

## Electronic Supplementary Information (ESI)

# Topotactic Transformation of Single-Crystalline TiOF<sub>2</sub> Nanocubes to Ordered Arranged 3D Hierarchical TiO<sub>2</sub> Nanoboxes

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### 1. Experimental Section,

#### Preparation of TiOF<sub>2</sub> nanocubes

The TiOF<sub>2</sub> nanocubes were synthesized by a facile one-step hydrothermal method. In a typical process, 5.0 ml (14.63 mmol) tetrabutyl titanate (Ti(OBu)<sub>4</sub>), 1.6 ml 47 % (w/v) hydrofluoric acid (HF), and 10.0 ml acetic acid (CH<sub>3</sub>COOH) were added in a Teflon-lined autoclave with 20 ml content. Then, the autoclave was transferred to an oven preheated to 200 °C, and kept at this temperature for 12 h. After cooled down naturally to room temperature, the white products were filtered with membrane and washed with ethanol for several times. 1.40g TiOF<sub>2</sub> products were finally obtained after dried at 60 °C overnight.

#### Preparation of ordered arranged 3D hierarchical TiO<sub>2</sub> nanoboxes

The hierarchical TiO<sub>2</sub> hollow nanoboxes were prepared via a simple solution based methods under the temperature of 80 °C. TiOF<sub>2</sub> nanocubes were employed as precursors. In a typical run, 100 mg TiOF<sub>2</sub> nanocubes were dispersed in 100 ml basic solutions with the pH value of 11, which is adjusted with NaOH (1 M) aqueous solutions. The solution was maintained at 80 °C for 8 hours with magnetic stirring to ensure the complete transformation from TiOF<sub>2</sub> to anatase TiO<sub>2</sub>. Then, the white powders were filtered and washed with deionized water for several times and dried at 60 °C overnight. 75 mg TiO<sub>2</sub> samples (yield 95 %) were finally obtained after the above procedures. In order to investigate the transformation process, samples prepared under different reaction times, e. g., 2 h, 4 h, 6 h, 16 h, 24 h, and 36 h, were also prepared under identical conditions.

## Characterizations of samples

The structures of the samples were characterized by the powder X-ray diffraction (XRD) performed on a Bruker D8 Advanced X-ray diffractometer with monochromatized Cu K $\alpha$  radiation. The morphologies and crystal structures of as-prepared samples were determined by scanning electron microscopy (SEM, Hitachi S-4800, 7 kV) and high-resolution transmission electron microscopy (HR-TEM, JEM 2100, 300 kV). The surface area of the samples was measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption and desorption isotherms on a Micrometrics ASAP 2020 system.

## Photocatalytic hydrogen evolution experiments

Before photocatalytic hydrogen evolution experiments, Pt co-catalyst were supported on TiO<sub>2</sub> hollow nanoboxes by a UV-Vis light induced reduction procedure, and the Pt loading was fixed at 1.0 wt%. Typically, 150 mg as-prepared TiO<sub>2</sub> hollow nanoboxes were initially dispersed in 100 ml deionized water by ultrasonic for 10 min. Then, 101  $\mu$ l H<sub>2</sub>PtCl<sub>6</sub> aqueous solutions with concentration of 0.0772 M were impregnated into the above suspension. The suspension was vigorously stirred and irradiated under UV light irradiation for 30 min at room temperature. The precipitates were collected by filtration and washed by ethanol twice and dried at 60 °C for 5 h. After this process, 1.0 wt% Pt were deposited on the surface of TiO<sub>2</sub> nanoboxes.

The photocatalytic H<sub>2</sub> evolution experiments were carried out on LABSOLAR II (Perfect light, Co. Ltd.) photocatalytic water splitting testing system. Typically, 100 mg of 1.0 wt% Pt loaded samples were dispersed in 100 ml aqueous methanol solution (20 ml of methanol, 80 ml of deionized water) under magnetic stirring. The experiments were carried out at room-temperature with a cooling water circulation. A 300 W Xe lamp (PLS-SEX-300UV, Trusttech Co. Ltd.) was employed as the light source. Before irradiation, the system was pumped to remove the air, and the amount of H<sub>2</sub> evolved was determined with a gas chromatograph (Techcomp-GC7890-II, nitrogen as a carrier gas), which connected to a circulation line and equipped with thermal conductivity detector (TCD).

