Electronic Supplementary Information

Solid state precursor strategy for synthesizing hollow TiO_2 boxes with high percentage of reactive {001} facets exposed

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1. Experimental section

Fabrication of $TiOF_2$ cubes

The $TiOF_2$ cubes were synthesized via a facile one-step hydrothermal reaction. Typically, 5.0 mL tetrabutyl titanate ($Ti(OBu)_4$), 1.6 mL 47% hydrofluoric acid solution (HF), and 10.0 mL acetic acid (C_2H_5OOH) were added together in a teflon-lined autoclave with 20 mL content. Then, the reactants were heated rapidly to 200 °C in 60 min, and kept at this temperature for 12 hours in an oven. After cooled down naturally to room temperature, white products were collected and washed by ethanol for several times and dried at 60 °C for 10 hours.

Preparation of hollow anatase TiO_2 boxes

The hollow anatase TiO_2 boxes, each of which consists of six anatase {001} facets exposed plates, were simply fabricated by calcining treatment of the as-prepared $TiOF_2$ cubes with a muffle furnace in the ambient. The amount of the $TiOF_2$ used was 0.400 g for each time. Five TiO_2 products were independently prepared at 300 °C, 400 °C, 500 °C, 600 °C, 900 °C for 120 min with a slow heating rate of 1 $^{o}C\bullet min^{-1}$, which were denoted as T300, T400, T500, T600 and T900, respectively.

Characterizations of samples

The powder X-ray diffraction (XRD) patterns of the samples were recorded on a panalytical X-pert diffractometer with the copper Kα irradiation. Morphologies and crystal structures of the as-synthesized products were determined by scanning electron mircoscopy (SEM, Hitachi S-4800, 10 kV) and transmission electron microscopy (TEM, FEI Tecnai-F30, 300 kV). The thermogravimetric analysis (TGA) was carried out on a SDT Q600 thermal analyzer under an air atmosphere at the temperature range of 30 ~ 900 ºC with a heating rate of 10 ºC•min^{-1}. The powder UV-visible absorption spectra were obtained with a Varian Cary-5000 UV-Vis-NIR Spectro-photometer. The surface area of the products was measured by the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption and desorption isotherms on a Micrometrics ASAP 2020 system.

Photocatalytic water splitting tests

Pt was selected as the co-catalyst for photocatalytic water splitting. The Pt/TiO_2 catalyst was conducted by a UV-vis light induced reduction method. Typically, hollow TiO_2 boxes (0.150 g) were dispersed in 100 mL deionized water by ultrasonic for 10 min. Then, 0.405 mL of 0.0193 M H_2PtCl_6 aqueous solution was impregnated into the above solution. In this prescription, the nominal weight ratios of Pt to TiO_2 was 1.0 wt%. The suspensions were stirred and followed by UV-vis illumination (300 W Xe lamp) for 30 min at room temperature. After that, the precipitates were collected by centrifuge and washed by ethanol for three times. Finally, the products were dried at 60 °C for 10 hours.

The photocatalytic H_2 production experiments were carried out in a top-irradiation vessel connected to a stainless steel closed gas circulation system. In typical, 50 mg of the 1.0 wt% Pt loaded photocatalyst was well dispersed in mixed solutioin of 80 mL deionized water and 20 mL methanol under magnetic stirring. The reaction was maintained at room-temperature by a cooling water circulation. A 300 W Xe lamp (Beijing Trusttech Co. Ltd, PLS-SEX-300UV) with the wavelength of 220~770 nm was employed as light source. Before irradiation, the system was pumped to remove the air, and then, Ar gas was inflated in as carrier gas untill the system reached the atmospheric pressure. The amount of the H_2 evolved was determined using a gas chromatography with a TCD detector.

