Supporting Information

Visible Light-Responsive Pristine Metal Oxide Photocatalyst: Enhancement of Activity by Crystallization under Hydrothermal Treatment

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Experimental details

Preparation of Bi_2WO_6 particles

Bi_2WO_6 particles were prepared by hydrothermal reaction. An aqueous solution of sodium tungstate (Na_2WO_4, 2.75 mmol) was added dropwise to a mixture of bismuth nitrate ($Bi(NO_3)_3$, 5.0 mmol) and water with vigorous magnetic stirring at room temperature. The resulting white slurry was stirred for 10 min, ultrasonicated for 10 min, and poured into a 100-mL Teflon-lined autoclave (San-ai Kagaku, HU-100). After the addition of water to ca. 80% of the capacity, the autoclave was heated in an oven. The hydrothermal treatment was performed under an auto-generated pressure at 373 or 403 K for 20 h. After the reaction, the precipitate was collected by centrifugation, washed three times with 50 mL of water, and dried in an oven at 393 K.

Photocatalytic oxidative decomposition of acetaldehyde

Photocatalyst powder (50 mg) was uniformly spread on a glass plate (15 mm × 15 mm) and placed on the bottom of a cylindrical glass vessel with a volume of ca. 330 mL. Gaseous acetaldehyde (2000 ppm, ca. 30 μmol) was injected into the vessel filled with ambient air. After adsorption of acetaldehyde had reached equilibrium in the dark, visible light photoirradiation (> 400 nm) was performed using a 300-W xenon lamp (ILC Technology CERMAX-LX300F) and a cut-off filter (Asahi Techno Glass L42) through a top window of the glass vessel. The amounts of acetaldehyde and carbon dioxide were measured by a gas chromatograph (Agilent Technologies 3000A Micro GC).

Action spectrum analysis

A suspension of photocatalyst powder (10 mg) was applied to a glass plate (9 mm × 38 mm) followed by drying at 393 K for 1 h. The thus-prepared film was placed in a glass vessel with a volume of ca.16.3 mL. Gaseous acetaldehyde (10000 ppm, ca. 7.1 μmol) was injected into the vessel filled with ambient air. After adsorption of acetaldehyde had reached equilibrium in the dark, monochromatic light was irradiated using a diffraction grating-type illuminator (Jasco CRM-FD) equipped with a 300-W xenon lamp (Hamamatsu Photonics). The intensity of irradiation was measured by an optical power meter (Hioki 3664). The optical power was in the range of 3.0–5.5 mW cm^{-2}. The amount of carbon dioxide was measured by an FID-gas chromatograph (Shimadzu GC-14B) equipped with a Porapak-Q column and a methanizer (Shimadzu MTN-1). The rate of carbon dioxide evolution during the initial 30 min of photoirradiation was used for calculation of apparent quantum efficiency. Acetaldehyde is decomposed into carbon dioxide with the following proposed stoichiometry:

$$CH_3CHO + 5/2O_2 \rightarrow 2CO_2 + 2H_2O.$$

Assuming that oxygen is reduced by photoexcited electrons and reduction of one oxygen molecule requires four electrons, this reaction is formally a ten-electron process. Therefore, the apparent quantum efficiency was calculated as a five-electron process for the evolution of one carbon dioxide molecule.

Time-resolved infrared absorption spectroscopy

The light source for photoexcitation was third harmonic light of a Q-switched Nd:YAG laser (Lotis, LS2124). The wavelength, pulse duration, repetition rate, and power were 355 nm, 10 ns, 1 Hz, and 1 mJ cm^{-2}, respectively. Photocatalyst powder was fixed on a calcium fluoride plate with a density of ca. 1 mg cm^{-2}. The thus-prepared film was placed in a stainless steel cell and evacuated at room temperature for 15 min. Infrared (IR) light emitted from an $MoSi_2$ source was focused on the sample film in a vacuum. The transmitted IR light was dispersed in a grating spectrometer (Acton, 2300i). The monocromatized IR output was transformed to an electric signal in a photovoltatic MCT detector (Kolmar). The MCT output was amplified in an ac-coupled amplifier (Stanford Research Systems, SR560) and recorded in a digital oscilloscope (Iwatsu, DS-4262) as a function of delay time. Transient absorbance change was obtained by signal averaging of 300 flashes at 1 Hz.

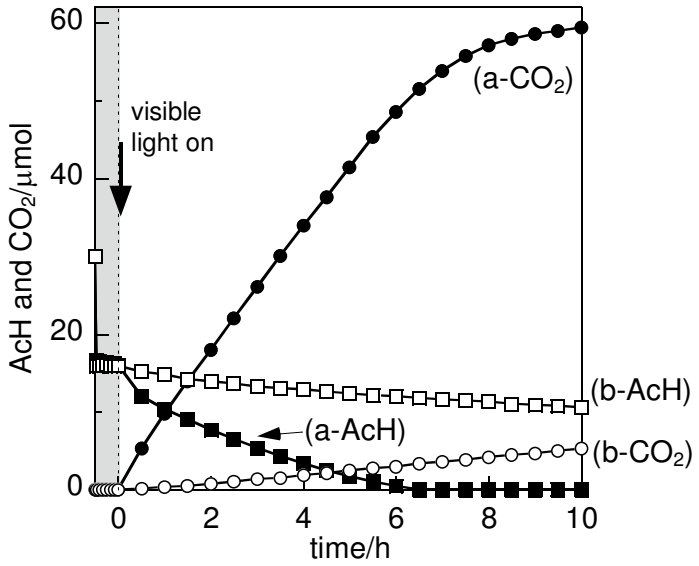

Figure S1. Photocatalytic oxidative decomposition of gaseous acetaldehyde (2000 ppm, ca. 30 μmol) in air over (a) 50 mg of Bi_2WO_6 crystallites autoclaved at 403 K and (b) 30 mg of titanium oxide P25 (Japan Aerosil) under visible light (> 400 nm) irradiation. The time courses of amounts of acetaldehyde (AcH) and carbon dioxide (CO_2) evolved are illustrated.

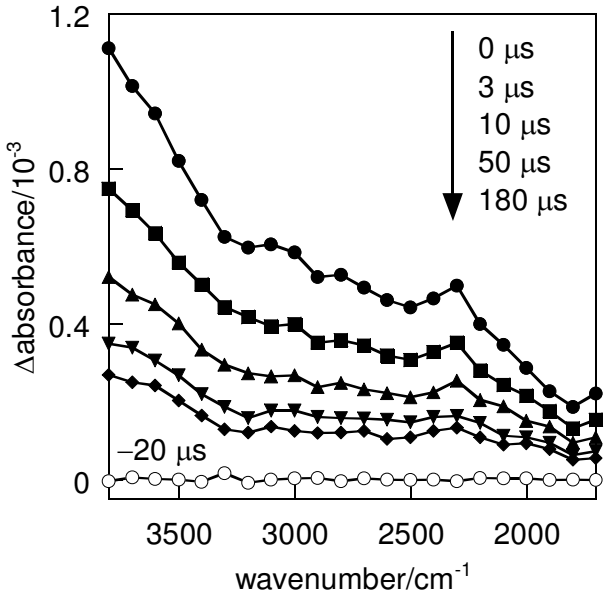

Figure S2. Transient IR absorption spectra of Bi_2WO_6 crystallites autoclaved at 403 K. The spectra were recorded at delay times of -20, 0, 3, 10, 50, and 180 μs after irradiation by 355-nm laser pulse in vacuum.