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Supporting Information

Achieving overall water splitting using titanium dioxide-based photocatalysts of different phases

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Sample preparation.

Anatase TiO_2 was prepared by a hydrothermal method.[1] 15 mL of titanium isopropoxide as Ti source and the desired volumes (1.0 mL, 1.5 mL) of HCl (37.0 %) were mixed in a Teflon-lined 100 mL autoclave at room temperature and then kept at 453 K for 36 hours. After reaction, the autoclave was cooled to room temperature; the resulting white precipitates were separated by centrifugal method (15000 r/min, 5min) and washed with H_2O for 5 times. The final products were dried in an oven at 353 K overnight. The as-prepared samples are anatase phase (denoted as A1 and A2).

Rutile TiO_2 was prepared as the similar method with anatase TiO_2, just by tuning the different amount of HCl reagent (2.0 mL, 2.5 mL, and 6 mL) . The as-prepared samples are rutile phase (denoted as R1, R2 and R3).

Brookite TiO_2 was prepared by hydrothermal method as reported.[2] In a typical synthesis, 1.65 mL of $TiCl_4$ was added dropwise into 60 mL deionized water, which was filled in a Teflon autoclave as cooled by an ice-water bath. After sufficient stirring, an acidic solution that contains a hydrosoluble titanium complex was formed. Subsequently, 5.0 g of urea was mixed and dissolved in this solution with agitation. Finally, 5.0 mL of sodium lactate liquor (60%) was dropped in the mixed solution while stirring for 30 min. The autoclave was sealed and heated in an oven at 473 K for 12 hours. After reaction, a white product was separated, washed respectively with ethanol and deionized water for 5 times, and dried in an oven at 353 K (denoted as B1).

Commercial rutile TiO_2 was purchased from Shanghai st-nano Science and Technology Company, commercial anatase TiO_2 was supplied by Alfa Aesar Company.

The TiO_2 film electrodes were prepared by doctor-blade technique on FTO substrate (1×2 cm^2) according to the references.[3-5] Grinding 100 mg TiO_2 powders with 0.2 mL of water containing 0.1 mL acetylacetone produces a viscous paste. Finally, 1 drop of Triton X-100 was added and the paste is smeared on a glass substrate immobilized by an adhesive tape strip, which determines the film thickness. After drying at room temperature, the film is annealed in an oven at 373 K for 2 hours.

Characterizations.

The as-prepared samples were characterized by X-ray powder diffraction (XRD) on a Rigaku D/Max-2500/PC powder diffractometer. The sample powder was scanned using Cu-Kα radiation with an operating voltage of 40 kV and current of 200 mA. The scan rate of 5°/min was applied to record the patterns in the range of 20-60° at a step size of 0.02°. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG ESCALAB MK2 spectrometer with monochromatized Al-Kα excitation, and the C 1s peak (284.8 eV) was used as reference. The morphologies and particle sizes were examined by scanning electron microscopy taken with a Quanta 200 FEG scanning electron microscope. HRTEM micrographs were taken on a FEI Tecnai G^2 F30 transmission electron microscope. SEM images were collected on a field emission scanning electron microscopy (FE-SEM, Quanta 200 FEG). Raman scattering measurements were recorded on a scanning double monochromator (Jobin–Yvon U1000) with a spectral resolution of 4 cm^{-1} and a 532 nm single-frequency laser (DPSS 532 Model 200) was used as the excitation source. The emission spectrum of Xe lamp was characterized by a commercial spectral radiometer, AvaSolar (Serialnr: S1101239U1, Grating: UA, 200-1100 nm. Option: Slit-50, OSC-UA. Software: AvaSolar Avasoft-full irrad.).

