

## Supporting Information for:

### Covalent Attachment and Growth of Nanocrystalline Films of Photocatalytic TiOF<sub>2</sub>

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## Experimental

### 1. Catalyst preparation

Each glass petri dish with  $\Phi$  60 mm (about 28 cm<sup>2</sup>) was treated by NaOH (0.20 M) and H<sub>2</sub>SO<sub>4</sub> (0.20 M) respectively, followed by washing with deionized water. After being dried, it was dip-coated with a 0.2 mL clear solution of ethanol (EtOH) containing desired amount of TiF<sub>4</sub> (from 0.10, 0.20, 0.30, 0.40 to 0.50 M) and then dried at 100 °C for 24 h in a fume cupboard. (Caution for TiF<sub>4</sub> excerpted from Sigma-Aldrich MSDS document. Harmful if swallowed or in contact with skin. Causes severe skin burns and eye damage. Harmful if inhaled.) During this process, the TiOF<sub>2</sub> was generated *via* alcoholysis of TiF<sub>4</sub>, together with the formation of HF which induced the corrosion of the glass surface via forming SiF<sub>4</sub> and the subsequent growth of TiOF<sub>2</sub> film. Then the as-made thin TiOF<sub>2</sub> film was washed with deionized water and dried at 100 °C for 24 h.

To show the influence of solvent, we also used water or tetra. butyl alcohol instead of ethanol to prepare TiOF<sub>2</sub> film. The process is similar to that of using ethanol as solvent. The desired amount of TiF<sub>4</sub> is 0.30 M.

As a comparison, the pure TiO<sub>2</sub> film has also been prepared by a sol-gel method. The process is similar to the above method to prepare TiOF<sub>2</sub> film. But we used TiCl<sub>4</sub> instead of TiF<sub>4</sub> as Ti resource, and the dried film should be calcined at 400 °C for 2 h.

### 2. Photoelectrochemical measurements

Photocurrents were measured using an electrochemical analyzer (CHI660D Instruments)

in a standard three-electrode system using the prepared samples as the working electrodes with an active area of *ca.* 1.0 cm<sup>2</sup>, a Pt piece as the counter electrode with area of 2.2 cm<sup>2</sup>, and Ag/AgCl (saturated KCl) as a reference electrode . A 300 W Xe arc lamp served as light source and the wavelength was controlled by a 420 nm cut filter. A 0.20 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. Bias voltage was 0.10 V. Working electrodes were prepared as follows: The samples were synthesized on ITO glass, which were dip coated with TiF<sub>4</sub> and alcohol solvent, and then dried in an oven at 100 °C for 24 h.

### 3. Activity test

Liquid phase photocatalytic degradation of rhodamine B (RhB) was carried out in a self-designed glass reactor at 10 °C. In each run of reactions, a photocatalytic film was settled in a 5.0 mL of RhB aqueous solution with a concentration of  $1.0 \times 10^{-5}$  mol/L. A 300 W Xe lamp with light strength of 64 mW/cm<sup>2</sup> was horizontally placed at the upper part of the reactor with a distance of 30 cm away from the reactor. Between the Xe lamp and reactor, two wave filters were used to achieve monochromatic light with wavelength of  $435 \pm 20$  nm. Before reaction, the film catalyst was placed in the dye solution for about 30 min in dark to achieve the adsorption/desorption equilibrium. The absorbance of RhB at 553 nm was measured by a UV-Vis spectrophotometer to calculate the decolorization rate. Photocatalytic degradation of methylene blue and fuchsin basic have also been carried out by the similar process. The initial concentration of methylene blue and fuchsin basic is  $1.0 \times 10^{-5}$  mol/L and  $5.0 \times 10^{-6}$  mol/L, respectively.

