

Electronic Supplementary Information

Nonstoichiometric rutile TiO₂ photoelectrode for improved photoelectrochemical water splitting

Sample preparation procedure. To prepare an amorphous TiO₂ nanotube array film, a titanium foil (30 mm × 10 mm × 0.25 mm) was immersed in a mixed solution of glycol and water with a volume ratio of 9:1 containing 0.25 wt% NH₄F in a two-electrode cell with a Pt foil as counter electrode. Anodization was conducted at 60 V for 3 h. As-prepared films were washed with deionized water several times to remove any residual dissolvable ions. Then the top amorphous nanotube array film can be easily removed through ultrasonic treatment in 30 wt% H₂O₂ solution, and a nanotube-free compact amorphous film was obtained.

To prepare stoichiometric and nonstoichiometric rutile TiO₂ films, the obtained compact amorphous films were heated at 550 °C for 1 h in air and argon atmosphere with a temperature ramping rate of 5 °C/min.

Characterization. X-ray diffraction patterns of the samples were recorded on a Rigaku diffractometer using Cu K α irradiation. Their morphology was determined by using scanning electron microscopy (SEM) performed on a Nova NanoSEM 430. The chemical states of Ti and O, and depth dependent component evolution in two rutile TiO₂ films were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al K α X-ray source). Binding energy was referenced to the C 1s peak (284.6 eV) arising from adventitious carbon. The Raman spectra of samples were recorded on LabRam HR 800 excited by a 632.8 nm laser. The Mott-Schottky curves and EIS were recorded on a PARSTAT 2273 electrochemical workstation (Princeton Applied Research). The Mott-Schottky plots were conducted at the AC frequency of 1 kHz in 0.2 M Na₂SO₄ aqueous electrolyte. The Nyquist plots were recorded from 10 mHz to 100 KHz at 0.3 V (vs Ag@AgCl) with an amplitude of 20 mV and fitted by ZSimpWin software using the proposed equivalent circuit models.

Photoelectrochemical water splitting measurements. The measurements were carried out in a quartz cell with a conventional three-electrode process, where a TiO₂ photoelectrode as an anode, a Pt foil and Ag/AgCl electrode served as the working electrode, counter electrode and reference electrode, respectively. Electrolyte was 0.2

M Na_2SO_4 aqueous solution. The light source in the above photoreactivity experiments was a 300 W Xe lamp (Beijing Trusttech Co. Ltd, PLS-SXE-300UV). The photoanode surface area illuminated was 1 cm^2 , and the scanning rate was 0.1 V s^{-1} . The scanning is from -0.6 V to 1.0 V . Visible light irradiation was obtained by using a 420 nm longpass glass filter to remove UV.

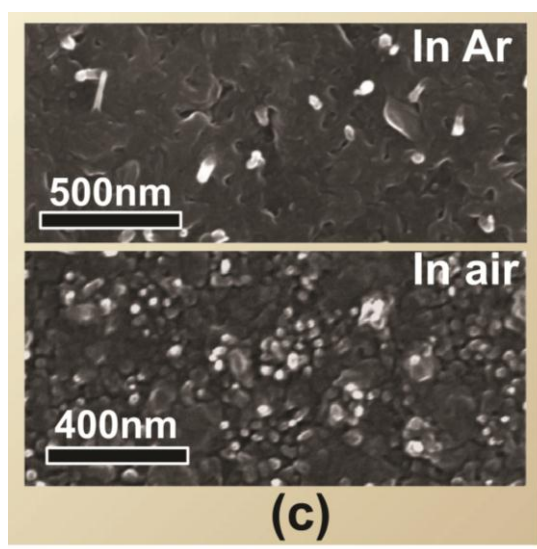


Fig. S1 The Fig. 1c in a large size.

