Supporting Information

Hollow TiO$_2$ Microspheres: Template-Free Synthesis, Remarkable Structure Stability, and Improved Photoelectric Performance

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Figure S1 The XRD patterns of products obtained at different reaction interval during the formation of HTS.

Figure S2 SEM images of products obtained under different reaction solvents. (a) water, (b) isopropanol, (c) ethylene glycol and (d) glycerol
**Figure S3** XRD patterns of HTS after different calcination temperatures.

**Figure S4** The comparison SEM images before and after calcination of TiO$_2$ hollow spheres obtained under the condition of without HCl.

**Figure S5** Cross-section SEM images of the three TiO$_2$ films: (a) THS-film, (b) NP-film and the HTS+NP bilayer film.
Figure S6 Photocurrent density-voltage curve of a DSSCs based on the bilayer structured photo-anode by introducing HTS as the light scattering layer over the NP film.

Table S1 Photovoltaic performance of DSSCs fabricated from NP and HTS TiO$_2$ photo-anode (the active area for all the cells is about 0.16 cm$^2$).

<table>
<thead>
<tr>
<th>Cells</th>
<th>$J_{SC}$/mA cm$^{-2}$</th>
<th>$V_{OC}$/V</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>Dye absorption/mol cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP</td>
<td>12.8</td>
<td>0.64</td>
<td>60</td>
<td>5.0</td>
<td>$1.9 \times 10^{-7}$</td>
</tr>
<tr>
<td>HTHS</td>
<td>15.3</td>
<td>0.72</td>
<td>58</td>
<td>6.3</td>
<td>$2.3 \times 10^{-7}$</td>
</tr>
</tbody>
</table>