Gas phase photocatalytic degradation of acetone was carried out on a self-made solid-gas photocatalytic reactor at 30 °C with a volume about 2.0 L containing 0.50 uL of acetone and the TiOF<sub>2</sub> film photocatalyst coated on a petri dish with a diameter of about 60 mm. After reaching adsorption/desorption equilibrium, the film sample was irradiated by a 300 W Xe lamp with a wave filter to cut off the lights at  $\lambda < 420$  nm. The remained acetone in reactor was analyzed by gas chromatography (Shimadzu, 17A) with a flame ionization detector, from which the degradation yield was calculated.

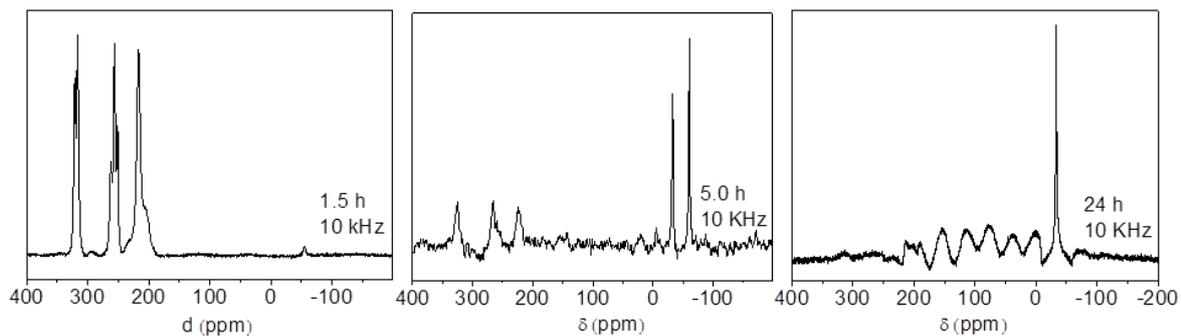
### 4. XPS analysis

The depth analysis of T3 (Fig. 3) was carried out on a ULVAC PHI 5000 Versaprobe X-ray photoelectron spectroscopy (XPS) by adjusting Ar<sup>+</sup> etching time (40 nm/min). Within the

depth less than 330 nm, no significant change in XPS spectra were found. All the F, Ti and O species are present in F-Ti-O bonds corresponding to binding energy (BE) of 686.0 eV, 531.4 eV and 458.9 eV for the F 1s, O 1s and Ti 2p levels, respectively. We observed no signal from the Si 2p level, implying that the glass surface was completely covered by the TiOF<sub>2</sub> film. At depth of 350 nm which was similar to the film thickness determined by cross-section FESEM image (Fig. 2c), a broad peak was observed from 104.0 eV to 104.4 eV in the Si 2p level, corresponding to the Si species in both Si-O-Ti and Si-O-Si bonds. Besides the F, Ti and O species in the F-Ti-O bond observed on the outer surface, the F species in the F-Si bond and the O species in the Si-O-Ti bond were also found at the interface, corresponding to the BE around 688.0 eV and 533.4 eV in F 1s and O 1S levels, respectively.

