Electronic Supporting Information

Decorating geometry- and size-controlled sub-20 nm Pd nanocubes onto 2D TiO_2 nanosheets for simultaneous H_2 evolution and 1,1-diethoxyethane production

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Table S5 Summarized results on the photocatalytic conversion of ethanol over TCs-7 composites with different H^+ ion concentration

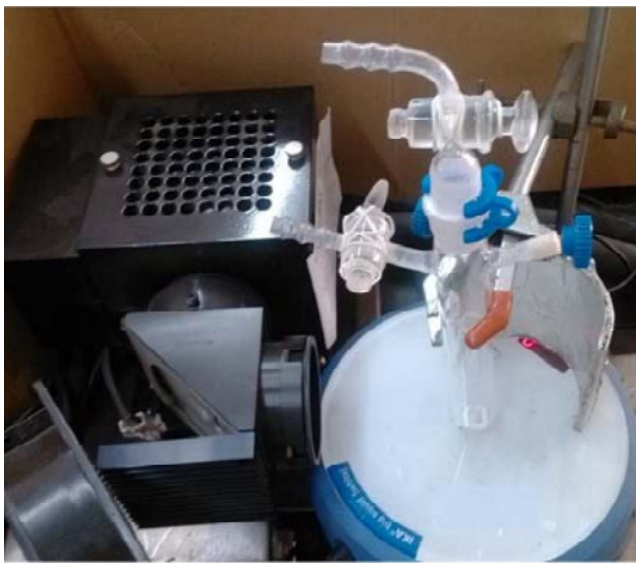


Fig. S1. Photograph of the experimental setup for simultaneous H_2 evolution and DEE production

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

Samples	Size (nm)	KBr (mg)	KCl (mg)	K_2PdCl_4 (mg)	PVP (mg)	AA (mg)
Pd NCs-7	7	5	185	63	105	60
Pd NCs-14	14	400	0	63	105	60
Pd NCs-17	17	600	0	63	105	60

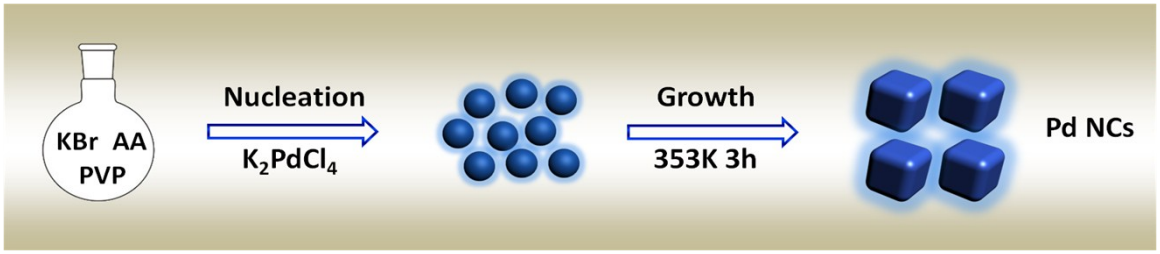
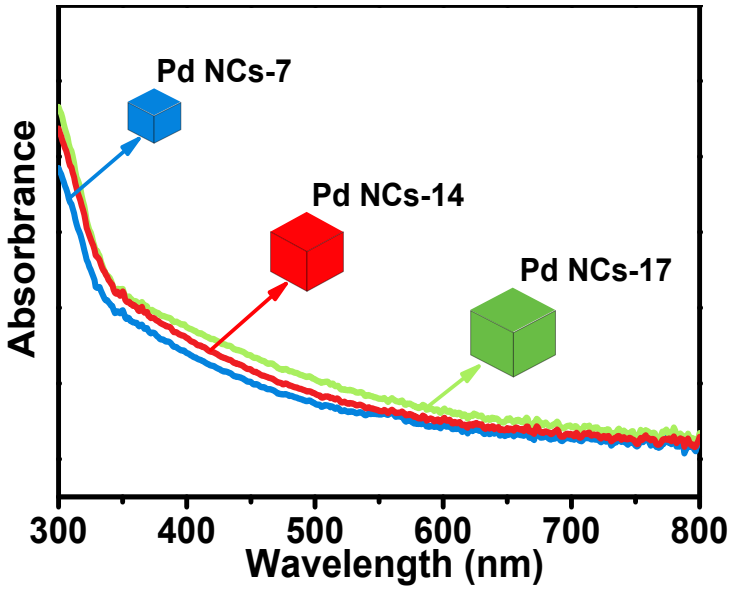


