Supplementary Information

Visible-light-driven Conversion of Organic Compounds over WO_3-based Microtubes with Mesoporous-walled Structure

Ying Lv,[a b] Zhanglian Xu,[c] and Lei Du*[a]

a. Zhejiang Provincial Research Center of Clothing Engineering Technology, Zhejiang Sci-Tech University, Hangzhou 310018, China.

b. College of Materials Science and Engineering, Xi’an Shiyou University, Xi’an 710065, China.

c. School of Nuclear Science and Technology, Xi’an Jiaotong University, Xi’an 710049, China.

Corresponding author
E-mail: dulei@zstu.edu.cn
Tel: +86-571-86843580
Fax: +86-571-86843249

Experimental Section

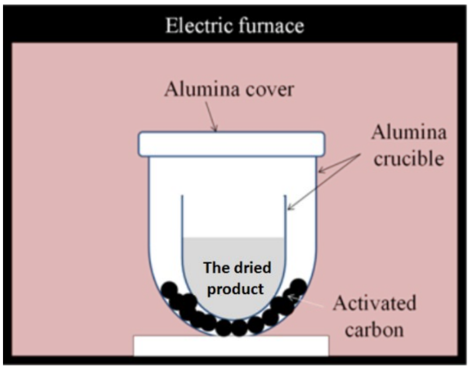
Materials

The raw materials of tungsten (VI) chloride (WCl_6, Wako Pure Chemicals Ind., Ltd., Japan.), palladium chloride ($PdCl_2$, Wako Pure Chemicals Ind., Ltd., Japan.), urea ($CO(NH_2)_2$, Wako Pure Chemicals Ind., Ltd., Japan), methylene blue ($C_{16}H_{18}ClN_3S$, Wako Pure Chemicals Ind., Ltd., Japan), acetaldehyde (AcH, Wako Pure Chemicals Ind., Ltd., Japan) and propan-2-ol (Wako Pure Chemicals Ind., Ltd., Japan) were commercially available and used directly without further purification. The solvents used in this communication are distilled water and absolute ethyl alcohol, respectively. Commercial WO_3 (~4 m^2/g) was obtained from Wako Pure Chemicals Ind., Ltd., Japan.

Experimental information

WCl_6 (2 mmol, 0.794 g) and a required amount of $PdCl_2$ (0.1 wt%(0.077 mg), 0.5 wt%(0.385 mg) and 1 wt%(0.77 mg), calculated relative to the amount of photocatalytsts) were first dissolved in 30 mL of absolute ethanol in the beaker. After completely dissolved, urea (20 mmol, 1.2 g) was added to the above solution through ultrasonic for 3 min. The mixture was then transferred into a 100 mL Teflon-lined autoclave and sealed and maintained at 180 ^{o}C for 8 h. After reaction, the grey precipitate was collected in plastic centrifuge tube. The as-obtained grey precipitate was washed three times with absolute ethanol and distilled water through centrifugation, respectively. After that, the product was then dried at 60 ^{o}C for 5 h.

The as-prepared dried product was subsequently transferred in a 30 mL alumina crucible. And then the 30 mL alumina crucible with the as-prepared sample was placed into a 100-mL alumina crucible containing activated carbon (3 g, Wako Chemical Co. Ltd.). An alumina cover was then placed on the 100-mL crucible, and this reaction container was transferred into the electric furnace. The temperature in the furnace was elevated to a given temperature (450 ^{o}C) in 4 h, and then maintained at 450 ^{o}C for another 3 h. After that, the sample was allowed to cool naturally to room temperature and light grey product was obtained for use. The schematic diagram of the above reductive calcination experiment is shown in Scheme. S1.



Scheme S1. Schematic diagram of heat-treatment under reductive atmosphere.

Characterization

The morphology and structure of the as-prepared products were characterized with field-emission scanning electron microscopy (FE-SEM, Zeiss Oberkochen, Germany), and high-resolution transmission electron microscopy (HR-TEM, JEM-2010F, JEOL, Japan). X-ray powder diffraction (XRD, D8 ADVANC, Germany) using a CuKα with a Ni filter (40 kV, 40 mA) was used to confirm the phases of the as-prepared samples. The chemical states of the as-prepared product were investigated by X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9010MCY). The porous properties of the as-prepared samples were characterized using N_2 adsorption at -196 °C on a specific surface area and porosity analyzer (Micromeritics, TRYSTAR 3000, Japan). The band energy information of the as-prepared samples was measured by UV-Vis diffuse reflectance spectroscopy (Shimadzu, UV-2400PC/2500PC, Japan).

