Electronic Supplementary Information (ESI)

A film of rutile TiO_2 pillars with well-developed facets on an α-Ti substrate as a photoelectrode for improved water splitting

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Sample preparation procedure. To prepare an amorphous TiO_2 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% NH_4F 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% H_2O_2 solution, and a nanotube-free compact amorphous film was obtained.

To prepare a rutile TiO_2 pillar film, the compact amorphous film was heated at 550 ^oC for 1 h in oxygen atmosphere with a pressure of 10^3 Pa. The temperature ramping rate used was 5 ^oC /min. A similar preparation procedure with a 3 ^oC/min ramping rate was also used to crystallize an anatase TiO_2 nanotube array film on a Ti foil.

Characterization. X-ray diffraction patterns of the samples were recorded on a Rigaku diffractometer using Cu irradiation. Their morphology was determined by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) performed on a Nova NanoSEM 430 and Tecnai F30. The chemical state of Ti

in TiO_2 was analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al Kα X-ray source). Binding energy was referenced to the C 1s peak (284.6 eV) arising from adventitious carbon. The optical absorbance spectra of the samples were recorded in a UV-visible spectrophotometer (JACSCO-550).

Photoelectrochemical measurements. Photoelectrochemical measurements were carried out in a quartz cell with a conventional three-electrode process, where a TiO_2 photoelectrode as 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 incident photon-to-current conversion efficiency (IPCE) was calculated according to the following equation:

IPCE (%) = [1240 × photocurrent density ($mAcm^{-2}$)] / [wavelength (nm) × photon flux ($mW\ cm^{-2}$)] × 100%

