

Hydrogen peroxide synthesis from water and oxygen by a three-component nanohybrid photocatalyst consisting of Au particle-loaded rutile TiO₂ and RuO₂ with heteroepitaxial junction

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Experimental details

Catalyst preparation

Au particles were loaded on TiO₂ particles with a crystal form of rutile and a specific surface area of 6.27 m² g⁻¹ (STG-1, SHOWA DENKO) by the deposition precipitation method using HAuCl₄ as a starting material. The pH of a 4.86 × 10⁻³ M aqueous solution (10 mL) of HAuCl₄ 4H₂O (Kanto Chemicals, >99.0%) was adjusted to 6.0 with 1 mol dm⁻³ NaOH. The solution turned from yellow to lighter yellow, accompanied by ligand exchange from [AuCl₄]⁻ to [Au(OH)_{4-x}Cl_x]⁻. To this solution, 1 g of the TiO₂ particles were added to be magnetically stirred at 70°C for 1 h. The resulting Au nanoparticle-loaded TiO₂ (TiO₂-Au) particles were washed with distilled water three times and then heated at 500°C in air.

RuO₂ were heteroepitaxially grown on TiO₂-Au particles by the following hydrothermal method. NaOH (0.375 g, > 97.0%, Kanto Chemical) was dissolved into water (25 mL), and RuCl₃ (0.01 g) was dissolved into the solution. TiO₂-Au particles (0.25 g) was added into the solution. The suspension was heated at 180°C in a Teflon-lined stainless-steel autoclave with an inner volume of 50 mL. The resulting solids were washed and dried in vacuo, and post-heating at 500°C in the air yielded TiO₂-Au particles covered with heteroepitaxial RuO₂ thin layers (RuO₂#TiO₂-Au). Also, RuO₂#TiO₂ particles were prepared by the same procedures using TiO₂ in the place of TiO₂-Au.

Catalyst characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) observations were carried out by using a JEM-2100F (JEOL) operated at 200 kV. X-ray photoelectron spectroscopy measurements were performed using a Kratos Axis Nova X-ray photoelectron spectrometer with a monochromated Al K α X-ray source operated at 15 kV and 10 mA using C1s as the energy reference (284.6 eV). Diffuse reflectance UV-Vis spectra of the samples were recorded on a Hitachi U-4000 spectrometer mounted with an integrating sphere at room temperature. The reflectance (R_{∞}) was recorded with respect to a reference of BaSO₄, and the Kubelka-Munk function [$F(R_{\infty})$] expressing the relative absorption coefficient was calculated by the equation $F(R_{\infty}) = (1 - R_{\infty})^2/2R_{\infty}$. The photoluminescence (PL) spectra were measured with an excitation wavelength of 320 nm at -196°C on a JASCO FP-6000 spectrofluorometer. Raman spectra were recorded on a Raman spectrometer (JASCO FP-1000). A green laser (532 nm) was used as an excitation source.

Photocatalytic synthesis of H₂O₂

Photocatalysts (10 mg) was added to aerated pure water (10 mL). After the suspension was stirred at 25 °C in the dark, irradiation was started using a 300 W Xe lamp (HX-500, Wacom) in a test tube (18 mm in diameter and 180 mm in length). The light intensity integrated from 360 to 780 nm ($I_{360-780}$) was adjusted to 30 mW cm⁻². The concentrations of H₂O₂ generated were determined by the spectrophotometric method using Cu(II) ion and 2,9-dimethyl-1,10-phenanthroline (DMP).^{S1} One mL each of DMP, copper(II) sulfate and phosphate buffer (pH 7.0) solutions was added to a 10-mL volumetric flask and was mixed. A measured volume of sample (3 mL) was added to the volumetric flask, and then the flask was filled up with pure water. After mixing, the absorption spectra were measured, and the concentration of H₂O₂ was determined by the absorbance at 454 nm. Oxygen evolution reaction (OER) was carried out for the RuO₂#TiO₂ photoatalyst system under the same conditions except that 10 mM AgNO₃ aqueous solution (10 mL) was used in the place of pure water. The amount of O₂ was determined by gas chromatography (Shimadzu. GC-8APT) with a

thermal conductivity detector, a Molecular Sieve 5A column (3.0 mm ϕ , 1m), and argon carrier gas. The injection and column temperatures were set at 60°C.