Fig. S2. Overall flowchart for the fabrication of Pd NCs



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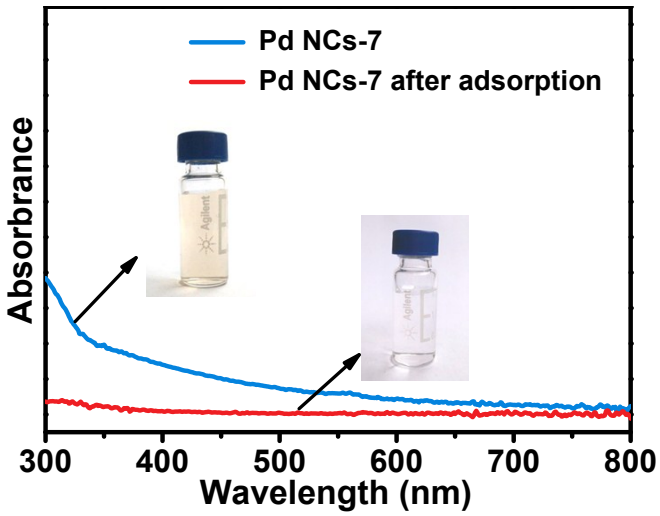

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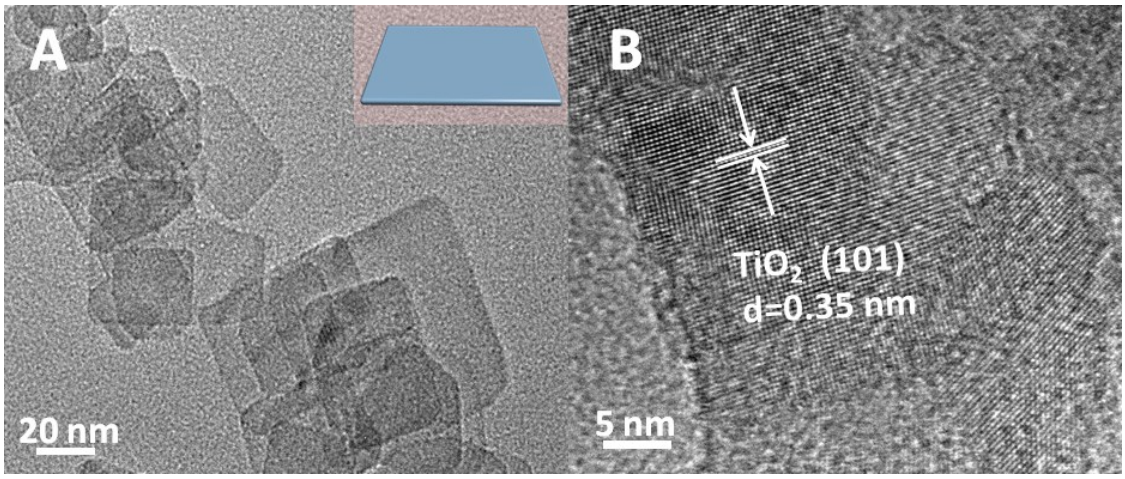