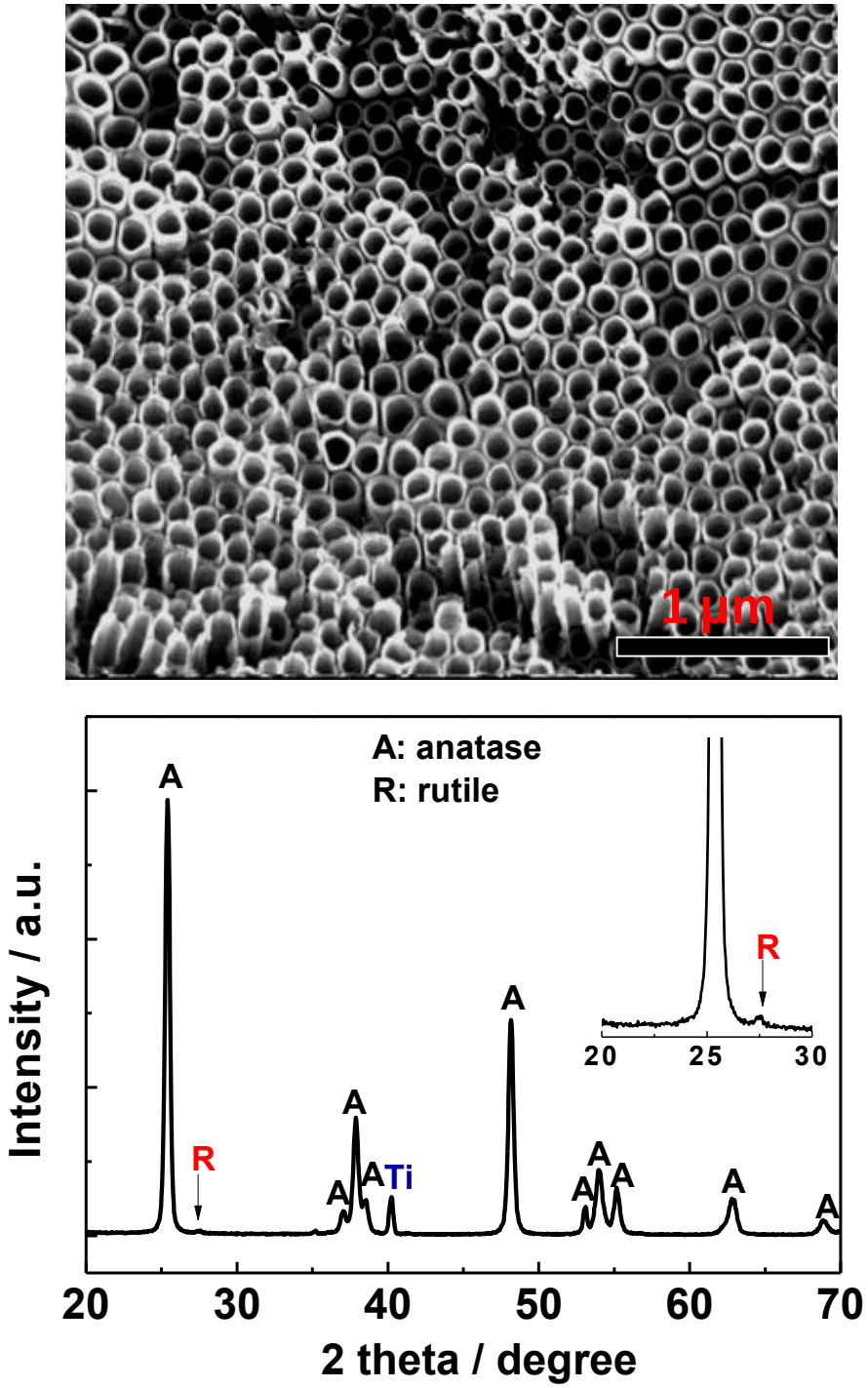

Fig. S1 SEM image and XRD patterns of a crystalline TiO_2 film on a Ti foil by directly heat treating an as-prepared amorphous TiO_2 film consisting of both the top nanotube and compact film.

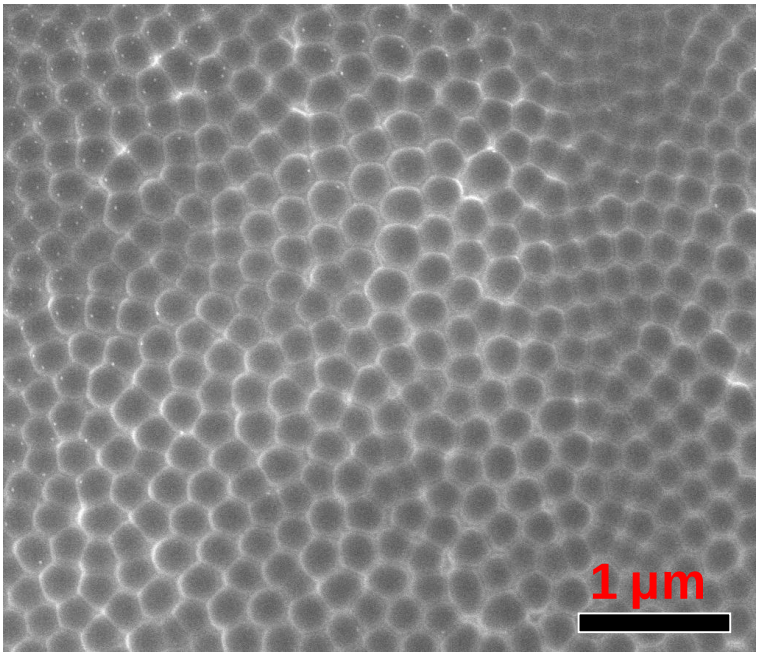

Fig. S2 SEM image of a compact amorphous TiO_2 film on a Ti foil left after removing the top amorphous nanotube array film. The topmost honeycomb-like pores were formed due to the slight embedding of the close ends of nanotubes in the compact amorphous TiO_2 film during anodization growth.

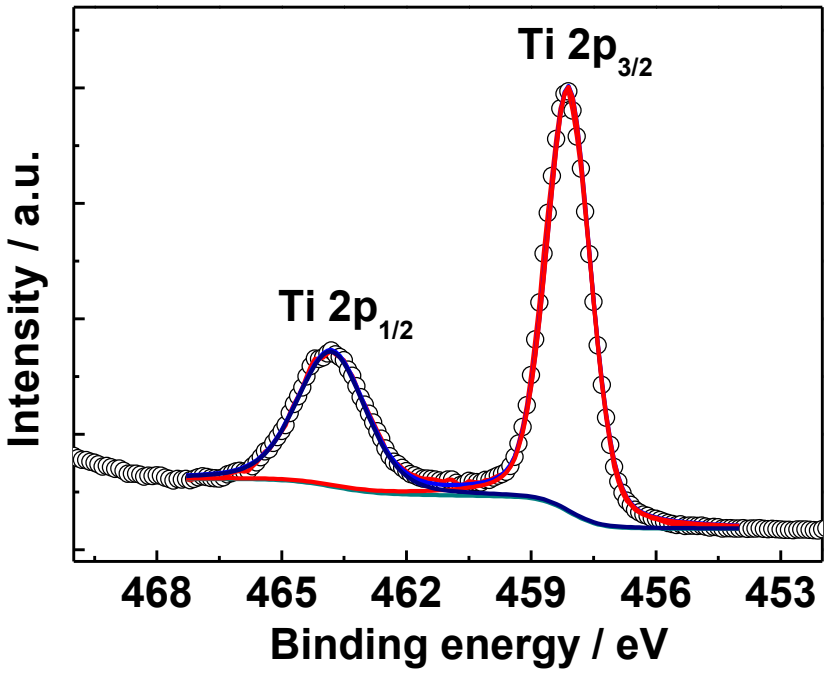

Fig. S3 High resolution XPS spectrum of Ti 2p in the prepared rutile TiO_2 pillars on a Ti foil.

