

## Supporting Information

### **Black and White Anatase, Rutile and Mixed Forms: Band-Edges and Photocatalytic Activity**

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## **Experimental Section**

### Materials:

Anatase nanopowders were purchased from Sigma Aldrich, purity: 99.8%, particle size: 25-35 nm. Rutile nanopowders were also purchased from Sigma Aldrich, purity: 99.8%, average particle size: 30 nm. Rutile single crystals and 0.05wt% Nb-doped rutile single crystals, (10×10×0.5 mm, one side polished, normal surface treated, 001 orientation) were purchased from Shinkosha Co. Ltd. (Japan). Anatase single crystals (5×5×0.5 mm) were purchased from SurfaceNet GmbH, Germany. These materials are used directly without further purification or cleaning.

### Hydrogenation treatment:

The hydrogenation treatment of the powders and single crystals were performed in a conventional tube furnace (Linn High Therm, FRV-40/220 V, Germany) in pure H<sub>2</sub> (Linde, 99.99%) at a flow rate of 8 L/h at 500 °C for 1 h. The loadings of the powders were 20 mg for each annealing experiment. The annealing treatment of P25 was performed from 450 °C to 600 °C for 1 h, respectively. Temperature ramping up was controlled to be 5 °C/min and temperature cooling down was by switching off the heating but still under hydrogen atmosphere. Afterwards, the collected powders or single crystals were stored in glass bottles.

### Preparation of electrodes:

Anatase or rutile powders (50 mg) were dispersed in 0.2 mL N,N-dimethylformamide under sonication for 30 min to get slurry. The slurry was then doctor bladed on FTO glass (15 Ω) using a single scotch tape frame. After the samples were dried in air, the scotch tapes were removed and the electrode was annealed at 450 °C for 30 min in air to improve adhesion. A copper wire cable was connected to the front side of FTO glass (on the sample layer) using silver glue. The uncoated FTO glass parts and silver connection point were coated with insulating silicon glue (transparent, BEST-Klebstoffe GmbH&Co. KG, Germany). Afterwards, the samples were dried in air for overnight. This method is described in detail in literature

(*Angew. Chem. Int. Ed.*, **2013**, 52, 3621). The single crystal substrates were connected with a copper wire cable from the back side using silver glue. To make an Ohmic contact on the single crystal, the back side was first sputtered with an Ar beam (to remove approx. 100 nm in depth) before fabricating the contact. Then the back side of the crystal was coated with a thin Ta layer (100 nm). After connection, the exposed parts (the rest of the back side and the connection point) were covered with the same insulating silica glue and dried in air.

#### Photoelectrochemical measurements:

Photoelectrochemical characterization was carried out with an electrochemical setup that consisted of a classical three-electrode configuration with a 3M Ag/AgCl reference electrode and a Pt plate (1 cm×1 cm) as a counter electrode. Photocurrent spectra were acquired in 0.1 M aqueous Na<sub>2</sub>SO<sub>4</sub> electrolyte at a potential of +500 mV (vs. 3 M Ag/AgCl). At each wavelength a photocurrent transient was recorded and the steady state photocurrent was evaluated. Photocurrent transients were recorded for 20 s using an electronic shutter system and A/D data acquisition. Before and after illumination, the dark current was recorded for 10 s. For the voltage-dependent photocurrent measurements, the wavelength of incident light was fixed at 350 nm. And the voltage applied was scanned from +500 mV to – 700 mV (vs. 3 M Ag/AgCl) in steps of 100 mV. At each applied voltage, the photocurrent transient was acquired by illuminating the sample for 20 s and subtracting the dark current for 10 s before and after light exposure.

The illumination part of the setup consists of a 150 W Xe arc lamp (LOT-Oriel Instruments) as irradiation source and a Cornerstone motorized 1/8 m monochromator. The monochromized light was focused to a spot of 5×5 mm<sup>2</sup> onto sample surface (through a quartz pass window in the electrochemical cell). The samples were placed in the middle of the electrolyte, leaving the front side perpendicular to the incident light.

Photoelectrochemical measurements of hydrogenated single crystals under 405 nm illumination was performed also in 0.1 M aqueous Na<sub>2</sub>SO<sub>4</sub> electrolyte. The electrochemical cell is configured the same as for photocurrent measurements. The voltage scan was conducted from 0. V to 0.2 V (vs. 3 M Ag/AgCl).

