Supporting Information

Synergistic Material Modifications Induced Optimization of Interfacial Charge Transfer and Surface Hydrogen Adsorption

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Experimental Details

Chemicals

All chemicals used in the material syntheses were reagent grade including sodium hydroxide, ethanol, nickel nitrate (98%), hydrochloric acid (37%), glucose (98%), ammonium fluoride and methanol from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and Degussa P25 TiO₂ nanoparticles from Evonik. Milli-Q water (18.2 mΩ/cm) were used throughout the experimental work.

Materials synthesis

To form an Ni-substituted TiO₂ the following approach was used. Preparation of Ni doped TiO₂ (NT): P25 TiO₂ nanoparticles (0.5 g) was dispersed in a 5 M sodium
hydroxide aqueous solution (30 mL) before being transferred into a Teflon-lined stainless-steel autoclave (50 mL in capacity) for hydrothermal reaction at 140°C for 10 h. The products were rinsed several times with water to remove residual sodium hydroxide and collected by centrifugation before being redispersed in 500 mL of 0.1 M hydrochloric acid solution. The precipitates were centrifugated and redispersed into 30 mL of aqueous solution containing nickel nitrate with various concentration (following a Ni/TiO2 ratio of 0, 0.5, 1.0, 2.0 and 3.0 wt%). The products were then collected by centrifugation and rinsed with water and ethanol several times before being dried under vacuum at room temperature, obtaining nickel titanates with varying nickel doping concentrations. With temperature ramping rate of 2°C/min to 450 °C, the samples were calcined in a muffle furnace for 2 h in air and labelled as NT0 (pure TiO2), NT0.5, NT1, NT2, and NT3, corresponding to the increasing nickel doping concentrations (0, 0.5, 1.0, 2.0 and 3.0 wt%).

Carbon coating of NTx were prepared as follow. 0.2 g NT2 was dispersed into 30 mL aqueous solution with 0.2 ml glucose aqueous solution (C:Ni=1:1) by sonication before hydrothermal reaction at 150 °C for 15 h in a 50 mL Teflon-lined stainless-steel autoclave. The products were rinsed by water and ethanol several times before being collected by centrifugation and dried at 60 °C for 10 h and denoted as CNTx - CNT0, CNT0.5, CNT1, CNT2 and CNT3, respectively, corresponding to the Ni-content. Carbon content was also investigated on the NT2 sample with Ni:C ratios of 2:1, 2:2 and 2:4.

Fluorinated carbon capping of NTs were prepared using glucose and ammonia
fluoride aqueous solution instead following the same process as carbon capping of the NTx with F: C: Ni of 1:2:2. The corresponding products were labelled as FNT0 (fluorinated carbon encapsulation of pure TiO$_2$), FNT0.5, FNT1, FNT2, and FNT3, respectively.

**Characterization**

A transmission electron microscope (TEM, JEM-2100F, JEOL) were used to investigate the morphology and conduct elemental mapping of the samples. X-ray diffraction (XRD) patterns of the obtained samples were obtained on an X-ray diffractometer (Ultima IV) using Cu K$_\alpha$ irradiation under a 40 kV working voltage and were used to determine the phase structures. Raman spectra were acquired on a HORIBA Lab-RAM HR-Evolution Raman spectrometer with laser excitation at 532 nm. The UV/Vis diffuse reflectance spectra (UV/Vis DRS) were obtained with a UV/Vis/NIR spectrophotometer (UH4150, Hitachi, Japan) in the wavelength range 300-800 nm. The photoluminescence spectra were recorded on a fluorospectrometer (F-280-Laser-NIR, Gangdong Science and Technology Development Co., LTD. Tianjin) with an excitation wavelength of 460 nm. X-ray photoemission spectra (XPS) were collected using a Thermo Escalab 250xi analyzer. Binding energies of Ti 2p, O 1s, C 1s and F 1s were recorded using Al K$_\alpha$ (1486.6 eV) as the excitation source and a pass energy of 23.5 eV. The position of the XPS peaks of the corresponding element is referenced to the C1s peak.

**Photocatalytic hydrogen generation**

The photocatalytic hydrogen evolution experiments were carried out at room
temperature (20 ± 1 °C) controlled by a cooling system and in a vacuum sealing reaction system. 10 mg of the powdered photocatalyst was dispersed in a 50 mL of 10% methanol aqueous solution by ultrasonication in a Pyrex flask (350 mL) equipped with a water jacket to exclude the temperature influence from illumination. Top illumination mode was used with a 300 W Xe lamp (Perfect Light, PLS-SXE300D) through the flat window of the reactor. Gas evolution was determined by an online gas chromatograph (GC-7860, Ar carrier gas).

