

Photocatalytic Activity of Octahedral Single-Crystalline Mesoparticles of Anatase Titanium(IV) Oxide

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Experimental

Characterization

Scanning electron microscopy (SEM) images were obtained by a JEOL JSM-7400F. Transmission electron microscopy (TEM) images were obtained by a JEOL 2010F with an acceleration voltage of 200 kV. Scanning transmission electron microscopy (STEM) images were obtained by a Hitachi HD-2000 with an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT ULTIMA diffractometer with Cu K α radiation. Brunauer-Emmett-Teller (BET) specific surface area was determined from nitrogen adsorption at 77 K on a Yuasa Ionics Autosorb-6-AG surface area and pore size analyzer.

Photocatalytic activity test

Photocatalytic activity of the samples was evaluated by three photocatalytic reactions in aqueous solutions: (a) oxidative decomposition of acetic acid (AcOH) under air, (b) oxidative decomposition of methanol (MeOH) under air, and (c) hydrogen (H₂) evolution from an aqueous methanol solution under argon. Photocatalytic reactions were performed in a glass tube with magnetic stirring at 1000 rpm. A photocatalyst (50 mg) was suspended in an aqueous solution (5.0 cm³) containing (a) 5.0 vol% AcOH and (b and c) 50 vol% MeOH. The concentration of powders in the suspension was high enough to prevent transmission of light. In the case of reaction (c), hexachloroplatinic acid (H₂PtCl₆·6H₂O), which is reduced in situ to platinum (Pt) metal deposits by photoexcited electrons, was added. The amount of Pt loading on photocatalyst powders was adjusted to 2.0 wt%. The suspension of (c) was bubbled with argon before irradiation. The glass tube sealed with a rubber septum was irradiated using a 400-W high-pressure mercury lamp (Eiko-sha). The wavelength of light was > 290 nm. The reaction temperature was kept at 298 K using a thermostated water bath. The molar amount of liberated products in the gas phase of reaction mixtures was measured using a TCD-gas chromatograph (Shimadzu GC-8A) equipped with MS-5A and Porapak-Q columns for (a and b) carbon dioxide (CO₂) and (c) H₂, respectively. The products in the liquid phase were not measured. Previous study indicates that CO₂ was liberated by complete oxidation of acetic acid ($\text{CH}_3\text{COOH} + 2\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$) [H. Kominami, J. Kato, M. Kohno, Y. Kera and B. Ohtani, *Chem. Lett.*, 1996, **25**, 1051]. In the case of methanol decomposition, CO₂ would be liberated by complete oxidation of methanol ($\text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$) and formaldehyde might be an intermediate ($\text{CH}_3\text{OH} + 1/2\text{O}_2 \rightarrow \text{HCHO} + \text{H}_2\text{O}$), although formaldehyde could not be measured in the present gas-chromatograph system. Figures S3, S4, and S5 show time courses of photocatalytic reactions in the presence of commercial titanium(IV) oxide P25 (Nippon Aerosil) and octahedral mesoparticles prepared by hydrothermal reaction of titanate nanowires. The steady rate of linear increase in product yields was used for the estimation of photocatalytic activity.