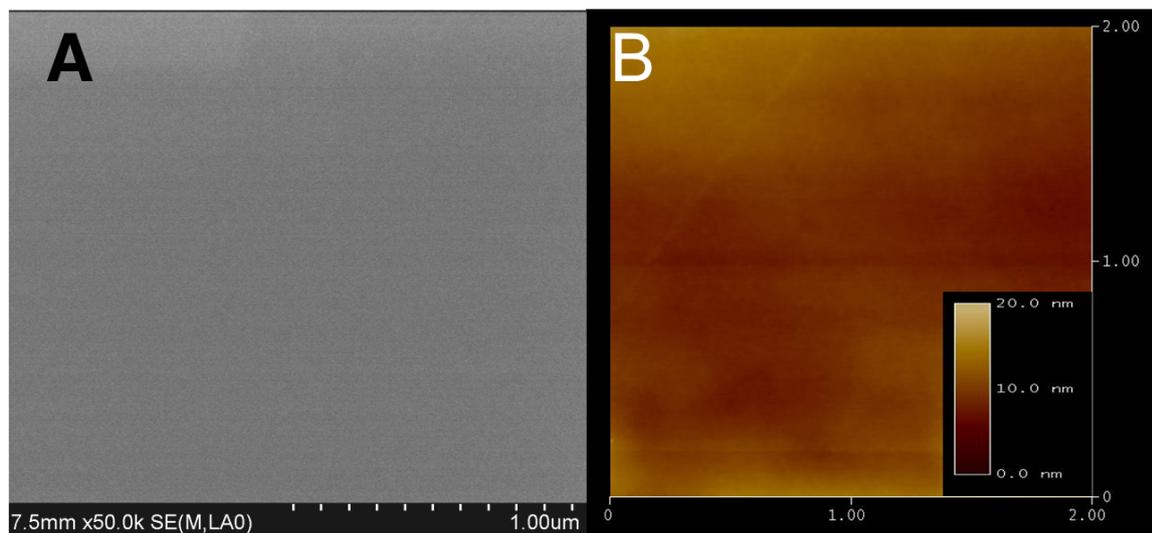
## 5. Other characterizations

Transmission electron micrographs (TEM) was recorded digitally with a Gatan slow-scan charge-coupled device (CCD) camera on a Hitachi JEM-2010 electron microscope operating at 200 kV. Scanning electron micrographs (SEM) images were collected on a Hitachi S-4800 microscope. The crystal structure was determined by X-ray diffraction (XRD) on D/Max-2000 with Cu K $\alpha$ 1 irradiation. Surface area measurements were carried out on a Micromeritics TriStar II 3020 system using N<sub>2</sub> adsorption at 77K at liquid nitrogen temperature. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method. About 100 mg sample was used in the procedure. Diffuse reflection (DR) UV-Vis spectra were obtained on a Shimadzu UV 2450 Spectrophotometer using BaSO<sub>4</sub> as a reference. Surface structure was detected by atomic force microscopy on a Veeco, Nanoscope IIIa AFM system.

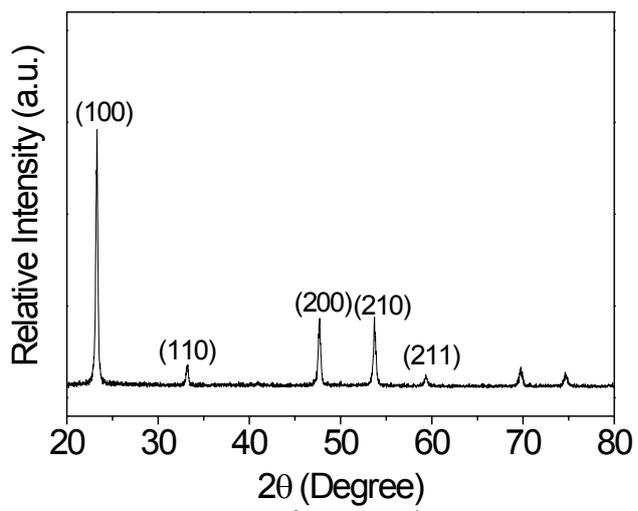


**Fig. S1**  $^{19}\text{F}$  NMR spectra of  $\text{TiOF}_2$  precursor in T3 sample obtained at different EIA time. The peak around -60 ppm also completely disappeared due to the release of gaseous  $\text{SiF}_4$ .