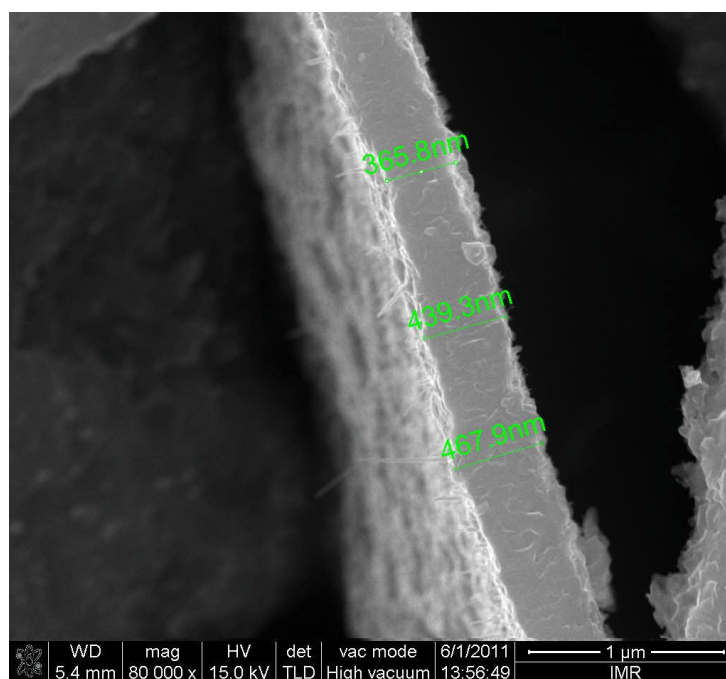


Fig. S2 SEM image showing the cross-sectional view of the nonstoichiometric rutile TiO_2 film.