#### Photocatalytic Measurements:

The photocatalytic H<sub>2</sub> evolution of the powder samples were measured under open circuit conditions. To prepare suspensions for H<sub>2</sub> measurements, 2 mg sample powders were dispersed in 10 mL aqueous methanol solution (50:50 vol%). The mixed solutions were placed in an ultra-sonication bath for 15 min to obtain a homogeneous suspension. Then, the suspensions were exposed to a laser with a monochromatic wavelength of 405 nm (400 mW) or a LED with a wavelength of 365 nm (90 mW) and AM1.5 solar simulator (100 mW/cm<sup>2</sup>). The illuminated area of the suspension was approx. 2 mm in diameter for the laser and 1 cm in diameter for the LED). During illumination, the suspensions were continuously stirred and kept at room temperature. The amount of H<sub>2</sub> accumulated in the head space of sealed-quartz reactor was measured using a Varian gas chromatograph (SHIMADZU GAS CHROMATOGRAPH GC-2010 plus) with a TCD detector. The molar amount of hydrogen produced is calculated based on the concentration detected from GC and volume of the head space of the reactor.

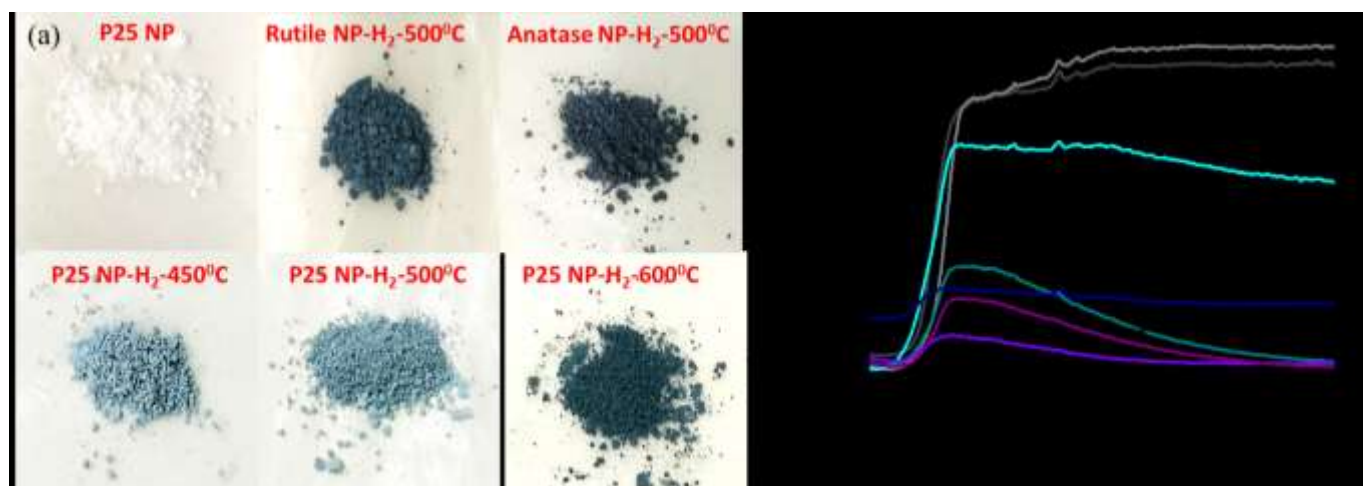
#### Reflectivity:

The absorbance of the samples was measured between 300-900 nm in air atmosphere (Avantes, AvaLight-DH-S-BAL, using cable IC-DB26-2). The reflectivity spectra were obtained in between quartz glass slides and a Teflon standard was used as background.

