One-Step Selective Aerobic Oxidation of Amines to Imines by Gold Nanoparticle-Loaded Rutile Titanium(IV) Dioxide Plasmon Photocatalyst

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Experimental details

Catalyst preparation and characterization

All the MO particles were heated at 923 K for 4 h prior to the use for the preparation of Au/MO, which enables to neglect the changes of MO with different T_c. In this case, no phase transition from anatase to rutile with the preheating was confirmed by X-ray diffraction measurements. Au particles were loaded on MO particles by the deposition-precipitation (DP) method using $HAuCl_4$ and NaOH as a starting material and a neutralizer, respectively. All the Au/MOs are stored in the dark. The mean diameters of the Au NPs were determined by transmission electron microscopy at an applied voltage of 300 kV (JEM-3010, JEOL). The loading amount of Au was quantified by inductively coupled plasma spectroscopy (ICPS-7500, Shimadzu).

Au/MO-photocatalyzed oxidation of amines.

After MOs or Au/MOs (50 mg) had been added to amines (5.0 g) and stirred at 298 K in dark for 15 min, irradiation was started using a 300 W Xe lamp (HX-500, Wacom) with a cut off filter Y-45 (AGC TECHNO

GLASS) in a double jacket type reaction cell (15 mm in diameter and 80 mm in length). Magnetic stirring of the suspension was continued throughout the reaction. The cell was kept at a given temperature by circulating thermostated water through an outer jacket around the cell. The light intensity integrated from 420 to 485 nm ($I_{420–485}$) through a Y-45 optical filter was adjusted to 6.0 mW cm^{-2}. For the study on the support- and Au particle size effects, MOs or Au/MOs (100 mg) were added to acetonitrile solutions of amines (0.1 mM, 0.1 L), and the photoreactions were carried out under the same conditions. The yield and selectivity determined by UV/Vis spectroscopy (UV-1800, Shimadzu) and high-performance liquid chromatography (LC-6 AD, SPD-6 A, C-R8A (Shimadzu)) [measurement conditions : column = Shim-pack CLC-ODS (4.6 mm×150 mm) (Shimadzu); mobile phase acetonitrile; flow rate = 0.5 mL min^{-1}; λ = 280 nm].

Photoelectrochemical measurements (photochronopotentiometry)

Slurry of Au/R-TiO_2 particles (0.5 g/H_2O 1 mL) was coated on fluorine-doped SnO_2-film coated glass substrates (FTO, sheet resistance = 12 Ω/□), and the sample was heated in air at 573 K for 1 h to form Au/mp-R-TiO_2/FTO electrodes. The electrode potential (E) was measured in a deaerated 0.1 M Bu_4ClO_4 electrolyte solution with $PhCH_2NH_2$ (0.1 mM) in a regular three-electrode electrochemical cell using a galvanostat/potentiostat (HZ-5000, Hokuto Denko). Irradiation by using a xenon lamp with a monochromator (fwhm, 10 nm) (HM-5, JASCO) led to a shift of E in the cathodic direction.

Adsorption measurement

Adsorption isotherms were obtained by exposing Au/R-TiO_2 or R-TiO_2 (10 mg) to solutions with different concentrations of 4-methoxybenzylamine solution (10 mL) at 275 K for 18 h in the dark. The concentration of 4-methoxybenzylamine in the solution were quantified by UV-Vis spectroscopy.

Table S1. Surface area, particle size, supplier, and isoelectric point (IEP) of metal oxide support.

Support	surface area / m^2 g^{-1}	particle size / nm	supplier	IEP
Anatase TiO_2	8.1	150	Ishihara Sangyo	6.0
Rutile TiO_2	12.5	100	TAYCA	6.0
$SrTiO_3$	20.3	50	Aldrich	2.4
WO_3	11.8	< 150	Aldrich	1.5
ZnO	15-25	50-70	Aldrich	9.8
Nb_2O_5	3.3	100	Aldrich	4.1
In_2O_3	20-30	15-25	Aldrich	2.5

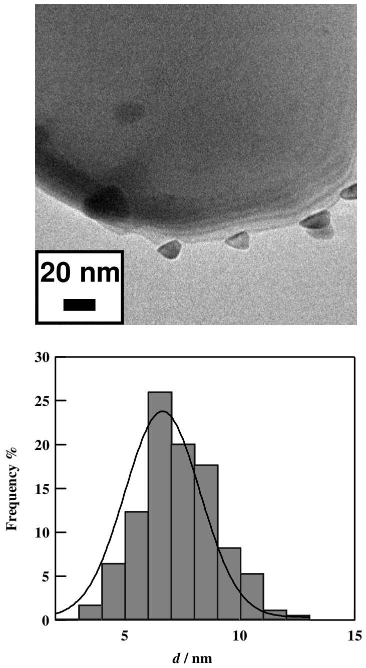

Figure S1a. TEM image and size distribution of Au/ZnO.

