

## Supporting information

### ‘Black’ TiO<sub>2</sub> nanotubes formed by high energy proton implantation show noble-metal-co-catalyst free photocatalytic H<sub>2</sub>-evolution

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## Experimental:

As substrates for TiO<sub>2</sub> nanotube growth we used titanium foils (99.6% purity, Goodfellow) with a thickness of 0.1 mm. Prior to tube formation the foils were cleaned by sonication in acetone and ethanol followed by rinsing with deionized (DI) water and drying in a nitrogen stream. To perform electrochemical TiO<sub>2</sub> nanotube formation, the foils were anodized using a power supply (Votcraft VLP 2403 pro) in a two electrode configuration with a counter electrode made from platinum gauze. The typical electrolyte for TiO<sub>2</sub> nanotubes was prepared from ethylene glycol (EG, Sigma–Aldrich, containing less than 0.2 wt% H<sub>2</sub>O), with addition of 1 M DI H<sub>2</sub>O and 0.1 M NH<sub>4</sub>F (Sigma–Aldrich, 98%). The anodization was carried out at 60V for 2, 5, 15 and 30 min, and TiO<sub>2</sub> nanotube layers of a thickness of about 1, 2, 7 and 12 μm were obtained.

Thermal treatments of the nanotube layers were carried out in air using a Rapid Thermal Annealer (Jipelec JetFirst 100) at 500 °C with heating/cooling rates of 1 °C/s. The samples were annealed at 450 °C for 1 h.

The single crystal anatase wafers were obtained from natural anatase to an epi-polished (001) surface (SurfaceNet GmbH, Germany).

Proton implantation was carried out at an energy of 30 keV and a nominal dose of 10<sup>16</sup> ions/cm<sup>2</sup> using a Varian 350 D ion implanter.

A Hitachi FE-SEM S4800 was used for morphological characterization of the samples. The length of the nanotubes was directly obtained from SEM cross-sections. XRD patterns were collected using an X'pert Philips PMD diffractometer with a Panalytical X'celerator detector, using graphite-monochromatized CuKα radiation ( $\lambda = 1.54056\text{\AA}$ ). The chemical composition of the layer was characterized with X-ray photoelectron spectroscopy (XPS, PHI 5600 XPS spectrometer, US).

Transmission electron microscopy (TEM) was performed with a Titan<sup>3</sup> Themis 300, a Phillips CM300 UltraTWIN and a Philips CM30 TWIN/STEM (FEI Company, Netherlands). The Titan<sup>3</sup> Themis 300 is equipped with a high-brightness field-emission gun (X-FEG), a monochromator system (energy resolution 0.2 eV), two C<sub>s</sub>-correctors (probe and image side) from CEOS (Corrected Electron Optical Systems GmbH), a Super-X detector (for energy dispersive X-ray spectroscopy), a Gatan Imaging Filter, a high-angle annular dark-field (HAADF) detector and a 4k CMOS camera. This microscope was operated at 200 kV acceleration voltage. The Philips CM300 UltraTWIN and the CM30 TWIN/STEM microscopes are equipped with LaB<sub>6</sub> filaments, 2k and 1k charged coupled device cameras from TVIPS (Germany), respectively, and were operated at 300 kV acceleration voltage. For TEM analysis the TiO<sub>2</sub> nanotubes are prepared on commonly used copper TEM grids coated with a holey carbon film. During TEM analysis no noticeable electron-beam-induced damage was observed. The free available software ImageJ (version 1.48r) and the commercially available software

DigitalMicrograph<sup>TM</sup> were used for image analysis. The evaluation of the electron diffraction patterns was performed by using the software JEMS<sup>1</sup> (version version 3.7624U2012) and the inorganic crystal structure database (ICSD).

The room temperature CW EPR spectra were recorded on an X-band ( $\nu_{mw} = 9.84$  GHz) EMXmicro BRUKER spectrometer and at 70 K using an Oxford flow cryostat with liquid nitrogen flow. The  $B_0$  modulation amplitude used was 0.4 mT, and the modulation frequency was adjusted to  $\nu_{mod} = 100$  kHz. The microwave power used was low enough to prevent the saturation of the spin systems.