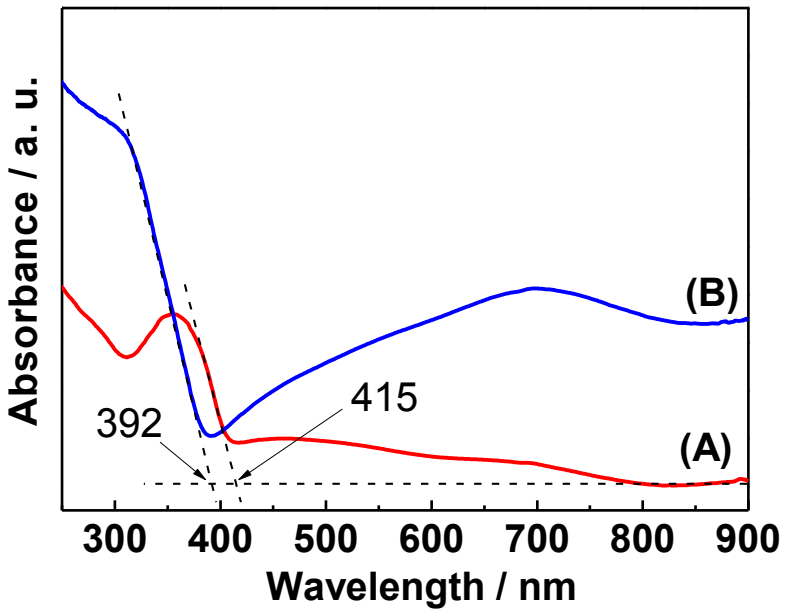

Fig. S4 UV-visible absorption spectra of (A) a rutile TiO_2 pillar film on a Ti foil and (B) an anatase TiO_2 nanotube array film on a Ti foil.

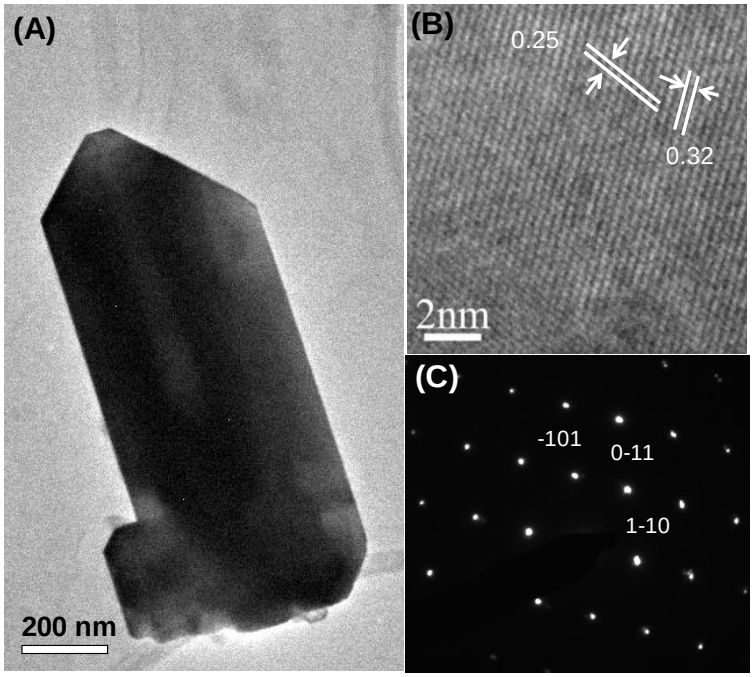

Fig. S5 (A), TEM image of a typical rutile TiO_2 pillar with well-developed facets; (B), high resolution TEM image of another single rutile TiO_2 pillar scraped from the rutile TiO_2 pillar film on a Ti foil; (C), corresponding selected area electron diffraction pattern of (B).