Electron paramagnetic resonance (EPR) of radicals trapped by 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) was recorded on a Brucker EPR A200 spectrometer. The samples containing 0.1 mg/mL TiO_2 (Anatase and Rutile) and 0.05 M DMPO were vacuumed following by ventilated with argon for 3 times. After that, the samples were introduced into home-made quartz cup inside the microwave cavity and illuminated with a 100 W Hg lamp. The distance between the sample and the lamp was fixed to 1.5 m. The settings for the EPR spectrometer were as follows: center field, 3486.70 G; sweep width, 100 G; microwave frequency, 9.82 GHz; modulation frequency, 200 kHz; power, 20.00 mW. Magnetic parameters of the radicals detected were obtained from direct measurements of magnetic field and microwave frequency.

Photo-induced carrier dynamics of TiO_2 films were measured using transient absorption spectroscopy on the μs-s timescale at room temperature. The TAS apparatus has been described in detail elsewhere.[6] Briefly, a 75 W Xe lamp and an Nd:YAG laser (355 nm, 6 ns pulse width) was used as a probe and pump beam, respectively. The change in transmitted light was detected by a Si PIN photodiode. Reasonably low laser intensity was used (~300 μJ cm^{-2} $pulse^{-1}$). Each TAS trace is the result of averaging between 50-500 scans.

Details of the setup for time-resolved infrared absorption-excitation scanning spectrum (TRIRA-ESS) can be seen as reported.[7, 8] Briefly, a quantum cascade laser continuously tunable from 4.69 to 4.88 μm, (TLC-21045, Daylight Solutions) was used as the mid-IR probe light, while 355 nm laser pulses from a Nd:YAG laser (Quanta Ray, Spectra Physics) with a pulse duration of 10 ns and a repetition rate of 10 Hz were used to pump an optical parametric oscillator (GWU premiScan-ULD/240, Spectra Physics) which acts as a wavelength-scanning excitation source (output signal beam tunable from 410 to 709 nm, and idler beam from 710 to 2630 nm) to excite the midgap states. A continuous working He-Cd UV-laser with an output wavelength of 325 nm (IK3301R-G, Japan) was used for UV-light irradiation of the film sample, the irradiation time was fixed to 3.5 hours. TIRA-ESS for TiO_2 probed at 2090 cm^{-1} at a delay time of 250 ns after the excitation pulse in a chamber with a vacuum of 1.0×10^{-6} mbar. The excitation energy is 0.5 mJ/pulse with a beam size of 4 mm in diameter, and the IR absorbance has been scaled by the excitation intensity in terms of the number of photons (10^{12} per pulse) The scanning excitation energy was converted to the midgap energy with the known bandgap for anatase TiO_2 of 3.2 eV, and setting the flat band of the VB as the reference point at which the midgap energy is set as zero eV.

The Mott-Schottky tests were conducted with an electrochemical work station (2273, Princeton) and a conventional three-electrode system. The single phase TiO_2 electrode, a saturated calomel electrode (SCE) and platinum plate were used as working, reference and counter electrodes, respectively; 0.5 M Na_2SO_4 aqueous solution (pH 6.8) was used as electrolyte. Mott-Schottky plots were evaluated at DC potential range of -0.2~ 0.2 V vs. RHE at a frequency of 1 kHz in dark.

Evaluation of photocatalytic water splitting.

The photocatalytic water splitting reaction was carried out in a closed gas circulation and evacuation system using a 300 W Xe lamp (R300-3J), the light intensity was tuned by changing the electricity of the lamp. The light intensity in the center of irradiation area was fixed to 1000 mW/cm^2. Normally, 50 mg photocatalyst was dispersed in 150 mL de-ionized H_2O in a Pyrex reaction cell. Before irradiation, the reaction system was thoroughly degassed by evacuation in order to drive off the air inside. 0.2wt% Pt was deposited as cocatalyst by in-situ photodeposition method before the reaction. The amount of evolved H_2 and O_2 was determined by an on-line gas chromatograph (Agilent, GC-7890, TCD, Ar carrier). Photocatalytic H_2 or O_2 production was carried out similarly to water splitting reaction, only changing the reaction solution to 10% CH_3OH-H_2O or 0.02 M $AgNO_3$ solution.