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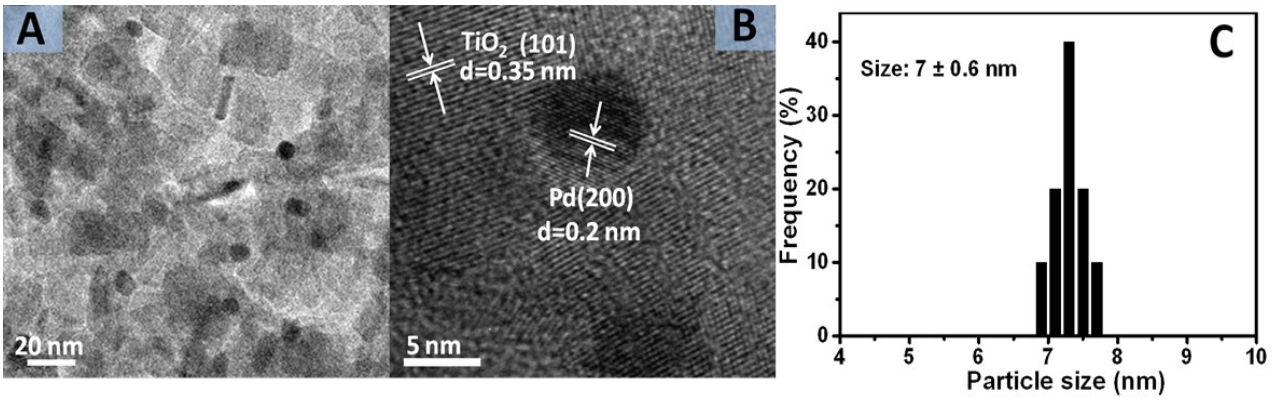

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Table S2. The average crystallite sizes of TiO_2 nanoparticles in TNS, TNS-Pd composites calculated from the (101) and (200) facets diffraction peaks of anatase TiO_2 on the basis of Scherrer formula[a]

Samples	Average crystallite sizes (nm)
TNS	12.8
TPs	12.6
TCs-7	11.1
TCs-14	11.2
TCs-17	11.2

[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, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle.

