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

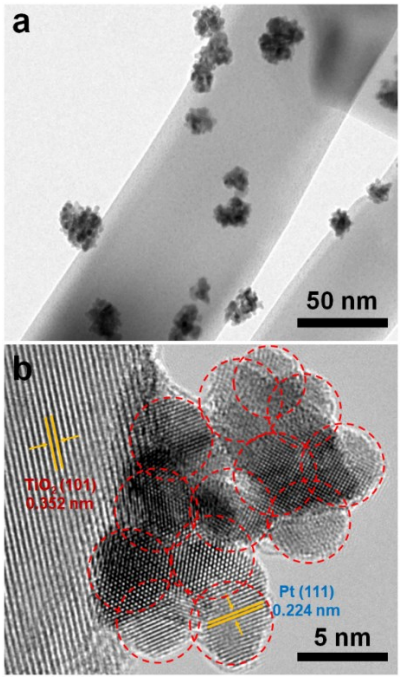

Figure S1. TEM (a) and HRTEM (b) images of Pt-NPs/TiO_2. By using $NaBH_4$ in aqueous solution to reduce Pt precursor, the obtained reduced Pt tends to aggregate to large nanoparticles. The large particles are composed of primary particles with a diameter of about 3.9 nm.

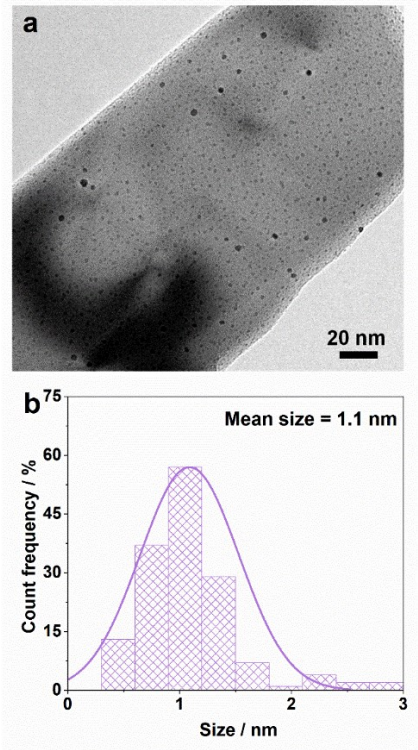

Figure S2. (a) TEM image of Pt-NCs/TiO_2. (b) Histograms of Pt clusters size distribution of Pt-NCs/TiO_2.

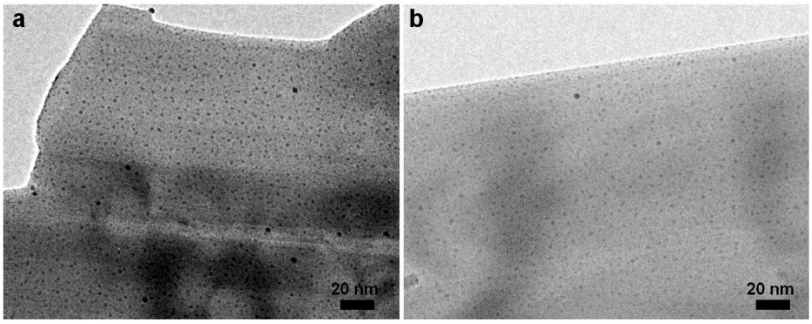

Figure S3. TEM images of the catalysts with Pt loading amount of (a) 0.5 wt.% and (b) 0.1 wt.% after treated in 10 vol.% H_2/Ar atmosphere at 700 °C.

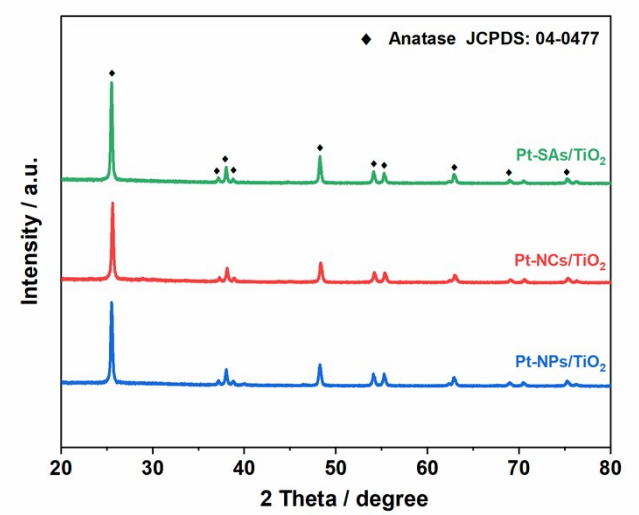

Figure S4. XRD patterns of Pt-NPs/TiO_2, Pt-NCs/TiO_2 and Pt-SAs/TiO_2. New peaks that can be attributed to the rutile TiO_2 phase can not be found, indicating that no phase transition would occur at the treatment temperature in this experiment.