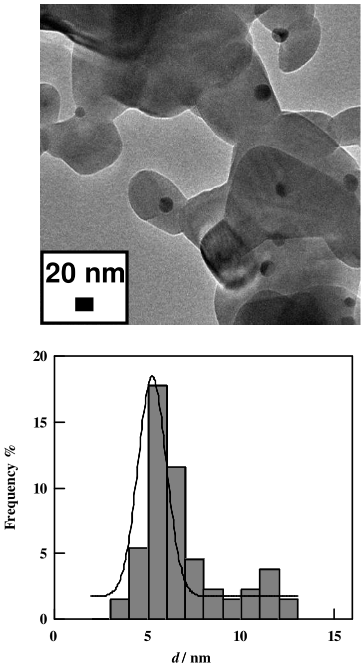

Figure S1b. TEM image and size distribution of Au/Nb_2O_5.

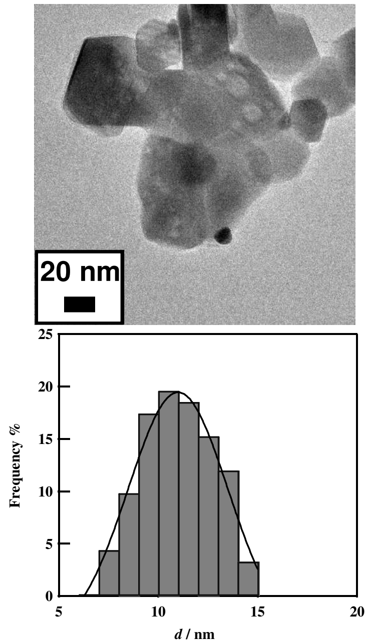

Figure S1c. TEM image and size distribution of Au/In_2O_3.

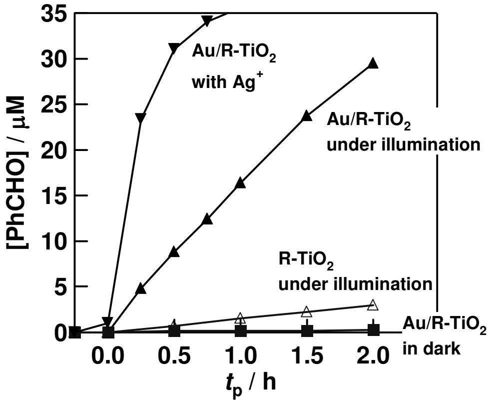

Figure S2. Visible-light-activity of Au/rutile TiO_2 (Au/R-TiO_2) and rutile TiO_2 (R-TiO_2) for the selective oxidation of benzylamine. Time course for the PhCHO generation.

Table S2. Amine oxidation by Au/rutile TiO_2.

	Yield / % [a]			v_0 /	E_{ox} / V
Amine	Aldehyde	Imine	conversion	μM h^{-1} [b]	vs SHE
$PhCH_2NH_2$	76	5	86	21	2.45
$PhCH_2NH_2$ [c]	35	24	83	9	2.45
4-Me-$C_6H_4CH_2NH_2$	87	6	99	23	2.34
4-Cl-$C_6H_4CH_2NH_2$	82	8	98	29	2.23
4-MeO-$C_6H_4CH_2NH_2$	92	0	92	38	1.93
$PhCH_2NHMe$	90	6	96	14	1.38
$(PhCH_2)_2NH$	75	25	100	12	1.61

[a] irradiation time = 24 h. [b] initial rate of aldehyde and imine generation. [c] removal of H_2O in the reaction solution using molecular sieves.

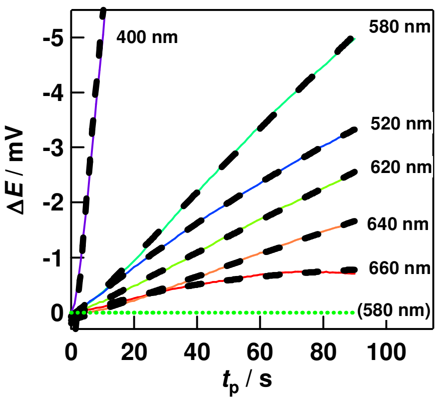

Figure S3. Photochronopotentiometry profiles of Au/rutile TiO_2 in a 0.1 M Bu_4ClO_4 aq. solution containing 0.1 mM $PhCH_2NH_2$ (solid lines) and fitting curves (bold broken lines) using equation of $E(t) = E_0 + (E_{max} - E_0)\ [1 - \exp(-k_{et}t)\ ]$, where E_0 is the rest potential of TiO_2, E_{max} is the potential of TiO_2 at $t = \infty$, and k_{et} is the rate constant. The dotted line shows the profile in a solution without $PhCH_2NH_2$.