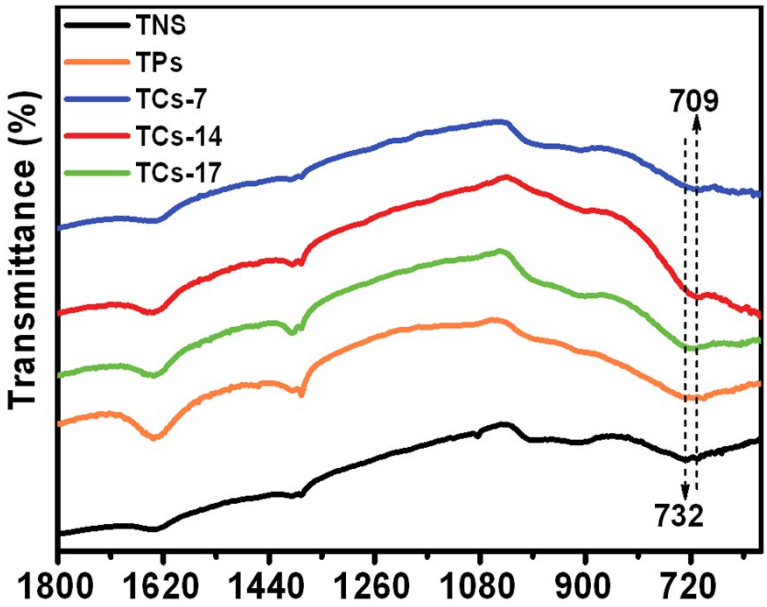


Fig. S7. FT-IR spectra of the TNS and TNS-Pd composites

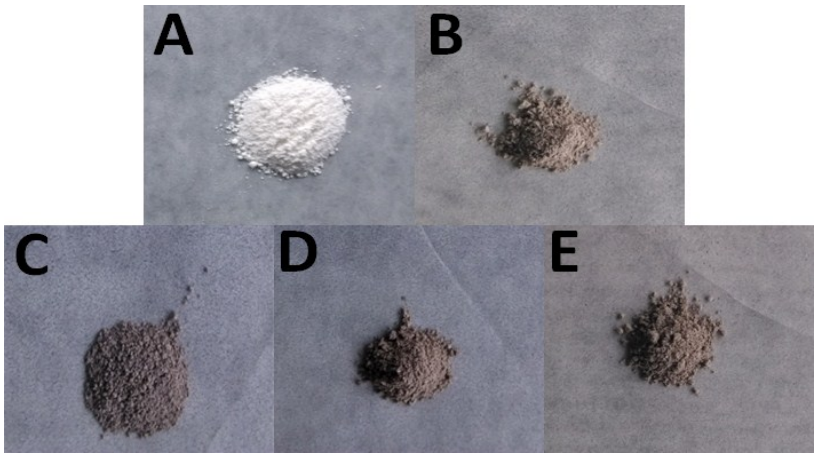


Fig. S8.The digital photographs of TNS (A), TPs (B), TCs-7 (C), TCs-14 (D) and TCs-17 (E)

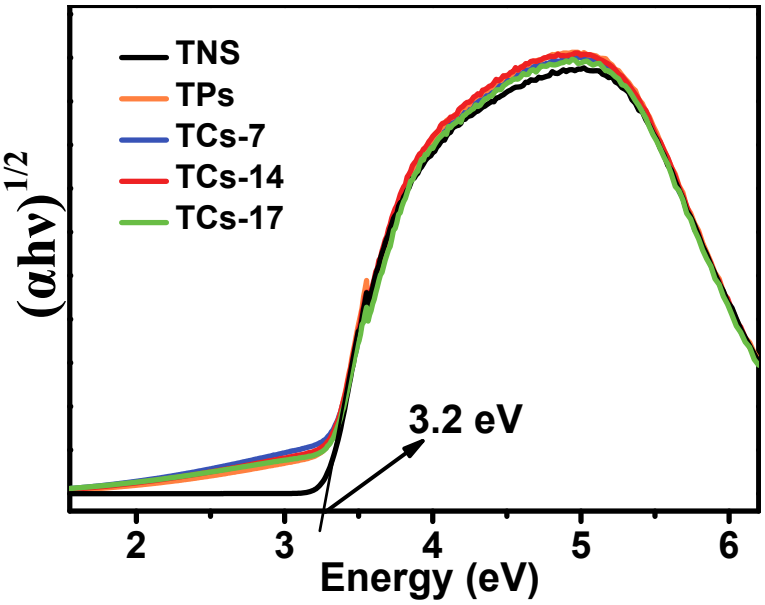


Fig. S9. The plots of transformed Kubelka-Munk function versus the energy of light over the TNS and TNS-Pd composites

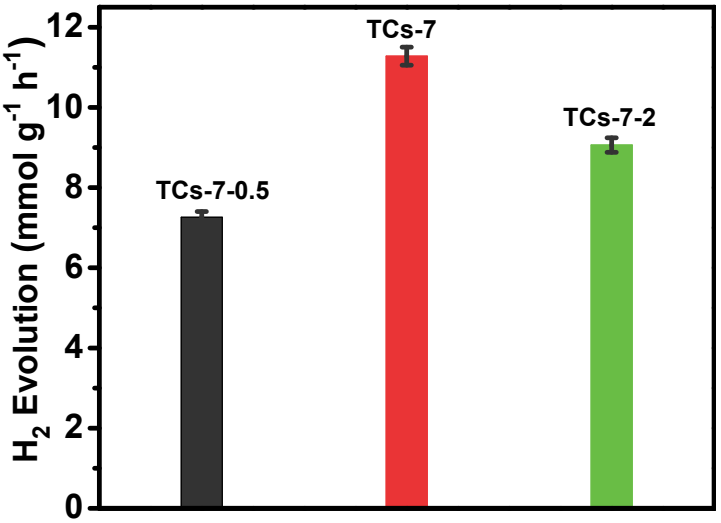


Fig. S10. Photocatalytic H_2 evolution over the TCs-7 composites with different addition amounts of Pd NCs-7. Reaction conditions: 15 mg sample in 2 mL ethanol with H^+ ion concentration of 1×10^{-3} mol L^{-1}, UV-Vis light ($300 \text{ nm} \leq \lambda \leq 800 \text{ nm}$), reaction time: **4 h**, 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.

