Supplementary Information

Surface oxygen vacancies promoted Pt redispersion to single-atom for enhanced photocatalytic hydrogen evolution

Jinmeng Cai,[a,b,+] Ang Cao,[c,+] Zhenbin Wang,[c] Siyu Lu,[a] Zheng Jiang,[d] Xi-Yan Dong,[a]

Xingang Li,*[b] and Shuang-Quan Zang*[a]

*a Henan Key Laboratory of Crystalline Molecular Functional Materials, Green Catalysis Center, and College of Chemistry, Zhengzhou University, Zhengzhou 450001, P. R. China

b Collaborative Innovation Center for Chemical Science & Engineering (Tianjin), Tianjin Key Laboratory of Applied Catalysis Science & Engineering, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, P. R. China

c Technical University of Denmark, Lyngby DK, 2800, Denmark

d Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, P. R. China

+ These authors contributed equally to this work.

*Corresponding authors

Email:

xingang_li@tju.edu.cn
zangsqzg@zzu.edu.cn
1. Figures

**Figure S1.** TEM (a) and HRTEM (b) images of Pt-NPs/TiO₂. By using NaBH₄ in aqueous solution to reduce Pt precursor, the obtained reduced Pt tends to aggregate to large nanoparticles. The large particles are composed of primary particles with a diameter of about 3.9 nm.
**Figure S2.** (a) TEM image of Pt-NCs/TiO$_2$. (b) Histograms of Pt clusters size distribution of Pt-NCs/TiO$_2$. 
Figure S3. TEM images of the catalysts with Pt loading amount of (a) 0.5 wt.% and (b) 0.1 wt.% after treated in 10 vol.% H$_2$/Ar atmosphere at 700 °C.
Figure S4. XRD patterns of Pt-NPs/TiO$_2$, Pt-NCs/TiO$_2$ and Pt-SAs/TiO$_2$. New peaks that can be attributed to the rutile TiO$_2$ phase can not be found, indicating that no phase transition would occur at the treatment temperature in this experiment.
**Figure S5.** Schematic illustration of the formation of Ti-OH and oxygen vacancy with the assistance of hydrogen spillover effect.
Figure S6. Pt 4f XPS spectra of the catalysts.
Figure S7. (a) TEM image of Pt-NPs/TiO$_2$ after the treatment in N$_2$ atmosphere at 700 °C for 5 h. (b) Histograms of Pt particle size distribution of the catalyst in (a).
Figure S8. (a) Side and (b) top views of anatase TiO$_2$(101) surface. The red means O atom and the grey means Ti atom.
2. Tables

Table S1. Binding energies (B.E.) of O element, and relative peak areas (P.A.) of different surface oxygen species of O 1s.

<table>
<thead>
<tr>
<th>Samples</th>
<th>B.E. O (eV)</th>
<th>P.A. (Counts)</th>
<th>O_{OH}/O_L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O_L</td>
<td>O_{OH}</td>
<td>O_L</td>
</tr>
<tr>
<td>Pt-NPs/TiO_2</td>
<td>529.7</td>
<td>531.5</td>
<td>10486</td>
</tr>
<tr>
<td>Pt-NCs/TiO_2</td>
<td>529.8</td>
<td>531.3</td>
<td>8604</td>
</tr>
<tr>
<td>Pt-SAs/TiO_2</td>
<td>529.8</td>
<td>531.0</td>
<td>9512</td>
</tr>
</tbody>
</table>
Table S2. Calculated adsorption energy and bader charge of a single Pt adatom on the pristine (Pt/P-TiO$_2$) and defective (Pt/V$_O$-TiO$_2$) TiO$_2$(101) surface.

| Catalyst       | Position                  | $E_{ad}$ (eV) | Bader charge (|e|) |
|----------------|---------------------------|---------------|----------------|
| Pt/P-TiO$_2$   | 2cO-2cO bridge            | 2.78          | -0.07          |
| Pt/V$_O$-TiO$_2$| $V_O$                     | 0.81          | +0.66          |