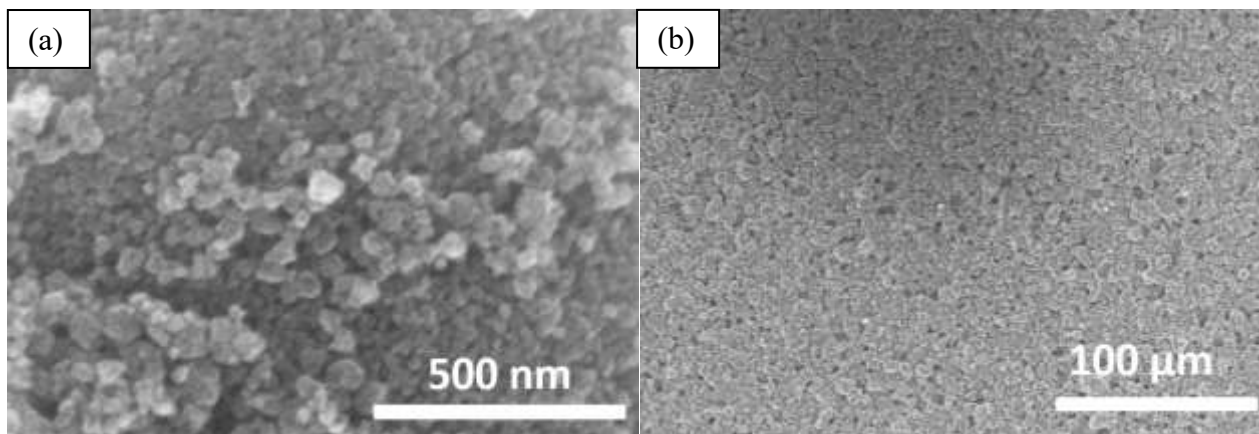
#### Other Characterization:

Chemical compositional analysis of the samples was performed by X-ray photoelectron spectroscopy (XPS, PHI 5600 XPS spectrometer, US). XPS spectra were acquired using monochromatic X-rays with a pass energy of 23.5 eV. All the XPS element peaks are shifted to the C1s standard position (284.8 eV).

The powder samples were taped on conductive carbon tapes as thin film. The single crystals were connected to the XPS stage by using welded tantalum wires. XPS fitting was conducted using casaXPS software. The difference of binding energy for splitting of  $Ti2p_{1/2}$  and  $Ti2p_{3/2}$  is kept at 5.65 eV for both  $Ti^{4+}$  and  $Ti^{3+}$ . And the peak areas are constrained to a 1:2 ratio for  $Ti2p_{1/2}$  to  $Ti2p_{3/2}$ . The valence band measurements were acquired from -5 eV to 10 eV. The valence band information obtained from XPS is a joint density of states information include valence band (UPS) and slight deeper orbital information. XRD patterns were collected using an X'pert Philips PMD diffractometer with a Panalytical X'celerator detector, using graphite-monochromatized  $CuK\alpha$  radiation ( $\lambda=1.54056\text{\AA}$ ). A Hitachi FE-SEM S4800 was used for morphological characterization of the powder samples after fabricating an electrode on FTO glass.



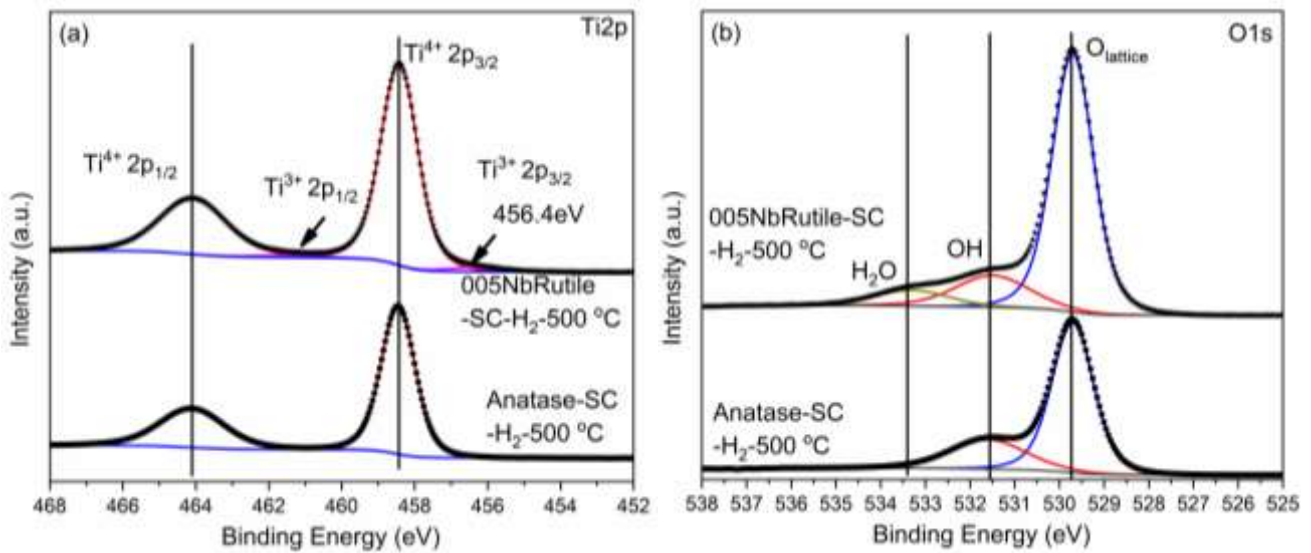
**Figure S1.** (a) Optical images of P25 before and after hydrogenation at various temperatures and anatase and rutile powders after hydrogenation at 500 °C, show darkening with increasing annealing temperature. The change in color can be quantified by DRS spectra shown in (b). Hydrogenated TiO<sub>2</sub> NP powders presented in (a) experience an increase in visible light absorption. Please note that from all spectra a primary absorption gap corresponding to anatase or rutile (3.0 to 3.2 eV) can be obtained while the visible light tail essentially corresponds to the colour of the sample. From the comparison with the photocurrent spectra (**Figure 1**) it is however evident that carriers on these visible states do not contribute to a photocurrent. I.e. they remain trapped and recombine. [*ChemSusChem*, **2017**, *10*, 62, *Chem. Soc. Rev.* **2015**, *44*, 1861, *Nano Lett.* **2011**, *11*, 3026].