**Electrochemical measurement**

The electrochemical catalytic performance throughout the measurement process was conducted in 0.5 M Na$_2$SO$_4$ solution using a (CHI 760E Electrochemical Workstation) with a three-electrode system. A platinum plate (1 × 1 cm$^{-1}$), a saturated Hg/Hg$_2$Cl$_2$ electrode and a fluorine doped tin oxide (FTO) coated glass plate (1 × 1 cm$^{-1}$) were used as the counter, reference and working electrode, respectively. The working electrode was prepared for testing samples, PVDF and NMP. In detail, a mixture of 300 mg sample, 2.7 g PVDF and 1 mL NMP were moderately stirring overnight before being coated on FTO, then calcination under 400 °C for 1h.

**Computational simulation details**

All calculations were based on the first principles of density functional theory (DFT) and performed by the Vienna Ab-initio Simulation Package (VASP). The exchange correlation energy was calculated by Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (GGA). The DFT-D3 method was used to describe the vdW interactions, and the DFT+U method was used to more accurately describe
the Coulomb interaction of the system, setting the effective U value on the Ti 3d orbit
to 4.2 eV. The vacuum space was set to 15 Å to avoid the interaction between two
periodic units. The plane wave energy cut-off was set to 450 eV and k-point was set to
$2 \times 4 \times 1$. A total energy convergence of $10^{-4}$ eV was used for the calculation of the
electron self-consistent field. The TiO$_2$ (101) surface was modeled with a ($2 \times 2$) three-
Ti-layer slab (24 Ti and 48 O atoms), the heterogeneous junction structure was modeled
using a ($2 \times 2$) supercell of TiO$_2$ (101) surface and a ($5 \times 3$) graphene supercell, and the
distance between the graphene layer and the TiO$_2$ (101) surface is 2.8 Å. One Ni atom
is doped in the TiO$_2$ surface model, corresponding a Ni doping concentration of ~4%,
which is comparable to the experiments results (0.5~3wt%). In all structures, the bottom
eight atoms (four oxygen and four titanium) were fixed.

The solvation effect is not taken into account in the calculations as our goal is to
investigate the effects of Ni-doping, carbon shield, and further fluorine-doping of the
thin carbon shield on the tendency of TiO$_2$ photocatalytic HER activity. Despite the
solvation effect may have some influence on the adsorption energy of hydrogen, but
the trend of TiO$_2$ photocatalytic activity will be maintained.

The adsorption energy and Gibbs free energy change of hydrogen adsorption was
defined as:

$$\Delta E_{H^*} = E_{H^* \text{cat}} - E_{\text{cat}} - \frac{1}{2}E_{H_2}$$
$$\Delta G_{H^*} = \Delta E_{H^*} + 0.24$$
where $E_{H^\bullet\text{cat}}$ and $E_{\text{cat}}$ is the energies of the catalyst with and without H adsorption, respectively. $E_{H_2}$ is the energy of the molecular hydrogen in the gas phase, and 0.24 is the free energy correction, which was proposed by Norskov et al.

The adsorption energy of hydroxyl was calculated by the following formula:

$$\Delta E_{OH^\bullet} = E_{OH^\bullet\text{cat}} - E_{\text{cat}} - E_{OH}$$

where $E_{OH^\bullet\text{cat}}$ and $E_{\text{cat}}$ is the energies of the catalyst with and without OH*, respectively. $E_{OH}$ is the energy of hydroxyl.
Figure S1. The most stable position for Ni atoms doped in TiO$_2$: (a) Ni$_a$@TiO$_2$, (b) Ni$_b$@TiO$_2$

Table S1. The adsorption energy of hydroxyl and hydrogen on TiO$_2$ and Ni$_a$/TiO$_2$.

<table>
<thead>
<tr>
<th></th>
<th>TiO$_2$</th>
<th>Ni$_a$/TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O site</td>
<td>Ti site</td>
</tr>
<tr>
<td>$E_{H^+}$/eV</td>
<td>0.37</td>
<td>-</td>
</tr>
<tr>
<td>$E_{OH^+}$/eV</td>
<td>0.26</td>
<td>-1.12</td>
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</table>
Figure S2. (a-c) TEM, HR-TEM and SAED images of 2% Ni-doped TiO$_2$, NT2; (d-f) XRD, Raman and UV-visible diffuse reflectance spectra of NTs for a varying Ni-doping level.
Figure S3. XPS analyses of (a) Ti 2p, (b) O 1s for TiO$_2$ (NT0).