To specify the reduction and oxidation sites of RuO₂#TiO₂-Au, the photodepositions of CdS and PbO₂ were carried out. In the CdS photodeposition, RuO₂#TiO₂-Au particles (10 mg) was dispersed into an ethanol solution of Cd(ClO₄)₂·6H₂O (15 mM) and S₈ (2 mM). After argon-bubbling for 0.5 h, irradiation ($\lambda_{\text{ex}} > 300$ nm) was carried out at 25 °C by Xe lamp (300 W) for 0.5 h. In the PbO₂ photodeposition, K₂O₂S₈ (0.5 mg) was dissolved into 1 mM Pb(ClO₄)₂ aqueous solution (10 mL). RuO₂#TiO₂-Au particles (10 mg) was dispersed into the solution. After argon-bubbling for 0.5 h, irradiation ($\lambda_{\text{ex}} > 300$ nm) was carried out at 25 °C by Xe lamp (300 W) for 0.5 h.

Reference

S1 K. Kosaka, H. Yamada, S. Matsui, S. Echigo, K. Shishida, *Environ. Sci. Technol.*, 1998, **32**, 3821-3824.

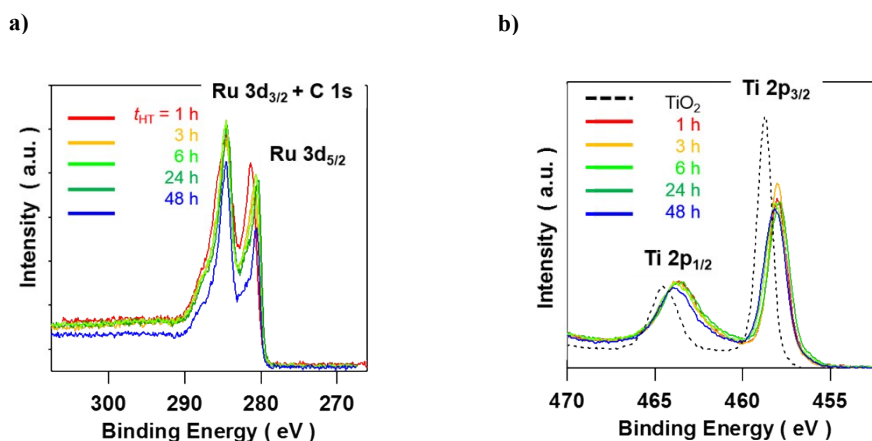


Fig. S1 Ru3d (a) and Ti2p (b) XP spectra of the samples obtained at varying t_{HT} .

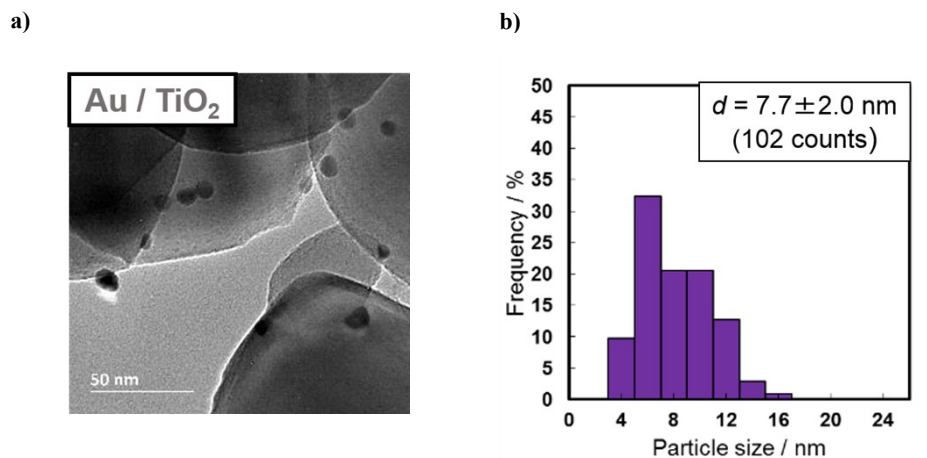


Fig. S2 (a) TEM image of Au/TiO₂ particles prepared by the deposition precipitation method. (b) Au particle size distribution of Au/TiO₂.