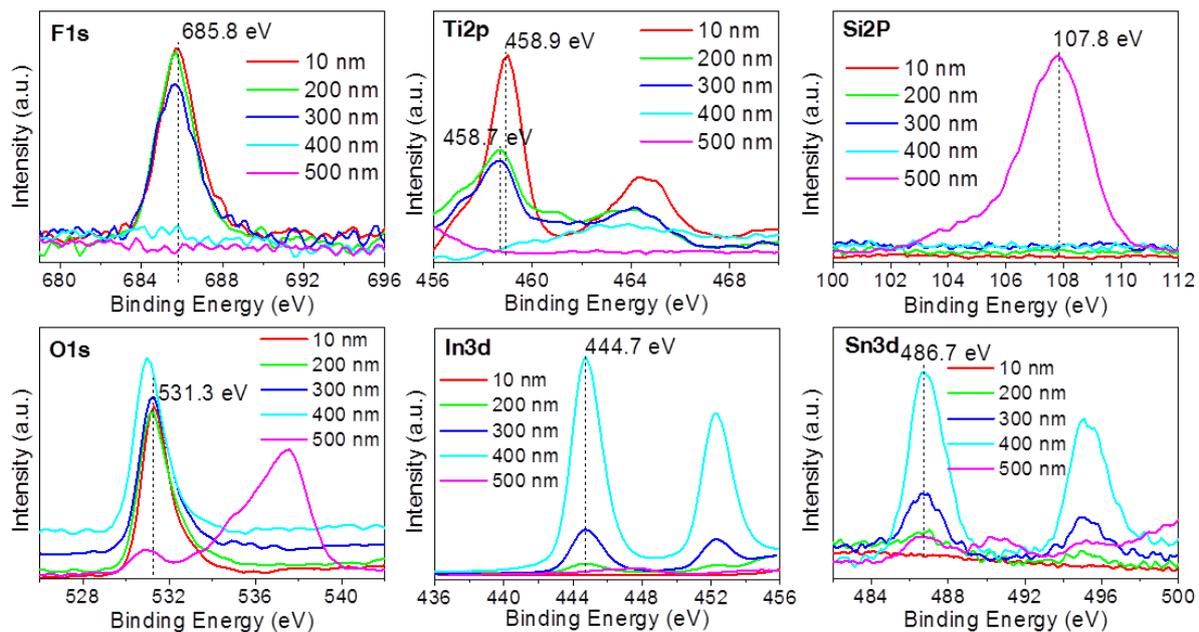
NMR spectra were recorded on a Bruker AV-400 spectrometer, and the spectra were calibrated in ppm displacements from the external primary standard NaF. The solid state NMR spectra were recorded with a spin rate of 10 kHz.



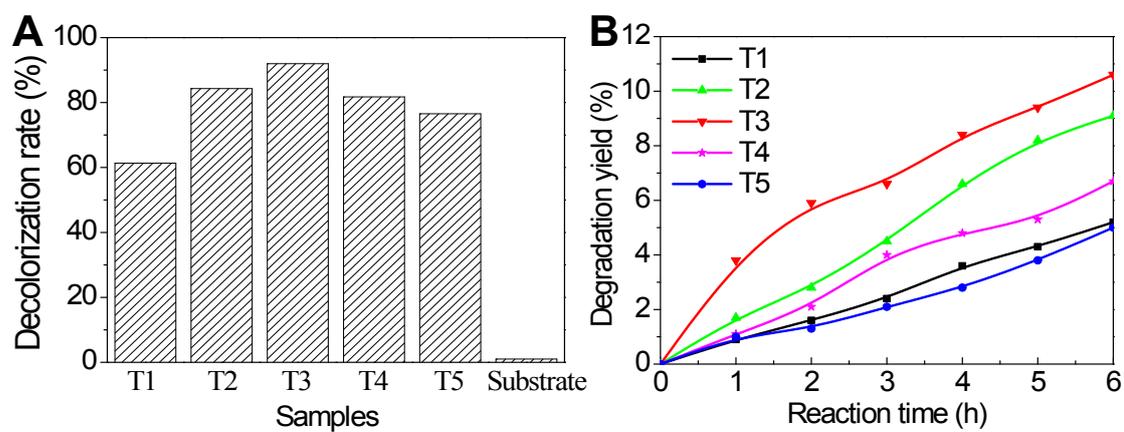
**Fig. S2** (A) Top view SEM image and (B) Image from atomic force microscopy of T3.