2. Experimental results

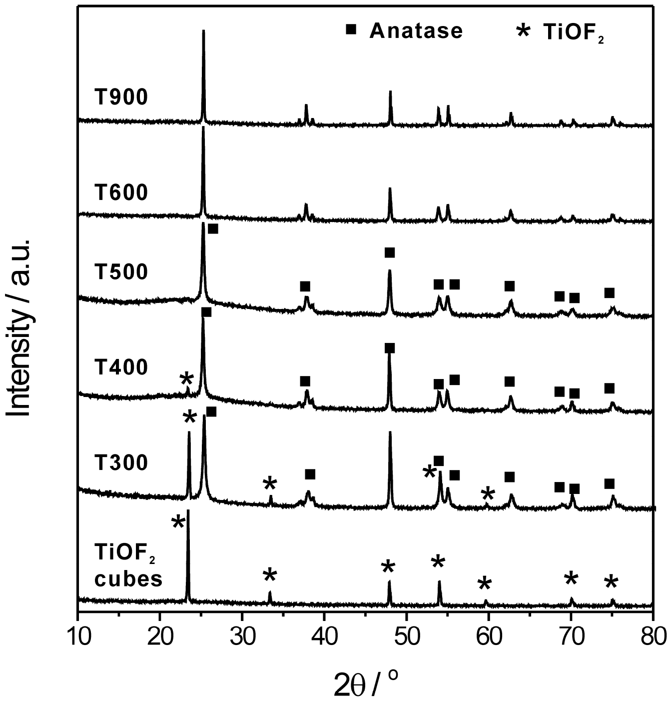

Fig. S1 XRD patterns of the $TiOF_2$ products before and after calcined at various temperatures for 120 min.

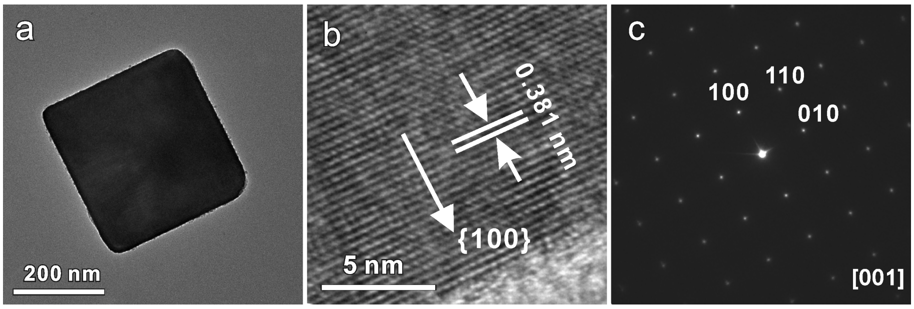

Fig. S2 TEM characterization of single $TiOF_2$ cubes. (a) TEM image of single $TiOF_2$ cube, (b) high-resolution TEM image on the edge of the $TiOF_2$ cube showing the exposed {100} facets, and (c) corresponding SAED pattern of the $TiOF_2$ cube.

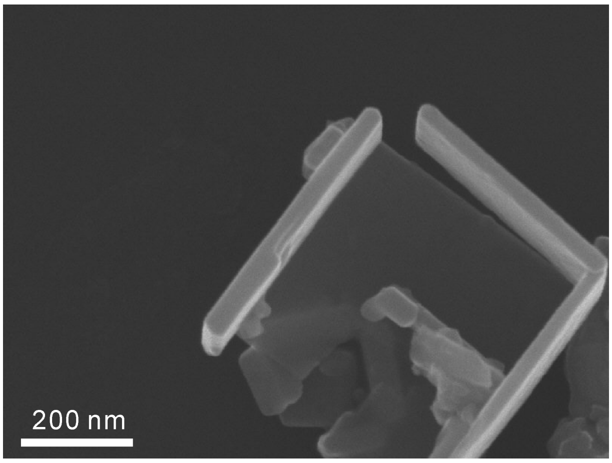

Fig. S3 The SEM image of the T500 products along the direction perpendicular to the side facets, showing the thickness of the plates.

