

Electronic Supplementary Information

Deciphering the reaction mechanisms of photothermal hydrogen production using H/D kinetic isotope effect

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Synthesis of Ti@TiO₂ nanoparticles

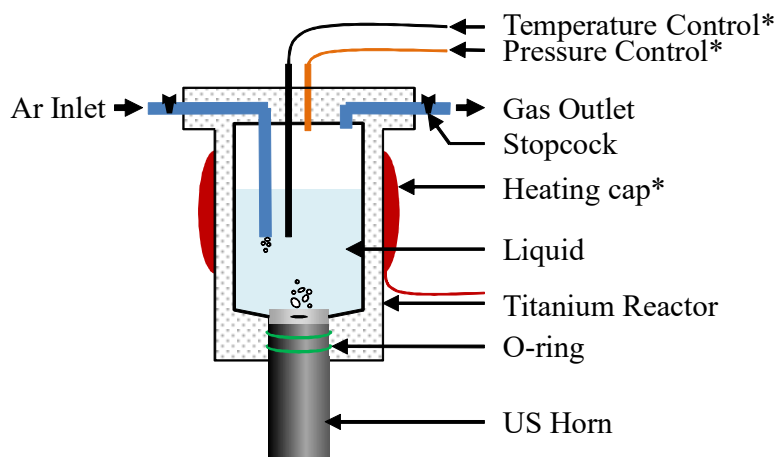


Figure S1. Graphical sketch of sonohydrothermal reactor.

The sonohydrothermal (SHT) reactor shown in Figure S1 was made from Ti-6Al-4V titanium alloy and equipped with a 19 cm² commercial ultrasonic horn made from the same alloy and powered by 20 kHz piezoelectric transducer and electric generator (130 W SONICS). The ultrasonic horn was tightly fitted in the bottom part of the reactor using O-rings made from Aflas[®] 75 rubber (ERIKS). Temperature control was provided by a removable heater fitted on the external surface of the vessel and two thermocouples inside and outside the reactor. Both thermocouples and the heater were connected to VULCANIC 30 656 control panel. The pressure inside the vessel was measured using calibrated digital manometer. Ultrasonic transducer was cooled with air flow. In a typical experiment, 2 g of air passivated Ti nanopowder (American Elements, Ti, 99%) was dispersed in 50 mL of water using ultrasonic bath, placed in SHT reactor and heated at T = 214 °C (autogenic pressure P = 19.0 bar) under simultaneous ultrasonic treatment (f = 20 kHz, P_{ac} = 17 W) for 3 hours. After cooling, the treated NPs were recovered by centrifugation, washed with pure water and dried at room temperature under reduced pressure.

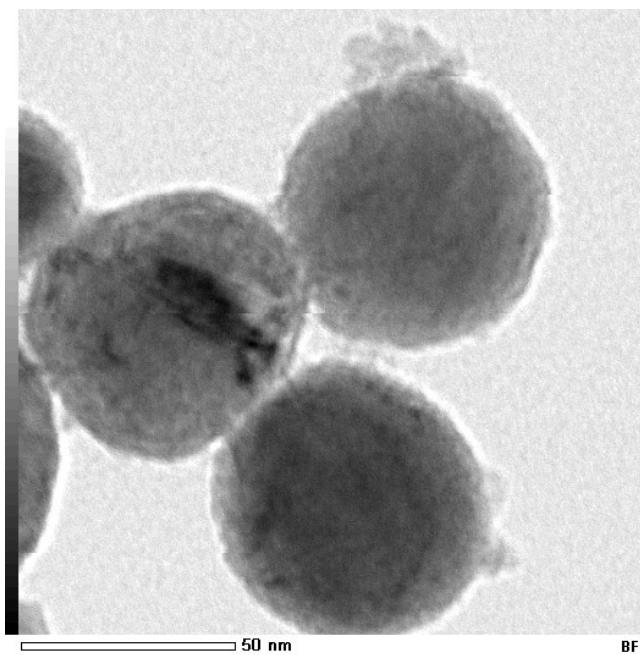


Figure S2. HR STEM image of air passivated nanoparticles of metallic titanium used for the preparation of Ti@TiO₂ photocatalyst. Reproduced from S. I. Nikitenko et al.¹⁴