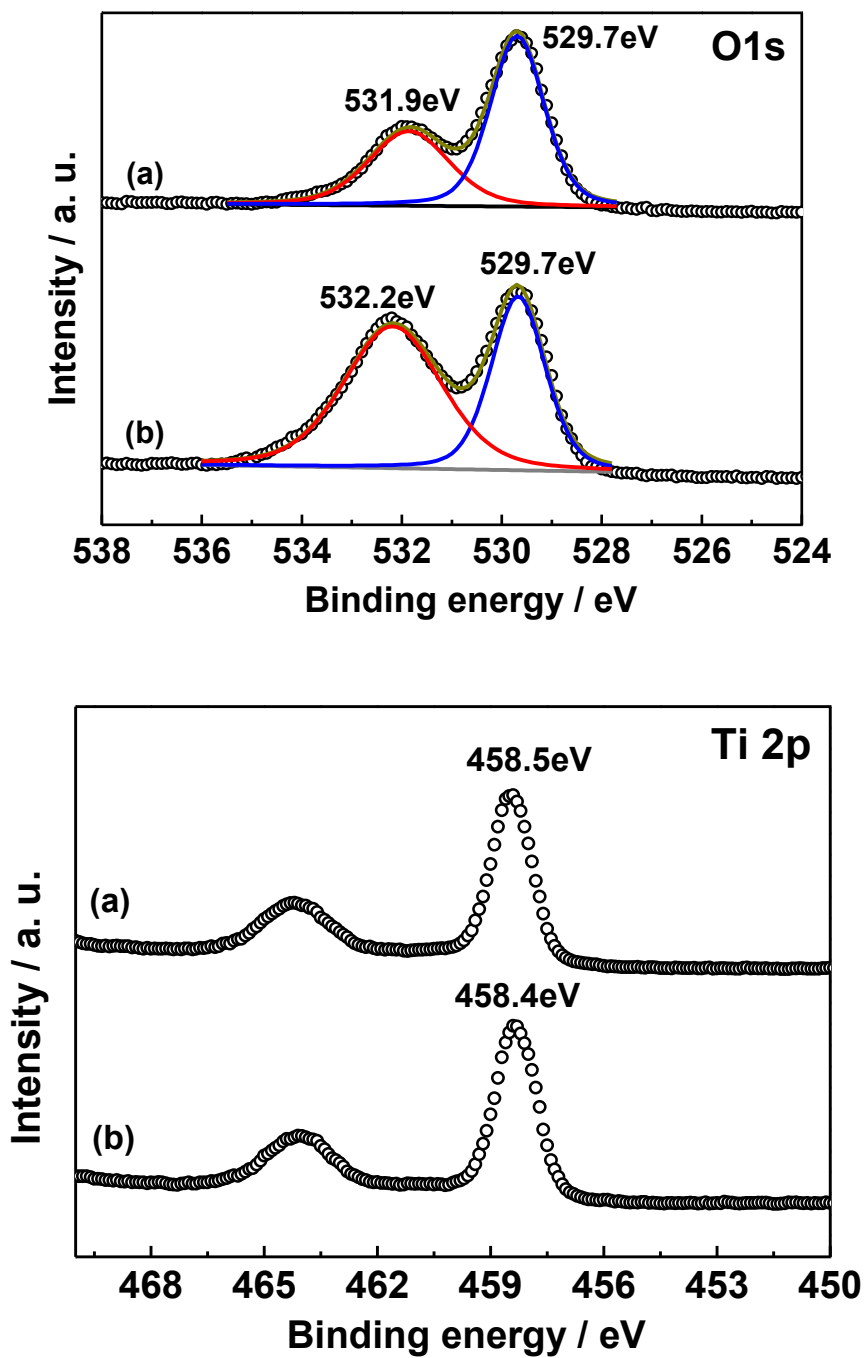


Fig. S3 High resolution XPS spectra of O 1s and Ti 2p recorded from the surface of the (a) stoichiometric and (b) nonstoichiometric rutile TiO₂ photoelectrodes.

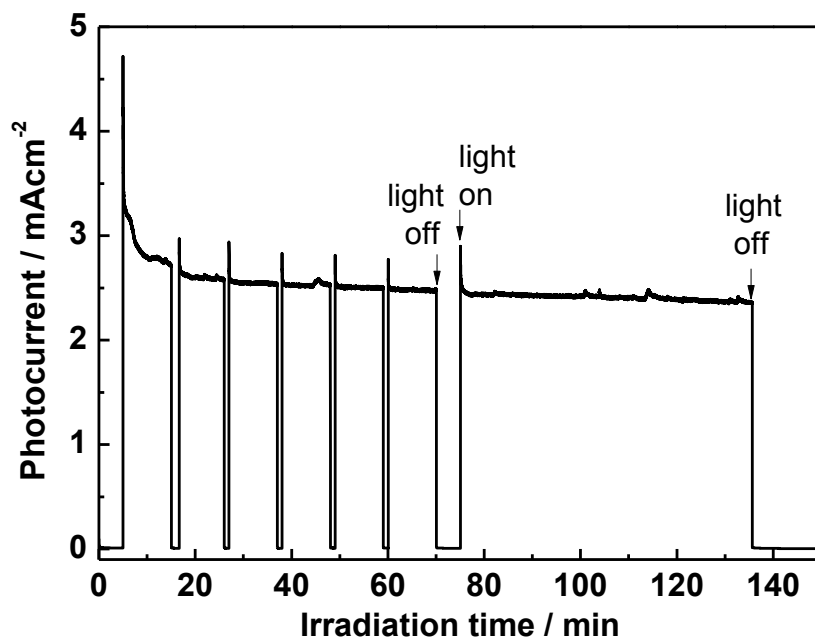


Fig. S4 Time-dependent photocurrent stability of the nonstoichiometric rutile TiO_2 photoelectrode measured at 0.3 V in 0.2 M aqueous Na_2SO_4 electrolyte.