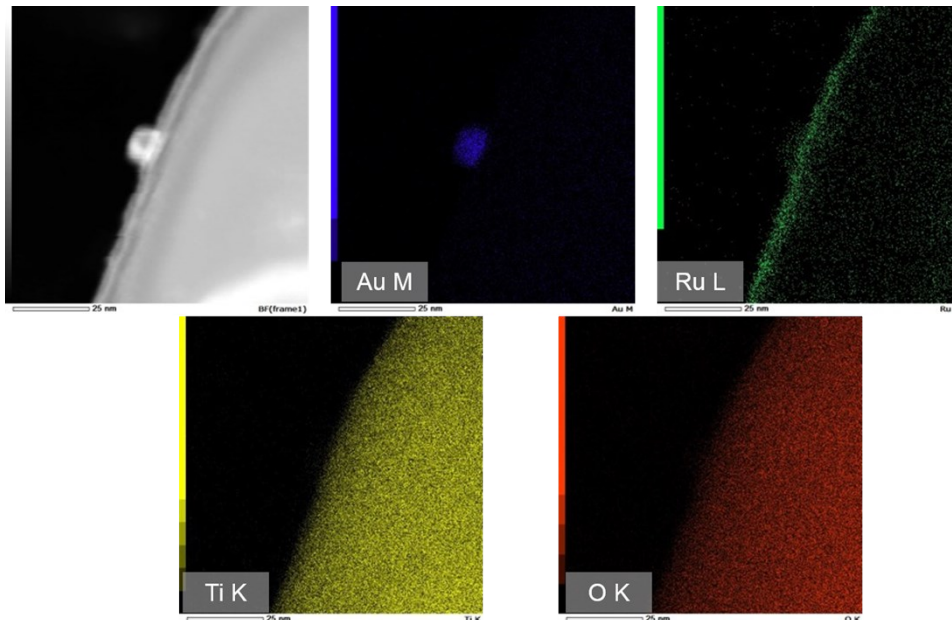


Fig. S3 High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of RuO₂#TiO₂-Au.

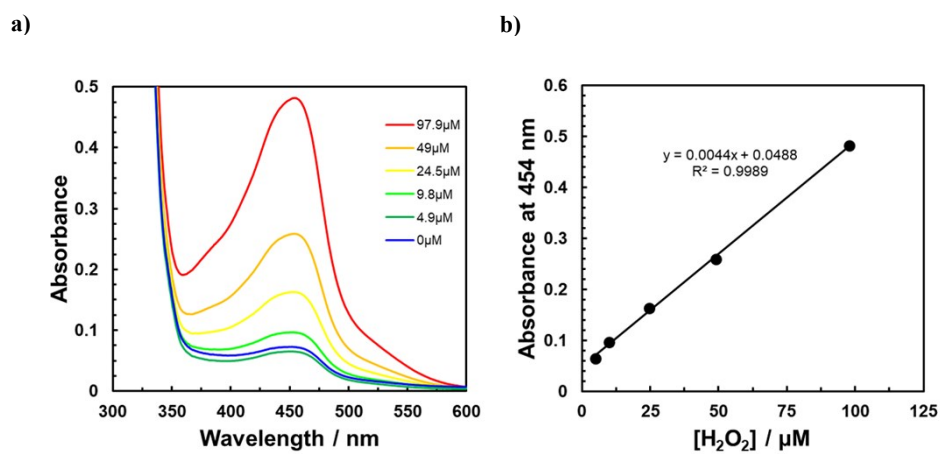


Fig. S4 (a) Absorption spectra of measurement solution containing H₂O₂ with varying concentrations. (b) Plots of the absorbance at 454 nm and H₂O₂ concentration ([H₂O₂]).

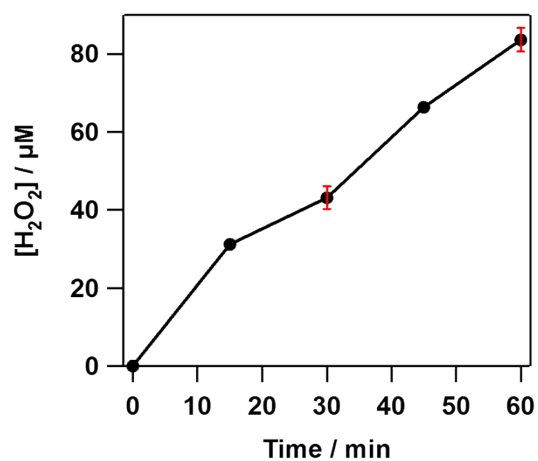


Fig. S5 Time courses for H₂O₂ generation in the RuO₂#TiO₂-Au system.

