Electronic Supplementary Information (ESI)

Engineering on the edge of Pd nanosheet cocatalysts for enhanced photocatalytic reduction of CO$_2$ to fuels

Yuzhen Zhu,$^a$ Zaixiang Xu,$^a$ Wenya Jiang,$^b$ Shuxian Zhong,$^a$ Leihong Zhao$^a$ and Song Bai$^{a,b}$

$^a$ Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Life sciences, Zhejiang Normal University, Jinhua, Zhejiang, 321004, P. R. China.

$^b$ School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China.

E-mail: songbai@zjnu.edu.cn
**Fig. S1** TEM and HRTEM images of TiO$_2$ nanosheets: (a) TEM image showing the flat surface of nanosheets; (b) TEM image showing the cross section and thickness of the nanosheets; (c) HRTEM image showing the lattice fringes of the flat faces; (d) HRTEM image showing the lattice fringes of side faces.
Fig. S2 XRD patterns of TiO$_2$-Pd NSs-M in reference to bare TiO$_2$ nanosheets. The standard diffraction patterns for anatase TiO$_2$ (JCPDS 21-1272) and fcc Pd (JCPDS 65-2867) are provided as references.
Fig. S3 TEM images of (a,b) large, (c,d) middle and (e,f) small Pd nanosheets.
Fig. S4 Edge length distribution histograms of the as-prepared Pd nanosheets on the TiO$_2$ nanosheets: (a) TiO$_2$-Pd NSs-L, (b) TiO$_2$-Pd NSs-M, (c) TiO$_2$-Pd NSs-S.
Fig. S5 AFM images and the corresponding height profiles of Pd nanosheets in (a,b) large, (c,d) middle and (e,f) small size.
Fig. S6 CO$_2$ adsorption behaviors for TiO$_2$-Pd NSs samples. The data are plotted based on the total weights of materials.
**Fig. S7** (a) Schematic illustration of the photocatalytic mechanism of TiO$_2$-Pd NSs samples under visible light irradiation; (b) H$_2$ and CO average evolution rates of TiO$_2$-Pd NSs samples in photocatalytic CO$_2$ reduction reaction with bare TiO$_2$ as a reference sample under visible light irradiation (400 nm $< \lambda < 780$ nm).
Fig. S8 TEM images of small Pd nanorings.
Fig. S9 (a) UV-vis-NIR diffuse reflectance spectra of bare TiO$_2$, TiO$_2$-Pd NSs-S and TiO$_2$-Pd NRs-S; (b) photocurrent vs. time (I-t) curves and (c) EIS Nyquist plots of bare TiO$_2$, TiO$_2$-Pd NSs-S and TiO$_2$-Pd NRs-S at 0.4 V vs. Ag/AgCl under UV light ($\lambda < 400$ nm) irradiation; (d) PL spectra of bare TiO$_2$, TiO$_2$-Pd NSs-S and TiO$_2$-Pd NRs-S excited at 310 nm.
Fig. S10 TEM images of middle Pd nanorings.
Fig. S11 (a) Schematic illustration, (b,c) TEM and (d) HRTEM images of TiO$_2$-Pd NRs-M.
Fig. S12 H₂, CO, and CH₄ average evolution rates of TiO₂-Pd NRs-M in photocatalytic CO₂ reduction reaction with TiO₂-Pd NSs-M as a reference sample.
Fig. S13 Stability studies of CO and CH₄ evolution rates as well as the selectivity for CO₂ reduction with (a) TiO₂-Pd NSs-S and (b) TiO₂-Pd NRs-S as catalysts in the photocatalytic cyclic process.
Fig. S14. TEM images of (a) TiO$_2$-Pd NSs-S and (b) TiO$_2$-Pd NR-S after the photocatalytic cyclic process.
Table S1. Chemical compositions of the TiO$_2$-Pd NSs and TiO$_2$-Pd NRs samples determined by ICP-MS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight ratio of Pd : TiO$_2$</th>
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<tr>
<td>TiO$_2$-Pd NSs-L</td>
<td>4.6%</td>
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<tr>
<td>TiO$_2$-Pd NSs-M</td>
<td>5.0%</td>
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<tr>
<td>TiO$_2$-Pd NSs-S</td>
<td>4.8%</td>
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<tr>
<td>TiO$_2$-Pd NRs-S</td>
<td>4.9%</td>
</tr>
<tr>
<td>TiO$_2$-Pd NRs-M</td>
<td>4.8%</td>
</tr>
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