Electronic Supplementary Information

Improving the Photocatalytic and Photoelectrochemical Activities of Mesoporous Single Crystal Rutile TiO₂ for Water Splitting

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Sample preparation. A seeded mesoporous silica template was prepared based on the method given in [1] and [2]. 16 ml H₂O, 9 ml ammonium hydroxide (30%, Aldrich) and 50 ml tetraethyl orthosilicate (Aldrich) were added to 375 ml ethanol. The reaction solution was stirred at 700 r.p.m. for 24 h, and then centrifuged at 7000 r.p.m. for 5 h to form a quasi-close-packed bead template. The unwashed template was collected and sintered at 500 °C in air for 30 min with a heating rate of 3 °C/min. To seed the template, 2.5 g template was immersed in 16 ml 15 mM TiCl₄ solution, obtained by diluting a 2 M TiCl₄ aqueous stock solution (the stock solution was prepared by diluting 100 ml TiCl₄ in 350 ml H₂O containing 1 ml 35% HCl in an ice/water bath), and heated at 70 °C for 1 h. The seeded template was thoroughly washed with deionized water. The dried template was re-heated at 500 °C in air for 30 min with a heating rate of 3 °C/min.

To prepare mesoporous single crystal rutile TiO_2 , 0.3 g of the seeded silica template was added to 40 ml of a 15 mM $TiCl_4$ aqueous solution containing NaF (15 mM) and HCl (3 M). The suspension was transferred to a Teflon-lined autoclave and heated at 220 $^{\circ}$ C for 12 h. The sample was collected by centrifugation and fully washed with deionized water to remove any dissolvable impurity. To selectively remove the silica template, the sample was heated at 80 $^{\circ}$ C in a 2 M NaOH solution for 60 min and then washed with deionized water. In a control experiment, solid single crystal rutile TiO₂ was prepared without the silica template. The synthesis parameters used were as given in the reports by Lai et al. [3]. To remove surface-terminated fluorine/chlorine species, the TiO₂ samples were heated at 600 $^{\circ}$ C in air for 2 h.

Photoelectrode fabrication. A doctor-blade technique was used to fabricate rutile TiO_2 films on fluorine-doped tin oxide-coated glass substrates. TiO_2 slurries were prepared by fully milling a mixture of 0.1 g TiO_2 , 1 mL distilled water, three drops of Triton X-100 and one drop of acetylacetone. The slurries were deposited on the substrates by the doctor-blade method with adhesive type as spacer. After coating, the films were calcined at 400 °C in air for 60 min.

Characterization. X-ray diffraction patterns of the samples were recorded on a Rigaku diffractometer using CuKα irradiation. Sample morphology and microstructure were determined using scanning electron microscopy (Nova NanoSEM 430) and transmission electron microscopy (JEOL 2010). Brunauer-Emmett-Teller (BET) surface area was determined by nitrogen adsorption-desorption isotherm measurements at 77 K (ASAP 2010). The optical absorption spectra of the samples were recorded in a UV-visible spectrophotometer (JASCO-550).

Photocatalytic water splitting measurements. Photocatalytic hydrogen and oxygen evolution reactions were carried out in a top-irradiation vessel connected to a glass-enclosed gas circulation system. 50 mg of the TiO₂ powder was dispersed in a 300 mL aqueous solution containing 10 vol% methanol for hydrogen evolution or 16.7 mM AgNO₃ for oxygen evolution. The reaction temperature was maintained around 20 0 C. The amount of H₂ and O₂ evolved was determined using a gas chromatograph (Agilent Technologies: 6890N). The light source in the photoreactivity experiments was a 300 W Xe lamp (Beijing Trustlech Co. Ltd, PLS-SXE-300UV).

Photoelectrochemical water splitting measurements. Photoelectrochemical water splitting was carried out in a three-electrode system, where the fabricated TiO_2 electrodes, Ag/AgCl electrode and Pt foil act as the working electrode, reference electrode and counter electrode, respectively. The electrolyte used was a 0.2 M Na₂SO₄ aqueous solution illuminated by AM 1.5G light with a density of 100 mWcm⁻² (Newport).

Photodeposition of Pt particles on rutile TiO₂ crystals. A certain amount of mesoporous or solid anatase single crystal TiO_2 powder was suspended in the H₂PtCl₆ solution containing methanol as sacrificial agent (water: methanol of 2:1 in volume). This suspension was irradiated under UV light for 60 min.

References

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Fig. S1 The nitrogen desorption isotherm curves and BJH pore size distribution of

mesoporous single crystal rutile TiO₂.



Fig. S2 UV-visible absorption spectra of solid single crystals and mesoporous single crystals of rutile TiO₂.



Fig. S3 a, TEM image of Pt-loaded mesoporous single crystal rutile TiO_2 produced by the photo-deposition method. b, Schematic of the dispersion of Pt nanoparticles in mesoporous single crystal rutile TiO_2 .



Fig. S4 TEM image of Pt-loaded solid single crystal rutile TiO_2 produced by the photo-deposition method.