Zinc-doping in TiO$_2$ films to enhance electron transport in dye-sensitized solar cells under low-intensity illumination

By Kai-Ping Wang and Hsisheng Teng*

[*] Prof. H. Teng
Department of Chemical Engineering and Center for Micro/Nano Science and Technology
National Cheng Kung University, Tainan 70101 (Taiwan)
E-mail: hteng@mail.ncku.edu.tw

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 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.

![Photocurrent-voltage characteristics](image)

**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]

$$Z = \frac{1}{3} R_t + \frac{R_{ct}}{1 + \frac{i\omega}{\omega_{ct}}}$$

(S1)

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

$$R_{dc} = \frac{1}{3} R_t + R_{ct}$$

(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]

$$Z_N = \frac{W}{\sqrt{i\omega}} \cdot \tanh \left( \frac{i\omega}{(D_t/\delta)^2} \right) = R_N \frac{1}{i\omega} \sqrt{\frac{D_t/\delta^2}{(D_t/\delta)^2}} \right)$$

(S3)

where $W = RT/(m^2F^2C^A\sqrt{D_1})$ is the Warburg parameter, $R_N = W\sqrt{\delta^2/D_1}$ 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 $\delta$ the thickness of the Nernst diffusion layer (here, $\delta = a$ 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. $R_{total} = R_S + R_{Pt} + R_{dc} + R_N$.\(^\text{[1]}\)

<table>
<thead>
<tr>
<th>TiO$_2$ specimen</th>
<th>$R_s$ /Ω</th>
<th>$R_{Pt}$ /Ω</th>
<th>$R_t$ /Ω</th>
<th>$R_{ct}$ /Ω</th>
<th>$R_N$ /Ω</th>
<th>$R_{total}$ /Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light intensity = 100 mW cm$^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bare-TiO$_2$</td>
<td>4.8</td>
<td>5.8</td>
<td>2.2</td>
<td>8.3</td>
<td>7.0</td>
<td>26.7</td>
</tr>
<tr>
<td>TZ04</td>
<td>4.9</td>
<td>4.3</td>
<td>1.3</td>
<td>7.4</td>
<td>7.0</td>
<td>24.0</td>
</tr>
<tr>
<td>Light intensity = 11 mW cm$^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bare-TiO$_2$</td>
<td>4.8</td>
<td>5.5</td>
<td>8.8</td>
<td>18.9</td>
<td>8.3</td>
<td>40.4</td>
</tr>
<tr>
<td>TZ04</td>
<td>4.9</td>
<td>4.5</td>
<td>4.2</td>
<td>17.3</td>
<td>8.3</td>
<td>36.4</td>
</tr>
</tbody>
</table>

References