



Supporting Information

© Wiley-VCH 2008

69451 Weinheim, Germany

Supporting Information

Nanoporous-walled Tungsten Oxide Nanotubes as Highly-active Visible-light-driven Photocatalysts

Zhi-gang Zhao and Masahiro Miyauchi*

Nanotechnology Research Institute

National Institute of Advanced Industrial Science and Technology

Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8565 (Japan)

[1] Experimental details:

Characterization: TEM images were collected by using a JEOL JEM 2010F microscope working at 200 kV. A Hitachi S-4800 field emission scanning electron microscope (FE-SEM, Hitachi Co. Ltd. S-4800) was used to investigate the morphology. X-ray powder diffraction (XRD, Rigaku Co. Ltd. Ultima-X) measurements were carried out using filtered CuK radiation. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micrometrics ASAP 2010 system after the sample was degassed in vacuum at 90 °C overnight. A Shimadzu UV-1601PC spectrophotometer was used to record the UV-vis spectra of the NTs.

Photocatalytic activity measurement: A typical indoor air pollutant, acetaldehyde, was chosen as the probe molecule for evaluating the photocatalytic activity. The experiments were performed in a cylindrical glass air-filled static reactor (500 mL total volume) with a quartz window. An O₂ (20 %)-N₂ gas mixture adjusted to a relative humidity of 30 % was used to fill the reaction vessel. The sample was illuminated with a 300 W Xe lamp (Hayashi Watch-works Co. Ltd.) in conjunction with an optical fiber coupler, an UV cutoff filter (Y43, Asahi Techno Glass Co. Ltd.), and an IR cutoff filter (C-50S, Asahi Techno Glass Co. Ltd.). A spectro-radiometer (USR-45D, Ushio Co.) measured the visible light intensity which was adjusted to 20 mW/cm². The catalyst (100 mg) was placed in a circular glass dish and mounted in the reactor. Then a certain amount of gas-phase acetaldehyde was introduced into the reactor by syringe until the concentration of acetaldehyde in the reactor reached to be about 500 ppmv. Before analysis, the catalyst and acetaldehyde were kept in the dark for 1 hour to ensure the establishment of an adsorption-desorption equilibrium between photocatalyst and acetaldehyde. The acetaldehyde and CO₂ concentrations were measured using a gas chromatography (Shimadzu model GC-2014) equipped with a 2 m Poropak-Q column, a methanizer, and a flame ionization detector, using N₂ as the carrier gas.

[2] Nitrogen adsorption-desorption isotherm plot of WO₃ NTs:

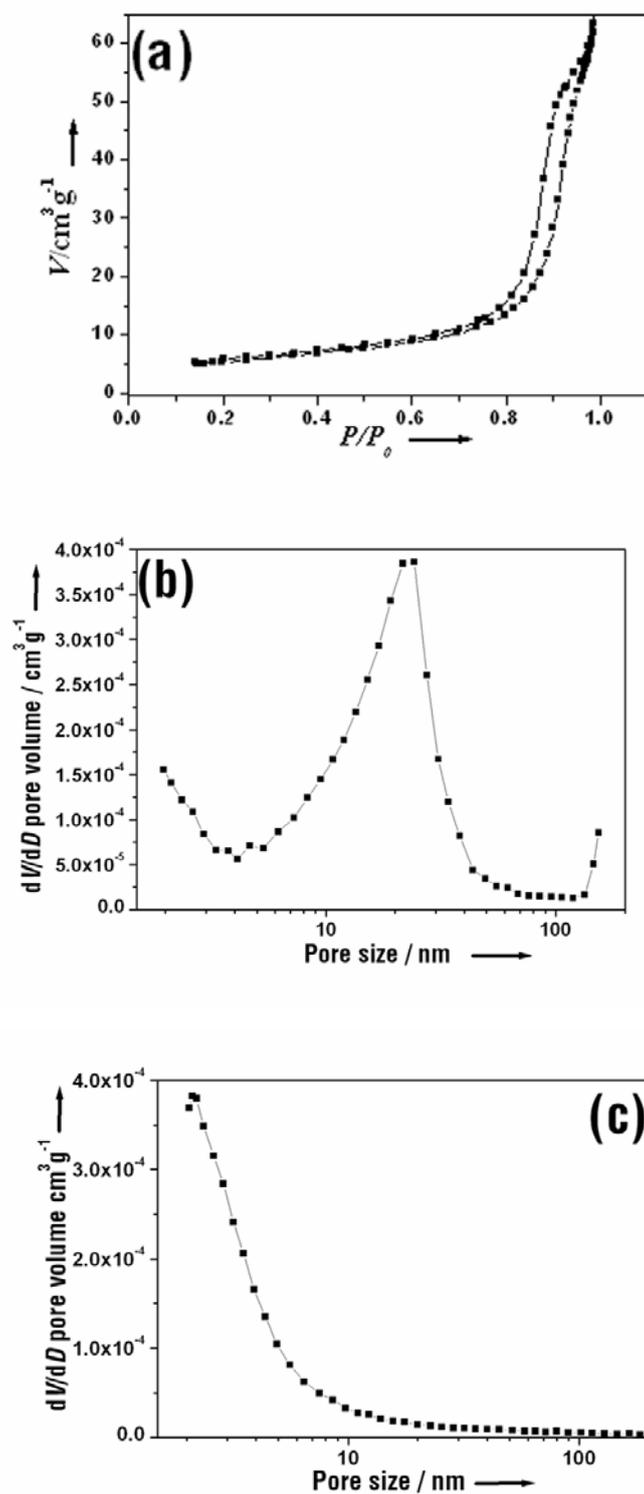


Figure S1: (a) Nitrogen adsorption-desorption isotherm plot of WO₃ NTs, and Barrett-Joyner-Halenda (BJH) pore size distribution plot of (b) WO₃ NTs and (c) tungstic acid hydrate NTs.

[3] UV-vis spectrum of WO_3 NTs:

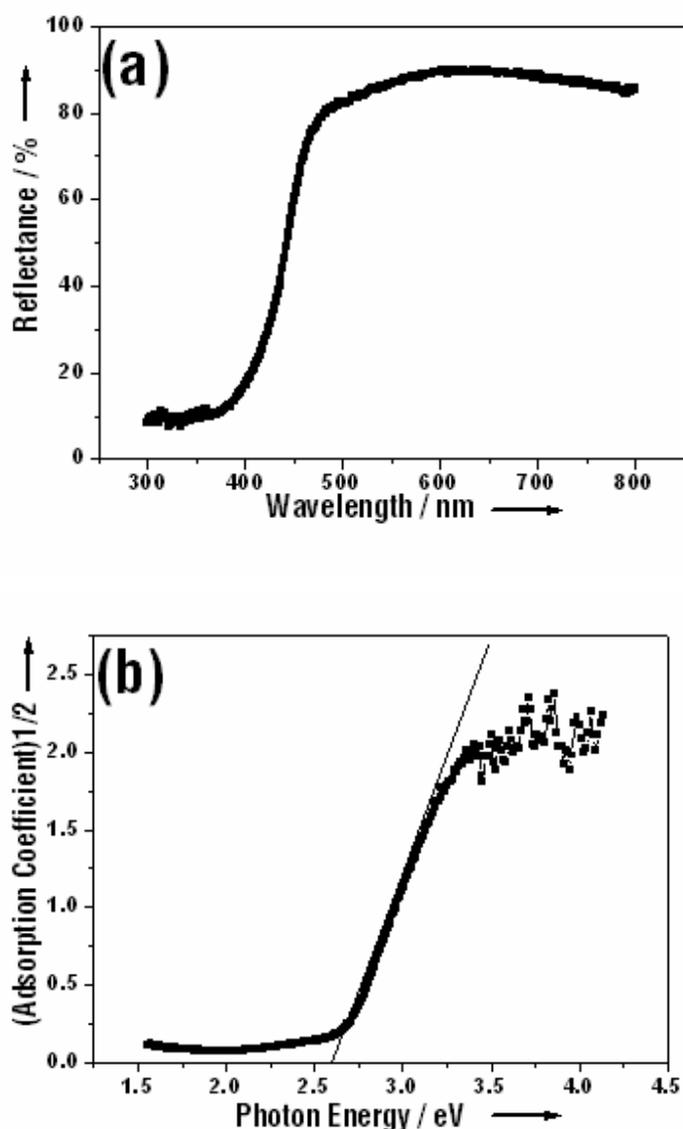


Figure S2: (a) UV-vis spectrum for NTs analyzed by the diffuse reflectance method. Adsorption coefficient (α) was obtained by the Kubelka-Munk method; (b) the square root of adsorption coefficient α vs. photon energy.