(c)

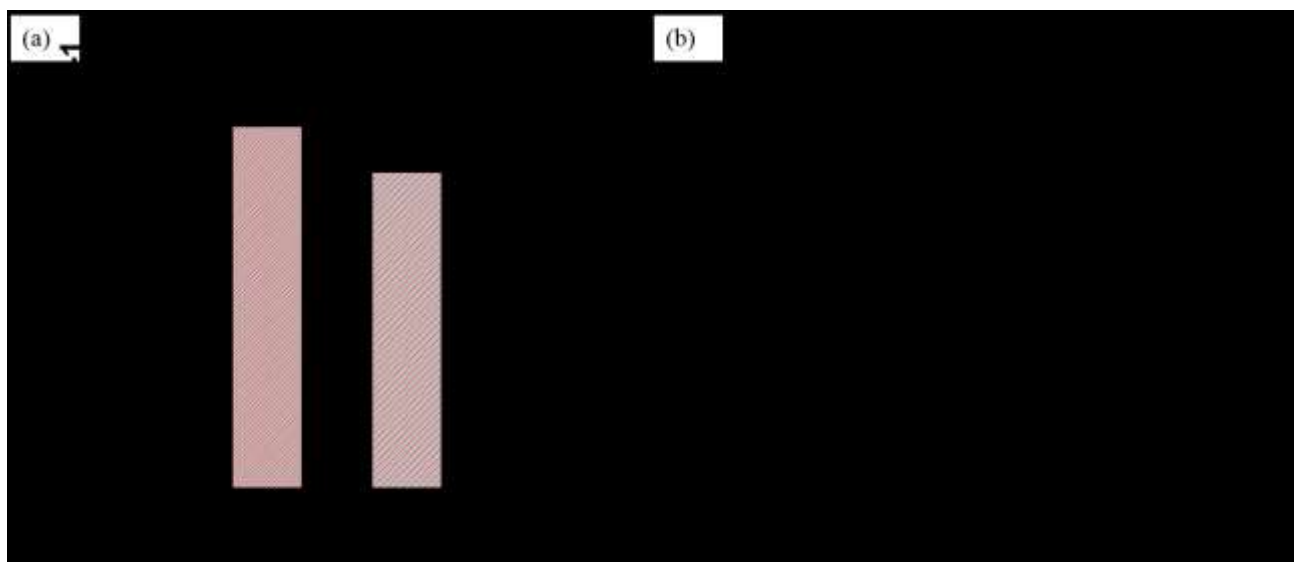
Samples	d anatase (101) (nm)	d rutile (110) (nm)
Anatase-NP	12.2	
Rutile-NP		40.8
P25-NP	15.0	56.8
P25-NP-H <sub>2</sub> -450 °C	18.4	55.8
P25-NP-H <sub>2</sub> -500 °C	17.9	56.8

**Figure S2.** (a-b) SEM images of anatase on FTO by doctor blading and annealed at 450°C for 30 min in air. (c) Particle size according to Scherrer equation used on XRD data from **Figure 3a**.