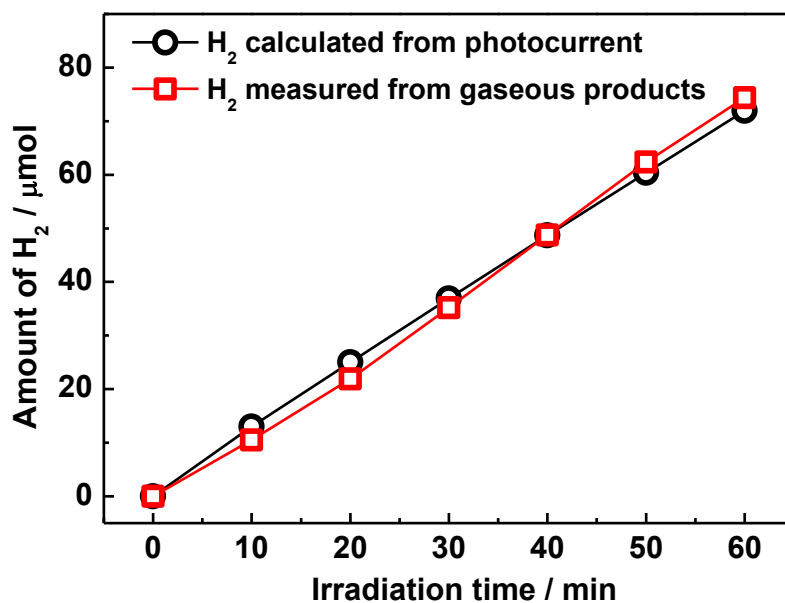


Fig. S5 Comparison between the amount of hydrogen measured from the gaseous products generated in the PEC cell and the amount of hydrogen calculated from the photocurrent generated with the nonstoichiometric rutile TiO_2 photoelectrode at 0.3 V.

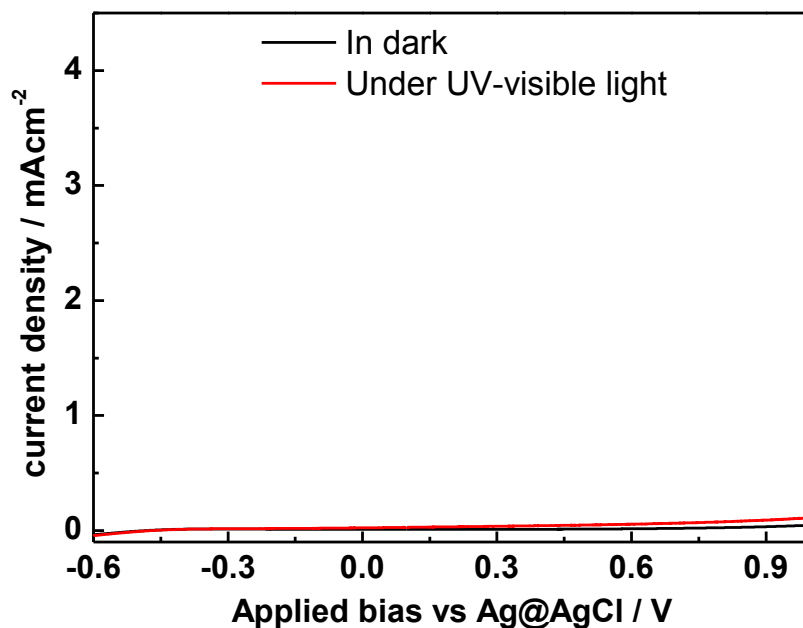


Fig. S6 Applied potential bias-dependent photocurrent density of the amorphous TiO₂ photoelectrode in the dark and under UV-visible light.

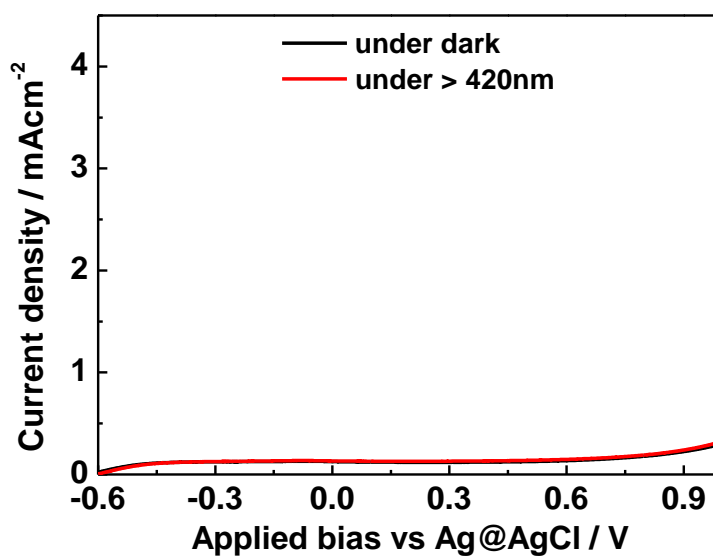


Fig. S7 Applied potential bias-dependent photocurrent density of the nonstoichiometric rutile TiO₂ photoelectrode in dark and under visible light ($\lambda > 420$ nm). Measurement conditions: 0.2 M aqueous Na₂SO₄ electrolyte, scanning rate of 0.1 V s⁻¹.