## 2. Experimental results

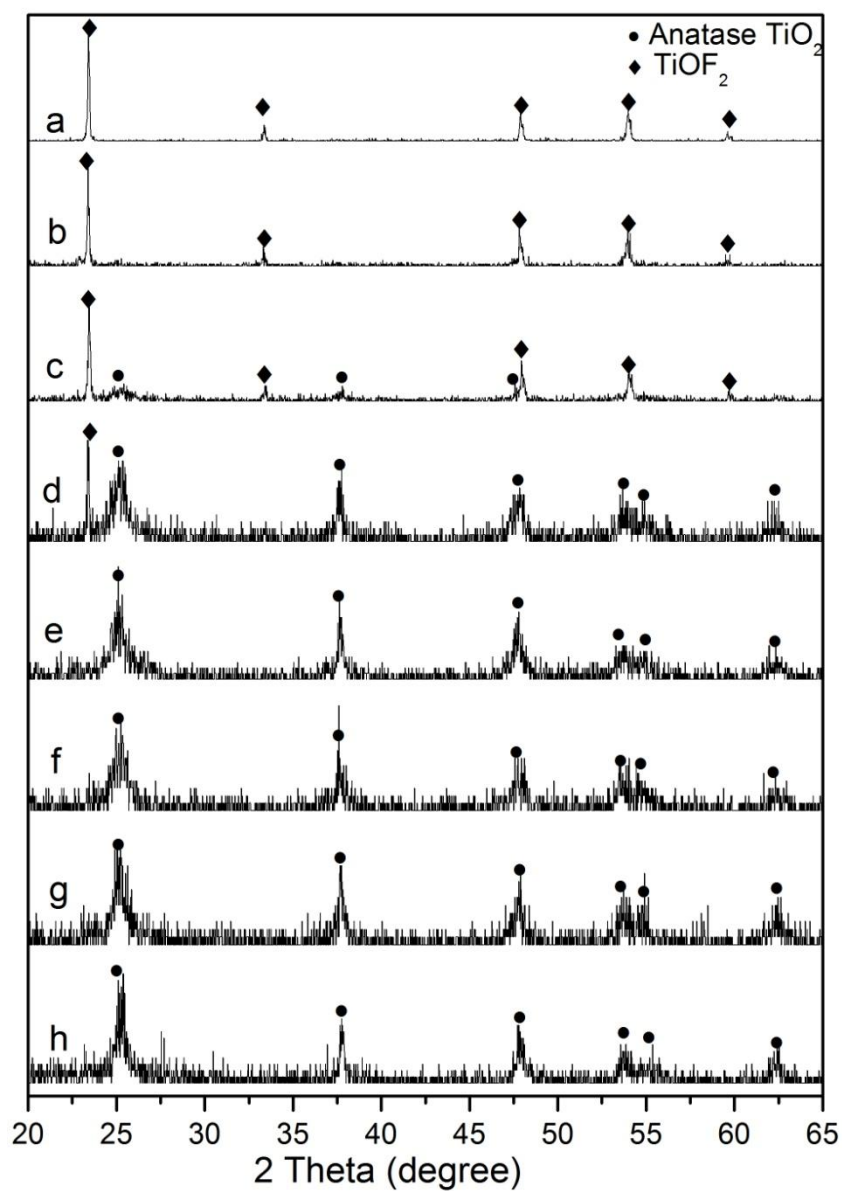


Fig. S1 XRD patterns of (a) the  $\text{TiOF}_2$  precursors and as-prepared samples produced with different reaction times. (The reaction time for the samples from (b) to (g) is 4 h, 6 h, 8 h, 16 h, 24 h, and 36 h, respectively.)

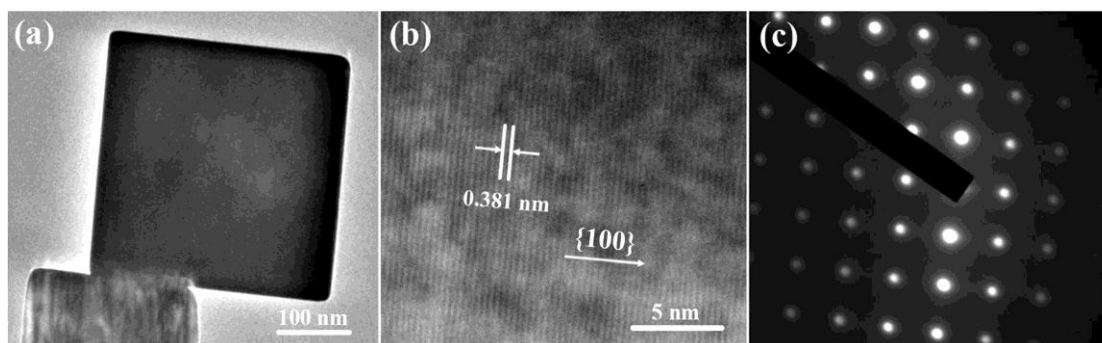


Fig.S2 TEM characterizations of as-prepared  $\text{TiOF}_2$  cubes. (a) TEM image of  $\text{TiOF}_2$  precursors, (b) HR-TEM image of  $\text{TiOF}_2$  cube showing the exposed  $\{100\}$  facets, and (c) corresponding SAED patterns of the  $\text{TiOF}_2$  cubes.