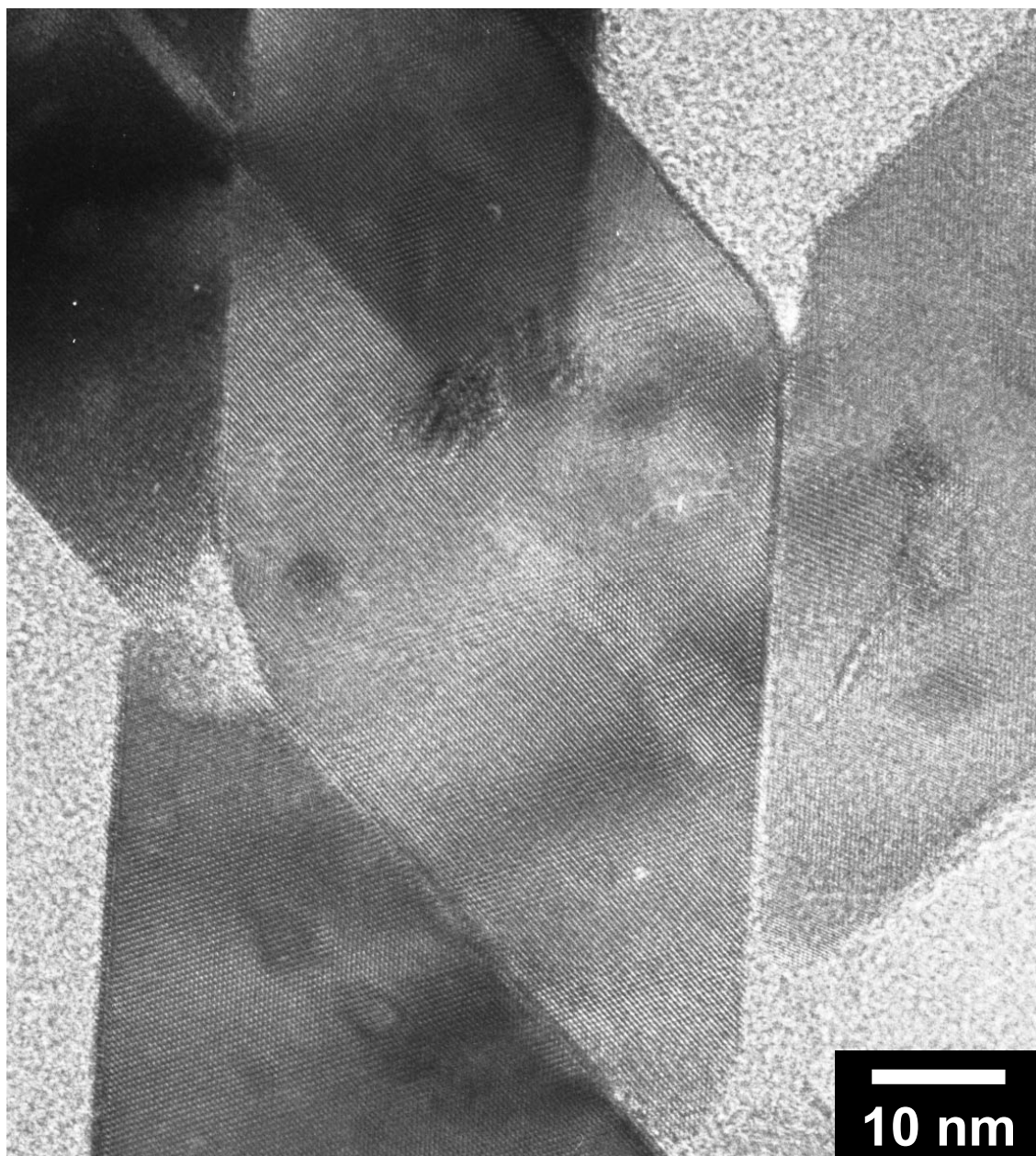


Figure S1. TEM image of particles after hydrothermal reaction of titanate nanowires. Each particle was found to be a single crystallite of anatase.

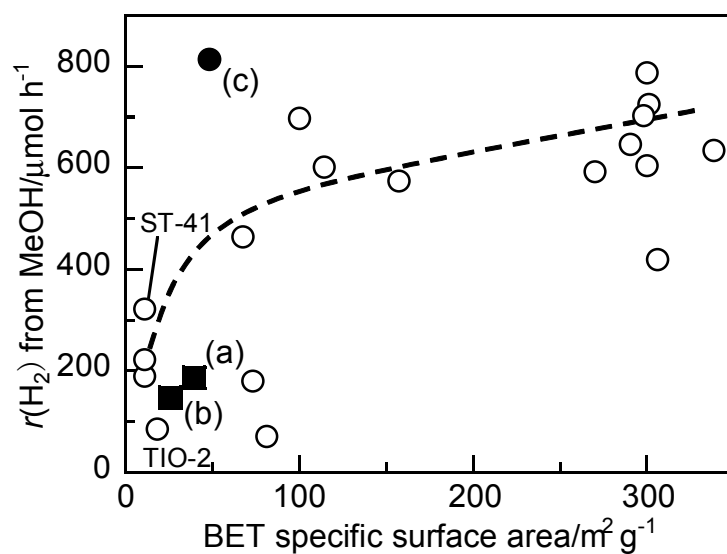


Figure S2. Effect of specific surface area on photocatalytic activities for dehydrogenation of MeOH in an aqueous solution: (a, b) particles containing octahedral crystallites prepared from (a) titanate nanowires and (b) bundled titanate nanowires, (c) P25, and (open circles) commercial anatase TiO_2 particles.