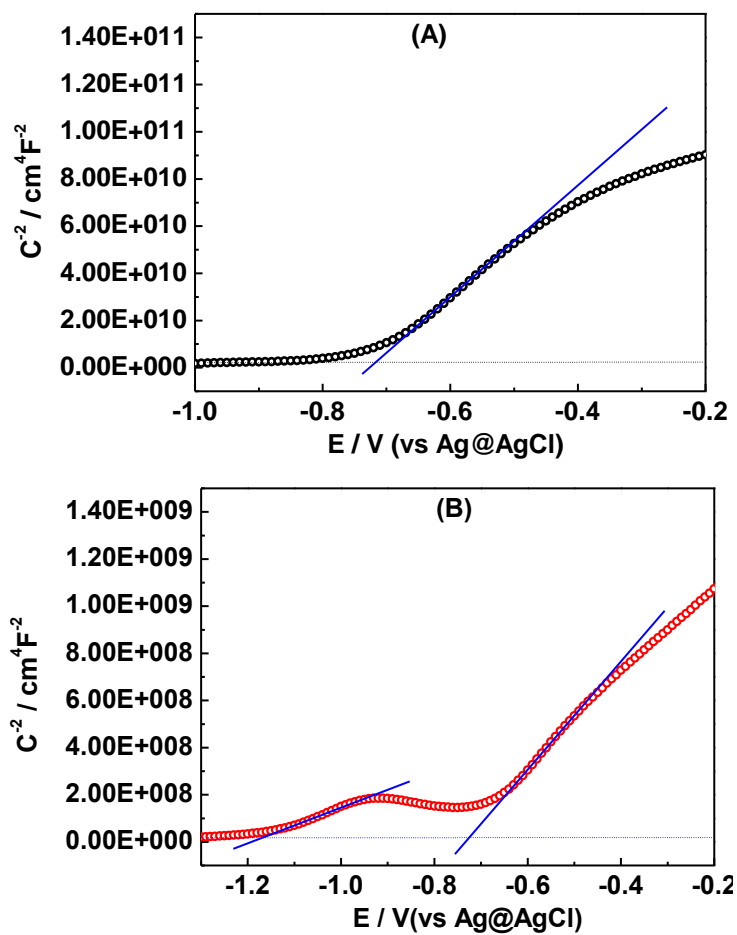


Fig. S8 Mott-Schottky curves of the (A) stoichiometric and (B) nonstoichiometric rutile TiO_2 films.

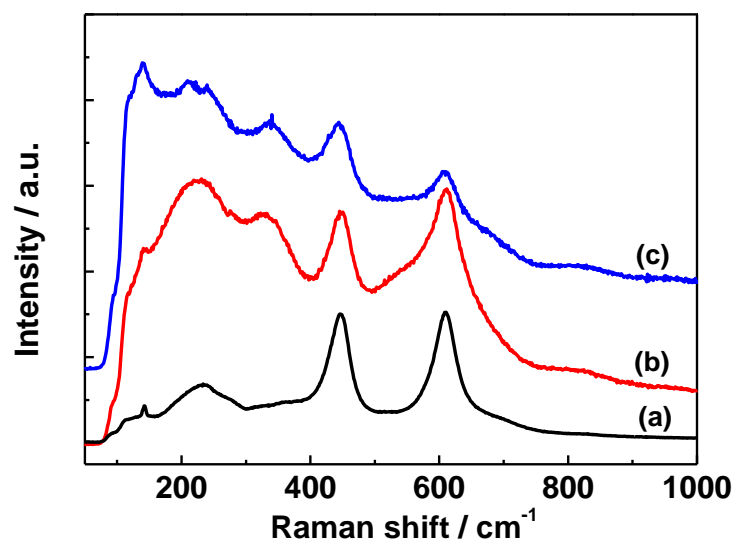


Fig. S9 Raman spectra of (a) reference rutile TiO_2 powders, (b) stoichiometric and (c) nonstoichiometric rutile TiO_2 films.