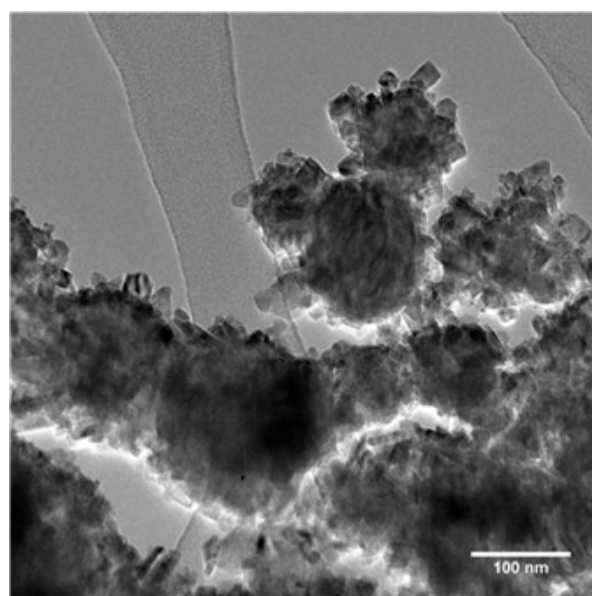


Figure S3. HR TEM image of Ti@TiO₂ NPs. Reproduced from S. I. Nikitenko et al.¹⁴ The images shown in Fig. S2 and Fig. S3 were taken using a Jeol 2200FS (200 kV) microscope.

Photocatalytic experiments

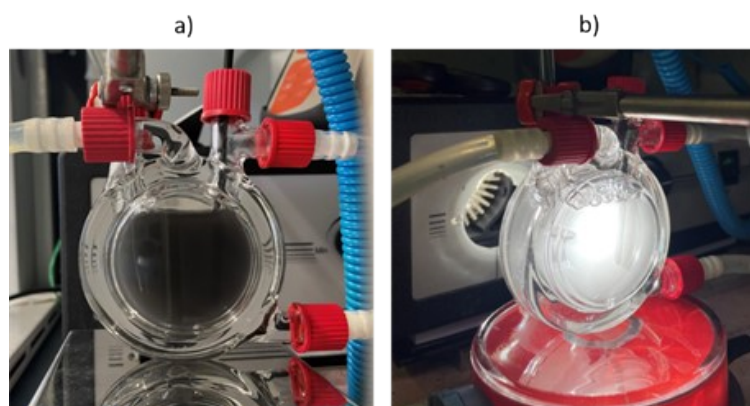


Figure S4. Image of the thermostated photocatalytic cell made from borosilicate glass before (a) and during (b) Xe lamp illumination.

In a typical run, 6 mg of photocatalyst was ultrasonically dispersed in 50 mL of H₂O/D₂O/1M Glycerol solution and placed into the photoreactor. Photolysis was carried out using a white light of ASB-XE-175W xenon lamp equipped with ozone blocking coatings. The lamp was placed at 8 cm away from the reactor and the light power at this distance was measured by X1-1 Optometer (Gigahertz-Optik) using UV-3710-4 (300-420 nm) and RW-3705-4 (400-1100 nm) calibrated detectors. The obtained values of light power were equal to 8.9 W and 0.6 W for vis/NIR and UV spectral ranges respectively, which provides the close spectral match to solar spectra. The solutions inside the reactor were stirred continuously and the temperature was gradually increased up to 94 °C during photolysis using Julabo F12 thermostat. The temperature was measured by J-KEM thermocouple inserted into the photolyte. The Ar gas flow through the reactor was kept constant at 58 mL·min⁻¹ and controlled by a volumetric flowmeter.

