Electronic supplementary information

Enhanced charge transfer and separation of hierarchical hydrogenated TiO$_2$ nanothorns/carbon nanofibers composites decorated by NiS quantum dots for remarkable photocatalytic H$_2$ production activity

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**Fig. S1** SEM images of H-TiO$_2$/CNFs precursors prepared from different reaction time. (A) 0.5 h, (B) 6 h, (C) 12 h, and 24 h.

**Fig. S2.** SEM image of the pure TiO$_2$ precursor.
**Fig. S3.** The survey XPS spectrum of the NiS/H-TiO$_2$/CNFs.

**Fig. S4.** The energy dispersive spectrum (EDS) of the NiS/H-TiO$_2$/CNFs.
**Fig. S5.** (A), (B), (C) and (D) are the water contact angle photographs of TiO$_2$, TiO$_2$/CNFs, H-TiO$_2$/CNFs, and NiS/H-TiO$_2$/CNFs after AM 1.5 irradiation, respectively.

**Fig. S6.** Nitrogen adsorption–desorption isotherms and the pore size distribution plots (inset) of TiO$_2$, TiO$_2$/CNFs, H-TiO$_2$/CNFs, and NiS/H-TiO$_2$/CNFs.
Table S1: Summary of the photoluminescence decay time (τ) and their relative intensities of the different samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>τ₁(ns)</th>
<th>τ₂(ns)</th>
<th>I₁ (%)</th>
<th>I₂ (%)</th>
<th>Average lifetime (τ, ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiS/H-TiO₂/CNFs</td>
<td>3.93</td>
<td>8.07</td>
<td>35.52</td>
<td>64.48</td>
<td>7.19</td>
</tr>
<tr>
<td>H-TiO₂/CNFs</td>
<td>3.75</td>
<td>7.41</td>
<td>36.95</td>
<td>63.05</td>
<td>6.57</td>
</tr>
<tr>
<td>TiO₂/CNFs</td>
<td>3.50</td>
<td>6.33</td>
<td>38.27</td>
<td>61.73</td>
<td>5.61</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.64</td>
<td>5.96</td>
<td>39.99</td>
<td>60.01</td>
<td>5.29</td>
</tr>
</tbody>
</table>

The average lifetime was calculated using equation: 

\[ \langle \tau \rangle = \frac{I_1 \tau_1^2 + I_2 \tau_2^2}{I_1 \tau_1 + I_2 \tau_2} \]

Fig. S7. (A), (B), and (C) are SEM images of TiO₂/CNFs prepared from 30, 20, and 10 mg carbon fibers, respectively.

We control the relative content of TiO₂ and CNFs according to the dosage of carbon fiber (CNFs) under the fixed 0.5 mL tetrabutyl titanate. The TiO₂/CNFs prepared from 10, 20, 30 mg CNFs were obtained. The SEM images were shown in Fig. S7. When the CNFs content is high, there are fewer TiO₂ nanothorns grown on the surface of CNFs. With the decrease of CNFs amount, more TiO₂ nanothorns can be found.
Fig. S8. The photocatalytic H$_2$ evolution activities of TiO$_2$/CNFs prepared from 10 (a), 20 (b), and 30 mg (c) carbon fibers, respectively.

The relative content of TiO$_2$ and CNFs also influence the photocatalytic activity (Fig. S8). Only proper content of TiO$_2$ and CNFs can exhibit optimal photocatalytic activity. When the content of CNFs is too high, there would have strong shading effect of CNFs. Meanwhile, the amount of TiO$_2$ catalyst is relatively low (Fig. S7A). So the photocatalytic hydrogen evolution activity is relative low. When the content of CNFs is too low, additional TiO$_2$ separated from CNFs can exist (Fig. S7C). There would have relatively weak interaction between TiO$_2$ and CNFs, not contributing to the photogenerated charge transfer and separation, leading to the decrease of photocatalytic hydrogen evolution activity.
Fig. S9. The photocatalytic H\textsubscript{2} evolution activities of these catalysts under visible light irradiation ($\lambda > 420$ nm).

Fig. S10. The photocatalytic H\textsubscript{2} evolution rates of the NiS/H-TiO\textsubscript{2}/CNFs with different NiS contents (A). The amounts of photocatalytic H\textsubscript{2} evolution plotted against AM1.5 irradiation time.
**Fig. S11.** SEM image (A), TEM images (B, C), and XRD pattern of the NiS/H-TiO$_2$/CNFs after photocatalytic H$_2$ evolution reaction.

**Fig. S12.** Comparison of the photocatalytic H$_2$ evolution rate of NiS/H-TiO$_2$/CNFs and the crushed NiS/H-TiO$_2$/CNFs (C-NiS/H-TiO$_2$/CNFs) (A), and corresponding amounts of photocatalytic H$_2$ evolution plotted against AM1.5 irradiation time (B).
Fig. S13. Comparison of the photocatalytic H₂ evolution rate of NiS/H-TiO₂/CNFs (a) and the physically mixed NiS/H-TiO₂ and CNFs (b) (A), and corresponding amounts of photocatalytic H₂ evolution plotted against AM1.5 irradiation time (B).