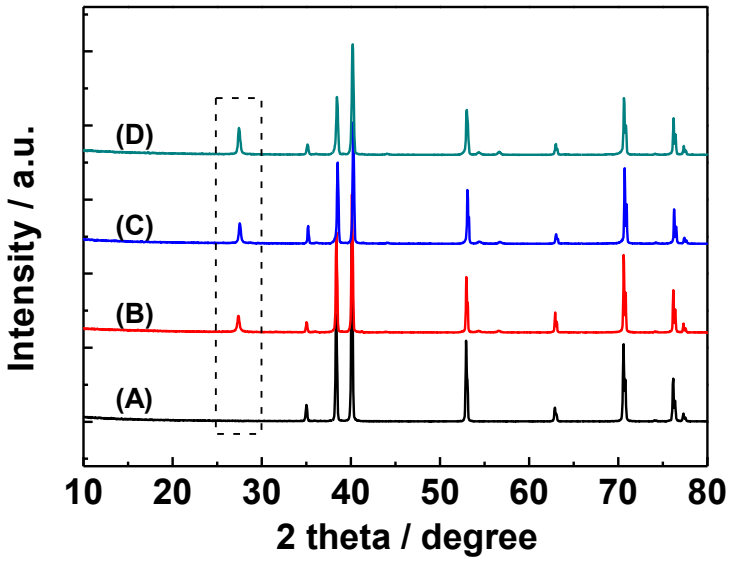

Fig. S6 Time dependence X-ray diffraction pattern evolution of an amorphous compact TiO_2 film on a Ti foil by heating at 550 ^oC in oxygen atmosphere with a pressure of 10^3 Pa: (A), 0 min; (B), 10 min; (C), 30 min; (D), 50 min.

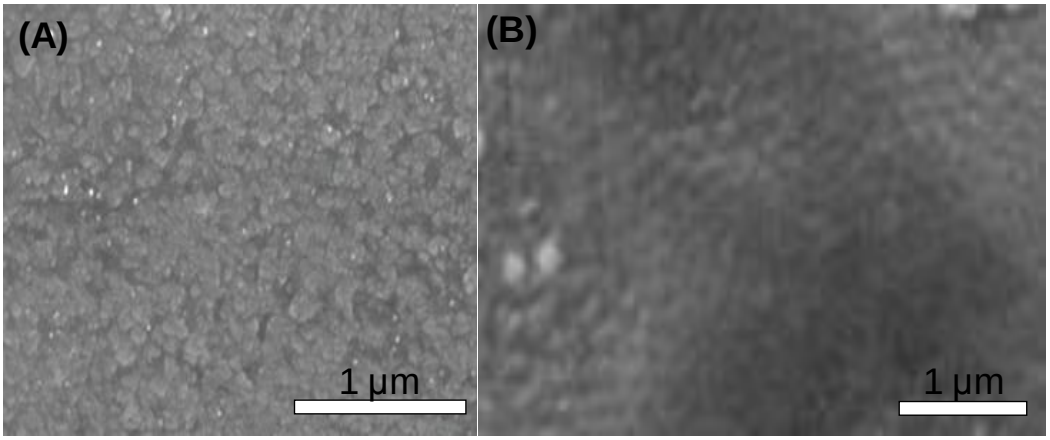

Fig. S7 SEM images of the rutile TiO_2 films on a Ti foil obtained by heating a compact amorphous TiO_2 film at 550 ^oC for 1 h in oxygen atmosphere with a pressure of (A) 10 Pa and (B) 10^5 Pa.

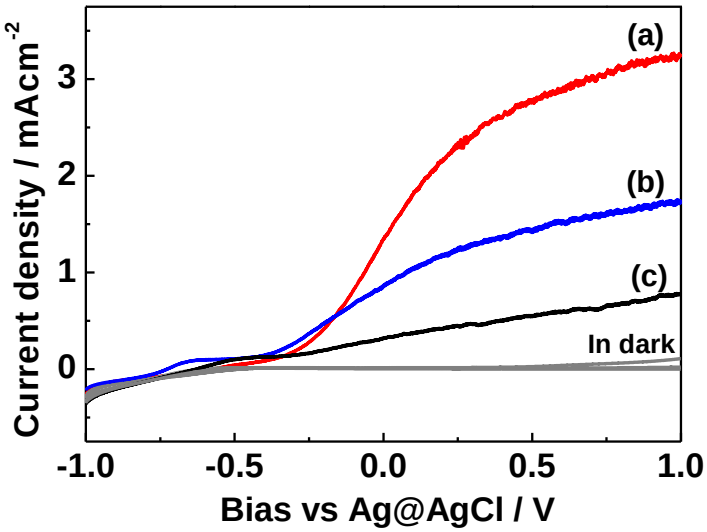

Fig. S8 Applied potential bias-dependent photocurrent density: a rutile TiO_2 pillar photoelectrode (a), the rutile TiO_2 films on a Ti foil obtained by heating a compact amorphous TiO_2 film at 550 ^oC for 1 h in oxygen atmosphere with a pressure of (b) 10^5 Pa and (c) 10 Pa.