Electronic Supporting Information

Decorating geometry- and size-controlled sub-20 nm Pd nanocubes onto 2D TiO₂ nanosheets for simultaneous H₂ evolution and 1,1-diethoxyethane production

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Fig. S17. Photocatalytic H₂ evolution over the TCs-7 composites with different H⁺ ion concentration. Reaction conditions: 15 mg sample in 2 mL ethanol, UV-Vis light (300 nm ≤ λ ≤ 800 nm), reaction time: 4 h, reaction temperature, 298 K.

Table S5. Summarized results on the photocatalytic conversion of ethanol over TCs-7 composites with different H⁺ ion concentration
Fig. S1. Photograph of the experimental setup for simultaneous H₂ evolution and DEE production

Table S1. Composition of the growth solution for synthesis of various sized Pd NCs

<table>
<thead>
<tr>
<th>Samples</th>
<th>Size (nm)</th>
<th>KBr (mg)</th>
<th>KCl (mg)</th>
<th>K₂PdCl₄ (mg)</th>
<th>PVP (mg)</th>
<th>AA (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd NCs-7</td>
<td>7</td>
<td>5</td>
<td>185</td>
<td>63</td>
<td>105</td>
<td>60</td>
</tr>
<tr>
<td>Pd NCs-14</td>
<td>14</td>
<td>400</td>
<td>0</td>
<td>63</td>
<td>105</td>
<td>60</td>
</tr>
<tr>
<td>Pd NCs-17</td>
<td>17</td>
<td>600</td>
<td>0</td>
<td>63</td>
<td>105</td>
<td>60</td>
</tr>
</tbody>
</table>

Fig. S2. Overall flowchart for the fabrication of Pd NCs
Fig. S3. UV-vis absorption spectra of Pd NCs with various sizes (The insets are the models of Pd NCs)

Fig. S4. UV-vis absorption spectra and the digital photographs of Pd NCs-7 aqueous solution before and after dipping with TNS for 24 h
**Fig. S5.** TEM (A) and HRTEM (B) images of TNS

**Fig. S6.** TEM (A) and HRTEM (B) images of TNS-Pd nanoparticles composites and the corresponding histogram of particle size distribution of Pd nanoparticles (C)

**Table S2.** The average crystallite sizes of TiO$_2$ nanoparticles in TNS, TNS-Pd composites calculated from the (101) and (200) facets diffraction peaks of anatase TiO$_2$ on the basis of Scherrer formula$^a$

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average crystallite sizes (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNS</td>
<td>12.8</td>
</tr>
<tr>
<td>TPs</td>
<td>12.6</td>
</tr>
<tr>
<td>TCs-7</td>
<td>11.1</td>
</tr>
<tr>
<td>TCs-14</td>
<td>11.2</td>
</tr>
<tr>
<td>TCs-17</td>
<td>11.2</td>
</tr>
</tbody>
</table>

$^a$ Scherrer equation: $D = K\lambda/\beta \cos \theta$, where $D$ is the mean size of the ordered crystalline domains, $K$ is the shape factor, $\lambda$ is the X-ray wavelength, $\beta$ is the line broadening at half the maximum intensity (FWHM) in radians, and $\theta$ is the Bragg angle.
**Fig. S7.** FT-IR spectra of the TNS and TNS-Pd composites

**Fig. S8.** The digital photographs of TNS (A), TPs (B), TCs-7 (C), TCs-14 (D) and TCs-17 (E)
**Fig. S9.** The plots of transformed Kubelka-Munk function versus the energy of light over the TNS and TNS-Pd composites.

**Fig. S10.** Photocatalytic H$_2$ evolution over the TCs-7 composites with different addition amounts of Pd NCs-7. Reaction conditions: 15 mg sample in 2 mL ethanol with H$^+$ ion concentration of $1 \times 10^{-3}$ mol L$^{-1}$, UV-Vis light (300 nm $\leq \lambda \leq$ 800 nm), reaction time: 4 h, reaction temperature, 298 K.

**Note:** The weight addition ratio of Pd NCs-7 in the TCs-7-0.5, TCs-7 and TCs-7-2 composites is 0.5%, 1% and 2%, respectively.
**Fig. S11.** Photocatalytic H$_2$ evolution over the TCs-7 composites under UV light ($\lambda = 365 \pm 15$nm) illumination. Reaction conditions: 15 mg sample in 2 mL ethanol with H$^+$ ion concentration of $1 \times 10^{-3}$ mol L$^{-1}$, UV light ($\lambda = 365 \pm 15$nm), reaction time: 12 h, reaction temperature, 298 K.