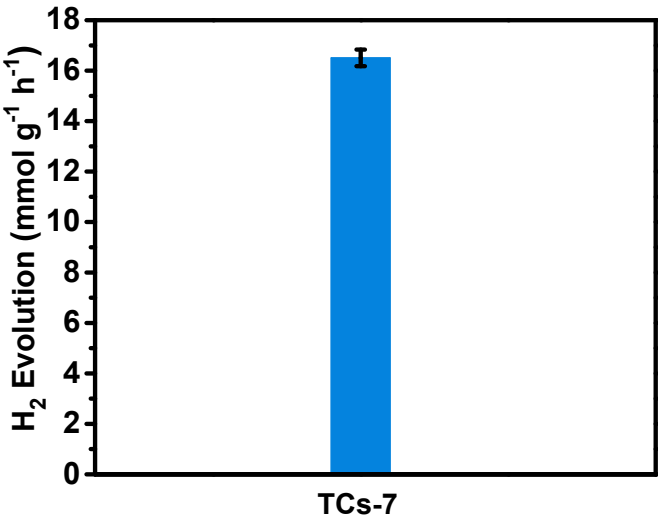


Fig. S11. Photocatalytic H_2 evolution over the TCs-7 composites under UV light (λ = 365 ± 15nm) illumination. Reaction conditions: 15 mg sample in 2 mL ethanol with H^+ ion concentration of 1 × 10^{-3} mol L^{-1}, UV light (λ = 365 ± 15nm), reaction time: 12 h, reaction temperature, 298 K.

Note: **Fig. S11** shows the photocatalytic H_2 evolution under UV light (λ = 365 ± 15nm) 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.

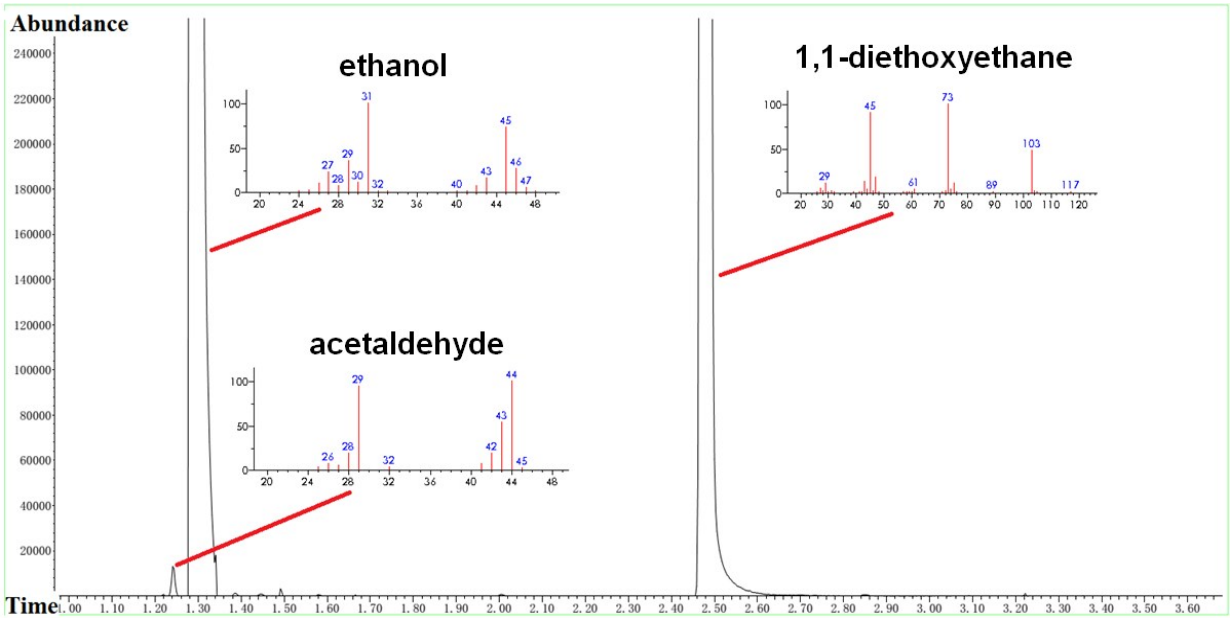


Fig. S12. GC-MS analysis of the products of the photocatalytic conversion of ethanol over TCs-7 composites

