Supporting Information

Photocatalytic Evolution of Nitrous Oxide from Nitric Monoxide over Pt-loaded Titanium Dioxide under UV irradiation.

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Preparation of photocatalyst

Titanium dioxide (P25, TiO_2) used in this paper was purchased from Sigma-Aldrich, which is a mixture of anatase and rutile types. Prior to Pt loading, TiO_2 was calcined at 400°C (1 h to raise and 5 h to keep) to remove impurities. Hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Wako) was used as a platinum source. Platinum was loaded on the calcined P25 by three methods, such as photo-deposition, [1] impregnation [2]and chemical reduction. [3]

Photo-deposition method

0.5 g of calcined TiO_2 was dispersed in mixture of water (900 mL) and methanol (100 mL). 24.1 mg of $H_2PtCl_6 \cdot 6H_2O$ was added and the mixture was irradiated with light while stirring at room temperature. The wavelength of the light was 300–800 nm and the light intensity was 100% (HAMAMATSU L9588-04). After the solution turned into black, the mixture was washed, filtered, and dried 80 °C overnight. This photocatalyst was denoted as "Pt/TiO_2-pd".

Impregnation method

1.0 g of calcined TiO_2 and 48 mg of $H_2PtCl_6 \cdot 6H_2O$ were dispersed in 25 mL water and heated with stirring at 60 °C for 24 h. The resultant solid was crushed and calcined at 500°C. The obtained sample was calcined at 400 °C for 2 h under hydrogen flow. This photocatalyst was denoted as "Pt/TiO_2-imp".

Chemical reduction method

0.8 g of TiO_2 was dispersed in 500 mL of ethylene glycol. The solution was heated to 160 °C with stirring, and 38 mg of $H_2PtCl_6 \cdot 6H_2O$ was added with a small amount of water. The solution was then washed, filtered, and dried overnight. This photocatalyst was denoted as "Pt/TiO_2-cr."

Characterization

The crystallite structure was analysed by SmartLab X-ray diffractometer (Rigaku). Crystalline sizes of TiO_2 were calculated by Scherrer's equation (equation S1).[4] The calculated values were shown in Table S1.

$$D = \frac{k\lambda}{\beta cos\theta} \qquad \text{(Eq. S1)}$$

where D is the crystallite size (nm), k is a constant (0.90 for this paper), λ is the wavelength of the X-ray radiation, β is the full width at half maximum (FWHM) of the intense and broad peaks, while θ is the Bragg's or difraction angle.

UV-Vis spectra was measured by a UV-Vis spectrophotometer (JASCO, V-670). Transmission Electron Microscope (TEM) images and Pt particle size was measured by JME-2100 (JEOL). Pt content in photocatalysts was calculated from X-ray fluorescence spectroscopy (XRF) spectra. The XRF measurements were carried out using EA1400 (Hitachi). The dispersion of Pt particle was measured by BELCAT II (MICROTRAC MRB) using CO-pulse, and particle size was calculated from equation S2.

$$d = \frac{6000}{A_m \times \rho}\left(A_m = \frac{V \times SF/22414 \times 6.02 \times 10^{-23} \times \sigma_m \times 10^{-18}}{c}\right) \qquad \text{(Eq. S2)}$$

where d is particle size, ρ is the metal density, V is the absorption volume, SF is the stoichiometric factor, σ_m is metal cross-sectional area of one atom and c is the metal weight.

Photocatalytic activity measurement

The photocatalytic test was conducted using a home-made, fixed-bed reactor. The reactor was composed of a quartz tube of 4 mm (with an inner diameter) covered by an electric furnace and a 300 W Xenon lamp (Asahi Spectra MAX-303). Flow rate was controlled by a mass flow controller. The top surface of the quartz tube was covered with a quartz plate to allow light (at wavelengths of 300-600 nm) to pass through. When calculating AQY (Apparent quantum efficiency), 365 nm cutoff filter (Asahi Spectra HQBP365-UV) was used. The photocatalyst powder (0.1 g) was fixed by quartz wool. The height of the photocatalyst placed on the quartz tube (the distance from the light source) was aligned for all measurements so that the intensity of irradiated light was constant. When water was introduced, the feed gas was passed through a water tank by a 4-way switching valve. Prior to the catalytic test, the photocatalyst powder was kept at 450 °C in 1% NO/He gas to remove carbon species in the photocatalysts, followed by cooling to 50 °C. Typically, the catalytic reaction was performed at 50 °C with 1% NO/He gas flowing at 10 cc·min^{-1} as the feed gas, corresponding to at an SV of 3500 h^{-1}. The concentration of N_2O, O_2 and N_2 in the outlet gas was analyzed using a gas chromatograph (Shimadzu GC-2014) equipped with a thermal conductivity detector.

