Supporting information for

Visible light-induced photocatalytic reaction of gold-modified titanium (IV) oxide particles: Action spectrum analysis

Experimental details

Materials

Fifteen powder titanium(IV) oxide (titania; TiO₂) samples (Aldrich, Merck, Ishihara, Degussa P-25, Titan Kogyo PC series, Showa Titanium ST series, reference catalysts supplied from the Catalysis Society of Japan JRC-TIO series and Ultra-fine rutile supplied from Newcastle University) were used in this study. Hydrogen tertrachloroaurate (III) tetrahydrate (HAuCl₄·4H₂O) (Nakalai Tesque and Wako Pure Chemicals) were used as received as metal loadings. Methanol, acetic acid, 2-propanol (Wako Pure Chemicals) were used without further purification.

Gold photodeposition

2 wt.% of gold, which corresponds to 0.81 % in moles, was photodeposited onto the surface of commercial titania powders of different physical properties and crystalline forms (anatase or rutile), according to the procedure shortly described below.

Au/TiO₂ powder was prepared simultaneously in six Pyrex tubes to obtain sufficient amount of photocatalyst powders. In every Pyrex tube, 572 mg of titania powder was suspended in a 28.6-mL 50vol% aqueous methanol in the presence of HAuCl₄·6H₂O, purged of air with argon for at least 15 min, and then sealed off with a rubber stopper. The suspension was photoirradiated with a 400-W high-pressure mercury lamp under magnetic stirring (500 rpm). The temperature of the suspension during photoirradiation was maintained at 298±5K by the use of a thermostatically controlled water bath. During the irradiation, the amount of generated hydrogen was measured at every 15 min by gas chromatography (Shimadzu GC-8A-IT). Au/TiO₂ photocatalyst was centrifuged, washed at least three times with distilled water, dried overnight at 393K and grinded in an agate mortar.

Characterization of photocatalysts

To characterize the light-absorption properties of modified photocatalysts, diffuse reflectance (DR) spectra were recorded, and data were converted to obtain absorption spectra. DR spectra were taken both for solid and suspended photocatalysts. The measurements were carried out on a Hamamtsu Photonics C7473-6 photonic multi-channel analyzer (BaSO₄ and bare photocatalysts used as reference materials) and on Jasco V-670 spectrophotometer equipped with a PIN-757 integrating sphere where the baseline was recorded using a poly(tetrafluoroethylene) reference.

The morphology of gold photodeposited onto titania was observed by Field Emission Scanning Electron Microscopy (FE-SEM, JEOL JSM-7400F). Au/TiO₂ powders were dispersed in water in an ultrasound bath for a few minutes. Some drops of suspension were deposited on copper tape. Some powder samples were also dusted on conductive carbon paint. The samples prepared by both methods were dried under vacuum overnight. The images were acquired at wide range of magnification (30.000-600.000) in the secondary electron imaging mode (SEI) and lower electron

imaging mode (LEI) using 3 mm and 6 mm working distance, respectively; 4-5 kV accelerating voltage and 10 μ A emission current.

X-ray diffraction (XRD) patterns were recorded with a diffractometer (Rigaku, RINT Ultima+) using Cu K α radiation (tube voltage: 40kV, tube current: 20 mA) equipped with a graphite monochromator. Measurements were carried out for two scan speeds: 2 and 0.2° min⁻¹ and three scan ranges: 10-90°, 35-40° and 42-47°, where slower one for narrower ranges was used for particle sizes determination. To determine primary particle size of titania (PC101A) and gold, XRD data were calculated using Scherrer equation with appropriate corrections (ref. 10). The sizes of almost all titania particles (except PC101A which was determined in this study) and surface areas (using the BET Brunauer, Emmett and Teller-BET method) were determined by our group and will be reported (ref. 14).

Photocatalytic activity tests

Polychromatic irradiation: A metal-loaded photocatalyst (50 mg) was suspended in an aqueous solution of acetic acid or 2-propanol (5vol%, 5 mL) and photoirradiated under magnetic stirring (1000 rpm) in the same set-up as for the gold photodeposition. For the test of visible-light induced activity, an additional sample holder with cut-off filter Y48 mounted in the irradiation window was installed, so that light of wavelengths > 450 nm reached the suspension. During the irradiation of acetic acid solutions, a portion (0.2 mL) of the gas phase of reaction mixture was withdrawn with a syringe and subjected to gas chromatographic analysis of carbon dioxide (CO₂) (Shimadzu GC-14B equipped with a flame ionization detector and a methanizer). Due to relatively small yield of CO₂ under visible irradiation, enhancement of FID sensitivity by converting CO₂ into methane in the methanizer was required. For the irradiated sample in a 2-propanol solution, generated acetone was detected using a GC-FID (Shimadzu GC-14B equipped with a flame ionization detector). Before liquid sample injection to GC, photocatalyst powder was separated from the suspension using a filter (Whatman Mini-UniPrep, PVDF).

Monochromatic irradiation - action spectrum analysis

For action spectra analyses, 20 mg of photocatalyst was suspended in a 2-mL of acetic acid or 2propanol (5vol%) and irradiated for 2 or 4 h 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 and a Hioki 3664 optical power meter, was in the range of $1.24-3.9 \times 10^{-8}$ einstein s⁻¹. During experiments, reaction mixtures were continuously stirred. The stoichiometries of acetic acid and 2-propanol oxidations are assumed as follows.

 $\frac{1}{2}$ CH₃COOH + O₂ = CO₂ + H₂O (four-electron process since O₂ reduction requires 4e⁻) (CH₃)₂CHOH + $\frac{1}{2}$ O₂ = (CH₃)₂CO + H₂O (two-electron process)

Apparent quantum yield was calculated as the ratio of the rate of electron consumption (calculated from the rate of acetone generation) to the flux of incident photons.

Exemplary results

Characterization of Au/TiO2 powders

Size distribution and shape of Au on titanium oxide were strictly dependent on properties of used titanium oxide, such as particle sizes, surface defects and uniformity. Thus, on large, non-uniform rutile particles, huge variety of sizes and shapes of generated Au nanoparticles was noticed. The exemplary size distribution of Au on Au/TiO₂ (Aldrich rutile) obtained by measuring the sizes of 115 particles in SEM images is shown in Fig. S1.



Fig. S1. Distribution of size of Au deposits on Au/TiO_2 (Aldrich rutile), where the volumetric content was calculated assuming constant thickness (diameter) of rod-like (spherical) Au particles.

In contradiction to large rutile particles, on anatase particles with smaller sizes and higher density of defects, smaller Au nanoparticles with similar sizes were generated, as shown in Fig. S2.



Fig. S2. SEM and STM images of Au/TiO_2 : Aldrich rutile (left) and STO1 (right), respectively. The scale bars represent 100 nm for each image.





Fig. S3. Comparison of rate of photocatalytic CO_2 evolution from suspension containing CH_3COOH under UV irradiation between bare and gold-modified titania particles: A: predominantly anatase and R: predominantly rutile.