Electronic Supplementary Information

Band Engineering of Mesoporous TiO$_2$ with Turnable Defects for Visible-Light Hydrogen Generation

Jin Yan$^a$, Lei Dai$^a$, Penghui Shi$^{a,b,*}$, Jincheng Fan$^a$, Yulin Min$^{a,b}$, Qunjie Xu$^{a,b,*}$

$^a$ Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai University of Electric Power, Shanghai 200090, P.R. China

$^b$ Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200090, P.R. China

*Correspondence E–mail: shipenghui@shiep.edu.cn (P. Shi), xuqunjie@shiep.edu.cn (Q. Xu)
Table S1 below shows the particle size and unit cell parameters of Rh/B-TiO$_2$ with different doping amounts. XRD analysis demonstrates that all samples heated at 400 °C are in pure anatase phase and there is no observable structural difference between undoped and doped samples. The particle size obtained from the XRD data are assumed to be tetragonal crystal systems, which are listed in Table S1. The lattice expansion and contraction properties shown are consistent with previously reported B-doped TiO$_2$ data.

**Table S1.** Crystallite size and BET surface area of samples.

<table>
<thead>
<tr>
<th>Products</th>
<th>Crystallite size (nm)</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO$_2$</td>
<td>46</td>
<td>43.14</td>
</tr>
<tr>
<td>B-TiO$_2$</td>
<td>51</td>
<td>139.05</td>
</tr>
<tr>
<td>Rh-TiO$_2$</td>
<td>39.3</td>
<td>82.55</td>
</tr>
<tr>
<td>Rh$_{0.1}$/B-TiO$_2$</td>
<td>28.7</td>
<td>195.01</td>
</tr>
<tr>
<td>Rh$_{0.5}$/B-TiO$_2$</td>
<td>25.9</td>
<td>381.55</td>
</tr>
<tr>
<td>Rh$_1$/B-TiO$_2$</td>
<td>17.6</td>
<td>198.54</td>
</tr>
</tbody>
</table>
Table S2. Parameters obtained from time-resolved PL decay curves according to a Three-exponential decay.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_1$(ns)</th>
<th>$\tau_2$(ns)</th>
<th>$\tau_3$(ns)</th>
<th>$A_1$(%)</th>
<th>$A_2$(%)</th>
<th>$A_3$(%)</th>
<th>avllifetime(ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO$_2$</td>
<td>186.16</td>
<td>926.98</td>
<td>35.38</td>
<td>67.51</td>
<td>94.76</td>
<td>99.54</td>
<td>346.43</td>
</tr>
<tr>
<td>B-TiO$_2$</td>
<td>128.56</td>
<td>840.26</td>
<td>18.75</td>
<td>66.28</td>
<td>94.46</td>
<td>99.50</td>
<td>299.19</td>
</tr>
<tr>
<td>B/Rh$_{0.5}$-TiO$_2$</td>
<td>196.73</td>
<td>1020.73</td>
<td>34.99</td>
<td>67.79</td>
<td>95.49</td>
<td>99.61</td>
<td>380.97</td>
</tr>
</tbody>
</table>

Transient PL B-TiO$_2$ and Rh$_{0.5}$/B-TiO$_2$ nanoporous particle decay curves are compared in Fig. 4c. And use the three exponential function to mathematically fit the PL decay curve:

$$y = A_1\exp(-x / \tau_1) + A_2\exp(-x / \tau_2) + A_3\exp(-x / \tau_3) + y_0$$  \hspace{1cm} (1)

here $A_1$, $A_2$, $A_3$ are amplitude coefficient and $y_0$ is basal constant. $\tau_1$, $\tau_2$ and $\tau_3$ are the corresponding fluorescence lifetime, respectively. The calculated carrier lifetimes are shown in Table 2. After integrating through the formula, the average fluorescence lifetime is longer than other lifetimes:

$$\tau = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3}$$  \hspace{1cm} (2)
Fig. S1. The FESEM of pure TiO$_2$ (a) before annealing, (b) calcined for 1h, (c) after full annealing.

Fig. S2. The FESEM (a-b) images of the B doped-TiO$_2$ nanoparticle.

Fig. S3. The FESEM (a-b) images of the Rh-TiO$_2$ nanoparticle.

Fig. S4. The FESEM (a-b) images of the Rh$_{0.5}$/B codoped-TiO$_2$ nanoparticle.
Fig. S5. The TEM image of B-TiO$_2$: (a, b, d) TEM; (c) HRTEM; (e) Mapping of B-doped TiO$_2$.

Fig. S6. The TEM of (a-b) B-TiO$_2$. (c) TEM, (d) mapping of Rh, B-codoped TiO$_2$.

Fig. S7. (a) Nitrogen adsorption-desorption isotherms and (b) the corresponding pore size distribution curves of the Rhx/B-TiO$_2$ (x=0, 0.1, 0.5, 1).
Fig. S8. XRD patterns of the TiO$_2$ at different temperatures.

Fig. S9. FT-IR spectra of Rh$_x$/B-TiO$_2$ (x=0, 0.1, 0.5, 1).

Fig. S10. Raman spectra of the Rh$_x$/B-TiO$_2$ (x=0, 0.1, 0.5, 1).
Fig. S11. XPS survey spectra of the B-TiO$_2$ and Rh$_{0.5}$/B-TiO$_2$.

Fig. S12. High-resolution XPS spectra of B 1s for B-TiO$_2$ and Rh$_{0.5}$/B-TiO$_2$.

Fig. S13. High-resolution XPS spectra of Rh 3d for Rh$_{0.5}$/B-TiO$_2$. 
Fig. S14. High-resolution XPS spectra of pure TiO$_2$ and Rh-TiO$_2$.

Fig. 15. (a-b) The energy band structure, DOS and (c) crystal structures of the pure TiO$_2$.

Fig. S16. Cycling tests of photocatalytic hydrogen evolution of Rh$_{0.5}$/B-TiO$_2$. 
**Fig. S17.** Long-term cycling of transient photocurrents measurements of Rh$_{0.5}$/B-TiO$_2$.

**Fig. S18.** EPR spectra with Rh$_{0.5}$/B-TiO$_2$. 