Electronic Supplementary Information for

Hierarchical nanosheet assembled yolk-shell TiO$_2$ microspheres with improved photocatalytic activity

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![Element in at. %](image)

<table>
<thead>
<tr>
<th>Element in at. %</th>
<th>C</th>
<th>O</th>
<th>Ti</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Before acid washing</td>
<td>70.79</td>
<td>19.51</td>
<td>8.46</td>
<td>1.24</td>
</tr>
<tr>
<td>(b) After acid washing</td>
<td>76.97</td>
<td>15.23</td>
<td>7.65</td>
<td>0.15</td>
</tr>
</tbody>
</table>

**Fig. S1** EDS analysis results of the as-collected yolk-shell products (a) before and (b) after the acid washing procedure. Note the effective removal of K by the acid washing.
**Fig. S2** Raman spectra of microspheres achieved at various reaction durations. The powders here were subjected to a subsequent acid washing, but not calcinated.

**Fig. S3** XRD pattern of urchin-like TiO$_2$ microspheres achieved with a reaction duration of 36 h. The microspheres were achieved by the subsequent acid washing and calcination in air at 450 °C for 1 h.
Fig. S4 Low (a) and high (b) magnification FESEM images of the precipitates collected after the hydrolysis of K$_2$TiO(C$_2$O$_4$)$_2$ in the mixed solutions of H$_2$O$_2$ and HNO$_3$ at 80 ºC.
Fig. S5 FESEM images of the powders derived with varied chemicals in the reactants. The varied parameter was noted in the citation, with other parameters remained the same as the reactant utilized for the synthesis of the yolk-shell microspheres (10 % H$_2$O$_2$, 0.87 M HNO$_3$ and 500 mM K$_2$TiO(C$_2$O$_4$)$_2$). (a, b) 20 wt. % H$_2$O$_2$; (c, d) 30 wt. % H$_2$O$_2$; (e, f) 0 mL HNO$_3$; (g, h) 1.74 M HNO$_3$; (i, j) 200 mM K$_2$TiO(C$_2$O$_4$)$_2$. The powders were subjected to the intermediate acid washing and subsequent calcination in air at 450 ºC for 1 h.
Parallel experiments intending to clarify the effects of reactants, that is, the concentrations of H$_2$O$_2$, HNO$_3$, and K$_2$TiO(C$_2$O$_4$)$_2$, were carried out. The collected precipitates were subjected to the intermediate acid washing and calcination in air at 450 °C for 1 h. Fig. S5 and S6 show, respectively, the SEM images and XRD patterns of the achieved powders.

For the H$_2$O$_2$ concentration, a value below 10 wt. % achieved few precipitates. With increasing concentrations to 20 wt. % and 30 wt. %, the morphology changed to urchin-like microspheres consisted of short nanorods (Fig. S5a, b), and then to hollow microspheres consisted of nanoparticulate aggregates with interconnected nanopores (Fig. S5c, d).

For the HNO$_3$ concentration, the urchin-like microspheres consisted of nanorods were also achieved when the HNO$_3$ additive was doubled (Fig. S5e, f). In absence of the HNO$_3$ in the reactants, only solid nanoparticulate aggregates can be observed, which can be contributed to the higher hydrolysis and condensation rate arising from the improved pH value.

For the K$_2$TiO(C$_2$O$_4$)$_2$ concentration, hollow microspheres consisted of nanoparticulate aggregates with interconnected nanopores were achieved when decreasing the concentration to 200 mM (Fig. S5g, h), which is similar to that achieved by using 30 wt. % H$_2$O$_2$ (Fig. S5c, d).

The XRD analysis results show that, after the acid washing and calcination, hollow microspheres consisted of nanoparticulate aggregates with interconnected nanopores mainly consisted of rutile, with minor anatase; whilst other powders are phase pure anatase (Fig. S6).
**Fig. S7** XRD patterns of the yolk-shell powders after calcinations at 450 °C for 1 h in air. Note that the acid washing procedure was not performed here.

**Fig. S8** The N₂ adsorption-desorption isotherm of the urchin-like TiO₂ microspheres (NS-36h). The inset shows the corresponding pore size distribution curve.

The specific surface area of the urchin-like TiO₂ microspheres (NS-36h) is determined to be 186.8 m²·g⁻¹. The pore volume is ca. 0.566 cm³·g⁻¹.
**Fig. S9** Low (a) and high (b) magnification FESEM images of hierarchical nanosheet-assembled yolk-shell TiO$_2$ microspheres after being crushed.

![FESEM images](image)

**Fig. S10** Diffuse reflectance UV-Vis spectra of hierarchical nanosheet assembled yolk-shell TiO$_2$ microspheres before (NS) and after being crushed (NS-crushed).

![UV-Vis spectra](image)

**Fig. S11** Low (a) and high (b) magnification FESEM images of hierarchical nanosheet-assembled yolk-shell TiO$_2$ microspheres after cycling test.

![FESEM images](image)