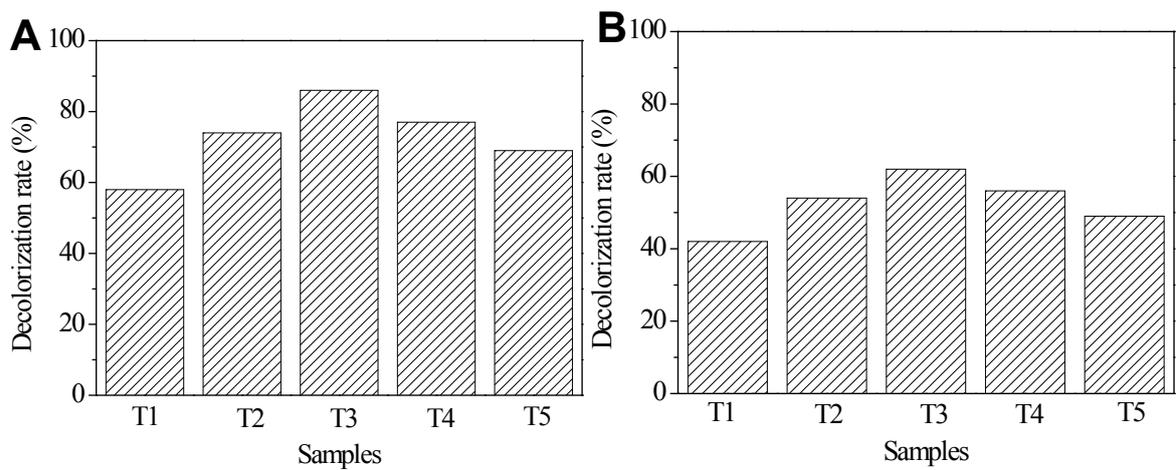
**Fig. S3** XRD pattern of T3 powder.



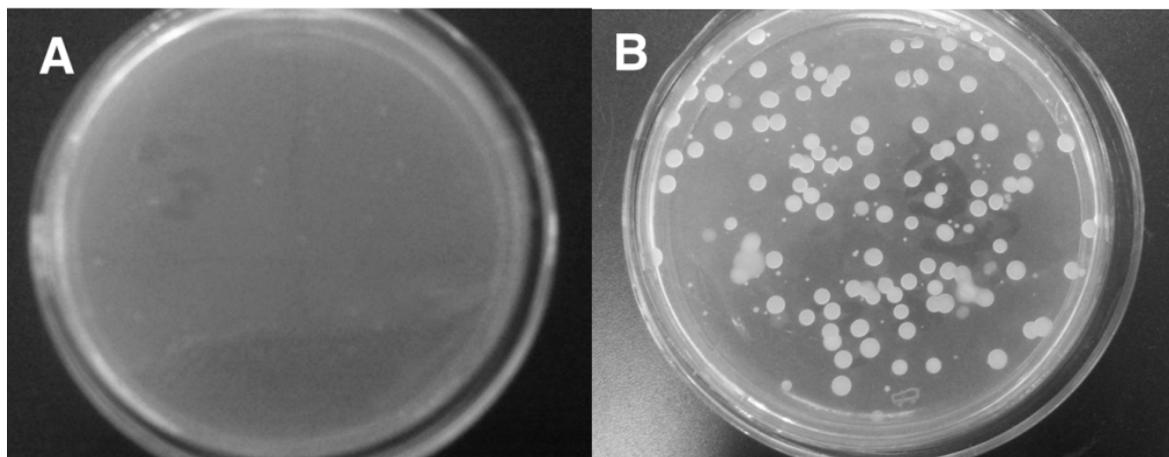
**Fig. S4** XPS spectra of TiOF<sub>2</sub> film on ITO glass substrate at different film depths obtained by adjusting Ar<sup>+</sup> etching time.