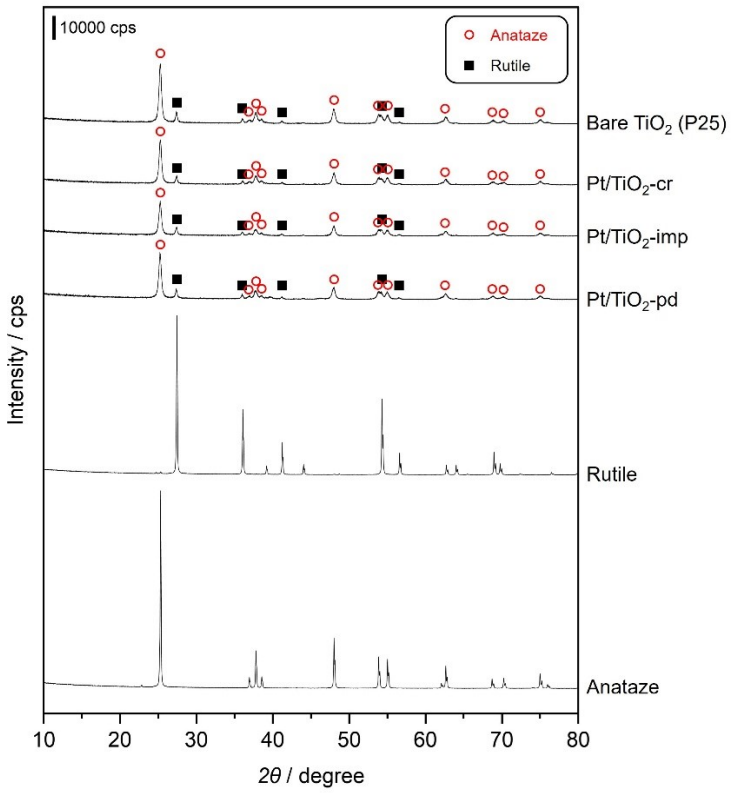

Figure S1. PXRD patterns of bare and Pt-loaded TiO_2 prepared by various loading methods. Diffraction peaks of rutile and anatase were observed in PXRD pattern of bare TiO_2 (P25), and there is no change in diffraction peaks after Pt loading.

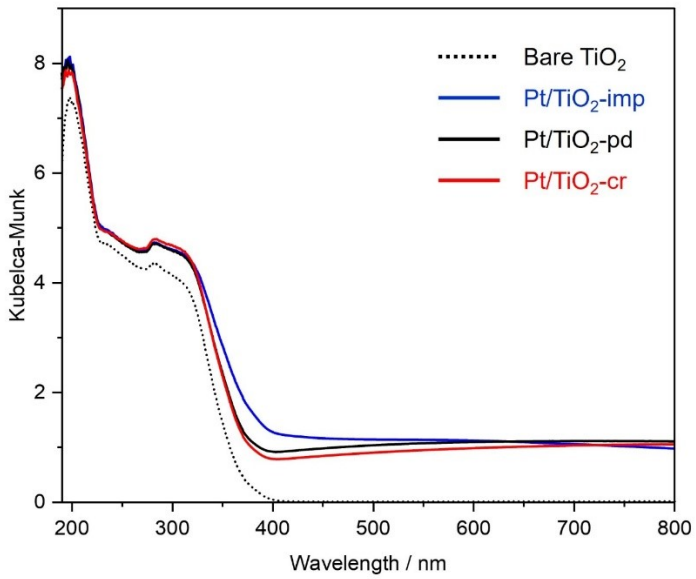

Figure S2. UV-Vis spectra of bare and Pt-loaded TiO_2 photocatalysts. TiO_2 has no absorption peak over 400 nm. After Pt loading, all of Pt-loaded TiO_2 photocatalysts exhibited light adsorption in the visible-light region due to the surface plasmon resonance of Pt NPs.