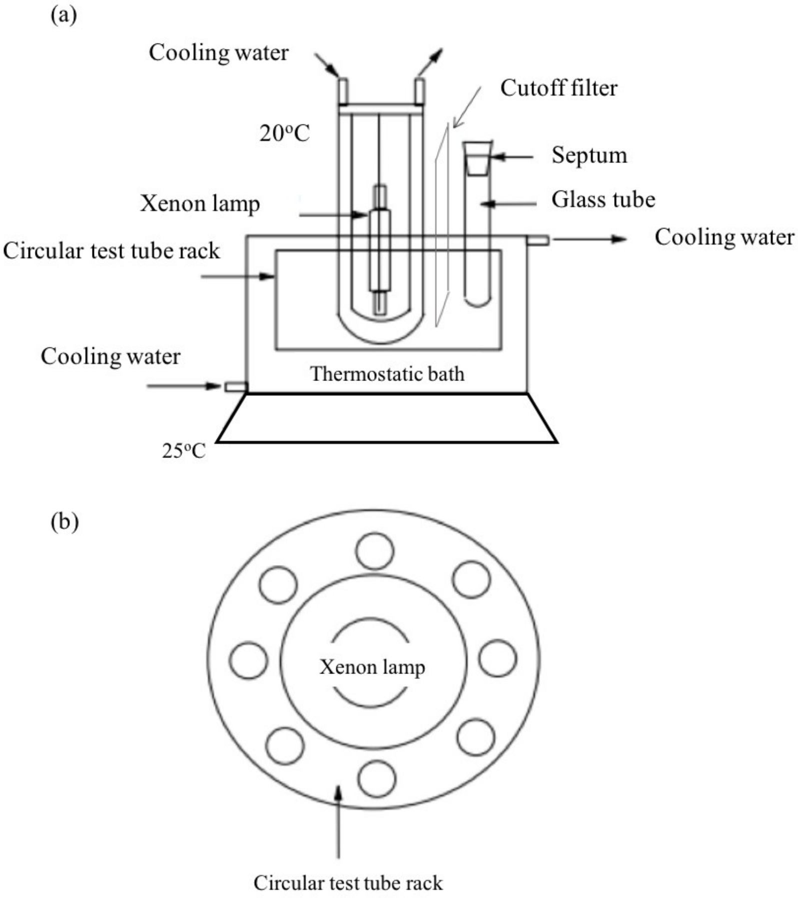
Photocatalytic reaction:

A photocatalytic reactor was used in this study and the schematic details are depicted in Schematic S2. A Xe lamp (LX-300F, Cermax 300 W, $300<\lambda<500$ nm) was located in the center of the reactor along the axis and protected by a water-cooled quartz jacket. At the bottom of the reactor a magnetic stirrer was used to achieve effective dispersion agitating mechanically. A circular test tube rack was inserted on the thermostatic bath to hold up the Pyrex glass tubes. Thus, the visible light (equipped with cutoff filter (L42, Hoya) between the Xe lamp and glass tubes) was collected into the glass tube and ensured the photocatalytic reaction performed uniformly and completely. The reactor was fitted with a magnetic stirrer for stirring at 700 rpm to keep the catalyst in suspension.

The photodegradation of methylene blue in water was used to evaluate the photoactivity of the samples as prepared through different methods, in our experiment, a consistent dosage of 50 mg samples was dispersed into 50 ml methylene blue solution with the initial concentration of 5×10^{-5} mol/L. The photodegradation experiment was carried out under the visible light irradiation. Four milliliters of test liquid were taken from this solution, centrifugated and fed in a quartz cell. The concentration of methylene blue in solutions were monitored and analyzed by measuring the absorbance at 665nm wavelength using UV-vis spectrometer (Shimadzu, UV-1800) at given irradiation time intervals.

The overall photocatalytic activity was tested in terms of the amounts of CO_2 gas that generated from the oxidation decomposition of aqueous acetaldehyde solution (0.1 vol%, ca.35 μmol) containing a suspension of the photocatalyst powder (50 mg) under the irradiation of Xe lamp with the cutoff filter (L42, Hoya) at 25 ^{o}C. For photocatalysis experiments, the rate of agitation was set at 700 rpm. The CO_2 concentrations were measured using a gas chromatography (Align model GC-6890N) equipped with a 2 m Porapak-Q column, a methanizer, and a flame ionization detector, using N_2 as the carrier gas.