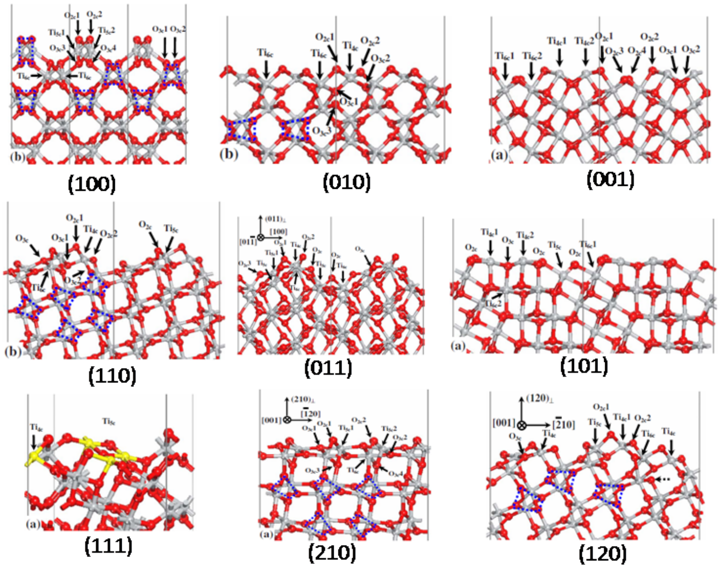
Computational Method

All the calculations were performed with the Vienna ab initio simulation package (VASP)[9, 10] and projector augmented wave (PAW) method.[11,12] The wave function was expanded by plane wave with kinetic cutoff of 400 eV. The generalized gradient approximation (GGA) with the spin-polarized Perdew-Burke-Ernzerhof (PBE) functional[13] was used for all of the calculations. For bulk TiO_2, calculated lattice parameters are in good agreement with experimental values (in parentheses): a = 4.605 Å (4.593 Å) and c = 2.963 Å (2.958 Å) for rutile, a = 3.802 Å (3.782 Å) and c = 9.490 Å (9.502 Å) for anatase.[14] Rutile TiO_2 (110) surface cleaved from bulk TiO_2 is a 5.91×13.03 Å^2 supercell, which contains four TiO_2 trilayers, while anatase TiO_2 (101) slab has three TiO_2 trilayers with an exposed surface area of 10.22×11.41 Å^2. The top half of slab and the adsorbed clusters are allowed to fully relax and the bottom half of slab is held fixed. The slabs are set by a 15 Å vacuum layer. The Monkhorst-Pack scheme was used for k-point with a (2×2×1) sampling grid for rutile TiO_2 (110) surface and a (4×2×1) sampling grid for anatase TiO_2 (101) surface. Structures were relaxed until all forces on atoms were less than 0.01 eV/Å. Transition states (TSs) were located by force reversed method.[15]

Adsorption energies are calculated by the following equation:

$$E_{\text{ads}} = E_{\text{surf}} - E_{\text{water}} - E_{\text{total}}$$

where E_{surf} is the energy of bare surface, E_{water} is the energy of free water molecule, and E_{total} is the total energy of water adsorbed the surface. A positive adsorption energy signifies that water adsorption is stable.



(100) (010) (001)

(110) (011) (101)

(111) (210) (120)

Figure S1. The structure of the relaxed stoichiometric for different exposed surfaces of Brookite TiO_2.

