Supporting Information

Dye Sensitized Nanostructured Crystalline Mesoporous Tin-doped Indium Oxide Films with Tunable Thickness for Photoelectrochemical Applications

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Figure S1. X–Ray diffraction patterns (a) and FE–SEM images (b) of templated nano-ITO films before thermal treatment.

Figure S2. FE–SEM images of templated nano-ITO films treated at various temperatures a) 300°C, b) 450°C, c) 550°C in air

Figure S3. EDX (a) and XPS (b) analyses for templated nano-ITO films heat-treated at 450°C in air
**Figure S4.** Small-angle X–ray diffraction of *templated nano–*ITO films calcined at 450°C. The most intense peak can be attributed to the (220) of mesopores organized into a cubic structure. The peaks before are due to interference.

**Table 1. Crystallites size as function of the heat-treatment.** Evolution of the crystallites size as function of the heat-treatment, determined from Debye and Scherrer formula (noted D(222)sherrer in the table), Dmean corresponds to mean diameter obtained by this method, and from Williamson et al. approach (noted D Williamson et hall in Table 1).

<table>
<thead>
<tr>
<th>Temperature</th>
<th>D (222)-Scherrer</th>
<th>D mean</th>
<th>D Williamson et Hall</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 °C</td>
<td>15 nm</td>
<td>15,6 nm</td>
<td>16,6 nm</td>
</tr>
<tr>
<td>450 °C</td>
<td>21 nm</td>
<td>20,4 nm</td>
<td>25 nm</td>
</tr>
<tr>
<td>550 °C</td>
<td>23 nm</td>
<td>21,5 nm</td>
<td>30 nm</td>
</tr>
</tbody>
</table>
**Figure S5.** *Top* Cyclic voltammograms of [Ru(bpy)$_3$]Cl$_2$, 1 mM in 0.1M aqueous HOTf at scan rates varying from 10 to 100 mV.s$^{-1}$, recorded at a non-functionalized nanostructured ITO electrode (10 layers, treated at 450°C for 1 hour in air; electrode surface: 1 cm$^2$). *Bottom* Linear evolution with the square root of the scan rate of the cathodic and anodic peak currents (capacitive current subtracted) related to the Ru$^{III}$/Ru$^{II}$ couple.

**Figure S6.** Dependence of the grafting density on the number of layers for multi-layered nanostructured ITO films.
Figure S7. Top Cyclic voltammograms of complex 1 adsorbed on planar ITO (electrode surface: 1 cm²), recorded in 0.1M aqueous HOTf at scan rates varying from 50 to 2000 mV s⁻¹. Bottom Linear evolution with the scan rate of the cathodic and anodic peak currents related to the RuIII/RuII couple.

Figure S8. Absorption spectrum of complex 1 adsorbed on templated nano-ITO (10 layers, treated at 450°C for 1 hour in air), after substraction of the absorption of the non-functionalized templated nano-ITO film.

Figure S9. Transmittance for the 10-layers dense nano-ITO film heat-treated at 450°C for 1 h in air
Figure S10. FE–SEM image (cross section view) of a 10 layers dense nano-ITO film treated at 450°C, in air.

Figure S11. Top Cyclic voltammograms of complex 1 adsorbed on dense nano-ITO (10 layers prepared in the absence of template, treated at 450°C for 1 hour in air; electrode surface: 1 cm²), recorded in 0.1M aqueous HOTf at scan rates varying from 10 to 100 mV.s⁻¹. Bottom Linear evolution with the scan rate of the cathodic and anodic peak currents related to the RuIII/RuII couple.
**Figure S12.** *In situ* electrical conductivity of films (thickness = 470 nm) heat-treated in air at 450°C: Evolution of the conductivity as a function of time for 10–layer *templated nano–ITO* films heated in 5% of H₂ in Ar at 200°C.

**Figure S13.** *Top* Cyclic voltammograms of complex 1 adsorbed on H₂-treated *templated nano–ITO* (10 layers, treated at 450°C for 1 hour in air then under 5% H₂ in Ar at 200°C for 30 min; electrode surface: 1 cm²), recorded in 0.1M aqueous HOTf at scan rates varying from 10 to 100 mV.s⁻¹. *Bottom* Linear evolution with the scan rate of the cathodic and anodic peak currents related to the Ru^{III}/Ru^{II} couple.
Figure S14. Sections of the cyclic voltammograms of non-functionalized A) 10-layer templated nano-ITO, B) 10-layer dense nano-ITO; C) 10 layers H$_2$-treated templated nano-ITO; recorded in 0.1M aqueous HOTf at scan rates varying from 10 to 100 mV.s$^{-1}$ (electrode surface: 1 cm$^2$).

Figure S15. Peak–to–peak splitting between the oxidation and the reduction peak of complex 1 grafted on a 10–layer templated nano–ITO electrode (●), a 10–layer H$_2$–treated templated nano–ITO electrode (▲), a 10–layer dense nano–ITO electrode (■) or a planar ITO electrode (○) (recorded in 0.1M aqueous HOTf at scan rates varying from 10 to 100 mV.s$^{-1}$).