For photocatalytic oxidation of propan-2-ol, the as-prepared photocatalysts (150 mg) were added in an aerated aqueous propan-2-ol solution (100 ml, initial amount 150 µmol). The reaction cell was tightly sealed with a rubber cap and then was irradiated by Xe lamp equipped by a cutoff filter (L42, Hoya). Sample aliquots were taken out from the reactor cell at given irradiation time intervals and then centrifugated for analysis. Sample analysis was carried out by ion chromatography (Shimadzu, CDD-10ASP, Shim-pack IC-SA2). The released CO_2 was measured using a gas chromatography (Align model GC-6890N) equipped with a 2 m Porapak-Q column, a methanizer, and a flame ionization detector, using N_2 as the carrier gas.



Sccheme S2. Schematic illustration of the cylindrical photocatalytic reactor (a) cross-sectional view, (b) top view.

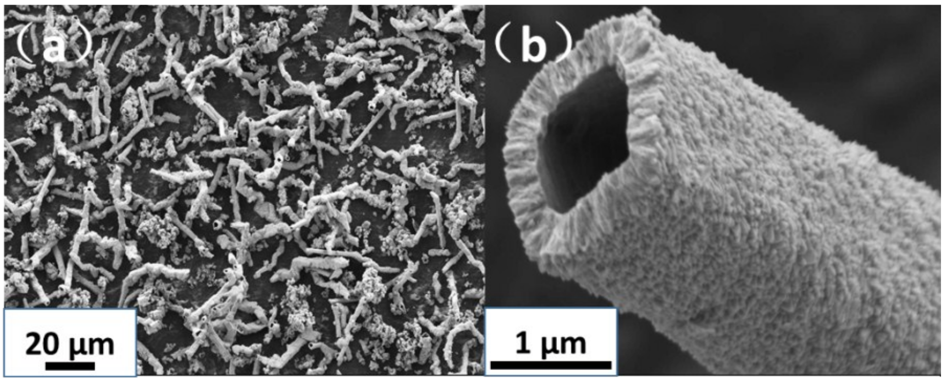


Fig. S1 The FE-SEM images of (a and b) the precursor of Pd-WO_3 microtubes before heat treatment.

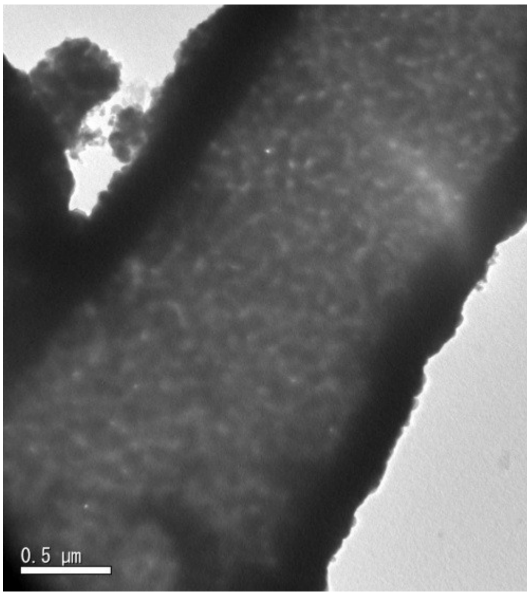


Fig. S2 TEM images of the Pd-WO_3 microtube obtained from the heat treatment under the reductive atmosphere.