**Note:** Fig. S11 shows the photocatalytic H$_2$ evolution under UV light ($\lambda = 365 \pm 15$nm) illumination for calculating the apparent quantum efficiency (AQE) of the TCs-7 composites. The AQE,$^{S1}$ defined as the ratio of the number of reacted electrons (that is, twice the number of H$_2$ molecules for the photocatalytic H$_2$ evolution reaction) to the number of incident photons, has been calculated to be 5.33% for TCs-7 composites under the present conditions.

**Fig. S12.** GC-MS analysis of the products of the photocatalytic conversion of ethanol over TCs-7 composites
**Fig. S13.** Schematic energy-band diagram of TiO$_2$-Pd composites (A) and schematic band diagram illustrating the charge transfer driven by the Schottky junction (B). $E_{\text{vac}}$, $E_{\text{F}}$, $\Phi_{\text{Pd}}$, $\Phi_{\text{b}}$, and $\chi$ denote vacuum level, Fermi level, work function of Pd, Schottky barrier height, and electron affinity of TiO$_2$ conduction band, respectively (in eV).

**Note:** Fig. S13A shows the schematic energy-band diagram of TiO$_2$-Pd composites, in which an appropriate height of Schottky barrier between TiO$_2$ and Pd is formed due to the difference between the work function ($\Phi_{\text{Pd}}$) of Pd (5.12 eV)$^{22}$ and the electron affinity ($\chi$) of TiO$_2$ conduction band (3.8 eV).$^{23}$ The Schottky barrier height at the TiO$_2$-Pd junction is determined to be about 1.32 eV according to following equation:$^{23}$

$$\Phi_{\text{b}} = \Phi_{\text{Pd}} - \chi$$

The as-formed Schottky barrier can act as a sink for the photoinduced electrons to inhibit the backflow of electrons from metal to semiconductor (Fig. S13B), thus preventing the recombination of photoexcited electron-hole pairs.

**Table S3.** Summary of mole of surface Pd atoms in Pd NCs participated in the catalytic reaction$^a$

<table>
<thead>
<tr>
<th>Size</th>
<th>7 nm</th>
<th>14 nm</th>
<th>17 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area per NC:$^b$</td>
<td>245 nm$^2$</td>
<td>980 nm$^2$</td>
<td>1445 nm$^2$</td>
</tr>
<tr>
<td>Volume per NC:</td>
<td>343 nm$^3$</td>
<td>2744 nm$^3$</td>
<td>4913 nm$^3$</td>
</tr>
<tr>
<td>$n_{\text{surface Pd atoms}}$$^c$</td>
<td>$2.0 \times 10^{-2}$ mol</td>
<td>$1.0 \times 10^{-7}$ mol</td>
<td>$8.2 \times 10^{-8}$ mol</td>
</tr>
</tbody>
</table>

$^a$ Calculations:
(a) General concepts
1. Since Pd cubes have a face-centered-cubic structure with a lattice constant of 0.39 nm. So, the volume of a unit cell in Pd nanocrystals is \((0.39 \text{ nm})^3 = 0.059 \text{ nm}^3\). Each unit cell contains 4 Pd atoms.

2. A cube with an edge length of \(b\) has a surface area of \(6b^2\) and a volume of \(b^3\). Considering that the Pd nanocubes have one face in contact with TiO\(_2\) nanosheets, the faces of Pd nanocubes which participate in the catalytic reactions are certified to be five. Therefore, the surface area of per Pd nanocube participated in the catalytic reactions is \(5b^2\).

(1) The surface area of per Pd NC-7 participated in the catalytic reactions is \(5b^2 = 5 \times 7^2 = 245 \text{ nm}^2\)

The volume of per Pd NC-7 is \(b^3 = 7^3 = 343 \text{ nm}^3\)

(2) The surface area of per Pd NC-14 participated in the catalytic reactions is \(5b^2 = 5 \times 14^2 = 980 \text{ nm}^2\)

The volume of per Pd NC-14 is \(b^3 = 14^3 = 2744 \text{ nm}^3\)

(3) The surface area of per Pd NC-17 participated in the catalytic reactions is \(5b^2 = 5 \times 17^2 = 1445 \text{ nm}^2\)

The volume of per Pd NC-17 is \(b^3 = 17^3 = 4913 \text{ nm}^3\)

3. Pd cube is enclosed by (100) facets. Each two-dimensional unit cell on the (100) facet contains 2 Pd atoms. The area of this unit cell is \((0.39 \text{ nm})^2 = 0.15 \text{ nm}^2\).