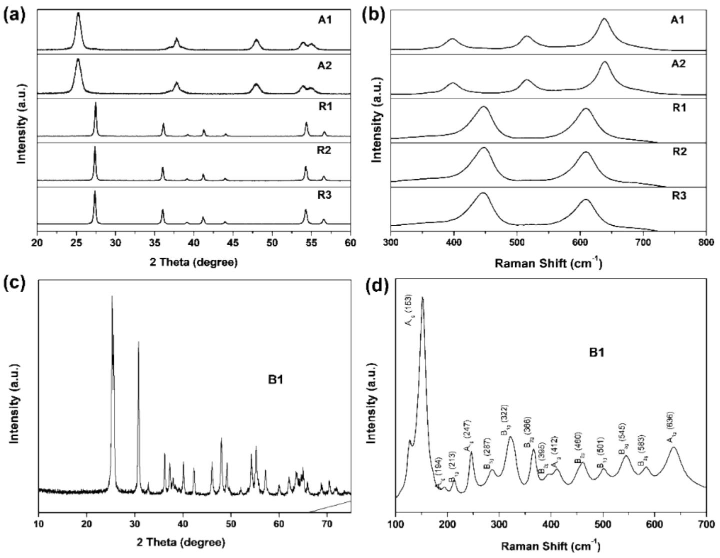


Figure S2. XRD patterns and Raman spectra for TiO_2 with different phases. (a)XRD patterns of A1-A2 and R1-R3 samples, (b) XRD patterns of B1 sample, (a) Raman shifts of A1-A2 and R1-R3 samples and (d) Raman shift of B1 sample.

All the samples are well-crystallized and all three TiO_2 samples are in good agreement with standard sample cards (anatase, PDF card: 21-1272; rutile, PDF card: 21-1276; brookite, PDF card: 29-1360). The Raman shifts of 397 cm^{-1}, 516 cm^{-1} and 639 cm^{-1} are well matched with anatase TiO_2, and rutile phase was confirmed with the Raman shifts of 447 cm^{-1} and 609 cm^{-1}. A rich scenario of Raman peaks was observed at 126.3, 152.3, 171.5, 194.1, 213.3, 246.5, 286.9, 321.1, 365.6, 395.5, 411.9, 454.1, 461.5, 501.8, 545.1, 585.1, and 636.2 cm^{-1}, which show the distinctive characteristic for brookite phase.

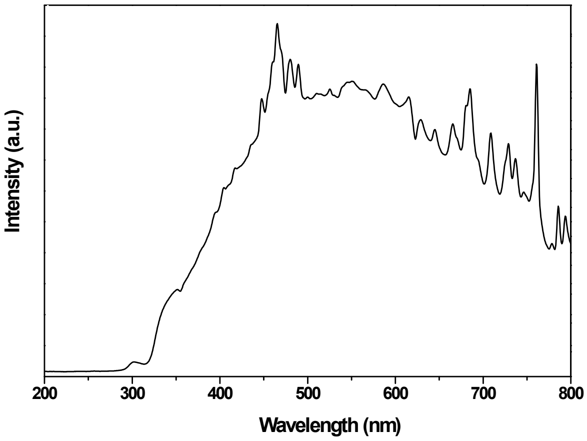


Figure S3: The spectrum of the Xe lamp (300 W, R300-3J). The electric current of lamp was set to 20 A in the experiment, the light intensity of Xe lamp was measured to be 1000 mA/cm^2.