**Fig. S5** Photocatalytic degradation of RhB (A) and acetone (B) on various TiOF<sub>2</sub> film photocatalysts.

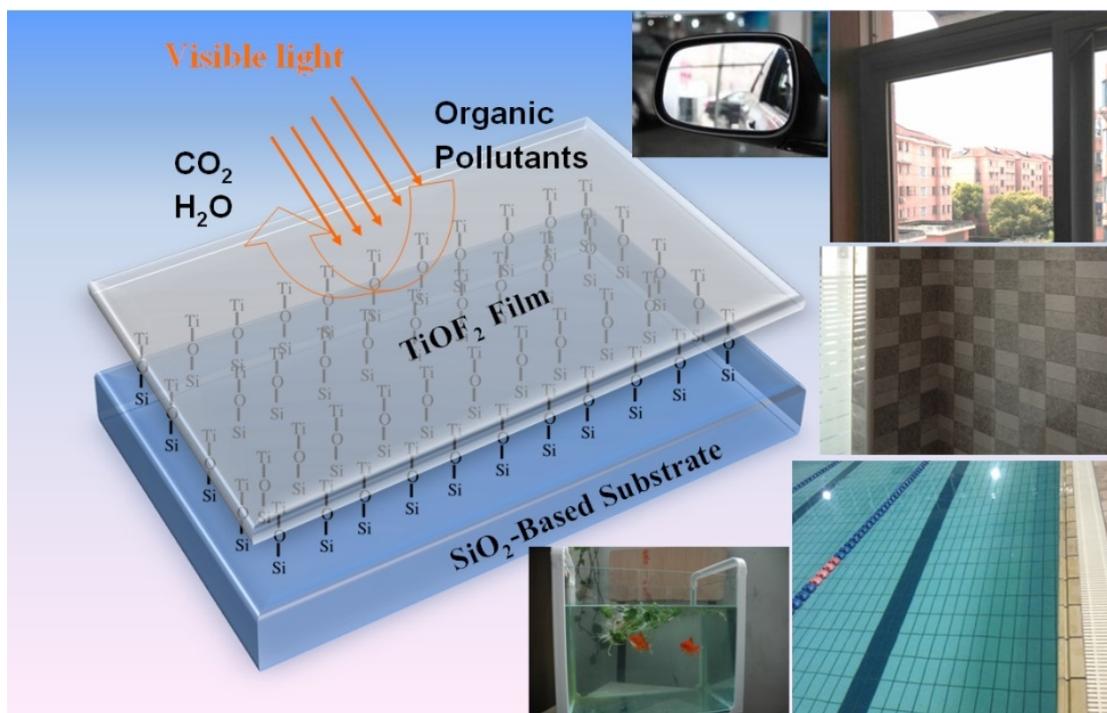


**Fig. S6** Photocatalytic degradation of methylene blue (A) and fuchsin basic (B) on various TiOF<sub>2</sub> film photocatalysts.



**Fig. S7** Bacterial colony growth with (A) and without (B) T3 TiOF<sub>2</sub> film.

In a typical antibacterial experiment, 5 mL of sterile maximum recovery diluent (MRD) and 500  $\mu$ L of overnight grown *Staphylococcus aureus* bacterial culture ( $10^5$  CFU/mL) were mixed and stirred for 15 min. Then the solution was dropped onto glass slide with or without TiOF<sub>2</sub> film. After that, the glass slide was irradiated under visible light generated by a fluorescent lamp (20 W) with a filter (420 nm) for 6 h. Aliquots (100  $\mu$ L) of test solution samples were withdrawn, diluted and spread on freshly prepared Mueller Hinton agar plates. These plates were kept overnight in an incubator at 37 °C, and bacterial colonies were counted on next morning.



**Fig. S8** Further applications of as-prepared  $\text{TiO}_2$  films on house and car windows, kitchen and house walls, aquariums and swimming pools.