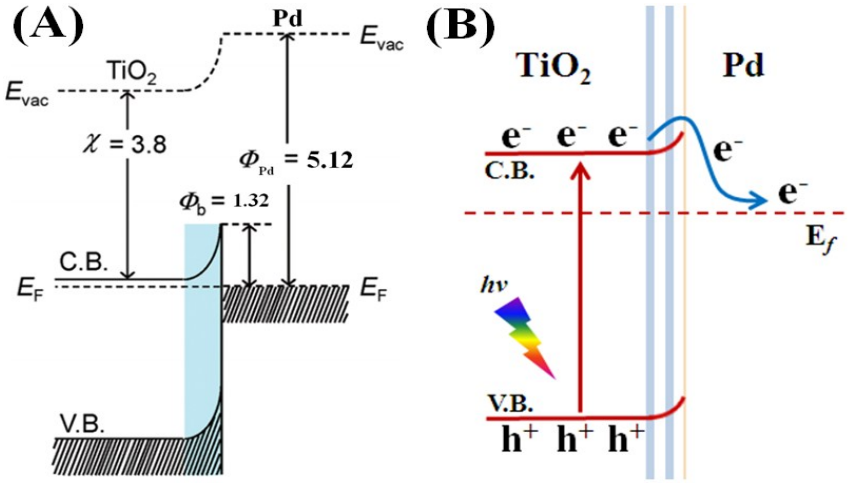


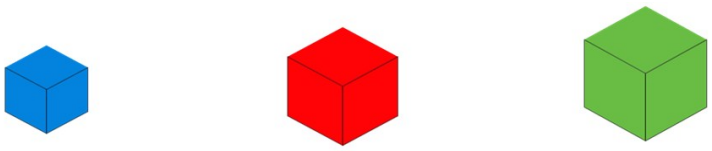
Fig. S13. Schematic energy-band diagram of TiO_2-Pd composites (A) and schematic band diagram illustrating the charge transfer driven by the Schottky junction (B). E_{vac}, E_F, Φ_{Pd}, Φ_b, and χ denote vacuum level, Fermi level, work function of Pd, Schottky barrier height, and electron affinity of 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 (Φ_{Pd}) of Pd (5.12 eV)[S2] and the electron affinity (χ) of TiO_2 conduction band (3.8 eV).[S3] The Schottky barrier height at the TiO_2-Pd junction is determined to be about 1.32 eV according to following equation:[S3]

$$\Phi_b = \Phi_{Pd} - \chi$$

The as-formed Schottky barrier can act as a sink for the photoinduced electrons to inhibit the back-flow 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]



Size:	**7 nm**	**14 nm**	**17 nm**
Area per NC:[b]	**245 nm²**	**980 nm²**	**1445 nm²**
Volume per NC:	**343 nm³**	**2744 nm³**	**4913 nm³**
$n_{surface\ Pd\ atoms}$:[c]	**2.0×10^{-7} mol**	**1.0×10^{-7} mol**	**8.2×10^{-8} mol**

[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 $(0.39\ nm)^3 = 0.059\ nm^3$. 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 $5b^2 = 5 \times 7^2 = 245\ nm^2$

The volume of per Pd NC-7 is $b^3 = 7^3 = 343\ nm^3$

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

The volume of per Pd NC-14 is $b^3 = 14^3 = 2744\ nm^3$

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

The volume of per Pd NC-17 is $b^3 = 17^3 = 4913\ nm^3$

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 $(0.39\ nm)^2 = 0.15\ nm^2$.