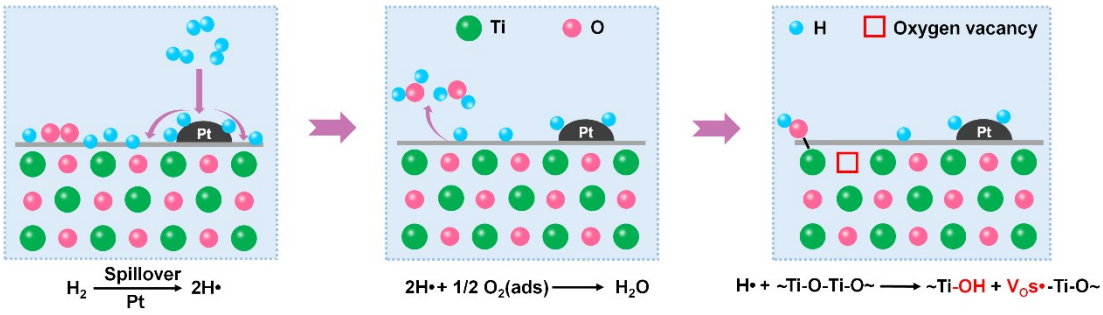

Figure S5. Schematic illustration of the formation of Ti-OH and oxygen vacancy with the assistance of hydrogen spillover effect.

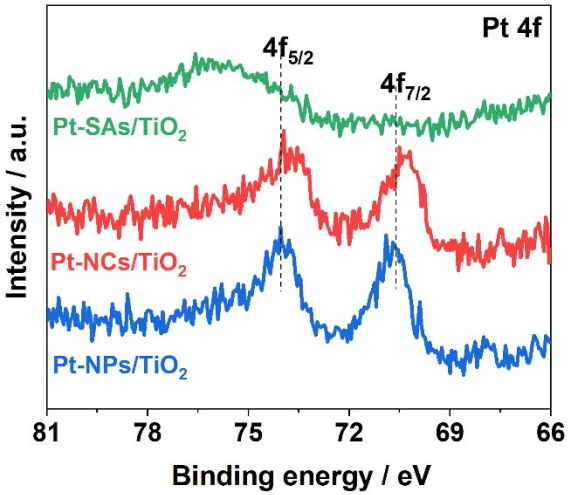

Figure S6. Pt 4f XPS spectra of the catalysts.

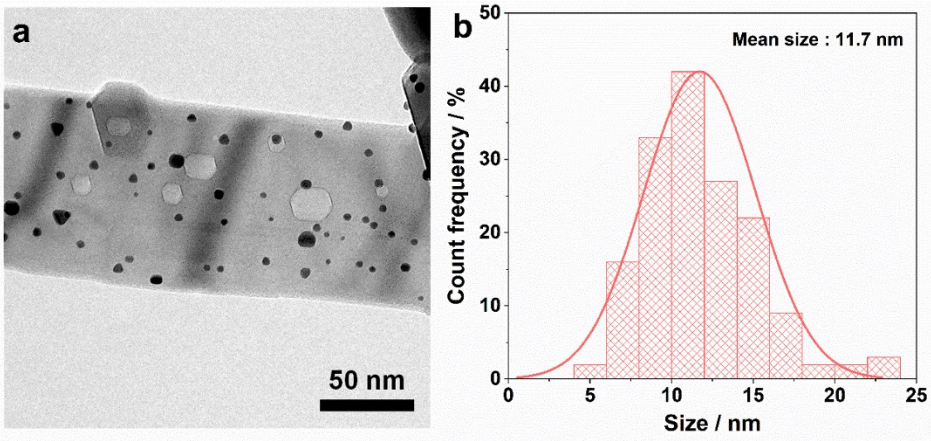

Figure S7. (a) TEM image of Pt-NPs/TiO_2 after the treatment in N_2 atmosphere at 700 °C for 5 h. (b) Histograms of Pt particle size distribution of the catalyst in (a).

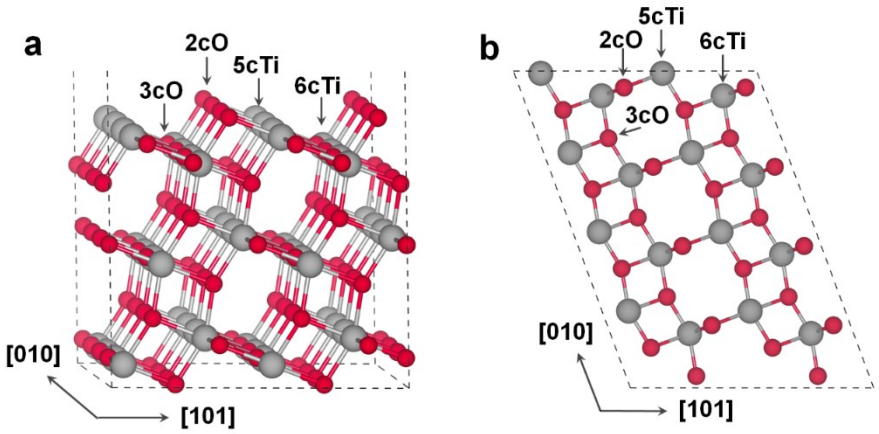

Figure S8. (a) Side and (b) top views of anatase TiO_2(101) surface. The red means O atom and the grey means Ti atom.

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.

Samples	B.E. O (eV)		P.A. (Counts)		O_{OH}/O_L
	O_L	O_{OH}	O_L	O_{OH}	
Pt-NPs/TiO_2	529.7	531.5	10486	726	0.07
Pt-NCs/TiO_2	529.8	531.3	8604	4152	0.48
Pt-SAs/TiO_2	529.8	531.0	9512	4646	0.49

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