The photoluminescence (PL) of the powder samples was excited with a 375 nm diode laser and the spectra were recorded at room temperature with an iHR320 monochromator and Synergy Si CCD camera (both Horiba Jobin-Yvon). The spectra are corrected for the spectral sensitivity of the setup, determined with the help of a calibrated halogen lamp.

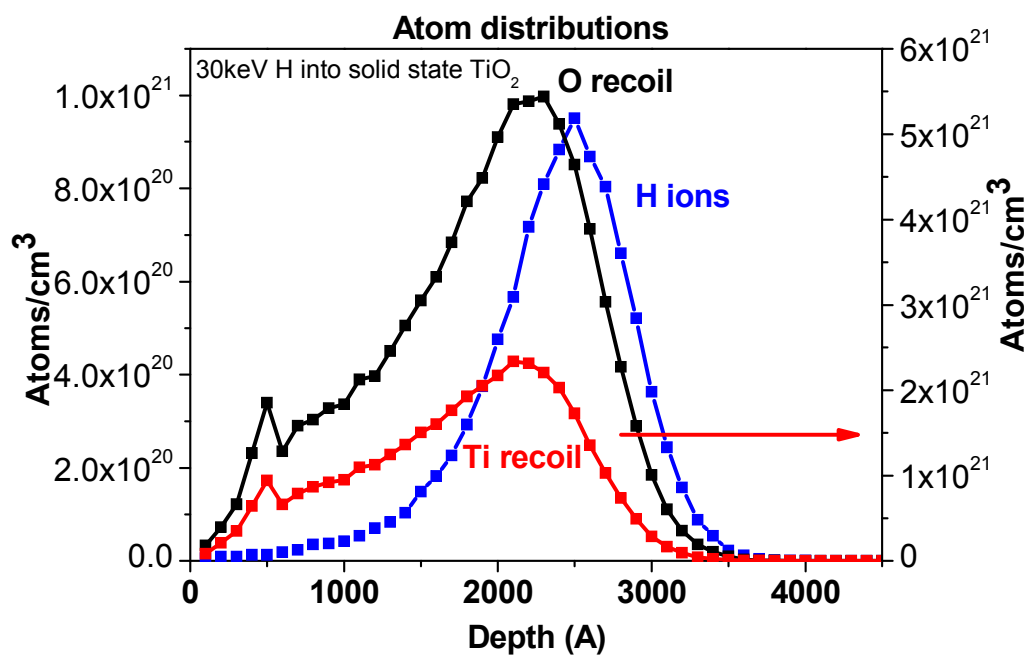
Measurements of Raman spectra were performed on a Spex 1403 Raman Spectrometer. A line (632 nm) of a HeNe laser was taken as the excitation source.

Photocatalytic hydrogen generation was measured under open circuit conditions from an aqueous methanol solution (50 vol%) under AM 1.5 ( $100 \text{ mW/cm}^2$ ) solar simulator illumination. The amount of  $\text{H}_2$  produced was measured using a Varian gas chromatograph with a TCD detector. For rate determination, data were taken approximately every 24 h during solar simulator irradiation. To prepare suspensions for  $\text{H}_2$  measurements, 2 mg  $\text{TiO}_2$  powders were dispersed in 10 mL of DI water/methanol (50/50 v%) with ultrasonication for 30 min. During illumination, the suspensions were continuously stirred.