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

Number of Pd atoms in each cubic Pd nanocrystals = (volume of each nanocube / volume of each unit cell) ×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 = (surface area of each nanocube participated in the catalytic reactions / surface area of each two-dimensional unit cell on the (100) facet) × 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 = (number of Pd atoms on the surface of each cubic Pd nanocrystals participated in the catalytic reactions / number of Pd atoms in each cubic Pd nanocrystals) × mole of cubic Pd nanocrystals = $66.7\ b^2 / 67.8\ b^3 \times (15 \times 10^{-5}\ g) / (106.4\ g/mol) = 1.4 \times 10^{-6} / b\ mol$

(1) The mole of surface Pd atoms of Pd NC-7 participated in the catalytic reactions is 1.4×10^{-6} / b = 1.4×10^{-6} / 7 = 2.0×10^{-7} mol

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

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

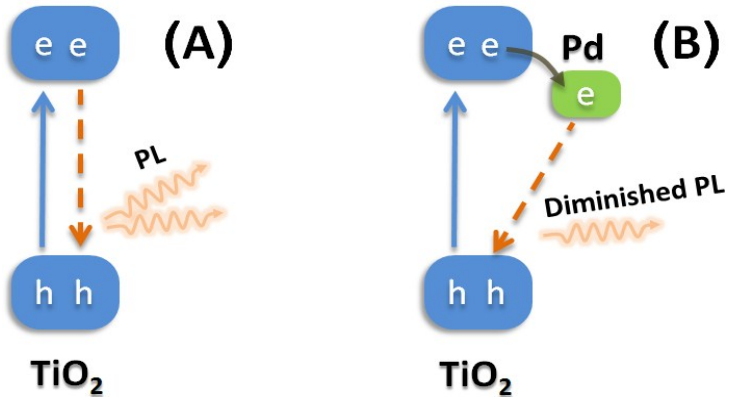


Fig. S14. Schematic of dynamics mechanisms followed by the photoexcited charge carriers involved in the TNS (A) and TNS-Pd composites (B)

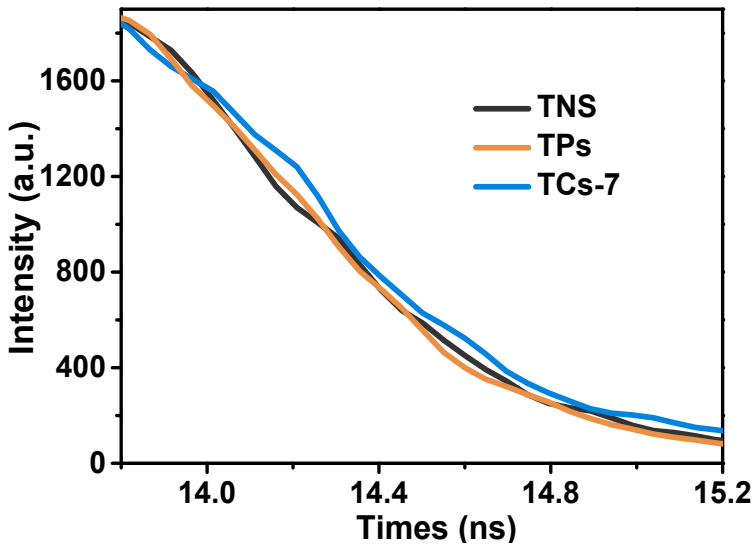
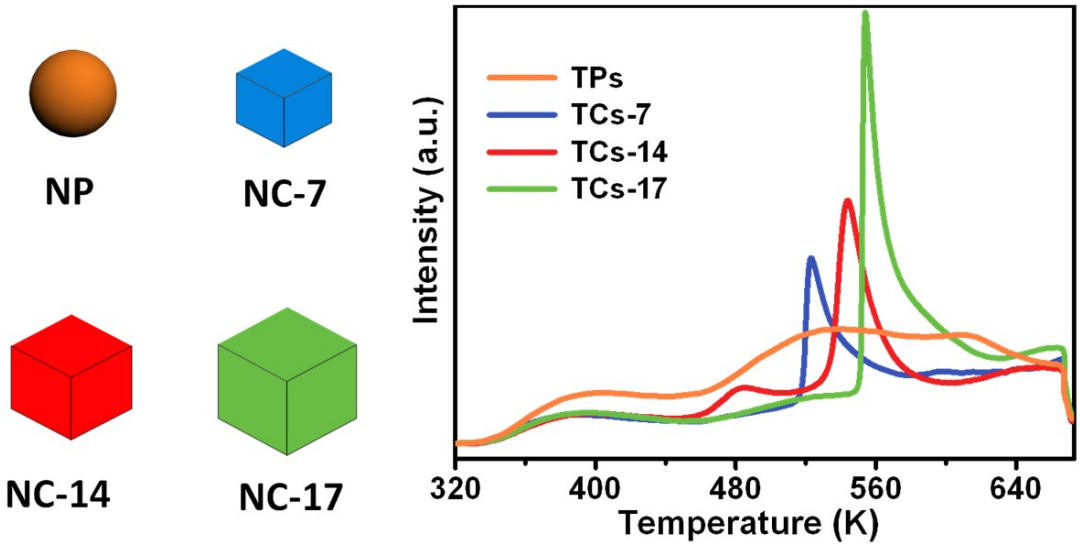


