Electronic Supplementary Information

Titanate Nanotubes Confined Merger of Organic Photocatalysis with TEMPO for Highly Selective Aerobic Oxidation of Sulfides†

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† TEMPO, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl.

1. Experimental section

1.1 Reagents and solvents

All the reagents were procured from commercial suppliers such as Sigma-Aldrich, Alfa Aesar and TCI, J&K Scientific, etc. The solvents were supplied by Merck, Fischer Scientific and Sinopharm Chemical Reagent Co. Ltd., China. Methanol-D_4 was purchased from Cambridge Isotope Laboratories, Inc. Aeroxide P25 TiO_2 was obtained from Evonik Industries. All the reagents and solvents were directly used without further purification.

2.2 Preparation of $H_2Ti_3O_7$

The $H_2Ti_3O_7$ nanotubes were synthesized according to a reported procedure [20]. In detail, put 250 mg of P25 TiO_2 into 40 mL of 10 M NaOH solution for 30 min of ultrasonication and then shifted into a Teflon-lined autoclave, afterwards the autoclave was put in oven at 150 ℃ for 48 h. The $Na_2Ti_3O_7$ precipitates were collected, and washed with deionized water and 0.1 M HCl solution, after that were cleaned with deionized water and absolute alcohol to remove excess HCl until pH close to 7 was reached. The $H_2Ti_3O_7$ nanotubes samples were collected by centrifugation and dried in a vacuum oven at 60 ℃ for 12 h. The $H_2Ti_3O_7$ nanorods were prepared *via* the same method as the $H_2Ti_3O_7$ nanotubes except the hydrothermal temperature is 180 ℃.

2.3 Characterization of the Materials

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were collected on a JEOL JEM2012-FEF operated at 200 kV. Energy dispersive spectrometry (EDS) analysis was studied. X-ray

powder diffraction (PXRD) measurement was carried out using a Rigaku/Miniflex 600 diffractometer with filtered Cu Kα radiation, and the data were collected from 3° to 55°. The UV-visible absorbance of ErB and $H_2Ti_3O_7$ samples were measured on UV-2600 and UV-3600 UV-vis spectrophotometer (Shimadzu, Japan) equipped with a diffuse reflectance measurement accessory, $BaSO_4$ was used as a reflectance standard. The specific surface areas were determined by N_2 physisorption using an ASAP automated system and the Brunauer-Emmet-Teller (BET) method. Each sample was degassed under vacuum ($<1\times10^{-5}$ bar) in the Micromertics system at 120 ℃ for 12 h prior to N_2 physisorption. The Fourier transform infrared spectroscopy (FTIR) spectra of catalysts were performed. The EPR tests were executed on an electron paramagnetic resonance (EPR) spectrometer (JEOL, JES-FA300).

2.4 Typical Procedure for the photocatalytic selective oxidation of sulfides with air

Firstly, 10 mg of $H_2Ti_3O_7$, 0.5 mmol of thioanisole, 2.5 μmol of TEMPO, 0.2 μmol of ErB, and 1 mL of CH_3OH were mixed in a 10 mL Pyrex vessel. Secondly, the mixture was maintained for 5 min at ultrasonication and stirred for 30 min in dark to reach adsorption equilibrium. Thirdly, the Pyrex vessel was put on a magnetic stirring apparatus and the reactive mixture was stirred at 1500 rpm. Afterwards, irradiated with 520 nm green LED irradiation (3 W × 4) connected to air by a hole in the rubber septum. Finally, the photocatalyst $H_2Ti_3O_7$ nanotubes were separated from the reaction mixture by centrifugation. And the reaction product was analyzed by gas chromatography equipped with a flame ionization detector (GC-FID, Agilent 7890B) using chlorobenzene as the internal standard. The structures of products were confirmed by

comparison with the retention time of standard samples and further confirmed by gas chromatography–mass spectrometry (GC–MS).

Table S1. Influence of application amount of $H_2Ti_3O_7$ on the selective aerobic oxidation of thioanisole towards the reaction endpoint [a]

Entry	$H_2Ti_3O_7$ [mg]	T [min]	Conv. [%][b]	Sel. [%][b]
1	10	20	98	96
2	20	50	94	97
3	30	65	92	98
4	40	80	93	99
5	50	90	94	99

[a] Reaction conditions: thioanisole (0.5 mmol), TEMPO (0.0025 mmol), ErB (2×10^{-4} mmol), aerial O_2, green LED irradiation (λ_{max}=520 nm, 3 W × 4), CH_3OH (1 mL). [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of thioanisole, selectivity of methyl phenyl sulfoxide.

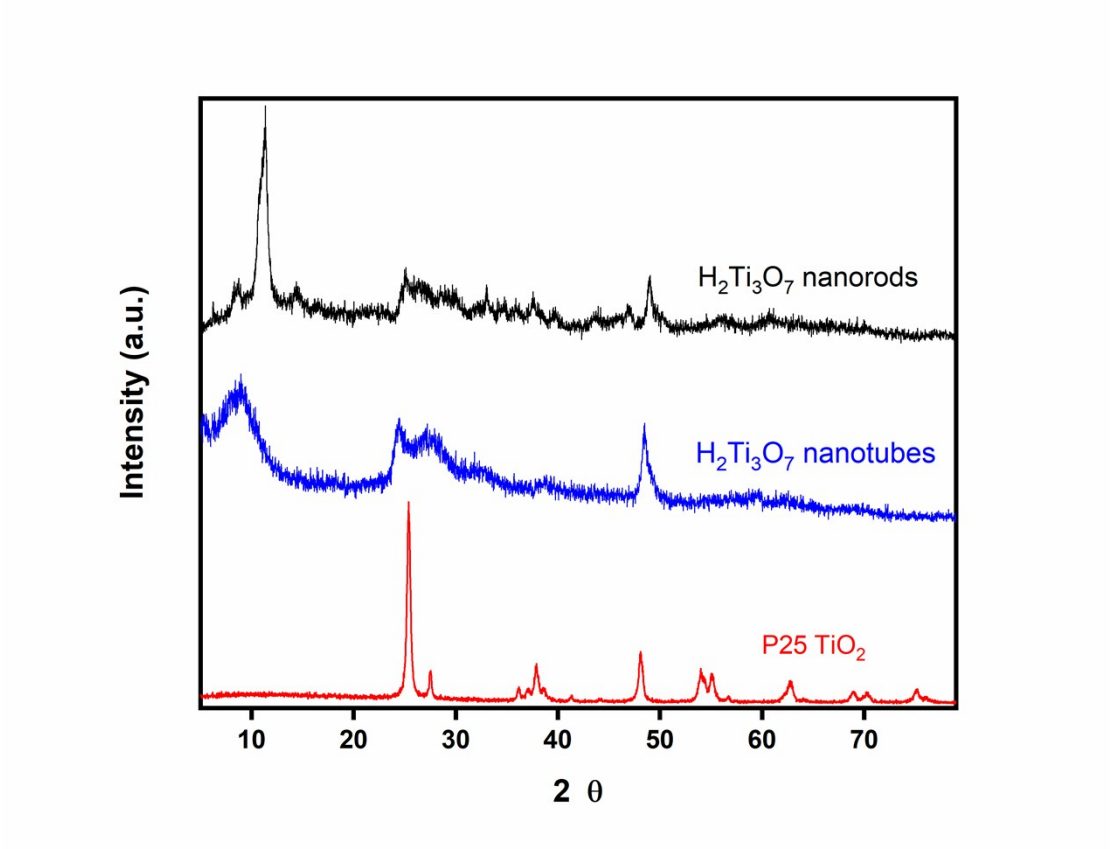

Fig. S1. XRD patterns of P25 TiO_2, $H_2Ti_3O_7$ nanotubes and $H_2Ti_3O_7$ nanorods.

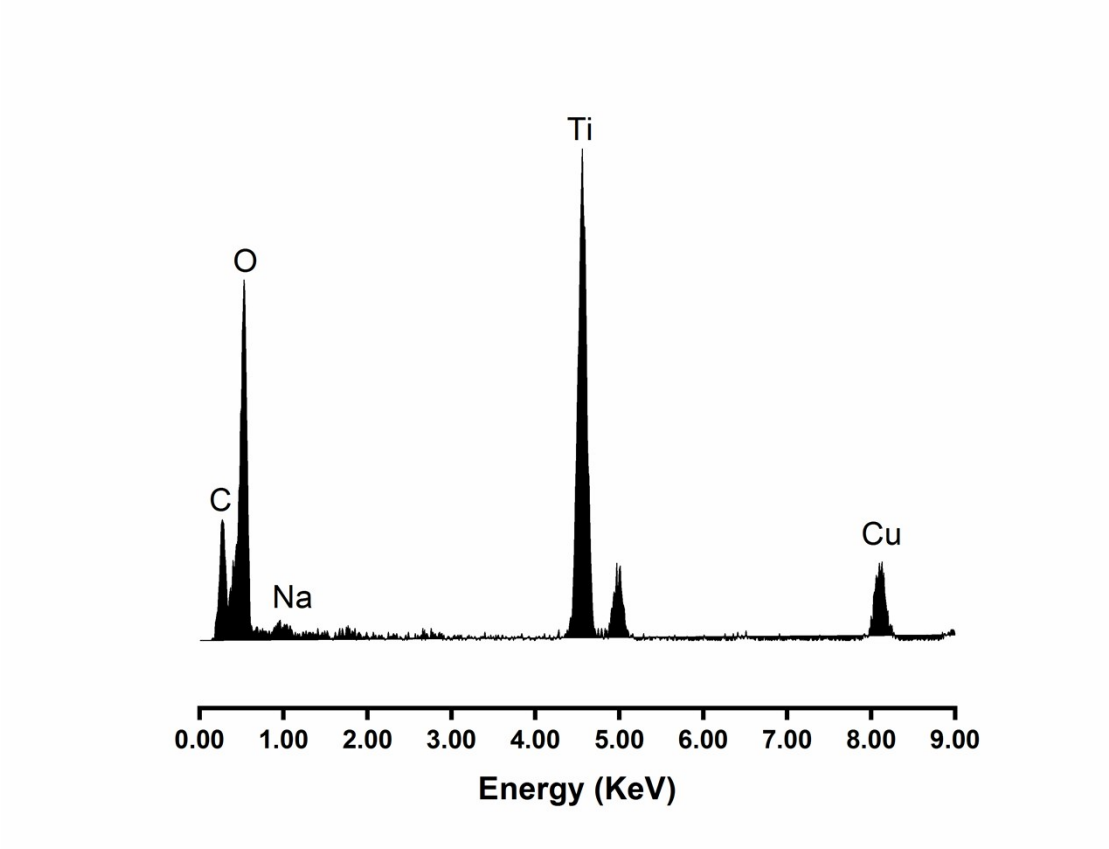

Fig. S2. The EDS spectrum of $H_2Ti_3O_7$ nanotubes synthesized by treating P25 TiO_2 with NaOH for 48 h at 150 ℃

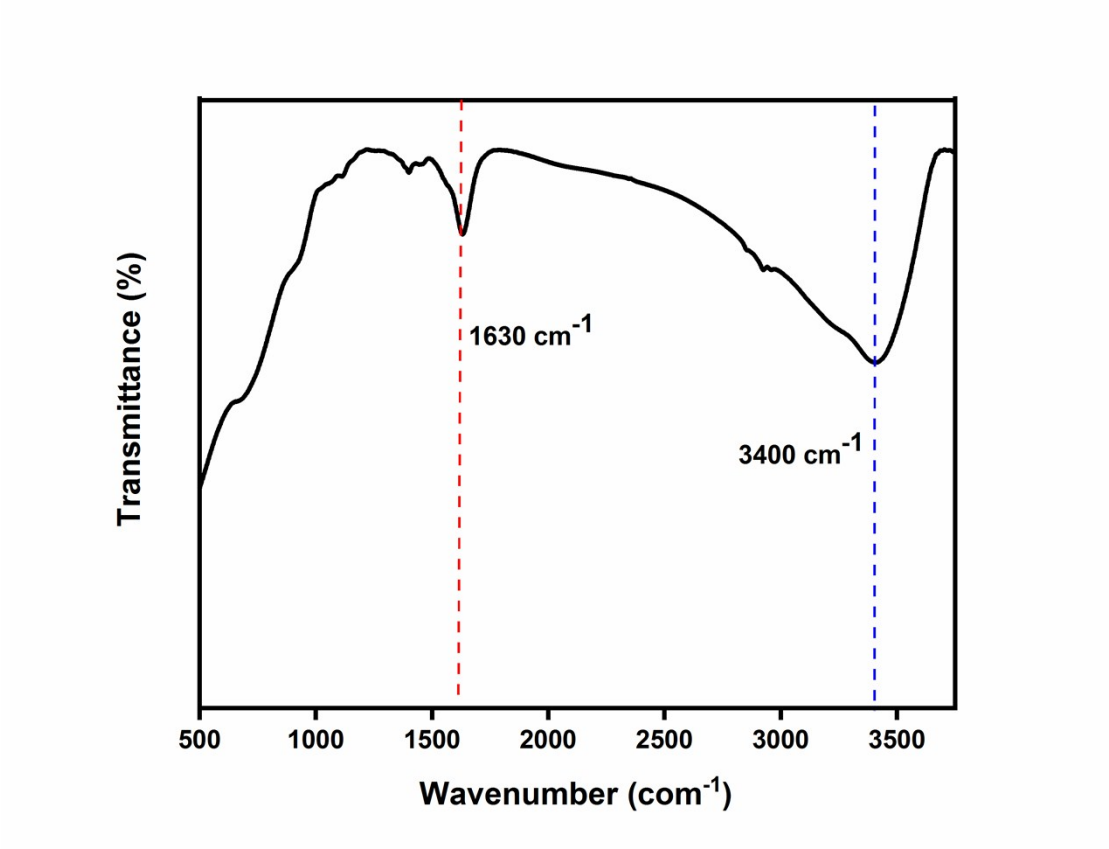

Fig. S3. The FTIR spectrum of $H_2Ti_3O_7$ nanotubes dried in a vacuum oven at 100 ℃ for 3 h

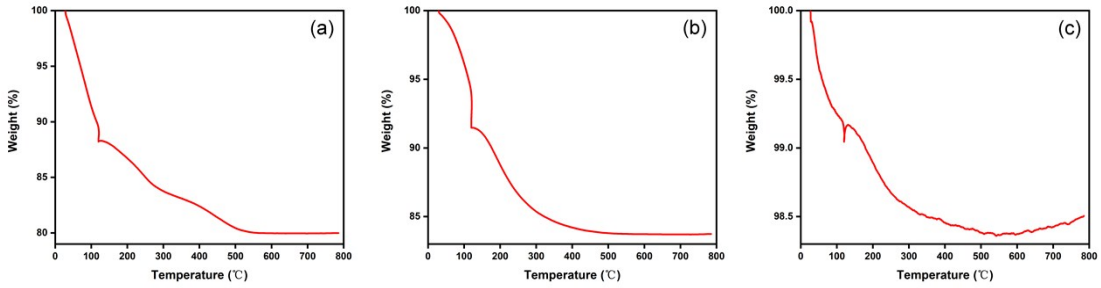

Fig. S4. Thermal gravimetric analysis (TGA) traces of a) $H_2Ti_3O_7$ Nanotubes, b) $H_2Ti_3O_7$ Nanorods and c) P25 TiO_2.