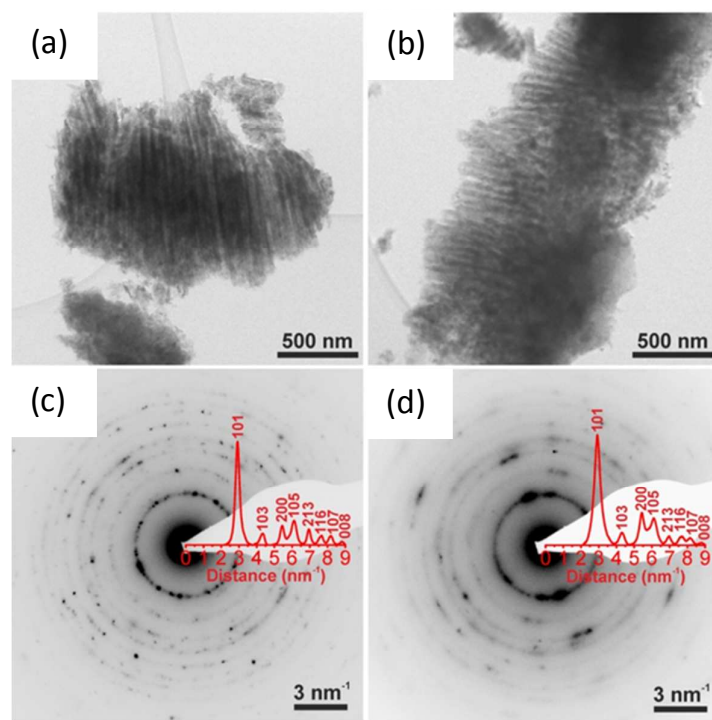
Monte-Carlo simulations of the implant and damage depth-distributions were carried out using TRIM 2008 and 2013 [2]. (We consider the small peaks appearing in the profiles at energies  $\sim 180$  nm (tube) and 50 nm (single crystal) as artifacts of the TRIM code).

[1] P. A. Stadelmann, Jems Electron Microscopy Software, (1999–2012), java version 3.7624U2012, CIME-EPFL, Switzerland.

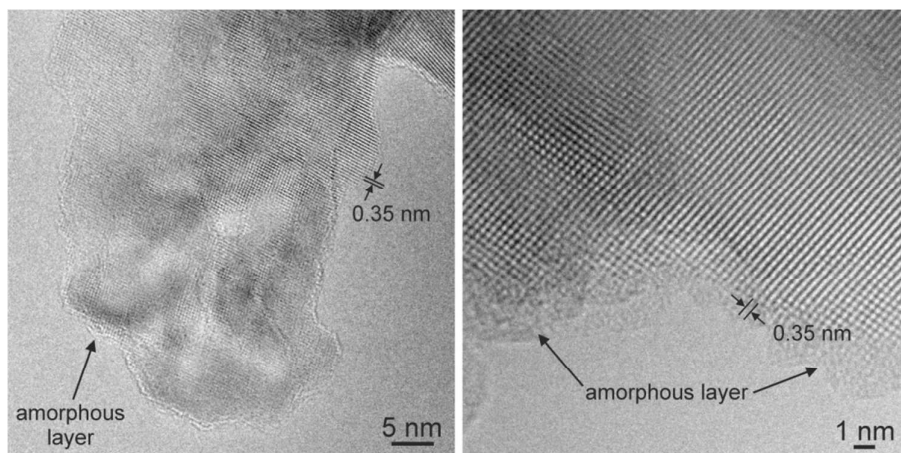
[2] Ziegler, J. F.; Biersack, J. P.; Littmark, U. The Stopping and Range of Ions in Solids; Pergamon Press: New York, 1985.



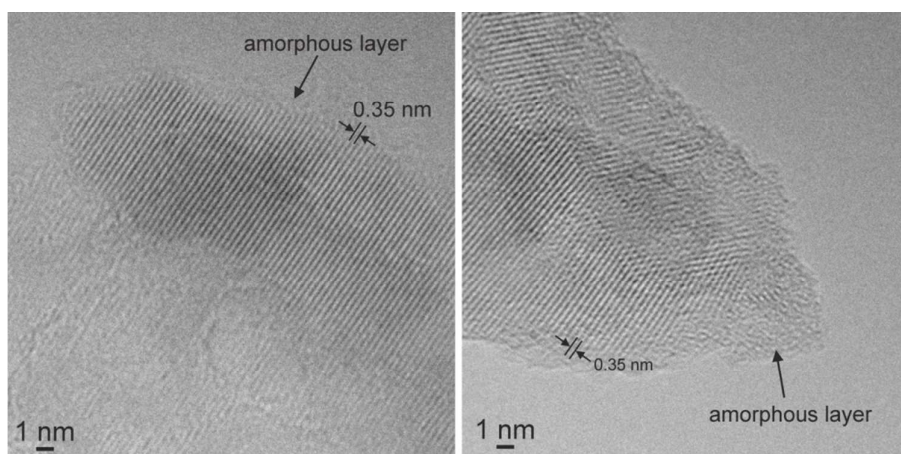
**Fig. S1** Calculation depth distribution of implanted protons (H ions) and crystal damage (titanium and oxygen recoil) in pure  $\text{TiO}_2$  anatase substrate.