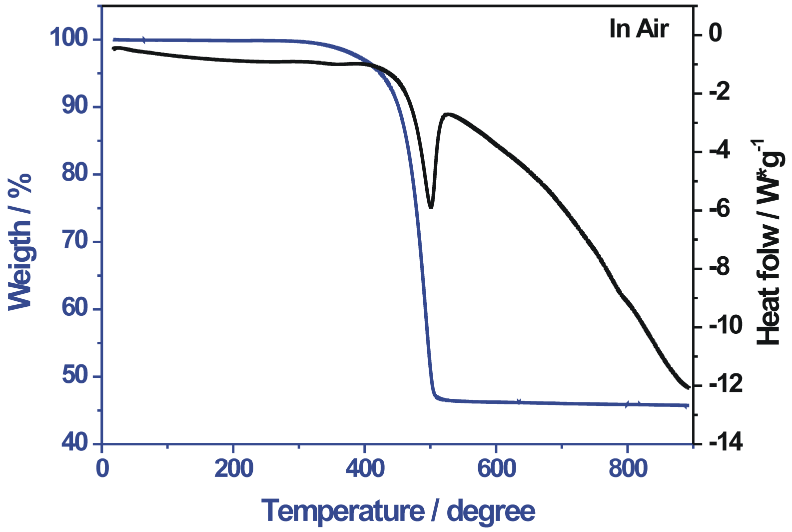

Fig. S4 TGA measurements of the $TiOF_2$ cubes: the weight losing curve (Blue) and the heat flow curve (Black).

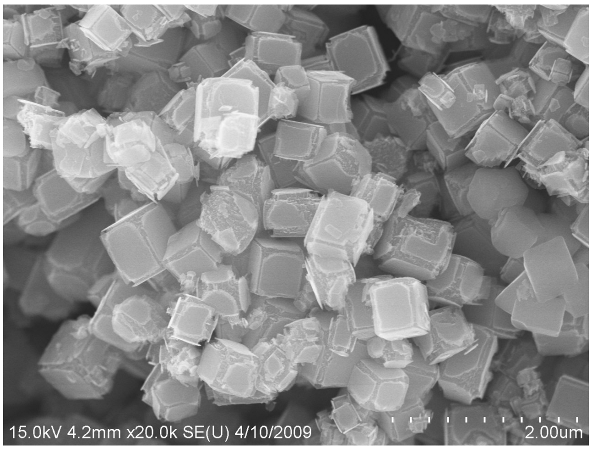

Fig. S5 The SEM image of the T300 product.

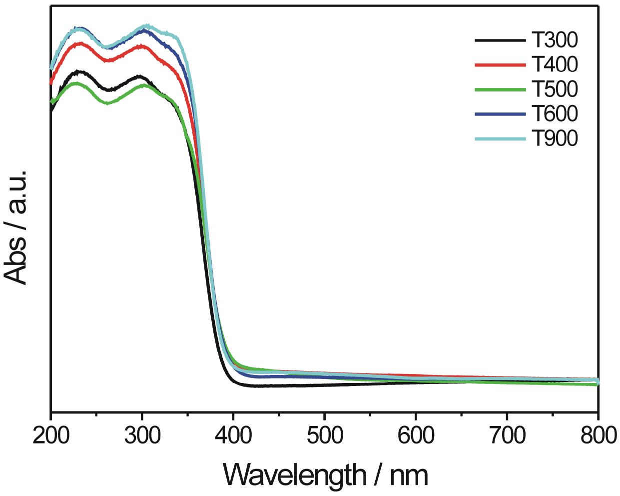

Fig. S6 The UV-vis diffuse reflection spectra of the products calcined at various temperatures.

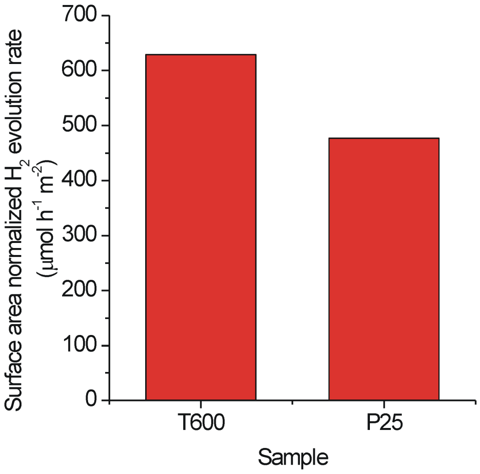

Fig. S7 The comparison of the photocatalytic H_2 evolution rates between T600 and P25, which have been normalized with their surface areas (T600:12.0 $m^2 \cdot g^{-1}$; P25: 52.8 $m^2 \cdot g^{-1}$).