Since the electronic structure of WO_3 gives an indirect transition, the square root of α is linear with photon energy, and the intercept with the x axis was used to estimate the band gap energy. The estimated band gap value for WO_3 NTs was 2.6 eV, comparable with that of the bulk WO_3 (2.4-2.8 eV).

[4] The complete decomposition of acetaldehyde to CO₂ on Pt- loaded NTs:

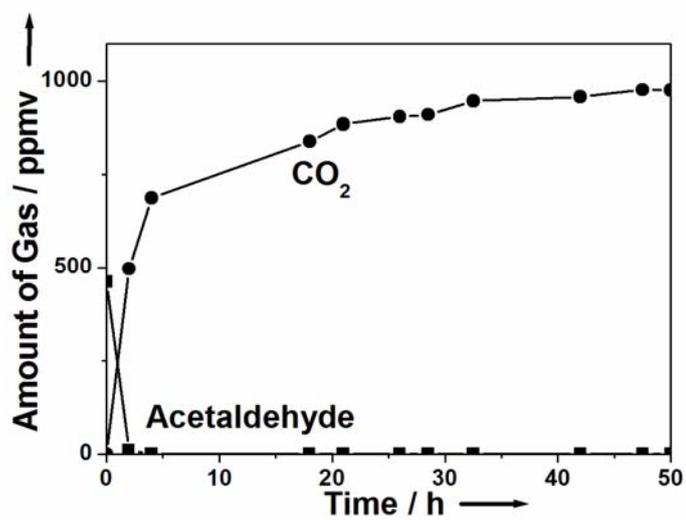


Figure S3: changes in the acetaldehyde and CO₂ concentration as a function of exposure time on 0.5 wt% Pt-loaded WO₃ NTs under 100 mW/cm² irradiance.

[5] The incomplete decomposition of acetaldehyde to CO₂ on pure NTs:

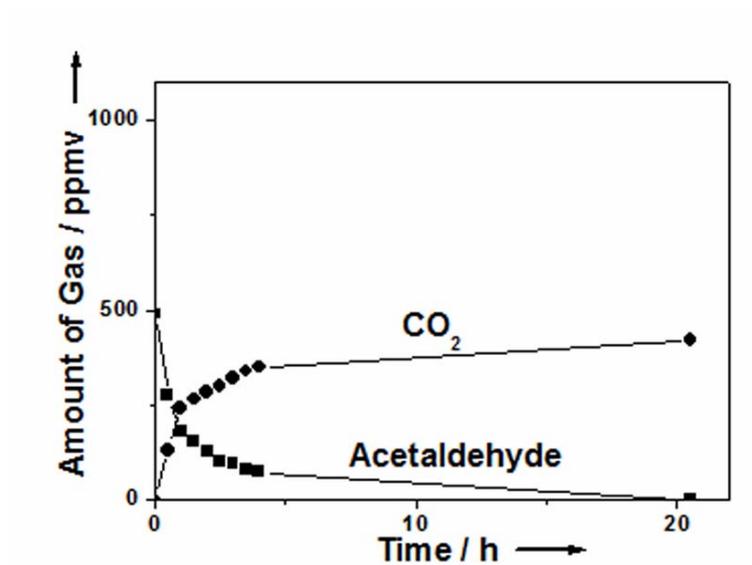


Figure S4: changes in the acetaldehyde and CO₂ concentration as a function of exposure time on pure WO₃ NTs under 100 mW/cm² irradiance.

[6] The Calculation of Apparent Quantum Yield (QY) values:

Apparent quantum yield (QY) is one of the basic parameters of semiconductor photocatalysis. The QY values for the photocatalytic degradation of acetaldehyde were calculated using the following equations:

$$\text{QY} = (1 + 1/2) \text{ Number of generated CO}_2 \text{ molecules} / \text{ Number of absorbed photons}$$

The initial amount of CO₂ generated, which were determined after 30 min of illumination was used to discuss the QY values. The QY values for 0.5 % Pt-loaded WO₃ nanotubes, 0.5 % Pt-loaded commercial WO₃ particles, and nitrogen-doped TiO₂ were calculated to be 1.03%, 0.24% and 0.22%, respectively (initial concentration: 500 ppmv). It should be stressed that the QY values decreased with increasing absorbed photons flux (light intensity). In our case, the absorbed photons flux for 0.5 % Pt-loading WO₃ nanotubes (1.9×10^{16}) is relatively high, thus the obtained QY value is lower than that at low light intensity. However, this QY value for 0.5 % Pt-loaded WO₃ nanotubes is very similar to that of TiO₂ under UV illumination with an absorbed photon flux level of 10^{16} reported by Y. Ohko (*J. Phys. Chem B* 98, 102, 2699). Also the QY value for 0.5 % Pt-loading WO₃ nanotubes is about 4 times than that of 0.5 % Pt-loading commercial WO₃ particles, and nitrogen-doped TiO₂.