**Fig. S2** Representative bright-field (BF) TEM images in Figure 1a) and b) show bundles of TiO<sub>2</sub> nanotubes after conventional annealing in air (to anatase) and after H implantation, respectively and corresponding electron diffraction patterns (see Fig. 2c and d).



**Figure S3.** HRTEM images of reference TiO<sub>2</sub> nanotubes.



**Figure S4.** HRTEM images of TiO<sub>2</sub> nanotubes after H-implantation.

**Fig. S3 and Fig. S4** Additional HRTEM images of samples are provided, which support statements given in the manuscript. A careful analyses under HRTEM conditions also revealed that electron beam irradiation does not introduce effects, such as re-crystallization, amorphization and/or pore formation in the nanotubes. These images indicate that amorphous layers are present in as annealed and implanted tubes.

## Raman Spectra:

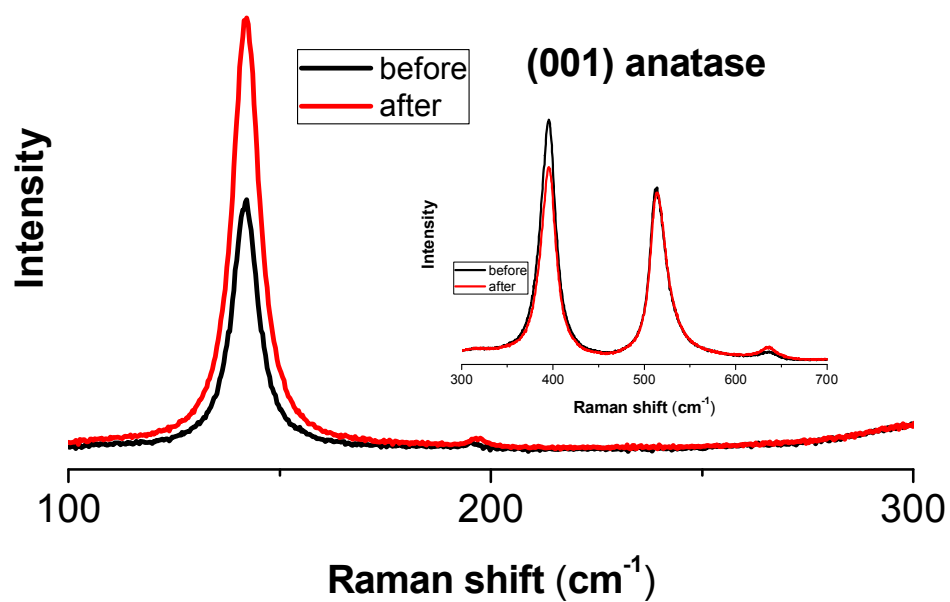


Fig. S5 Raman spectra of (001) anatase single crystal before and after H-implantation.