Fig. S15. Time-resolved fluorescence decays of TNS and TNS-Pd composites

Table S4 Fluorescence lifetimes of TNS and TNS-Pd composites

Samples	Lifetime (ns)
TNS	1.3
TPs	1.42
TCs-7	1.53



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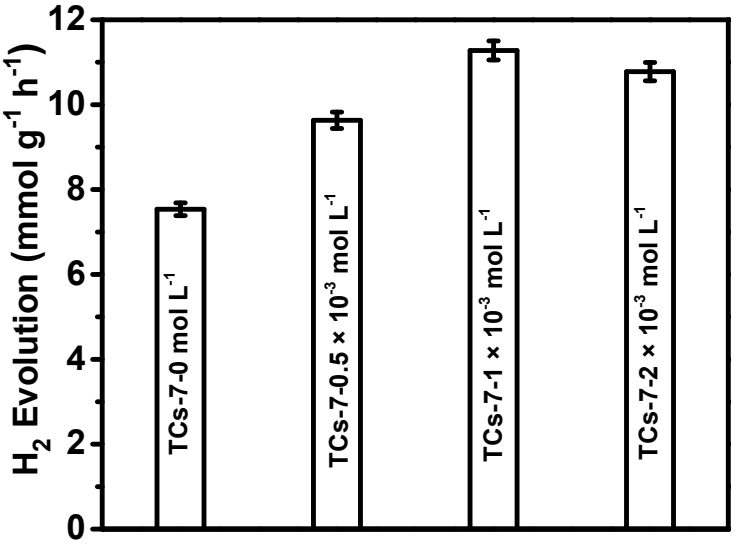

Fig. S17. Photocatalytic H_2 evolution over the TCs-7 composites with different H^+ ion concentration. Reaction conditions: 15 mg sample in 2 mL ethanol, UV-Vis light (300 nm ≤ λ ≤ 800 nm), reaction time: **4 h**, reaction temperature, 298 K.

Table S5 Summarized results on the photocatalytic conversion of ethonal over TCs-7 composites with different H^+ ion concentration

Samples	Con.[a]	Sel.[b]	Y. DEE[c] (μmol)	Y. Ald.[d] (μmol)	C_H[e] (mol L^{-1})
TCs-7	0.7%	22.5%	77	267	0
TCs-7	4.5%	94.7%	512	29	0.5×10^{-3}
TCs-7	5.0%	92.6%	563	45	1×10^{-3}
TCs-7	3.7%	92.0%	394	36	2×10^{-3}

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. [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:

(S1) N. Zhang, C. Han, Y.-J. Xu, J. J. Foley Iv, D. Zhang, J. Codrington, S. K. Gray, Y. Sun, *Nat. Photon.* 2016, **10**, 473-482.

(S2) A. C. Schmitz, A. T. Ping, M. A. Khan, Q. Chen, J. W. Yang, I. Adesida, *Semicond. Sci. Tech.* 1996, **11**, 1464-1467.

(S3) D. Tsukamoto, A. Shiro, Y. Shiraishi, Y. Sugano, S. Ichikawa, S. Tanaka, T. Hirai, *ACS Catal.* 2012, **2**, 599-603.