.

Electronic property measurements with electrochemical impedance spectroscopy: The semiconducting properties of the Zn-doped TiO_2 films were analyzed by impedance spectroscopy. Fig. S2 shows the capacitance variation with applied potential for TZ07 and TZ12.

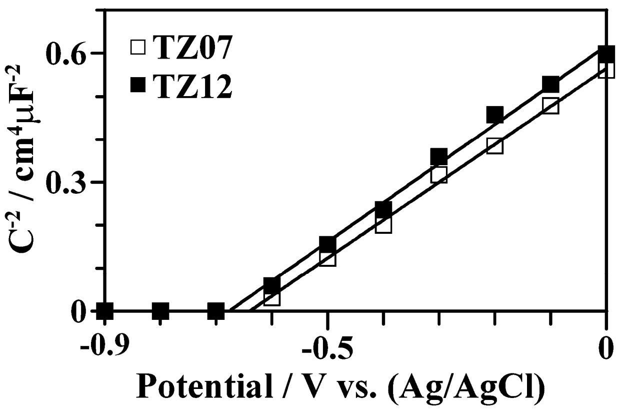

Fig. S2 Variation of capacitance of the TZ07 and TZ12 films with the applied potential in 1 M KNO_3 presented in the Mott-Schottky relationship. The capacitance was determined by electrochemical impedance spectrum. The capacitance was determined by electrochemical impedance spectroscopy. The TiO_2 films had a thickness of ca. 10 μm.

Photocurrent-voltage characterization of DSSCs under varying light intensity: Because 0.4 at% of Zn-doping exhibited an optimum performance for DSSCs, we further compare the performance of the bare-TiO_2 and TZ04 cells under illumination with reduced light intensity. Fig. S3 shows the photocurrent-voltage characteristics of the bare-TiO_2 and TZ04 cells at varying light intensity.

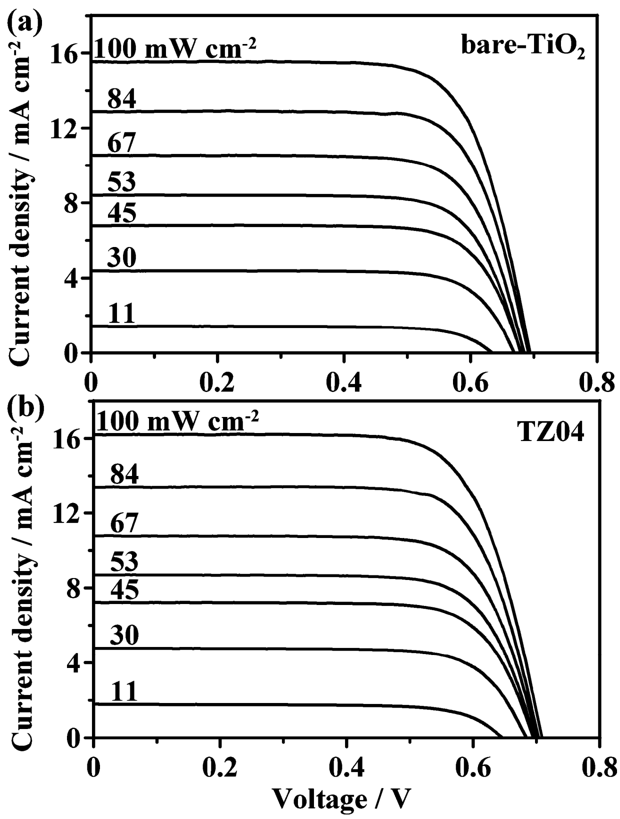

Fig. S3 Photocurrent-voltage characteristics of the cells assembled with the bare-TiO_2 and TZ04 films under AM1.5-type solar illumination of varying light intensity. The TiO_2 films had a thickness of ca. 15 μm.

Electrochemical impedance spectroscopic analysis of DSSCs: The spectrum is composed of three arcs situated in high, intermediate, and low frequency regimes.[1,2]

(a) The high-frequency impedance is typical of a RC circuit that represents a charge-transfer resistance R_{Pt} in parallel with an interfacial capacitance C_{Pt}.

(b) The intermediate-frequency impedance can be solved from the continuity equation in the TiO_2 conduction band and expressed by an equation:[1,2]

$$Z = \frac{1}{3}R_{\mathrm{t}} + \frac{R_{\mathrm{ct}}}{1 + i\omega / \omega_{\mathrm{ct}}} \qquad \text{(S1)}$$

where ω_{ct} is the angular frequency of the recombination process. The dc resistance (R_{dc}) at $\omega = 0$ is given as[1,2]

$$R_{\mathrm{dc}} = \frac{1}{3}R_{\mathrm{t}} + R_{\mathrm{ct}} \qquad \text{(S2)}$$

This value of R_{dc} corresponds to the width of the intermediate-frequency arc.

(c) The Z_{N} impedance corresponding to the low-frequency arc, is given by the following equation[1-3]

$$Z_{\mathrm{N}} = \frac{W}{\sqrt{i\omega}} \cdot \tanh\sqrt{\frac{i\omega}{(D_1/\delta^2)}} = R_{\mathrm{N}} \frac{1}{\sqrt{\frac{i\omega}{D_1/\delta^2}}} \tanh\sqrt{\frac{i\omega}{(D_1/\delta^2)}} \qquad \text{(S3)}$$

where $W\ (= RT/(m^2F^2C^*A\sqrt{D_1}))$ is the Warburg parameter, $R_{\mathrm{N}}\ (= W\sqrt{\delta^2/D_1})$ the diffusion resistance, D_1 the diffusion constant of I_3^-, R the gas constant, T the absolute temperature, m the number of electrons transferred in each reaction (m = 2 in this case), F the Faraday constant, C^* the concentration of I_3^- in the bulk, A the electrode area, and δ the thickness of the Nernst diffusion layer (here, δ = a half of the distance between the electrodes).

Simulation results for the electrochemical impedance spectra: We used the equivalent circuit shown in Fig. 11 to simulate the impedance spectra in the Fig. 10 and obtained the resistance values at different interfaces. The results are summarized in Table S1.

Table S1 The sheet resistance (R_S) of the conducting glass, the charge transfer resistance (R_{Pt}), the electron transport resistance (R_t) in the TiO_2 film, the interfacial charge recombination resistance (R_{ct}), electrolyte diffusion resistance (R_N), and the total resistance (R_{total}) determined from the electrochemical impedance spectroscopy measurements shown in Fig. 10. The total resistance is the sum of all the contributions, i.e. $R_{total} = R_S + R_{Pt} + R_{dc} + R_N$.[1]

TiO_2 specimen	R_s /Ω	R_{pt} /Ω	R_t /Ω	R_{ct} /Ω	R_N /Ω	R_{total} /Ω
Light intensity = 100 mW cm^{-2}						
bare-TiO_2	4.8	5.8	2.2	8.3	7.0	26.7
TZ04	4.9	4.3	1.3	7.4	7.0	24.0
Light intensity = 11 mW cm^{-2}						
bare-TiO_2	4.8	5.5	8.8	18.9	8.3	40.4
TZ04	4.9	4.5	4.2	17.3	8.3	36.4

References

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