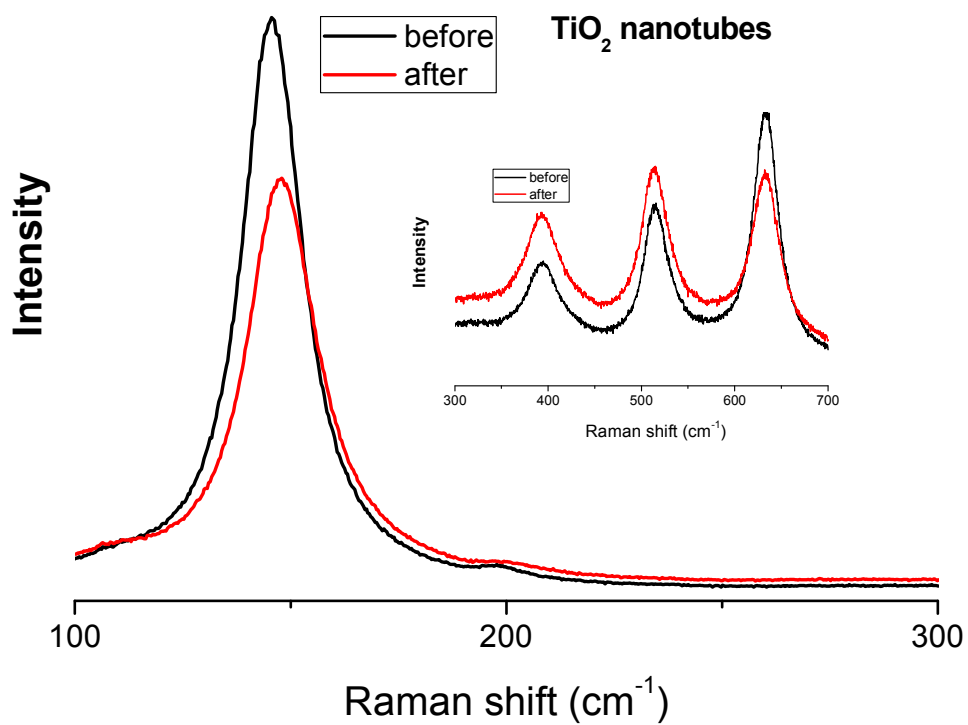
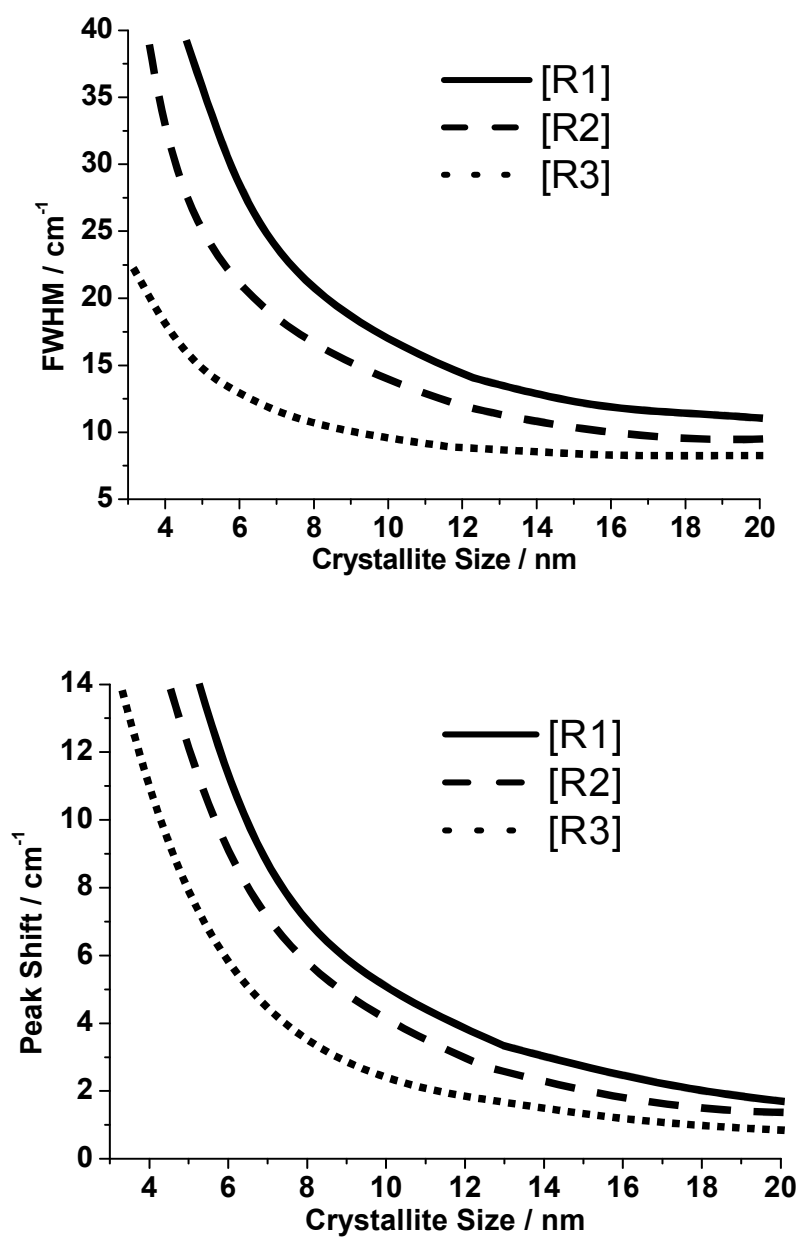


Fig. S6 Raman spectra for  $\text{TiO}_2$  nanotubes before and after H-implantation.