Isotopic analysis

The formation of H₂, HD, and D₂ species was monitored in the outlet gas with Prima BT Benchtop mass spectrometer (Thermo Scientific). The water vapors were trapped with molecular sieve (Sigma-Aldrich, 5 Å) prior to mass spectrometric analysis. The H/D isotope separation factor, α_H , was calculated as the ratio $\alpha_H = \left(\frac{H}{D}\right) / \left(\frac{H}{D}\right)_0$, where the initial ratio $\left(\frac{H}{D}\right)_0$ is equal to the molar composition of H₂O/D₂O mixture in the presence of 1M of glycerol, and

the experimental $\left(\frac{H}{D}\right)$ value is obtained as $\frac{H}{D} = \frac{I(H_2) + 1/2I(HD)}{I(D_2) + 1/2I(HD)}$, where I is the mass spectrometric ion intensity of the corresponding hydrogen isotopologue at steady-state after background subtraction. The H_0 value was calculated as a sum of H atoms from H₂O and exchangeable H atoms from 1 M Glycerol. Regarding H/D isotopic exchange, in the molecule of glycerol there are two kinds of hydrogen atoms. Hydrogen atoms strongly bonded to carbon are kinetically inert in the H/D exchange. By contrast, hydrogen atoms bonded to oxygen are

easily exchangeable with D atoms from D₂O or HDO. Therefore, only kinetically exchangeable

H atoms of glycerol were taken into account for the calculation of $\left(\frac{H}{D}\right)_0$ ratio. It is noteworthy that the contribution of the exchangeable H atoms from glycerol did not exceed 11% of H atoms originated from H₂O (25H₂O/75D₂O). The H₂O/D₂O/Glycerol solutions were prepared by mixing weighted amounts of ultrapure H₂O (18.2 MΩ cm), D₂O (99.90% D), and ultra-pure glycerol with a precision better than 0.1%. The concentration of hydrogen has been quantified using external calibration curves prepared with standard gas mixtures H₂/Ar (Messer).

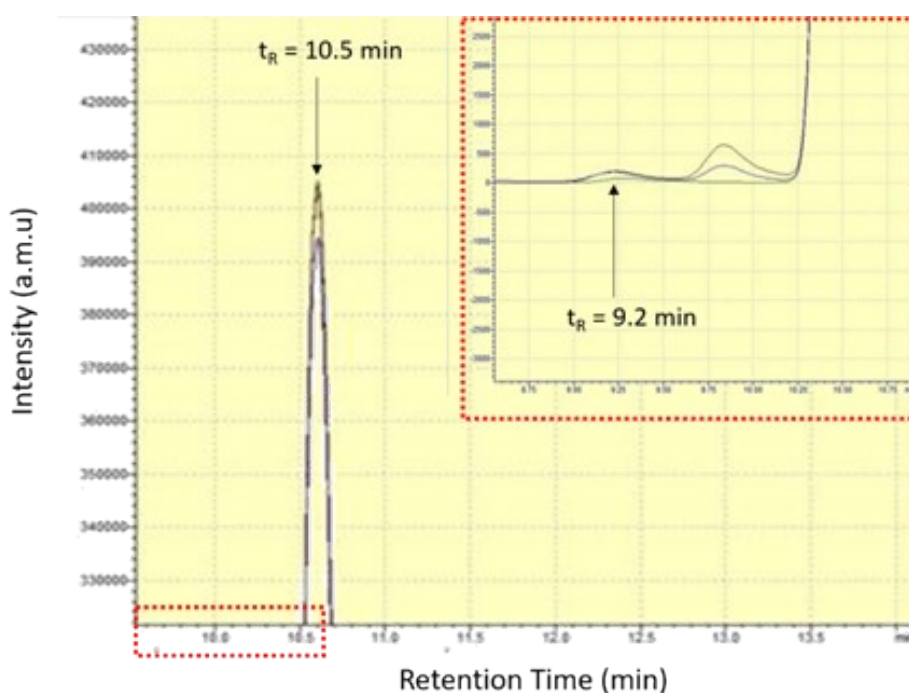


Figure S5. HPLC analysis of 0.5 M glycerol samples before and after 3 h and 8 h of photothermal treatment at 94 °C in the presence of Ti@TiO₂ nanoparticles (0.12 g⁻¹·L⁻¹). The analysis has been performed using Varian Pro Star HPLC analyzer on an Aminex HPX 87-H (Bio Rad) column. Signals at the retention time of 10.5, 9.85, and 9.20 min correspond to glycerol, glyceraldehyde and glyceric acid respectively (N. Wörz et al. J. Phys. Chem. C, 2010, 114, 1164–1172).