Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Photochromic Nano-system *via* Self-recovery for Stable Photocatalytic Hydrogen Evolution by Optimizing TiO_2 Surface Energy

Jinghui Jiang,[a] Liping Tong, [a] Han Zhou, [a] Fan Zhang, [a] Jian Ding, [a] Di Zhang,[a] Tongxiang Fan [a, *]

State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University, Dongchuan Road 800, Shanghai 200240, P. R. China

1) The fitting analyses for XPS high-resolution spectrum of Cu2p and Ti2p in TPN

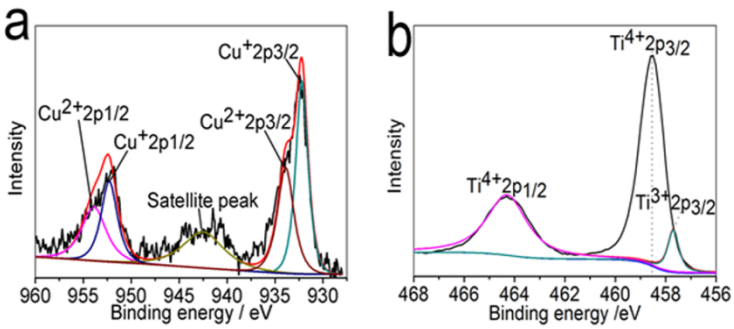

Figure S1. a) and b) are the fitting analyses for XPS high-resolution spectrum of Cu2p and Ti2p in TPN, respectively.

2) ***Table S1.*** Atomic concentration percentage (At %) of components in TPN analyzed by XPS

Samples	Ti 2p	Cu 2p	Ag 3d	Br 3d	O 1s
Pristine	25.92	3.62	0.37	0.27	57.78
Unrecovered	23.97	2.63	1.09	0	56.43
Recovered	21.59	3.31	0.30	0.18	51.44

3) ESR and UV-Vis analyses for as-prepared samples

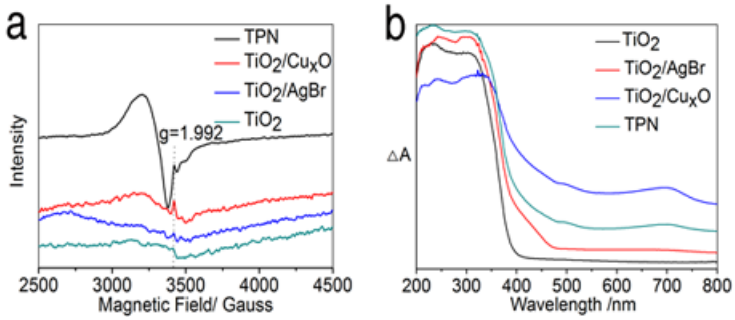

Figure S2. a) ESR (X-band) spectra for four degassed titania-based photocatalysts in 20 % methanol solution measured at 100 K without light irradiation; b) UV-Vis analyses for four as-prepared samples

4) XRD analysis for unrecovered TPN

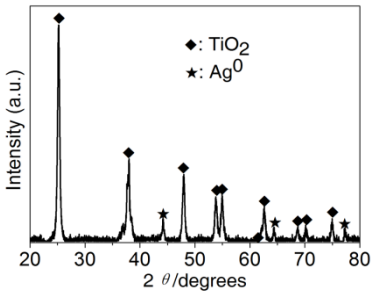

Figure S3. The XRD pattern of unrecovered TPN

6) **The fitting analyses for the XPS high-resolution spectra of Cu2p in TPN**

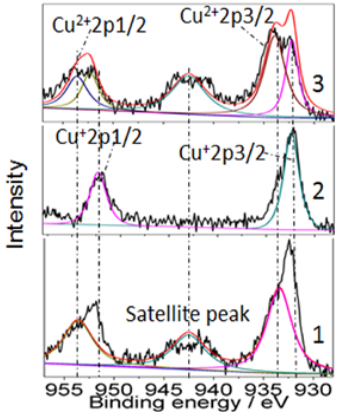

Figure S4. 1, 2, and 3 represent the corresponding valences of Cu2p in pristine, unrecovered, and recovered TPN, respectively.