**Fig. S7** Various calculated models predicting the relationship of FWHM and peak shift of main Eg Raman line as a function of TiO<sub>2</sub> feature size.

[R1]: M. Ivanda , S. Music , M. Gotic , A. Turkovic , A. M. Tonejc , O. Gamulin , J. Mol. Struct. 1999 , 480 , 641.

[R2]: S. Balaji ,Y. Djaoued , J. Robichaud , J. Raman Spectrosc. 2006 , 37 , 1416 .

[R3]: D. Bersani , P. P. Lottici , X-Z. Ding , Appl. Phys. Lett. 1998 , 72 , 73.



**Rietveld analysis** of XRD spectra was carried out using the RIETAN-FP program [1] and Toroya's split pseudo-Voigt profile function for the calculations of structural parameters and integrated intensity. The diffraction patterns of the reference and H-implanted TiO<sub>2</sub> nanotubes were fitted by using a TiO<sub>2</sub> anatase model.

## TiO<sub>2</sub>

Structural model: Anatase TiO<sub>2</sub>

Space group:  $I 4_1/a m d$  (VOL. A, 141)

$R_{WP} = 7.623\%$ ,  $R_e = 4.164\%$

$a = 3.7877(2) \text{ \AA}$ ,  $c = 9.5090(4) \text{ \AA}$ ,  $V = 136.42(1) \text{ \AA}^3$

Atom	$x$	$y$	$z$	$B$
Ti	0	0	0	1.07(8)
O	0	0	0.2085(3)	0.5(1)

## H:TiO<sub>2</sub>

Structural model: Anatase TiO<sub>2</sub>

Space group:  $I 4_1/a m d$  (VOL. A, 141)

$R_{WP} = 9.627\%$ ,  $R_e = 6.057\%$

$a = 3.7904(6) \text{ \AA}$ ,  $c = 9.530(2) \text{ \AA}$ ,  $V = 136.93(4) \text{ \AA}^3$

Atom	$x$	$y$	$z$	$B$
Ti	0	0	0	1.2(3)
O	0	0	0.204(2)	0.8(5)

Calculated intensity of reference and H-implanted nanotubes

Index	$2\theta / ^\circ$	$d / \text{\AA}$	Integrated intensity		
			Theoretical	Reference	H-implanted
101	25.308	3.51629	100000	31223	27111
103	36.951	2.43073	6700	4294	1723
004	37.79	2.37865	20586	100000	7955
112	38.572	2.33222	7844	2466	2076
200	48.047	1.8921	29051	7032	6707
202	51.969	1.75815	0	0	0
105	53.885	1.70007	18812	21987	15665
211	55.072	1.66619	18637	4663	4124
213	62.117	1.49308	3353	924	621
204	62.692	1.48076	14761	6168	3432
116	68.756	1.3642	6674	5664	2370
220	70.303	1.33792	7278	1760	1507

The (001)-orientation degree was evaluated in terms of the Lotgering factor  $F(001)$ , which is

calculated from the following equation,<sup>\*2</sup>  $F = (P - P_0) / (1 - P_0)$  where  $P_0 = \Sigma I_0(hkl) / \Sigma I_0(HKL)$  and  $P = \Sigma I(hkl) / \Sigma I(HKL)$ .  $I_0$  and  $I$  are the integrated intensities of each of the diffraction peaks in X-ray diffraction patterns as presented in ICSD database and in experimental data, respectively.  $F(001)$  values of the reference and H-implanted nanotubes were calculated to be 49.2% and 2.2%, respectively.

[\*1] F. Izumi and K. Momma, *Solid State Phenom.*, 2007, **130**, 15.

[\*2] F. K. Lotgering, *J. Inorg. Nucl. Chem.*, 1959, **9**, 113.