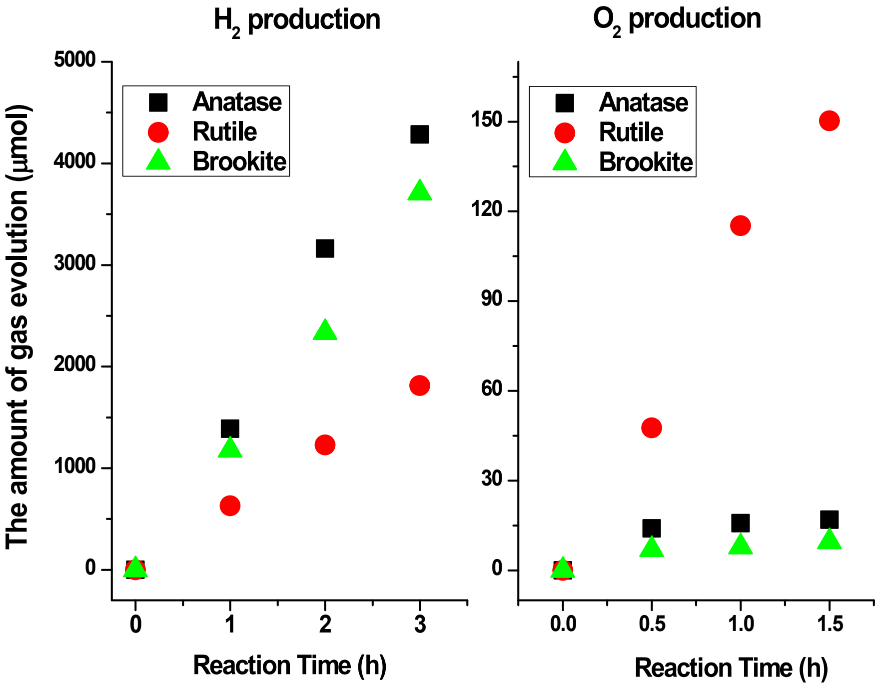


Figure S4. The photocatalytic H_2 and O_2 production performances of different phases TiO_2 in the presence of CH_3OH and $AgNO_3$. (a) H_2 production reaction using CH_3OH as hole acceptor and (b) O_2 evolution reaction using $AgNO_3$ as electron acceptor. Reaction condition: (a) 50 mg Cat., 150 ml 20% CH_3OH solution, 0.2wt% Pt was deposited by in-situ photo-deposition method, 300 W Xe lamp as light source. (b) 50 mg Cat., 150 ml 0.02 M $AgNO_3$ solution, 300 W Xe lamp as light source. A2, R3 and B1 samples in Table 1 were used in this experiment.

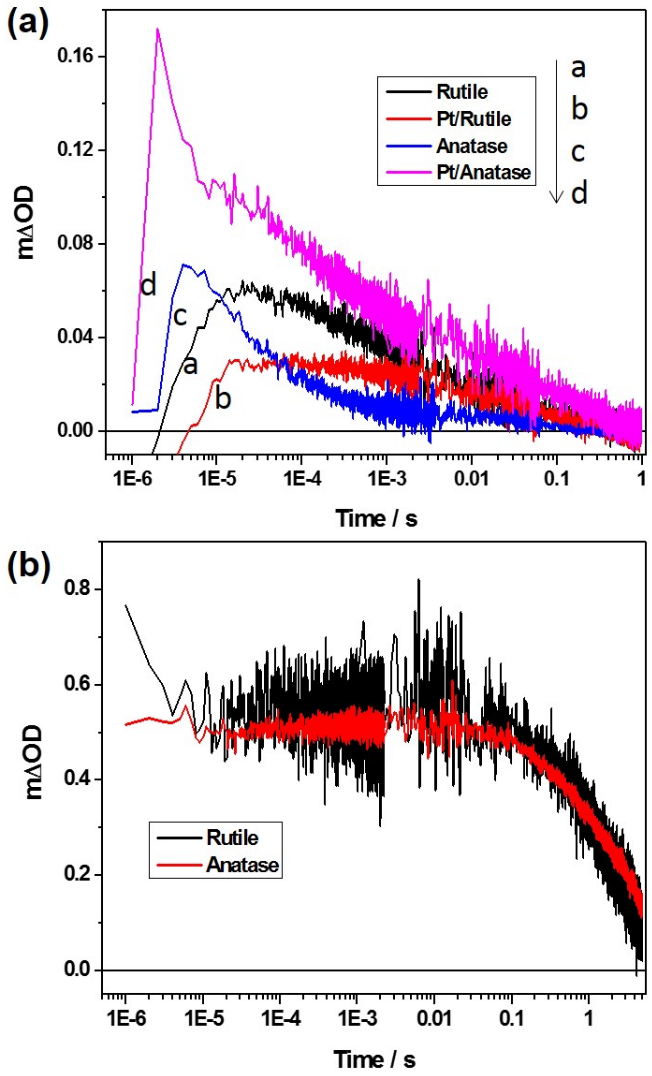


Figure S5. Transient absorption dynamic of a TiO_2 (h^+) in the presence of H_2O or $AgNO_3$ as electron acceptor. (a)H_2O; (b) $AgNO_3$.