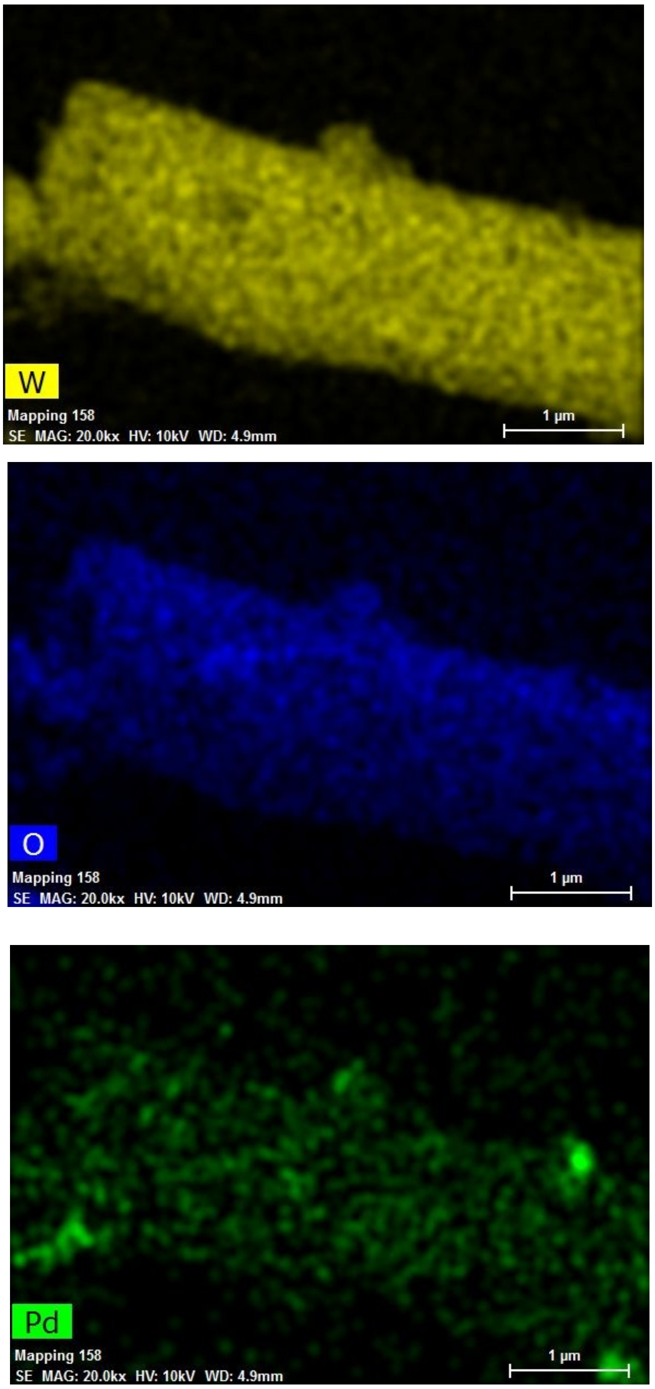


Fig. S3 The element mappings of W, O and Pd within a single tube under SEM.

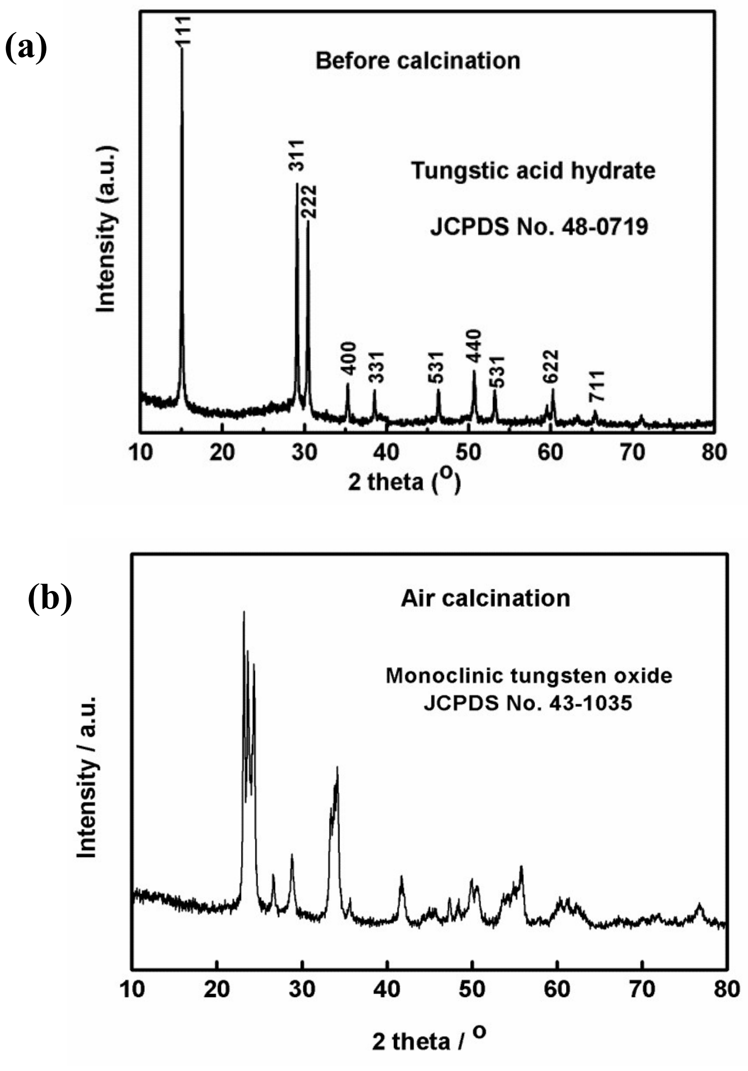


Fig. S4 XRD spectra of (a) the Pd-WO_3 precursor before heat treatment and (b) PdO-WO_3 microtubes after heat treatment under air atmosphere.