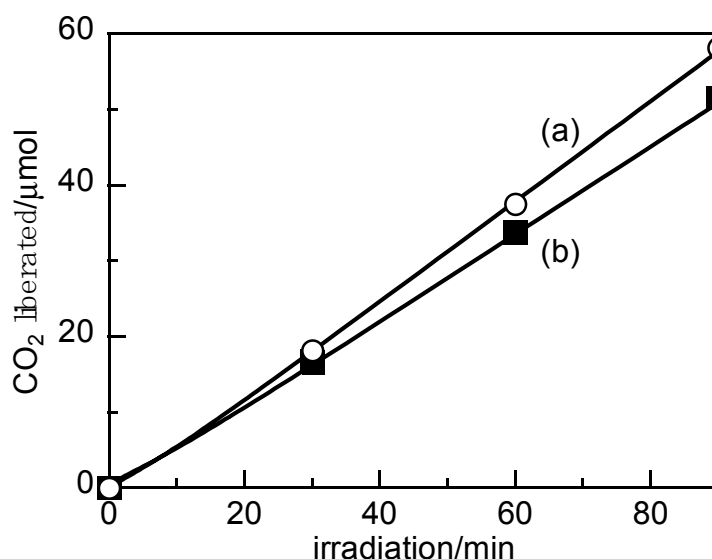


Figure S3. Photoinduced CO_2 liberation from oxidative decomposition of AcOH in an aerated aqueous solution in the presence of (a) P25 and (b) mesoparticles containing octahedral crystallites.

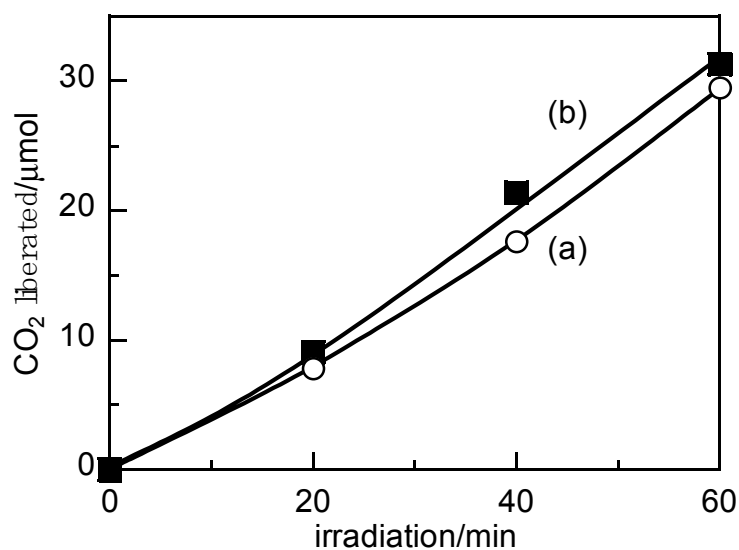


Figure S4. Photoinduced CO_2 liberation from oxidative decomposition of MeOH in an aerated aqueous solution in the presence of (a) P25 and (b) mesoparticles containing octahedral crystallites.

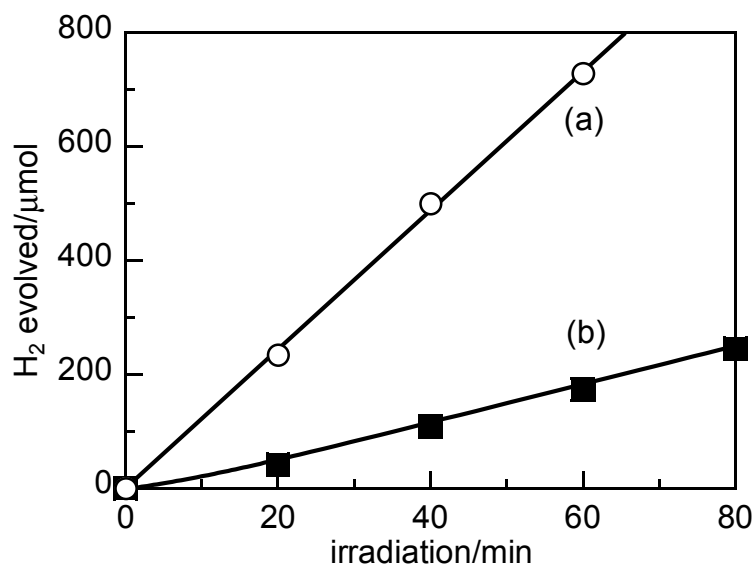


Figure S5. Photoinduced H_2 liberation from dehydrogenation of MeOH in a deaerated aqueous solution in the presence of (a) P25 and (b) mesoparticles containing octahedral crystallites.

