Supporting information

Hierarchical heterostructures of Sn$_3$O$_4$ on N doped TiO$_2$ nanotubes with enhanced photocatalytic performances

Xin Yu$^{ab1}$, Longfei Wang$^{ab1}$, Jian Zhang$^{ab}$, Weibo Guo$^{ab}$, Zhenhuan Zhao$^c$, Yong Qin$^a$, Xiaoning Mou$^a$, Aixue Li$^{a*}$, Hong Liu$^{ac*}$

$^a$Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Science, Beijing 100083, China
$^b$University of Chinese Academy of Science, Beijing 100049, China
$^c$State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

*Corresponding author. E-mail addresses: hliu@binn.cas.cn (H. Liu), liaixue@binn.cas.cn (A. Li)

Xin Yu and Longfei Wang are contributed equally to this work.

Fig. S1 XRD patterns of Sn$_3$O$_4$/TiO$_2$ heterostructures.
**Fig. S2** SEM image of the TiO$_2$ nanotubes.

<table>
<thead>
<tr>
<th>Sample number N-TiO$_2$ : Sn$_3$O$_4$</th>
<th>N-TiO$_2$</th>
<th>SnCl$_2$·2H$_2$O</th>
<th>Na$_3$C$_6$H$_5$C$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0.016 g</td>
<td>0.27 g</td>
<td>0.882 g</td>
</tr>
<tr>
<td>2:1</td>
<td>0.032 g</td>
<td>0.27 g</td>
<td>0.882 g</td>
</tr>
<tr>
<td>3:1</td>
<td>0.048 g</td>
<td>0.27 g</td>
<td>0.882 g</td>
</tr>
<tr>
<td>4:1</td>
<td>0.064 g</td>
<td>0.27 g</td>
<td>0.882 g</td>
</tr>
</tbody>
</table>

**Table. S1** The detailed experimental conditions for the fabrication of molar ratio of N-TiO$_2$: Sn$_3$O$_4$ = 1:1, 2:1, 3:1 and 4:1
Fig. S3 TEM image of the (a, b) N-TiO$_2$ nanotubes, (c, d) HRTEM of the N-TiO$_2$ nanotubes.
Fig. S4 (a, b) TEM images of the Sn$_3$O$_4$ nanosheets, (c, d) HRTEM images of the Sn$_3$O$_4$ nanosheets.
Fig. S5 SEM images Sn$_3$O$_4$/N-TiO$_2$ hierarchical heterostructures on different molar ratio (a) N-TiO$_2$: Sn$_3$O$_4$ = 1:1 (b) N-TiO$_2$: Sn$_3$O$_4$ = 2:1 (c) N-TiO$_2$: Sn$_3$O$_4$ = 3:1 (d) N-TiO$_2$: Sn$_3$O$_4$ = 4:1

The morphology of the samples was observed by FESEM. As observed in Fig. S5, four kinds of Sn$_3$O$_4$ nanostructures grew on the surface of TiO$_2$ nanotubes after solvothermal reaction for 12 h. Fig. 5 show the SEM images of samples, respectively. From Fig. 5d, it was found that a number of Sn$_3$O$_4$ nanoparticles uniformly grew on the surface of TiO$_2$ nanotubes. And nanoparticles possess an average diameter of less than 50 nm. When the concentration of precursor Sn$_3$O$_4$ was increased 2 times, the morphology of Sn$_3$O$_4$ nanostructures grew on TiO$_2$ nanotubes changed significantly. As shown in Fig. 5c, several Sn$_3$O$_4$ nanosheets instead of nanoparticles grew on the surface of TiO$_2$ nanotubes and the nanosheets distribute uniformly. From the high magnification SEM image (inset of Fig. 5c), it could be seen that the Sn$_3$O$_4$ nanosheets were about 10 nm in thickness and 40–60 nm in length. In Fig. 5a and b, when the Sn$_3$O$_4$ concentration was further increased, Sn$_3$O$_4$ nanosheets instead of nanoparticles grew on the surface of TiO$_2$ and the density of the nanoparticles was dramatically increased compared with sample Fig. 5d. Notably, the nanoparticles were still uniformly distributed over each fiber without aggregation, although their density increased significantly. This might be due to the fact that the high porosity and large surface area of TiO$_2$ nanotubes were beneficial for the growth and uniform distribution of secondary nanostructure nanomaterials.
In addition, the energy dispersive X-ray spectrometry (EDS) analysis was conducted to confirm the composition of N-TiO₂. The elements, Al and C (from the SEM sample holder), N, O and Ti were all detected. The EDS mapping clearly shows the strongest signals of N, Ti, and O, confirming that the N element was distributed uniformly.

**Fig. S6** EDS spectrum and mapping results from a single N-TiO₂ nanotube.

**Fig. S7** XPS fully scanned spectrum of the Sn₃O₄/N-TiO₂ hierarchical heterostructures.
Fig. S8 Photocatalytic degradation of MO without any catalyst and in the presence of photocatalysts but in dark.

To check if MO can be degraded under light irradiation, 20 mg/L of MO solution without photocatalyst was irradiated under UV and visible light, respectively, and the degradation rate of MO were checked. The result shows that there is no decrease of MO without photocatalyst under UV and visible light irradiation. And these results indicated that the adsorption-desorption equilibrium of MO was established within 30 min in the dark. And there was no appreciable degradation of MO after 50 min in the absence of photocatalysts.

Fig. S9 comparison of the photocatalytic activities of the Sn$_3$O$_4$/TiO$_2$ hierarchical heterostructures at different mole ratios of TiO$_2$ and Sn$_3$O$_4$ under either (a) visible or (b) UV light irradiation.
Fig. S10 Comparison of photocatalytic activities of the Sn₃O₄/N-TiO₂ hierarchical heterostructures (molar ratio N-TiO₂: Sn₃O₄ = 1:1) at different content of N under either (a) visible or (b) UV light irradiation.

Fig. S11 Photocatalytic H₂ evolution from the aqueous methanol solution by Sn₃O₄/N (5%)-TiO₂ hierarchical heterostructure at different ratio of Sn₃O₄ and N (5%)-TiO₂.
**Fig. S12** The amount of produced H2 and the concentration of used methanol.

**Fig. S13** UV-Vis diffuse reflectance spectra of Sn₃O₄/N (5%)-TiO₂ hierarchical heterostructures at different ratio of Sn₃O₄ and N-TiO₂.

The optical band gap of the as-prepared Sn₃O₄ was calculated using the Tauc model. By plotting \((\alpha hν)^2\) versus \(hν\) and extrapolating the linear portion of the spectrum in
the band edge region, the optical band gap of the Sn$_3$O$_4$ microflowers was determined to be 2.95 ev.

**Fig. S14** Digital pictures of the N-TiO$_2$, Sn$_3$O$_4$/N-TiO$_2$ and Sn$_3$O$_4$ anode.