Supporting information

Ethanol-Quenching Modified the Surface Environment of Titanium Dioxide for Visible Light-Assisted Hydrogen Production

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Experimental Section.

Chemicals. TiO_2 (P25, 20-30 nm, 20% rutile and 80% anatase) was purchased from Shanghai Macklin Biochemical Co., Ltd. Ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytical grade and without further purification in this study. Deionized water was used for all experiments.

Preparation of M-TiO_2.

The 2.0 g samples of P25 materials were weighed and poured into the sintering boat for use. The absolute ethanol was measured 100ml by a measuring cylinder and pour it into a beaker for use. The temperature of muffle furnace was raised to 700 °C in advance, and then the sintering boat equipped with P25 materials was quickly placed in the muffle furnace. After 20 minutes, P25 materials were immediately taken out and directly thrown into the beaker containing absolute ethanol for rapid quenching. The quenched samples were filtered and then dried at 80 °C for 12 h for further use. For the comparison, the P25 materials subjected to the 400 °C used the same preannealing procedure also were prepared. The quenched TiO_2 was labeled as M-TiO_2, respectively.

Material Characterizations.

Powder X-ray diffraction (XRD) data were obtained at room temperature using Cu Kα (λ = 1.5406 Å) operated at 36 kV tube voltage and 20 mA tube current at a scan rate of 8° min^{-1}. The JEOL JEM-2100F model was used to determine the size and morphology of the samples. Sample specimens to be measured by transmission electron microscopy (TEM) were prepared by briefly ultrasonicating the sample powders in ethanol, followed by placing a drop of the suspension onto lacey support films that were dried before imaging. Raman spectra were collected on a UV laser Raman spectrometer using a laser with an excitation wavelength of 785 nm. Diffusive reflectance UV–vis (DRUV-Vis) absorption spectra were recorded on an Evolution 220 UV–vis spectrophotometer. The X-ray photoelectron spectroscopy (XPS) experiments were carried out on ESCALAB 250Xi using the reference of C1 s (284.8 eV) with the excitation source of 150 W Al Kα (hυ = 1486.6 eV) X-rays. The electron paramagnetic resonance (EPR) spectra were recorded on a JES FA200 spectrometer at room temperature.

Photocatalytic hydrogen evolution.

Visible light photocatalytic H_2 generation

Photocatalyst (100 mg) loaded with Pt (0.5 wt.%) was placed into an aqueous methanol solution (100 mL, 20%) in a closed-gas circulation system. An Microsolar 300 solar light simulator system was used as light irradiation source. The visible wavelength light irradiation was obtained from a 400 W Xenon lamp cut off by a 400 nm filter.

Solar light photocatalytic H_2 generation

Photocatalyst (100 mg) was placed into an aqueous methanol solution (100 mL, 20%) in a closed-gas circulation system. An Microsolar 300 solar light simulator system was used as light irradiation source.

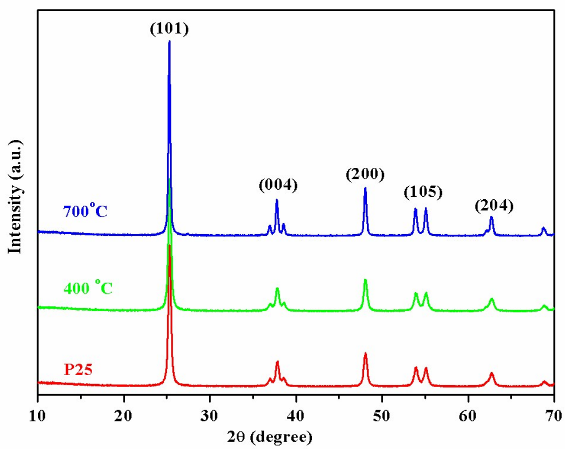

Figure. S1 Powder X-ray diffraction patterns of different samples.

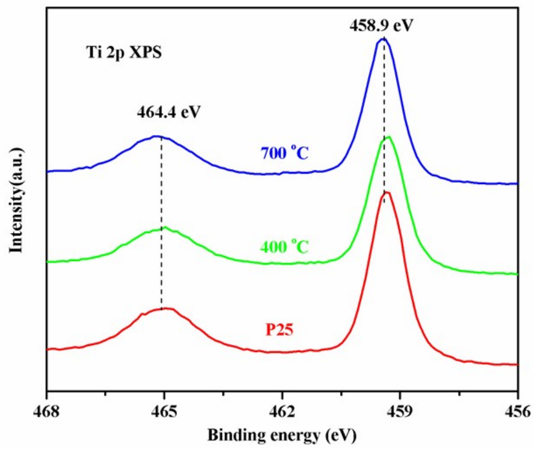

Figure S2. Ti 2p XPS spectra of the P25 and black M-TiO_2 nanocrystals.

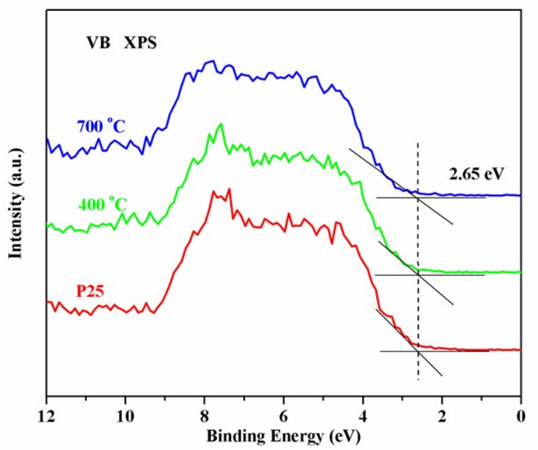

Figure S3. VB XPS spectra of the P25 and black M-TiO_2 nanocrystals.

Table S1. Rate of hydrogen generation obtained by using different black TiO_2 materials

Photocatalyst	**Reactant conditions**	**Light source**	**Visible light rate of hydrogen generation (μmol$h^{-1}g^{-1}$)**	**Refer.**
Hydrogenated Black TiO_2	50 % CH_3OH, 0.6 % Pt	AM-1.5 solar Stimulator	100	1
Hydrogenated TiO_2 nanotube	20 % CH_3OH, 1 % Pt	Xe arc lamp 500W	120	2
Al-reduce black TiO_2	25 % CH_3OH, 0.5 % Pt	Hg lamp, 300W	140	3
N doping Al-reduced black TiO_2	20 % CH_3OH, 0.5 % Pt	Xe lamp, 300 W	160	4
Al-reduced S doped TiO_2	50 % CH_3OH, 0.5 % Pt	AM 1.5 simulated solar power system	258	5
Ordered mesoporous hydrogenated black TiO_2	20 % CH_3OH, 1 % Pt	AM 1.5 solar power system	13.6	6
Mg-reduced black TiO_2	20 % CH_3OH, 1 % Pt	Xe lamp, 400 W	440	7
Current work	20 % CH_3OH, 0.5 % Pt	Xe lamp, 300 W	180	--

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