Figure S4. XPS analyses of (a) Ti 2p, (b) O 1s for NT2.
Figure S5. XPS analyses of (a) Ti 2p, (b) O 1s for CNT2.

Table S2. Detailed analysis of Ti$^{3+}$, oxygen vacancy (Ov), surface hydroxyl groups (OH) contents (%) in various catalysts from XPS spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti$^{3+}$</th>
<th>Ov</th>
<th>OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>5.7</td>
<td>14.8</td>
<td>6.1</td>
</tr>
<tr>
<td>NT2</td>
<td>6.0</td>
<td>16.8</td>
<td>6.4</td>
</tr>
<tr>
<td>CNT2</td>
<td>3.5</td>
<td>15.6</td>
<td>6.9</td>
</tr>
<tr>
<td>FNT2</td>
<td>2.8</td>
<td>12.8</td>
<td>7.0</td>
</tr>
</tbody>
</table>
Figure S6. (a) H₂ evolution rate, and (b) HER efficiency of NTx with varying Ni-doping level.

Figure S7. (a) H₂ evolution rate of CNTx with varying Ni-doping level.
Figure S8. (a) H$_2$ evolution rate, and (b) HER efficiency of the CNT2 as a function of the carbon content.
**Table S3.** Comparison of photocatalytic activity in hydrogen production of recent metal-doped TiO$_2$ photocatalysts composites.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Concentration (mg/ml)</th>
<th>Reactant solution</th>
<th>HER rate (mmol/g/h)</th>
<th>Incident light</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FNT2</td>
<td>0.2</td>
<td>10 % methanol</td>
<td>13.00</td>
<td>300 W xenon lamp</td>
<td>This work</td>
</tr>
<tr>
<td>Ni/TiO$_2$</td>
<td>0.2</td>
<td>50 % methanol</td>
<td>3.39</td>
<td>450 W Hg lamp</td>
<td>[9]</td>
</tr>
<tr>
<td>Ni/TiO$_2$/C</td>
<td>0.8</td>
<td>20 % methanol</td>
<td>3.56</td>
<td>300 W Xenon lamp</td>
<td>[10]</td>
</tr>
<tr>
<td>Mg/TiO$_2$</td>
<td>0.2</td>
<td>100 % water</td>
<td>0.85</td>
<td>AM 1.5 G solar simulator</td>
<td>[11]</td>
</tr>
<tr>
<td>Ga-TiO$_2$ nanoparticles</td>
<td>1</td>
<td>20 % methanol</td>
<td>5.77</td>
<td>150 W xenon arc lamp</td>
<td>[12]</td>
</tr>
<tr>
<td>Co/TiO$_2$</td>
<td>2</td>
<td>5% glycerol</td>
<td>11.02</td>
<td>400 W Hg vapor lamp</td>
<td>[13]</td>
</tr>
<tr>
<td>single atom Cu-TiO$_2$</td>
<td>0.065</td>
<td>25 % methanol</td>
<td>16.60</td>
<td>Xenon lamp (100 mW/cm$^2$)</td>
<td>[14]</td>
</tr>
<tr>
<td>Cu-TiO$_2$/C</td>
<td>0.25</td>
<td>10 % methanol</td>
<td>14.40</td>
<td>365 nm LED (80 mW/cm$^2$)</td>
<td>[15]</td>
</tr>
<tr>
<td>TiO$_2$/Pt/rGO</td>
<td>1</td>
<td>20 % methanol</td>
<td>0.48</td>
<td>Philips PL-S lamp (315 - 400 nm)</td>
<td>[16]</td>
</tr>
<tr>
<td>Pt/TiO$_2$</td>
<td>5</td>
<td>20 % methanol</td>
<td>11.20</td>
<td>AM 1.5 G solar simulator</td>
<td>[17]</td>
</tr>
<tr>
<td>Pt/TiO$_2$</td>
<td>0.5</td>
<td>25 % methanol</td>
<td>19.22</td>
<td>400 W Xenon lamp</td>
<td>[18]</td>
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</table>
Figure S9. UV-vis absorption spectra of pure TiO$_2$, NT2 and FNT2.
REFERENCES