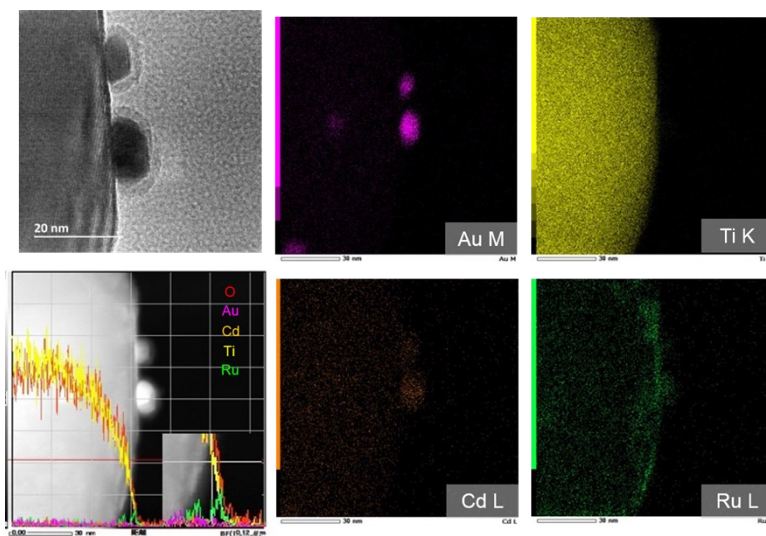


Fig. S6 STEM-EDS elemental mapping of CdS-photodeposited RuO₂#TiO₂-Au.

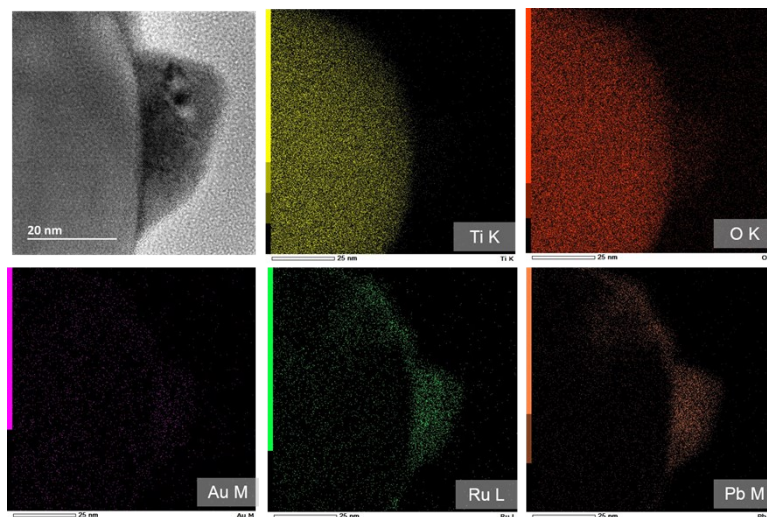


Fig. S7 STEM-EDS elemental mapping of PbO₂-photodeposited RuO₂#TiO₂-Au.

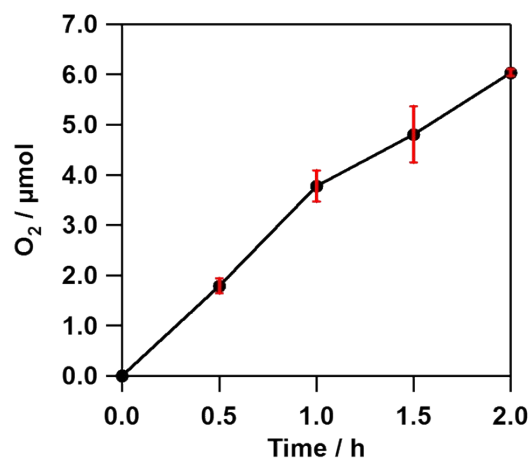


Fig. S8 Time courses for photocatalytic oxygen evolution reaction in the RuO₂/TiO₂ system.