7) Measurement and calculation of quantum yield

Quantum yield was measured and calculated according to previous methods [3]. The wavelength of 340 nm filter was used throughout the photocatalytic hydrogen evolution and the irradiation of iron (III) potassium oxalate trihydrate (IPOT) to get rid of other wavelength's incident light.

Table S2. The absorbances (ΔA) at 510 nm wavelength for three IPOT samples via 340 nm light irradiation for 60 s and three IPOT samples without light irradiation

Experiment	$\Delta A1$	$\Delta A2$	$\Delta A3$	Average ($\Delta \bar{A}$)
Irradiated IPOT	0.8516	0.9082	0.9477	0.9025
IPOT without irradiation	0.0194	0.0186	0.0210	0.0197

Table S3. Photochemical hydrogen evolution in 20% methanol (aq) under 340 nm UV irradiation for 5 h

Experiment	Total H_2 produced (μmol)	H_2 produced (μmol h^{-1})	Quantum yield [%]
TPN	1.472	0.290	14.3

8) Microstructure analysis for TPN from photodeposition of Pt nanoparticles

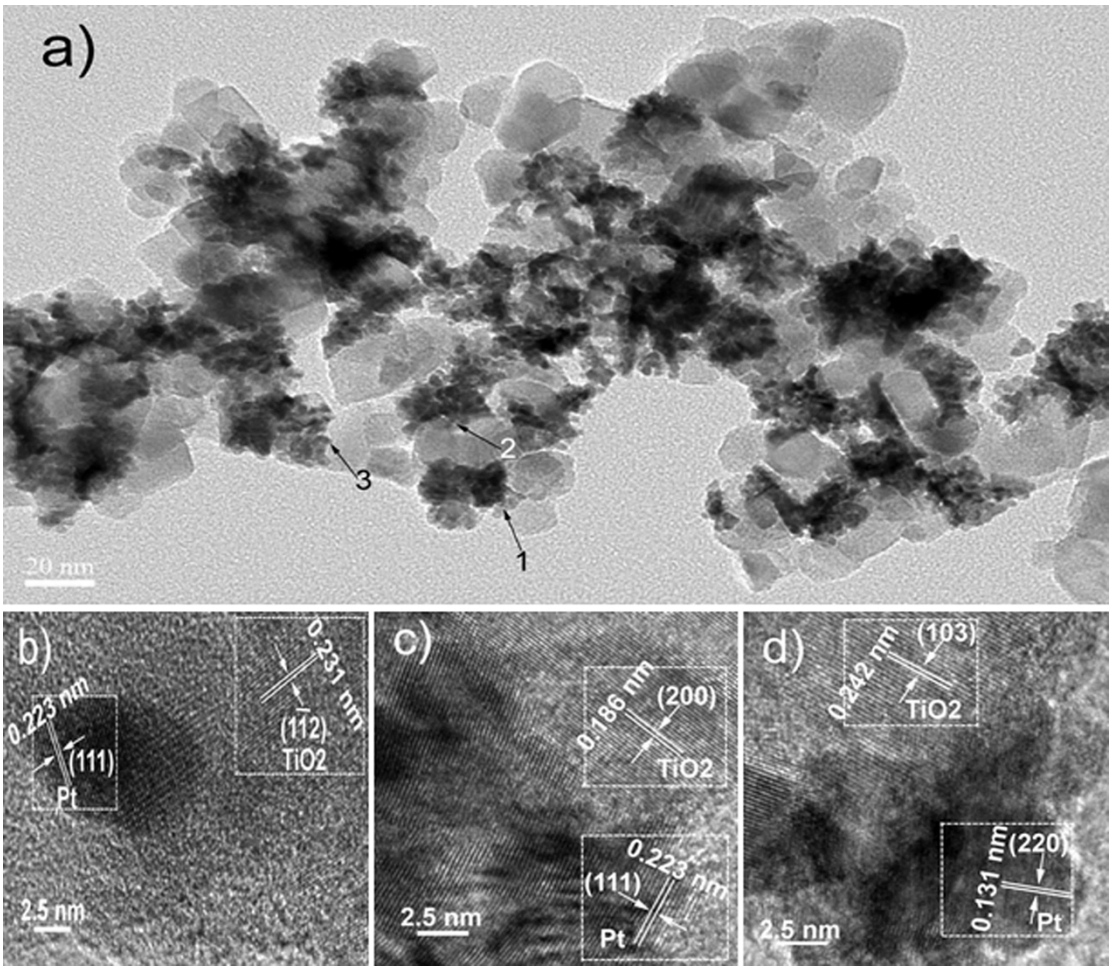

Figure S5. a) the TEM image of TPN via photodeposition of Pt; b), c), and d) the HRTEM images of interfaces between TPN and Pt taking from the zones of 1, 2, and 3 in a) as shown by arrows, respectively.

9) Calculation of surface energy

We used the first-principles density functional theory (DFT) calculations for the chemisorption of Br_2 on TiO_2 (101) surface. The calculations performed in this study were done using the CASTEP of Materials studio. This program evaluates the total energy of periodically repeating geometries based on density-functional theory and the pseudopotential approximation[1]. The calculations have been done using the