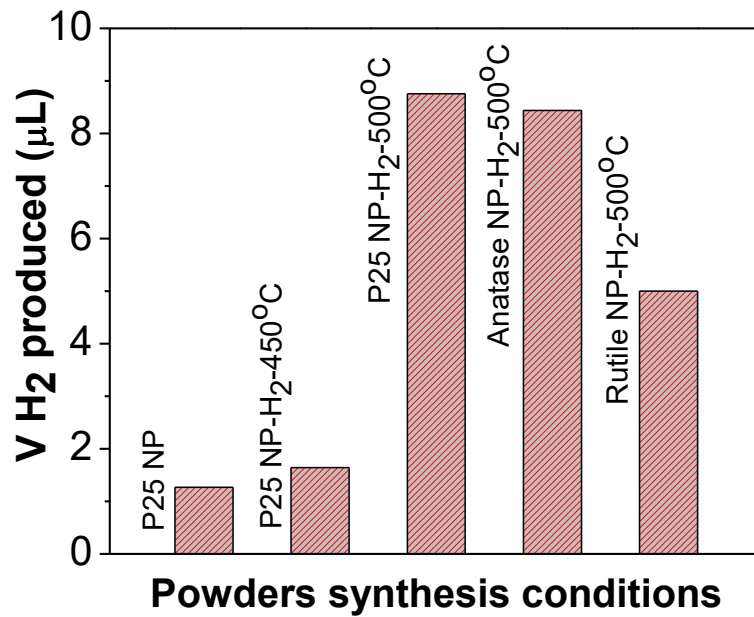
**Figure S3.** XPS measurements for (a) Ti2p peaks and (b) O1s peaks for hydrogenated anatase single crystal, and hydrogenated Nb-doped (0.05wt%) rutile single crystal. The data show that after annealing the single crystals in hydrogen at 500 °C, the effects are different on the anatase single crystal and the rutile single crystal. After deconvolution of the spectra, hardly any Ti<sup>3+</sup> states can be observed on the hydrogenated anatase surface, while visible tails can be seen on the hydrogenated rutile surface. On the surface of hydrogenated rutile single crystal, both hydroxide groups and surface adsorbed water are present from O1s spectrum. But on the surface of hydrogenated anatase single crystal, only surface hydroxide is visible. Overall, the XPS results for the hydrogenated single crystals show that no significant formation of surface Ti<sup>3+</sup> states or oxygen vacancies. This may be ascribed to two reasons: the defects are created below the surface layer (*J. Phys. Chem. C*, **2015**, *119*, 18160), and/or the partial re-oxidation of annealed crystals when transferring them to XPS.





**Figure S4.** The stability of P25 NP-H<sub>2</sub>-500 °C sample for H<sub>2</sub> evolution was tested by two types of experiments: a) after exposure of the sample to air for three month. 2 mg of the aged sample powder was again dispersed in 10 mL aqueous methanol (50:50 vol%) solution and exposed to 365 nm illumination during 24 hours. The obtained H<sub>2</sub> production rate only mildly lower than the fresh sample and confirms the stability of the powder. Additionally, (b) cycling experiments were conducted using a P25 NP-H<sub>2</sub>-450 °C sample. GC measurements of produced H<sub>2</sub> in volume were repeated three time after 17 and 24 hours exposure to 365 nm illumination, separated by 30 min purging with N<sub>2</sub> to remove the hydrogen from the system. These experiments verified linear and reproducible evolution of hydrogen and efficient desorption of hydrogen from the surface of the photocatalyst.

As a further control experiment, the P25 NP-H<sub>2</sub>-500 °C sample prepared in the same way as in a) was stored in reaction solution in the dark during 24 hours. After that time no hydrogen evolution was observed.



**Figure S5.** Photocatalytic H<sub>2</sub> evolution measurements under AM1.5 solar simulator (100 mW/cm<sup>2</sup>). Samples were taken after 24 hours and hydrogen evolution was evaluated from gas chromatography results. Obtained results are in line with experiment of H<sub>2</sub> evolution under 405 nm and prove that the rutile phase has a significant „antenna“ contribution to the photocatalytic H<sub>2</sub> production under solar excitation conditions.