A 75 W Xe lamp and an Nd:YAG laser (355 nm, 6 ns pulse width) was used as a probe and pump beam, respectively. The change in transmitted light was detected by a Si PIN photodiode. Reasonably low laser intensity was used (~ 300 μJ cm^{-2} $pulse^{-1}$). Each TAS trace is the result of averaging between 50-500 scans.

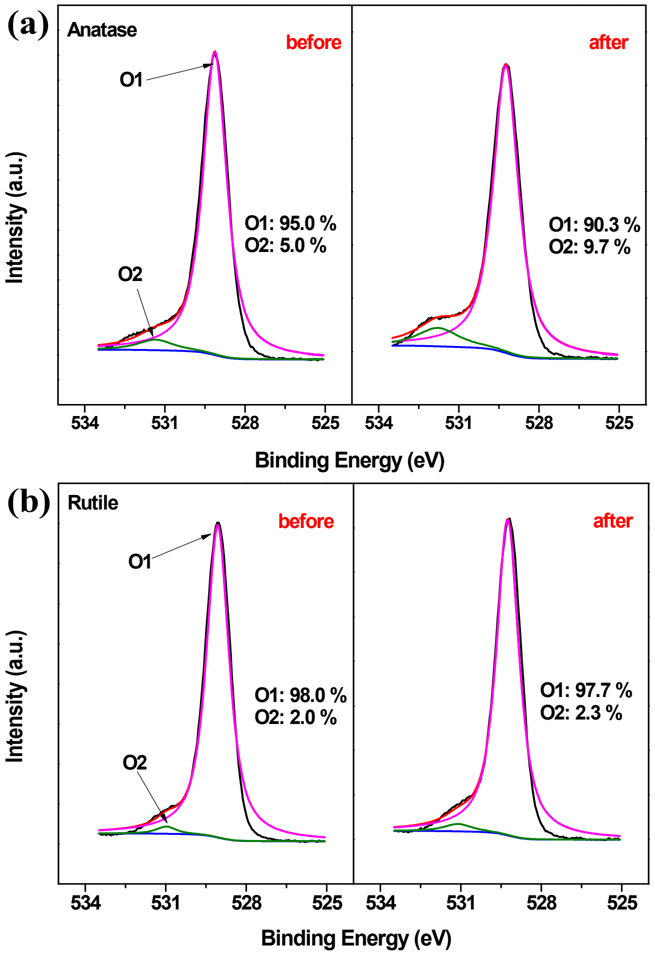


Figure S6. The O1s XPS spectra for anatase TiO_2 (a) and rutile TiO_2 (b) before and after photocatalytic reaction. Before: both as-prepared anatase and rutile TiO_2 was used for XPS characterization without treatment. After: both anatase and rutile TiO_2 were first used for photocatalytic reaction for 10 hours, and then filtered and dried under vacuum for XPS characterization.

Anatase TiO_2 exhibited obvious differences before and after the photocatalytic reaction but the rutile TiO_2 was unchanged. The peak at 531.5 eV can be ascribed to the hydroxyl oxygen, while the peak at 529.1 eV was recognized as the lattice oxygen in TiO_2.[16, 17] The proportion of hydroxyl oxygen for anatase is obviously increased after the photocatalytic reaction (from 5.0 % to 9.7 %), meaning that some of the photogenerated holes may be consumed to form hydroxyl oxygen species.