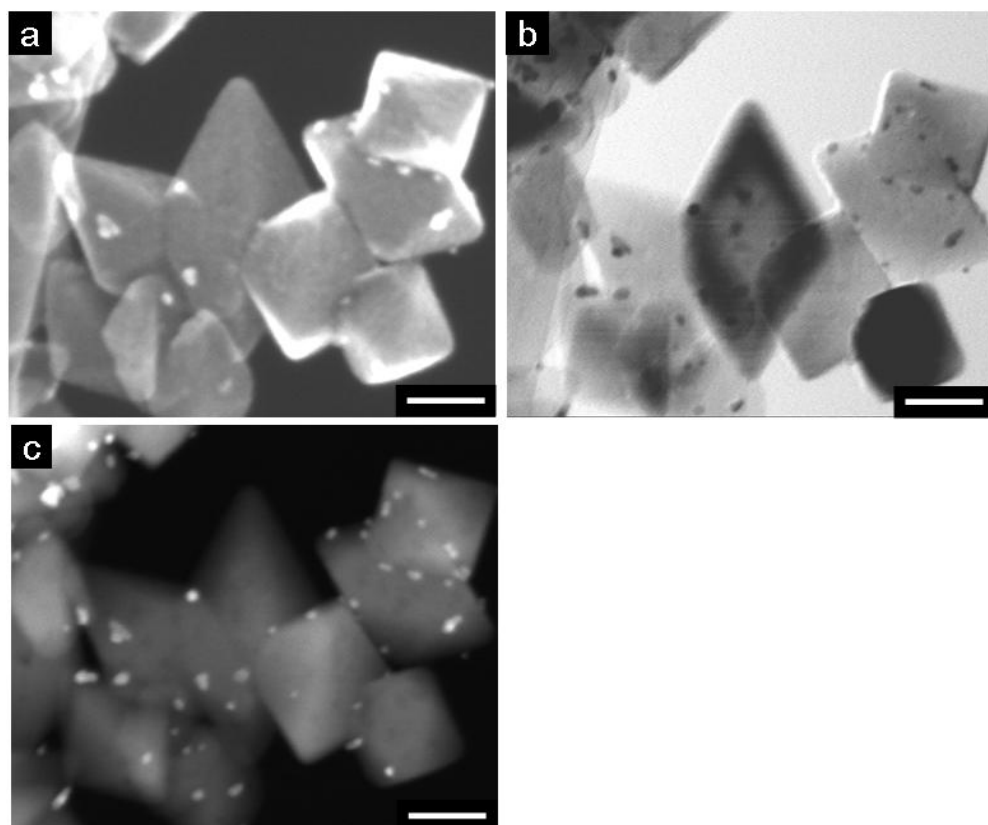


Figure S6. Electron microscopy images of Pt-loaded mesoparticles containing octahedral crystallites after photocatalytic dehydrogenation of MeOH: (a) secondary electron image, (b) bright-field STEM image, and (c) dark-field STEM (Z-contrast) image. The scale bars correspond to 30 nm. The amount of deposited Pt, which was dissolved using aqua regia for measurement, was quantified to be ca. 2 wt% by means of atomic absorption spectroscopy.

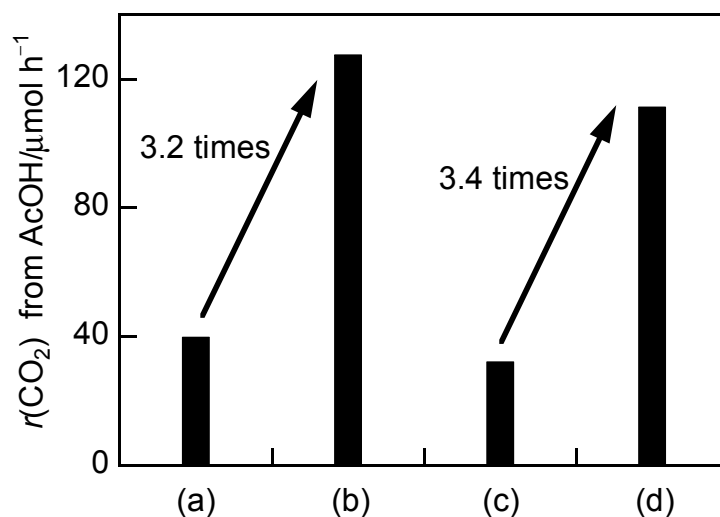


Figure S7. Photocatalytic activities of (a) P25, (b) Pt-loaded P25, (c) mesoparticles containing octahedral crystallites, and (d) Pt-loaded mesoparticles containing octahedral crystallites for oxidative decomposition of AcOH in an aerated aqueous solution. The Pt-loaded samples were collected after photocatalytic H_2 liberation from dehydrogenation of MeOH in a deaerated aqueous solution. The amounts of Pt loading were adjusted to 2.0 wt%.