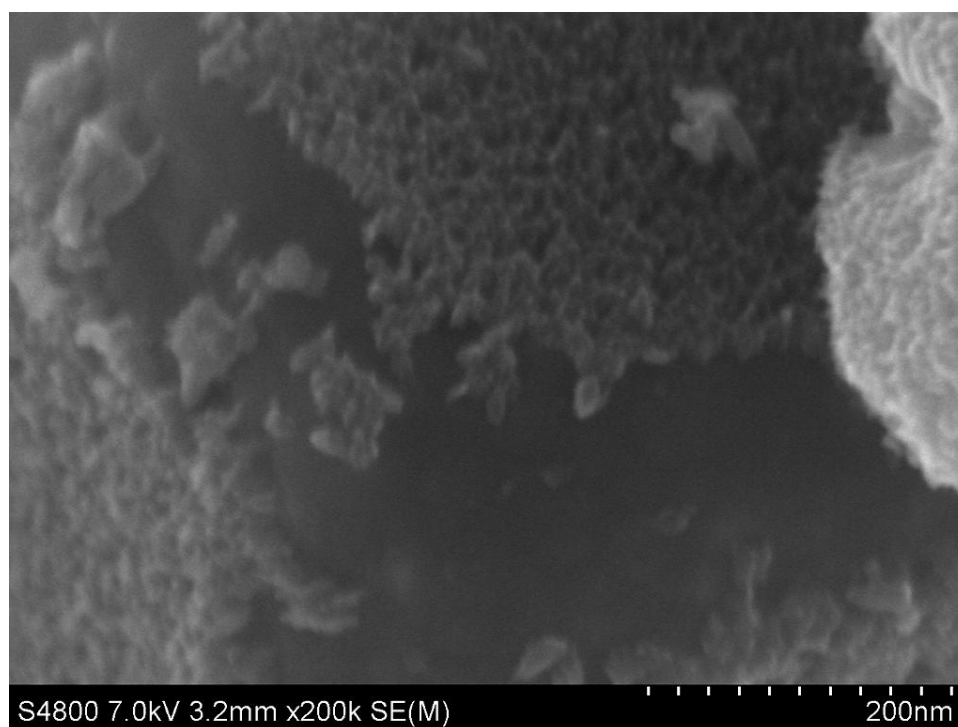


Fig.S3 Magnified SEM images for the sample prepared at  $80\text{ }^\circ\text{C}$  with 2 h reaction time, showing the  $\text{TiO}_2$  nanoparticles formed on  $\text{TiOF}_2$  surfaces are oriented arranged.

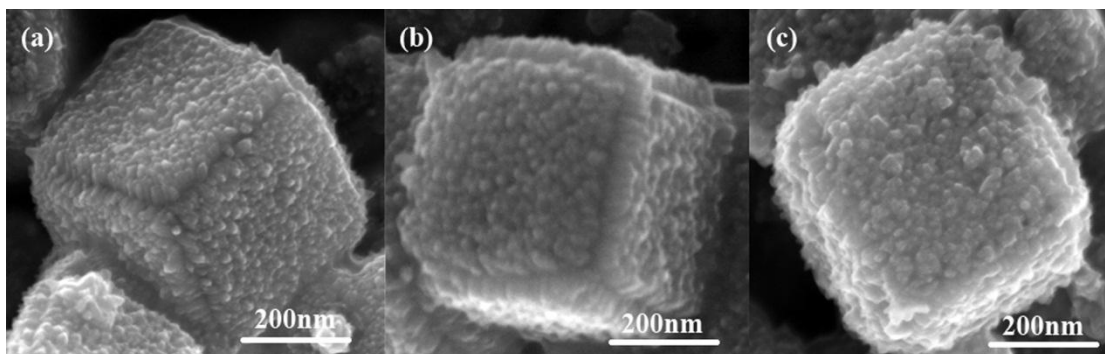


Fig. S4 SEM images for the samples prepared under different reaction times.  
(a) 16 h, (b) 24 h, and (c) 32 h.