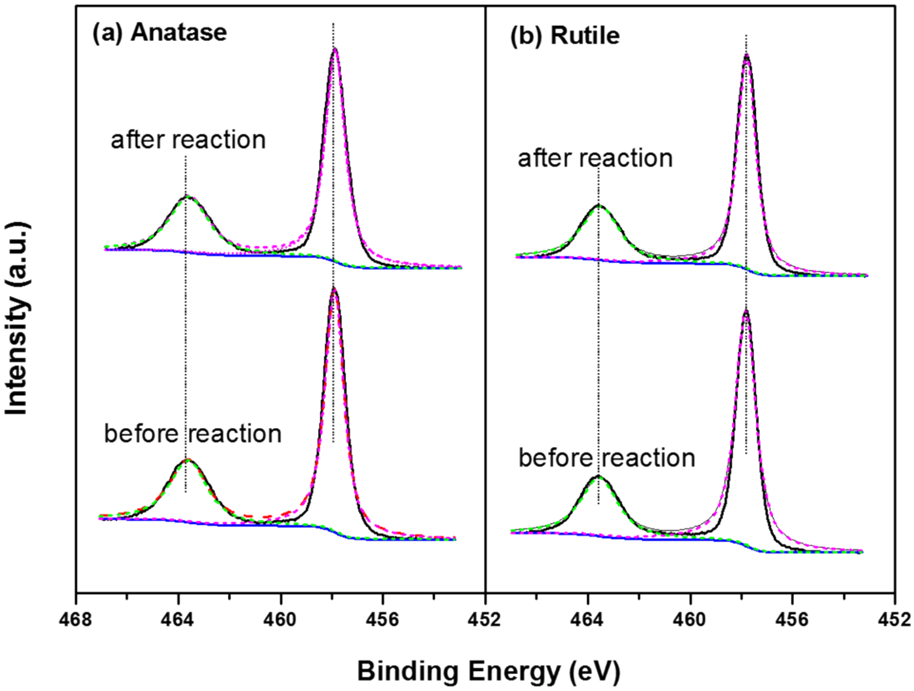


Figure S7. The Ti 3d XPS spectra for anatase TiO_2 (a) and rutile TiO_2 (b) before and after photocatalytic reaction.

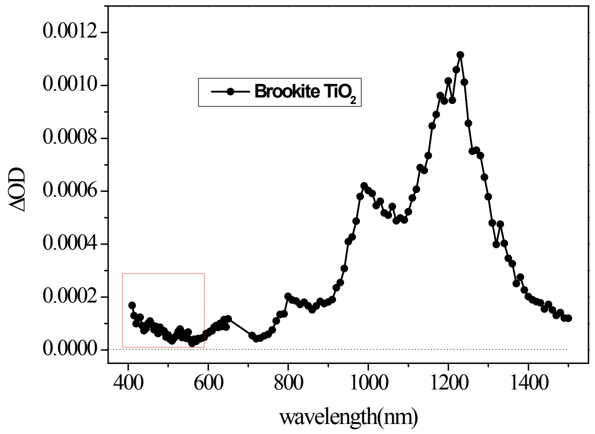


Figure S8. Transient IR absorption-excitation energy scanning spectra for brookite TiO_2.