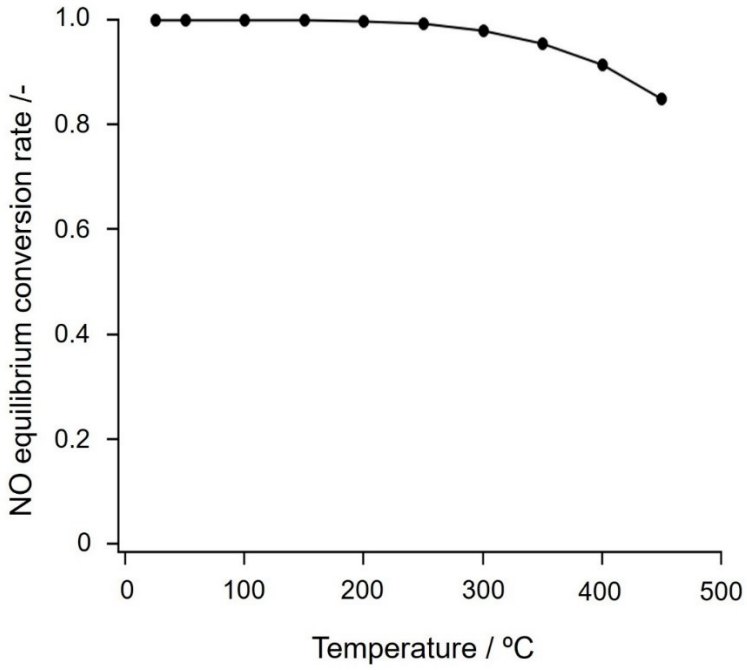

Figure S3. Calculated equilibrium conversion rate of NO for overall reaction ($^{4NO \rightarrow 2N_2O + O_2}$). The NO pressure before reaction P_{NO} is assumed to be P_{NO} = 1 kbar.

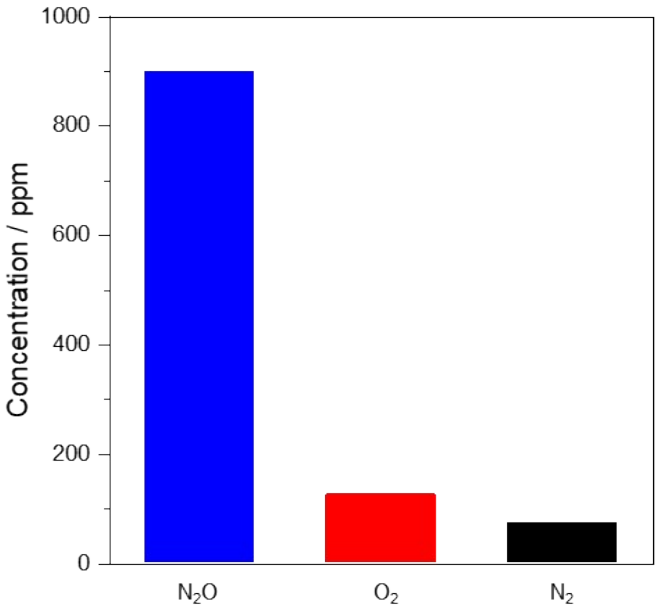

Figure S4. Gas evolution over Pt/TiO_2-pd under UV irradiation at an SV of 170 h^{-1}.

Table S1. Characteristics of bare and Pt-loaded TiO_2 photocatalysts.

Photocatalyst	Crystalline size of TiO_2 [a] / nm		Pt size [b] / nm	Pt size [c] / nm	Dispersion [c] / %	Pt amount [d] / wt%
	Anatase (101)	Rutile (110)				
TiO_2	22	35	-	-	-	-
Pt/TiO_2-pd	21	34	2.8	6.4	17	1.8
Pt/TiO_2-imp	21	33	1.9	4.1	27	1.7
Pt/TiO_2-cr	21	36	3.8	6.8	16	1.7

[a] calculated by Scherrer's equation.

[b] estimated from TEM image.

[c] determined by CO pulse technique.

[d] determined by XRF measurement.

Reference

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2. Lee, S., et al., *Low-coordinated surface atoms of CuPt alloy cocatalysts on TiO_2 for enhanced photocatalytic conversion of CO_2.* Nanoscale, 2016, **8**, 10043-10048.
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4. Mustapha, S., et al., *Facile synthesis and characterization of TiO_2 nanoparticles: X-ray peak profile analysis using Williamson–Hall and Debye–Scherrer methods.* International Nano Letters, 2021, **11**, 241-261.