spin-polarized Perdew-Wang 91 (PW91) generalized gradient approximation (GGA) exchange-correlation functional[2]. In all our calculations we have used a cutoff energy of 340 eV and the k-point of $1\times2\times1$. In order to investigate the influence of Br_2 adsorption position on chemisorption energy, we imitate a Br_2 binding on different sites of (101) TiO_2 facet (see Figure 4). According to the imitation results, we calculate the chemisorption energy (ΔE_{chem}) of different Br_2 adsorption sites with following formula:

$$\Delta E_{chem} = 1/4E_{Br2\ on\ (2\times2\times1)\ TiO2\ (101)} - [1/4E_{(2\times2\times1)\ TiO2\ (101)} + E_{Br2}]$$

Table S4. Chemisorption energy of Br_2 adsorbing on different sites of (101) TiO_2 facet corresponding to Figure 4

No.	E_{Br2}	$1/4E_{(2\times2\times1)\ TiO2\ (101)}$	$1/4E_{Br2\ on\ (2\times2\times1)\ TiO2\ (101)}$	ΔE_{chem}
a	-7.31392157×10^{2} eV	-0.24811834×10^{3} eV	-1.01082502×10^{4} eV	-0.68956747×10^{4} eV
b	-7.31392157×10^{2} eV	-0.24811834×10^{3} eV	-1.01080712×10^{4} eV	-0.68954956×10^{4} eV
c	-7.31392157×10^{2} eV	-0.24811834×10^{3} eV	-1.01082952×10^{4} eV	-0.68957197×10^{4} eV
d	-7.31392157×10^{2} eV	-0.24811834×10^{3} eV	-1.01096484×10^{4} eV	-0.68970729×10^{4} eV
e	-7.31392157×10^{2} eV	-0.24811834×10^{3} eV	-1.0107158×10^{4} eV	-0.68945832×10^{4} eV

Reference

1 D. C. Sorescu, J. T. Yates, Jr. *J. Phys. Chem. B*. **2002**, *106*, 6184-6199

2 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pedersen, D. J. Singh, C. Frolhais, *Phys. Rev*. **1992**, *22*, 6671-6687.

3 H. J. Kuhn, S. E. Braslavsky, R. Schmidt, *Pure Appl. Chem*. **2004**, *76*, 2105-2146.