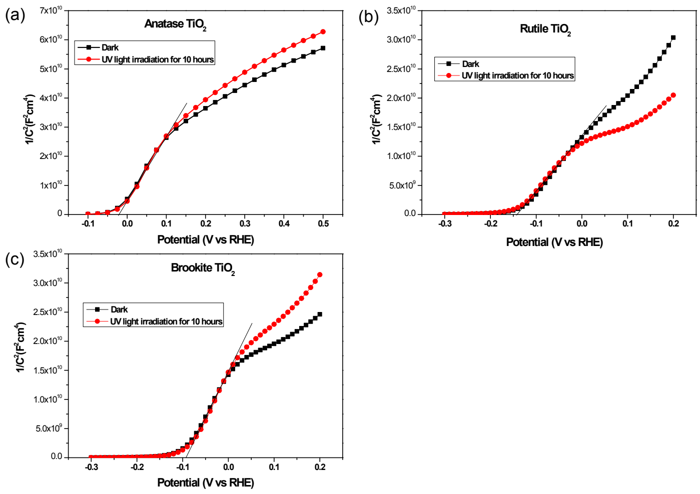
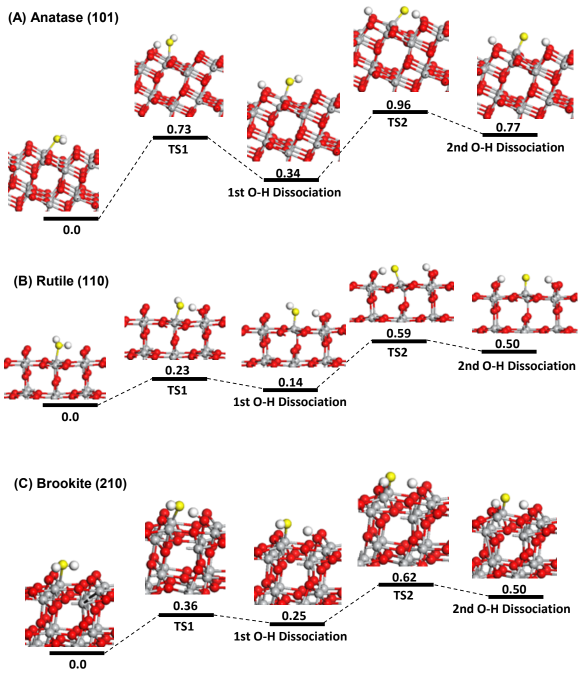


Figure S9. Mott-Schottky plots of different kinds of TiO_2 before and after the UV light irradiation. (a) anatase TiO_2; (b) rutile TiO_2 and (c) brookite TiO_2. The black line: fresh TiO_2 films; The red line: TiO_2 films were treated by UV light irradiation for 10 hours.



(A) Anatase (101)

(B) Rutile (110)

(C) Brookite (210)

Figure S10. Calculated potential energy surface of the two-step dissociation of H_2O on anatase TiO_2 (101) and rutile TiO_2 (110) surfaces. “TS” denotes the transition state and the unit of calculated energy is eV. The red balls represent the oxygen atoms of surface, the gray balls represent titanium atoms, the yellow balls represent the oxygen atoms of water, and the white balls represent hydrogen atoms.

Table S1. The surface energy of different exposed facets for different phases of TiO_2.

Anatase	Surf.	**(101)**	(100)	(001)	(110)						Ref. [18]
	Surf. Energy	**0.44**	0.53	0.90	1.09						
Rutile	Surf.	(101)	(100)	(001)	**(110)**						Ref. [19]
	Surf. Energy	1.01	0.67	1.21	**0.48**						
Brookite	Surf.	(100)	(010)	(001)	(110)	(011)	(101)	(111)	**(210)**	(120)	This work
	Surf. Energy	0.88	0.77	0.87	0.85	0.74	0.87	0.72	**0.70**	0.82	

Table S2. Photocatalytic water oxidation performance for anatase and rutile TiO_2 after treated under UV light irradiation.

Entry	**Photocatalyst**	**Irradiation time (h)**	**The amount of O_2 evolution ($\mu mol/h \cdot m^2$)**
1	Anatase TiO_2	0 h	1.7
2		2 h	5.0
3		8 h	9.5
4	Rutile TiO_2	0 h	30.4
5		2 h	31.9
6		8 h	32.5

Reaction conditions: photocatalyst, 50 mg; reaction solution, de-ionized H_2O, 150 mL; 0.2wt% Pt was deposited by in-situ photo-deposition method before the reaction; Light source, Xenon lamp (300 W), top-irradiation type. After the irradiation for different time, $AgNO_3$ solution (0.02M) was used as sacrificial reagent for photocatalytic water oxidation.

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