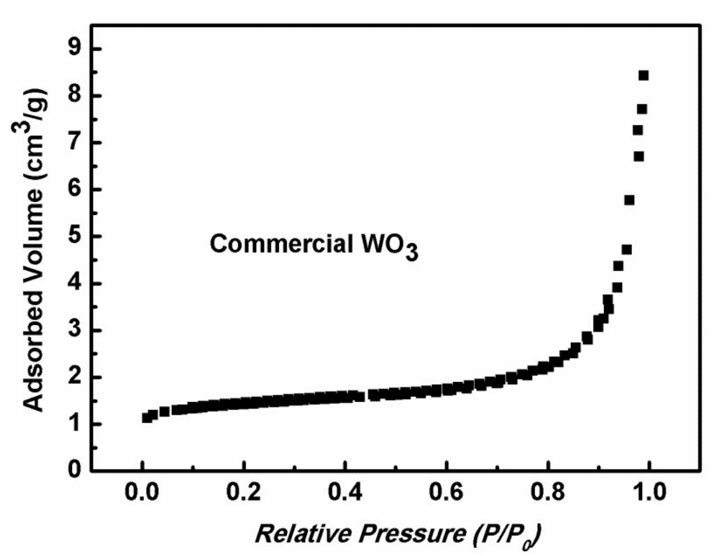
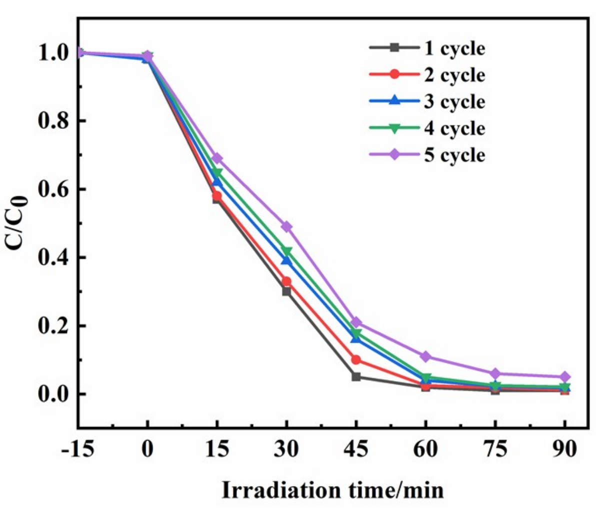


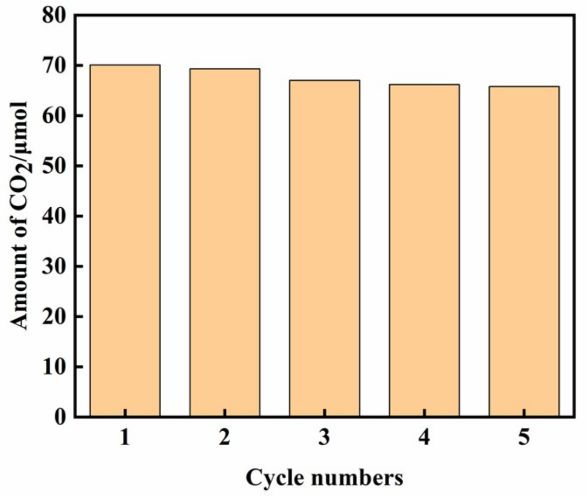
Fig. S5 Nitrogen adsorption-desorption isotherms of commercial WO_3 MTs。

(a)

(c)



(b)



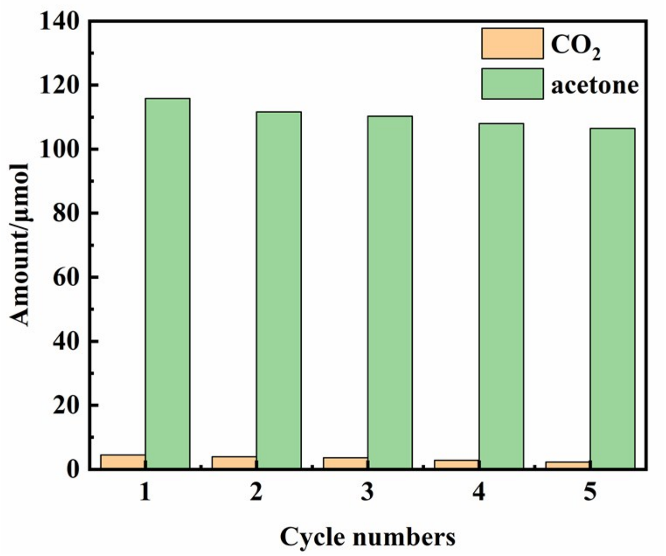


Fig. S6 Result of reusability experiments for (a) MB, (b) Ach and (c) propan-2-ol photocatalytic reaction using Pd-WO_3 microtubes.