SUPPORTING INFORMATION

Pristine Simple Oxides as Visible Light Driven Photocatalysts: Highly Efficient Decomposition of Organic Compounds over Platinum-loaded Tungsten Oxide

Ryu Abe,*[,†,§] Hitoshi Takami,[§] Naoya Murakami,[§] and Bunsho Ohtani[†]

Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan

RECEIVED DATE (automatically inserted by publisher); E-mail: ryu-abe@cat.hokudai.ac.jp

a) Preparation of Pt-loaded WO_3 photocatalysts

Fine particulate WO_3 with a particle size of 50–200 nm was separated from commercial WO_3 powder (99.99%, Kojundo Chemical Laboratory Co.) as follows. The WO_3 powder (5 g) was suspended in purified water (100 mL) with ultrasonic irradiation for 30 min, and then the suspension was centrifuged at 1000 rpm for 10 min. After the removal of precipitate containing large aggregates, fine particulate WO_3 with a particle size of 50–200 nm was collected by centrifugation (10000 rpm for 30 min). BET specific surface area of obtained WO_3 fine particles, which was determined by nitrogen-adsorption at 77 K, was ca. 10.5 m^2g^{-1}. (before the separation: ca. 2.4 m^2g^{-1})

Platinum-loaded WO_3 samples (Pt-WO_3) were prepared as follows. An aqueous suspension containing the fine particulate WO_3 and hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) was exposed to visible light ($\lambda > 400$ nm) provided by a 300 W Xe lamp (LX-300F, Cermax) fitted with a cutoff filter (L-42, HOYA). After 2 h of irradiation, methanol (10 vol%) was added and the suspension exposed to further irradiation for 2 h. This procedure resulted in a highly uniform dispersion of platinum particles (average size, 5 nm) on the WO_3 surface, as shown in Fig. S1. Titanium (IV) oxide (TiO_2 P25, Nippon Aerosil, Japan, ca. 55.4 m^2g^{-1}) was used as a reference photocatalyst. Nitrogen-doped TiO_2 (N-TiO_2) for comparative analysis was prepared by treatment of TiO_2 powder (ST-01, Ishihara Sangyo Kaisha Ltd., ca. 320 m^2g^{-1}) under NH_3 flow (50 mL min^{-1}) at 823 K for 3 h. This method is known as relatively reproducible procedure to prepare active N-TiO_2 sample, and applied in a considerable number of studies. We confirmed that the visible-light induced activities of prepared N-TiO_2 sample were comparable to those reported in the literatures. The specific surface area of N-TiO_2 sample was determined to be ca. 88.9 m^2g^{-1}.

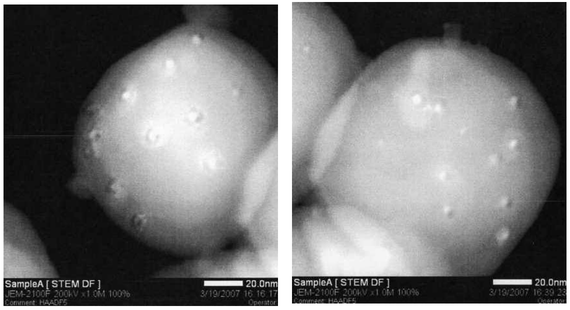

Figure S1 Scanning transmission microscopy images of Pt(1 wt%)-WO_3 samples.

b) Photoreactivity Experiments

Photocatalytic decomposition of acetic acid (AcOH) was carried out in a Pyrex reaction cell containing a suspension of the photocatalyst powder (50 mg) in an aerated aqueous AcOH solution (5 vol%, 250 mL) with continuous agitation using a magnetic stirrer. Photocatalytic decomposition of acetaldehyde (AcH) or isopropyl alcohol (IPA) was performed using a Pyrex reaction cell with internal volume of 330 mL. The photocatalyst powder (50 mg) was spread in a square (15×15 mm) on the bottom of the reactor, and gaseous AcH (1000 ppm, ca. 15 μmol) or IPA (1200 ppm, ca. 17 μmol) was introduced into the cell. In both cases, a 300 W Xe lamp was used as the light source. Components in the gas phase were analyzed by gas chromatography. Action spectrum analysis for AcOH decomposition was performed under monochromatic irradiation. In this case, 10 mg of photocatalyst powder was suspended in an aerated aqueous AcOH solution (5 vol%, 2 mL), which was subjected to monochromatic irradiation (with FWHM ~17 nm) in the range of 300-600 nm using a diffraction grating type illuminator (Jasco CRM-FD) equipped with a 300-W xenon lamp (Hamamatsu Photonics C2578-02). The intensity of irradiation, measured by a Molectron PM5200 laser power meter, was in the range of 1.98-6.52 10^{-8} einstein s^{-1}.

c) Photoacoustic Spectroscopic Measurements

Photoacoustic spectroscopic measurements were conducted using a home-made PA cell composed of an aluminum body (internal volume, ca. 1 mL) with a Pyrex window and two valves for gas flow. Three atmospheres were used in the reactions: flows of ambient air, nitrogen (N_2), or O_2 containing isopropyl alcohol (IPA) vapor. Monochromatic light (ca. 0.2 mW cm^{-2}) chopped at 80 Hz was obtained from a Xe lamp as modulated probe light, and an ultraviolet light-emitting diode (365 nm, ca. 2.8 mW cm^{-2}) was employed as continuous irradiation for excitation of WO_3. The PA signal was acquired by a condenser microphone buried in the cell, and amplified and monitored using a digital lock-in amplifier. In time-resolved analyses, a light-emitting diode (625 nm) was used as a probe light, and the output intensity was modulated by a digital function generator at 80 Hz. The PA spectrum of bare WO_3 under UV irradiation in the presence of air and IPA vapor exhibits an upward shift in the visible region at wavelengths longer than 470 nm, as shown in Fig. S2.

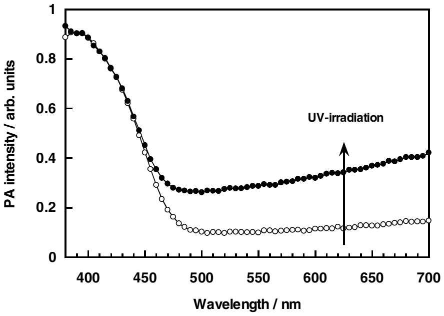

Figure S2 Photoacoustic spectra of a bare WO_3 powder before (open symbols) and after (closed symbols) UV irradiation for 30 min in air containing IPA vapor