(b) Number of Pd atoms in each cubic Pd nanocrystals

Number of Pd atoms in each cubic Pd nanocrystals = \((\text{volume of each nanocube} / \text{volume of each unit cell}) \times \text{atoms in each unit cell} = b^3 / 0.059 \times 4 = 67.8 b^3\)

(c) Number of Pd atoms on the surface of each cubic Pd nanocrystals participated in the catalytic reactions

Number of Pd atoms on the surface of each cubic Pd nanocrystals participated in the catalytic reactions = \((\text{surface area of each nanocube participated in the catalytic reactions} / \text{surface area of each two-dimensional unit cell on the (100) facet}) \times \text{atoms in each two-dimensional unit cell on the (100) facet} = 5b^2 / 0.15 \times 2 = 66.7 b^2\)

(d) Mole of surface Pd atoms of cubic Pd nanocrystals participated in the catalytic reactions \(n_{\text{surface Pd atoms}}\)

Mole of surface Pd atoms of cubic Pd nanocrystals participated in the catalytic reactions = \((\text{number of Pd atoms on the surface of each cubic Pd nanocrystals participated in the catalytic reactions} / \text{number of Pd atoms in each cubic Pd nanocrystals}) \times \text{mole of cubic Pd nanocrystals} = 66.7 b^2 / 67.8 b^3 \times (15 \times 10^{-5} \text{ g}) / (106.4 \text{ g/mol}) = 1.4 \times 10^{-6} / b \text{ mol}\)
(1) The mole of surface Pd atoms of Pd NC-7 participated in the catalytic reactions is $1.4 \times 10^{-6} / b = 1.4 \times 10^{-6} / 7 = 2.0 \times 10^{-7}$ mol

(2) The mole of surface Pd atoms of Pd NC-14 participated in the catalytic reactions is $1.4 \times 10^{-6} / b = 1.4 \times 10^{-6} / 14 = 1.0 \times 10^{-7}$ mol

(3) The mole of surface Pd atoms of Pd NC-17 participated in the catalytic reactions is $1.4 \times 10^{-6} / b = 1.4 \times 10^{-6} / 17 = 8.2 \times 10^{-8}$ mol

\[b\] The surface area of per Pd nanocube participated in the catalytic reactions;
\[c\] Mole of surface Pd atoms of cubic Pd nanocrystals participated in the catalytic reactions.

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**Fig. S14.** Schematic of dynamics mechanisms followed by the photoexcited charge carriers involved in the TNS (A) and TNS-Pd composites (B)

**Fig. S15.** Time-resolved fluorescence decays of TNS and TNS-Pd composites
Table S4 Fluorescence lifetimes of TNS and TNS-Pd composites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNS</td>
<td>1.3</td>
</tr>
<tr>
<td>TPs</td>
<td>1.42</td>
</tr>
<tr>
<td>TCs-7</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Fig. S16. Illustration of Pd nanocrystals (left) and TPD spectra (right) of TPs (orange), TCs-7 (blue), TCs-14 (red), and TCs-17 (green) at 10 K min⁻¹ heating rate. The colors of the cartoons correspond to the colors of the TPD profiles.

Fig. S17. Photocatalytic H₂ evolution over the TCs-7 composites with different H⁺ ion concentration. Reaction conditions: 15 mg sample in 2 mL ethanol, UV-Vis light (300 nm ≤ λ ≤ 800 nm), reaction time: 4 h, reaction temperature, 298 K.
Table S5 Summarized results on the photocatalytic conversion of ethonal over TCs-7 composites with different H$^+$ ion concentration

<table>
<thead>
<tr>
<th>Samples</th>
<th>Con.$^a$</th>
<th>Sel.$^b$</th>
<th>Y. DEE$^c$ (μmol)</th>
<th>Y. Ald.$^d$ (μmol)</th>
<th>C$\text{H}^+$ (mol L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCs-7</td>
<td>0.7%</td>
<td>22.5%</td>
<td>77</td>
<td>267</td>
<td>0</td>
</tr>
<tr>
<td>TCs-7</td>
<td>4.5%</td>
<td>94.7%</td>
<td>512</td>
<td>29</td>
<td>$0.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>TCs-7</td>
<td>5.0%</td>
<td>92.6%</td>
<td>563</td>
<td>45</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>TCs-7</td>
<td>3.7%</td>
<td>92.0%</td>
<td>394</td>
<td>36</td>
<td>$2 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Reaction conditions: 15 mg sample in 2 mL ethanol, UV-Vis light ($300 \text{ nm} \leq \lambda \leq 800 \text{ nm}$), reaction time: 4 h, reaction temperature, 298 K. $^a$ Con. is short for conversion of ethanol. $^b$ Sel. is short for selectivity of DEE, $^c$ Y. DEE is short for yield of DEE, $^d$ Y. Ald is short for yield of the acetaldehyde, $^e$ concentration of H$^+$ ion.

References:

