

Electronic Supplementary Information

Bridging green light photocatalysis over hierarchical Nb₂O₅ for selective aerobic oxidation of sulfides

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1. Experimental

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-D₄ was purchased from Cambridge Isotope Laboratories, Inc. Nb₂O₅ nanoparticles was purchased from Innochem. All the reagents and solvents were directly used without further purification.

1.2 Preparation of hierarchical Nb₂O₅

Hierarchical Nb₂O₅ was prepared by hydrothermal method by previous report. In detail, put 2 mmol of niobium oxalate into 25 mL of deionized water and stirred at 60 °C for 10 min under completely dissolve. Meanwhile, 1 mmol of L-Arginine was dissolved in 5 mL of deionized water and stirred for 5 min. Then the L-Arginine solution was added dropwise in the solution of niobium oxalate with stirring for 10 min. Next the mixed liquor was shifted into a 50 mL Teflon-lined autoclave and heated at 180 °C for 12 h. Naturally cooling autoclave to room temperature, the Nb₂O₅ precipitates were collected, cleaned with deionized water several times and dried in a vacuum oven at 60 °C for 12 h.

1.3 Characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were collected on a JEOL JEM2012-FEF

operated at 200 kV. Scanning electron microscopy (SEM) images of the solid samples were measured on Zeiss Merlin Compact field emission scanning electron microscope. X-ray powder diffraction (PXRD) measurement was carried out using a Rigaku/Miniflex 600 diffractometer with filtered Cu K α radiation, and the data were collected from 10° to 70°. The UV-visible absorbance of ARS, Nb₂O₅ and ARS-Nb₂O₅ samples were measured on UV-3600 UV-vis spectrophotometer (Shimadzu, Japan) equipped with a diffuse reflectance measurement accessory, BaSO₄ was used as a reflectance standard. The specific surface areas were determined by N₂ physisorption using an ASAP automated system and the Brunauer-Emmet-Teller (BET) method. Each sample was degassed under vacuum (<1×10⁻⁵ bar) in the Micromertics system at 120 °C for 6 h prior to N₂ physisorption. The EPR tests were executed on an electron paramagnetic resonance (EPR) spectrometer (JEOL, JES-FA300).

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

Firstly, 25 mg of Nb₂O₅, 0.25 mmol of thioanisole, 5 μ mol of TEMPO, 0.5 μ mol of ARS, and 0.5 mL of CH₃OH were mixed in a 10 mL Pyrex vessel. Then, the mixture was maintained for 10 min at ultrasonication and stirred for 30 min in dark to reach adsorption equilibrium. Next 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 \times 4) connected to air by a hole in the rubber septum. Finally, the photocatalyst ARS-Nb₂O₅ were separated from the reaction mixture by centrifugation. 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).

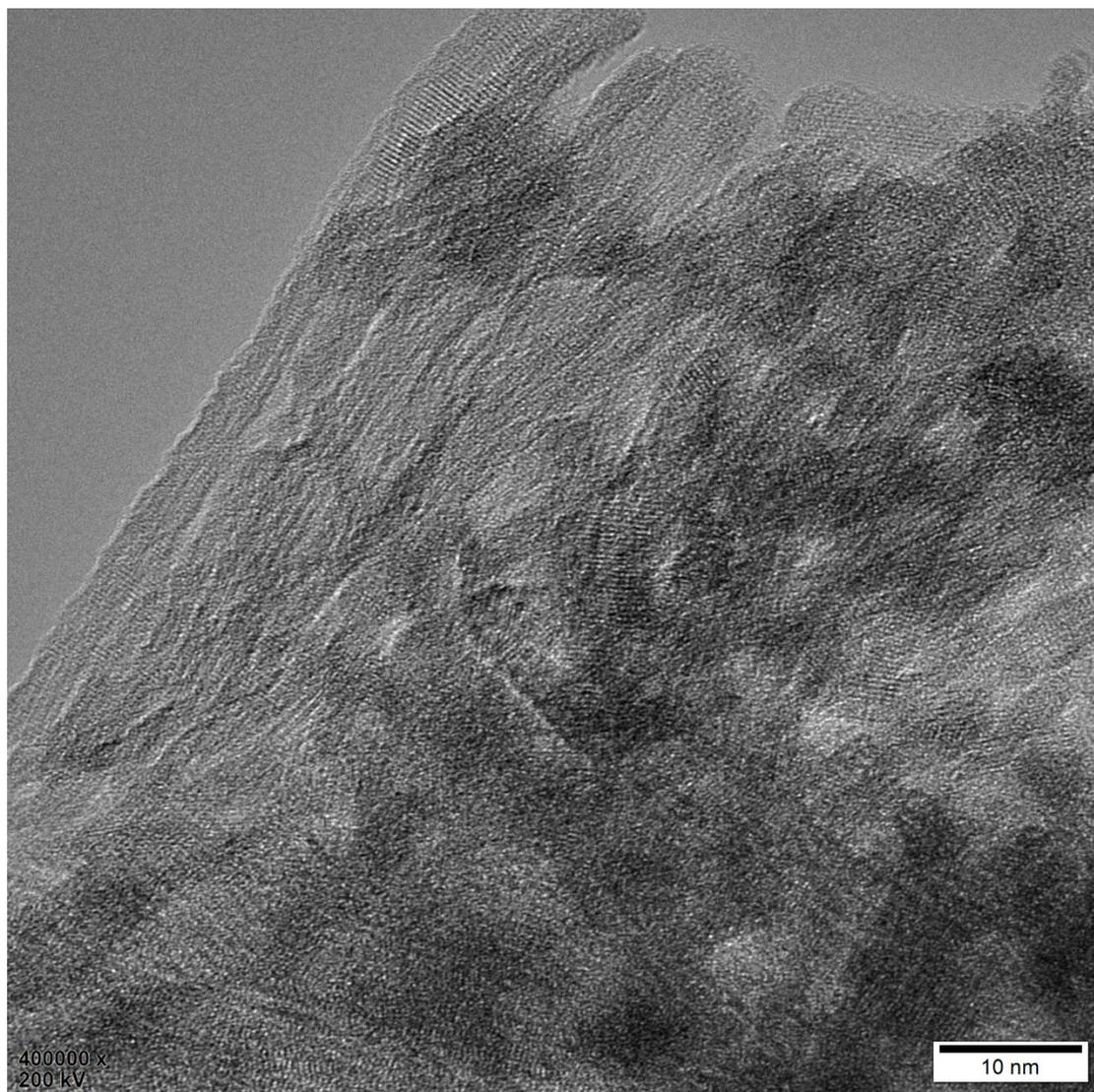


Fig. S1. The high-resolution transmission electron microscopy (HRTEM) image of hierarchical Nb₂O₅.

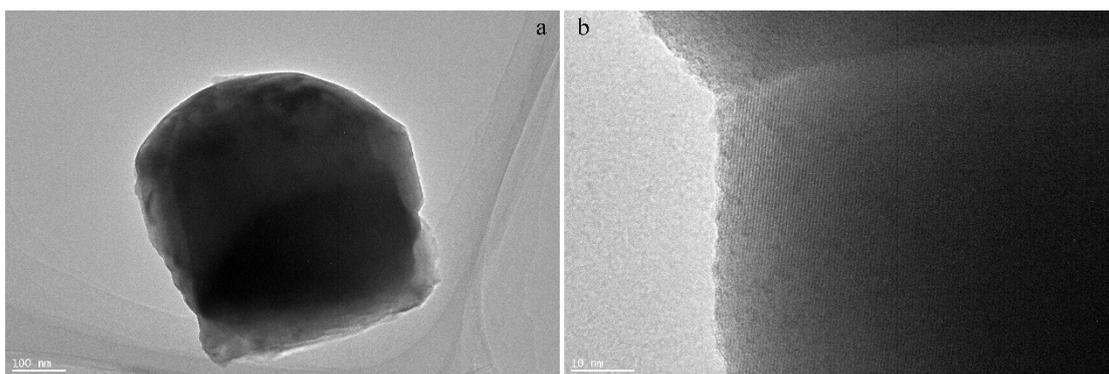


Fig. S2. The transmission electron microscopy (TEM) images of Nb_2O_5 nanoparticles.

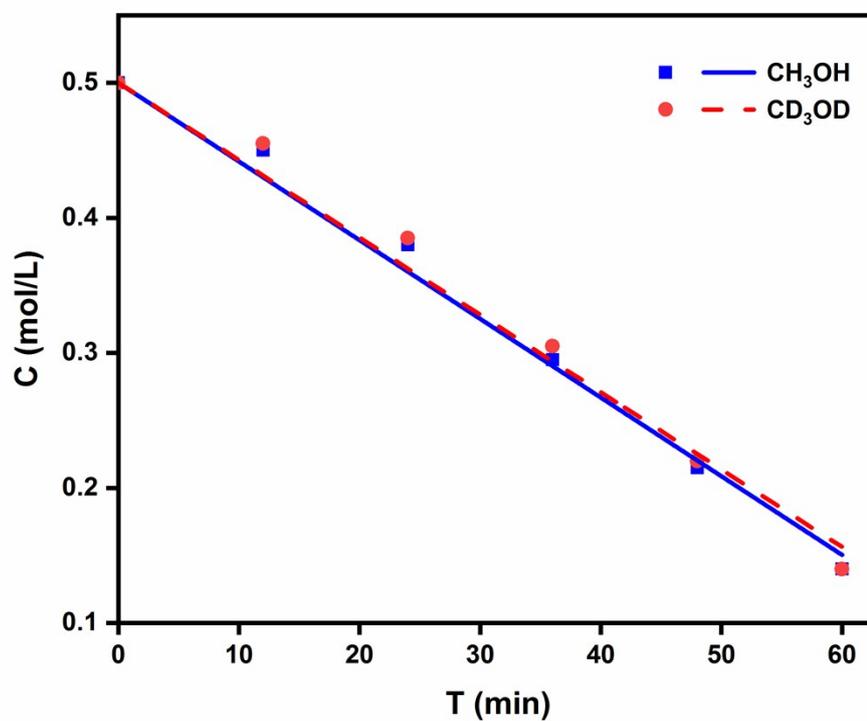


Fig. S3. The reaction kinetic curves studies of the visible-light-derived selective oxidation of sulfides into sulfoxides with air in the merger of ARS- Nb_2O_5 photocatalysis with TEMPO catalysis in CH_3OH and CD_3OD .

Table S1. Influence of solvent on the photocatalytic selective aerobic oxidation of methyl phenyl sulfide^[a].

Entry	Solvent	Conv.[%] ^[b]	Sel.[%] ^[b]
1	CH ₃ OH	66	99
2	C ₂ H ₅ OH	52	99
3	CH ₃ CN	1	-

[a] Reaction conditions: methyl phenyl sulfide (0.25 mmol), TEMPO (5 μ mol), Nb₂O₅ (25 mg), ARS (0.5 μ mol), aerial O₂, green LEDs (520 \pm 15 nm, 3 W \times 4), solvent (0.5 mL), 50 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of sulfides, and selectivity of sulfoxides.