[7] The characterization of Pt-loaded WO_3 nanotubes:

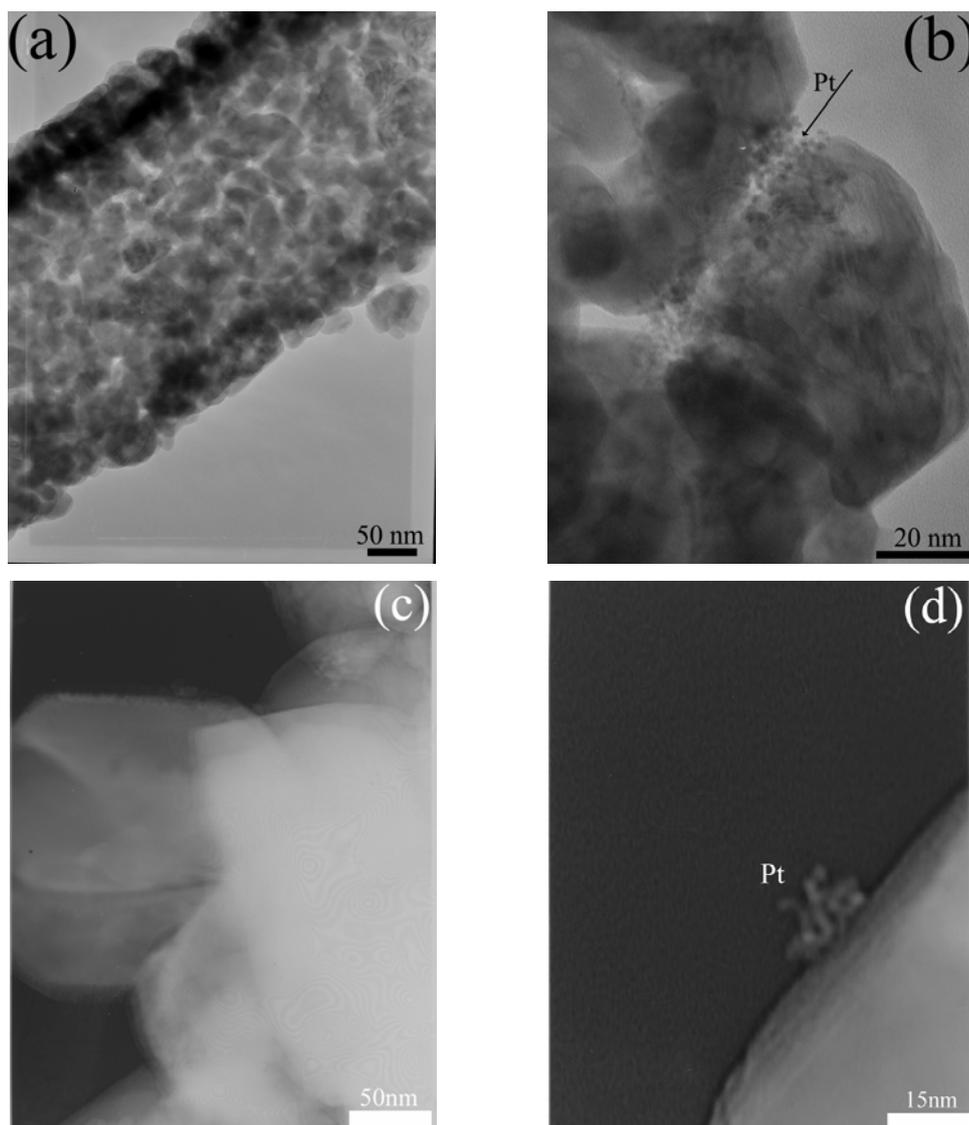


Figure S5: TEM images of Pt particles deposited on (a,b) WO_3 nanotubes; (c,d) commercial WO_3 particles