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Nickel(II) oxide surface-modified titanium(IV) dioxide as a visible-light-active photocatalyst

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Experimental details

Preparation of NiO/TiO_2. After P-25 (1 g) or mesoporous TiO_2 nanocrystalline film-coated SnO_2 substrates (mp-TiO_2/FTO, 25 mm x 50 mm) had been added to 100 mL of a $Ni(acac)_2(H_2O)_2$ solution (solvent, ethanol : n-hexane = 3:17 v/v), they were allowed to stand for 24 h at 298 K. The $Ni(acac)_2(H_2O)_2$ concentration was changed in the range of 1 x 10^{-5} to 5 x 10^{-3} M. The resulting samples were washed repeatedly with the solvent for the physisorbed complexes to be removed and dried, followed by heating in air at 773 K for 1 h. The complex adsorption and the subsequent heating were repeated to increase the Ni loading amount.

Preparation of mesoporous TiO_2 nanocrystalline films (mp-TiO_2). A paste containing TiO_2 particles with a mean size of 20 nm (PST-18NR, Nikki Syokubai Kasei) was coated on FTO-film coated glass substrates (12 Ω/□) by a squeegee method, and the sample was heated in air at 773 K to form mp-TiO_2 films.

Spectroscopic and TEM characterization. UV-Vis diffuse reflectance spectra were recorded on a Hitachi U-4000 spectrophotometer. The spectra were converted to the absorption spectra by using the Kubelka-Munk function. X-ray photoelectron spectroscopic (XPS) measurements were performed using a Kratos Axis Nova X-ray photoelectron spectrometer with a monochromated Al K_α X-ray source ($h\nu$ = 1486.6 eV) operated at 15 kV and 10 mA. The take-off angle was 90º, and multiplex spectra were obtained for Ni_{2p}, O_{1s}, and Ti_{2p} photopeaks. All the binding energies (E_B) were referenced with respect to the C_{1s} at 284.6 eV. TEM observation was carried out using JEOL JEM-3000F at an applied voltage of 300 kV.

Electrochemical measurements. Current-potential curves of the NiO/mp-TiO_2/FTO electrodes were measured in a 0.1 M Na_2ClO_4 electrolyte solution in a regular three-electrode electrochemical cell using a galvanostat/potentiostat (HZ-5000, Hokuto Denko). Glassy carbon and an Ag/AgCl electrode (TOA-DKK) were used as a counter electrode and a reference electrode, respectively.

Photocatalytic activity evaluation. In the decompositions of 2-naphthol (2-NAP), the reaction cells were irradiated with a Xe lamp (Wacom XRD-501SW) through a band-pass filter (D33S, AGC Techno Glass) superposed on a piece of FTO-coated glass transmitting only the 330-400 nm range (integrated light intensity = 0.5 mW cm^{-2}) for the UV-light photocatalytic activity evaluation and a high pass filter (L-42, Toshiba) to cut off UV-light for the visible-light-induced activity test (light intensity integrated from 420 to 485 nm = 1.0 mW cm^{-2}). P-25 or NiO/P-25 particles (0.1 g) was placed in 50 mL of 1.0×10^{-5} M solution of 2-NAP (solvent, acetonitrile : water = 1 : 9999 v/v) in a borosilicate glass container was irradiated. 2 mL of the solution was sampled every 15 min and the electronic absorption spectra of the reaction solutions were measured using a spectrometer (Shimadzu, UV-1800) to determine 2-NAP concentration from the absorption peak at 224 nm.

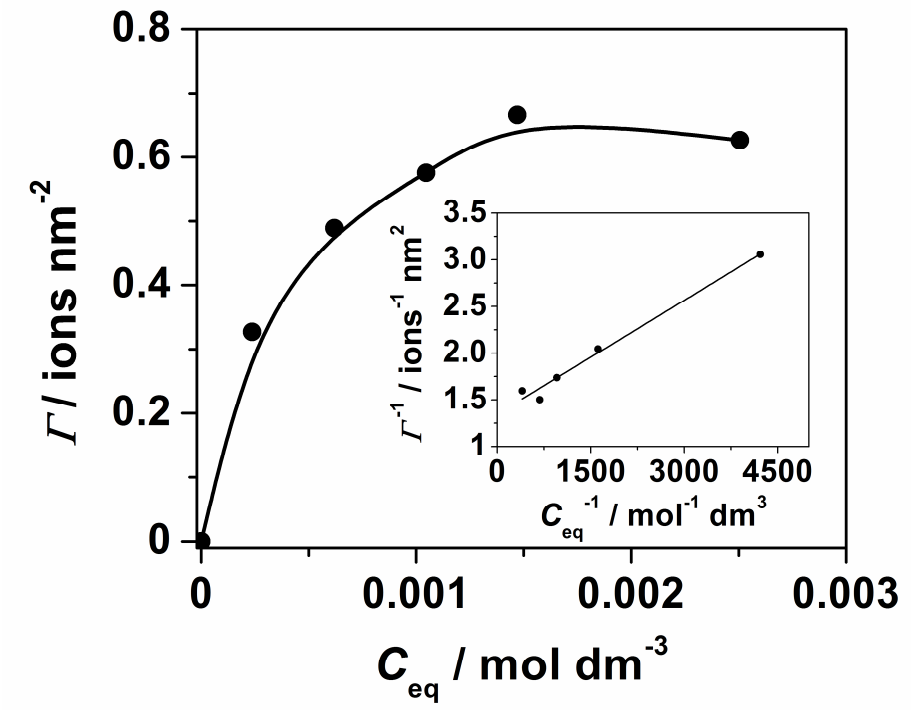

Fig. S1 Adsorption isotherm of $Ni(acac)_2(H_2O)_2$ on P-25 at 298 K: C_{eq} expresses the equilibrium concentration. The inset shows the Langmuir plot.

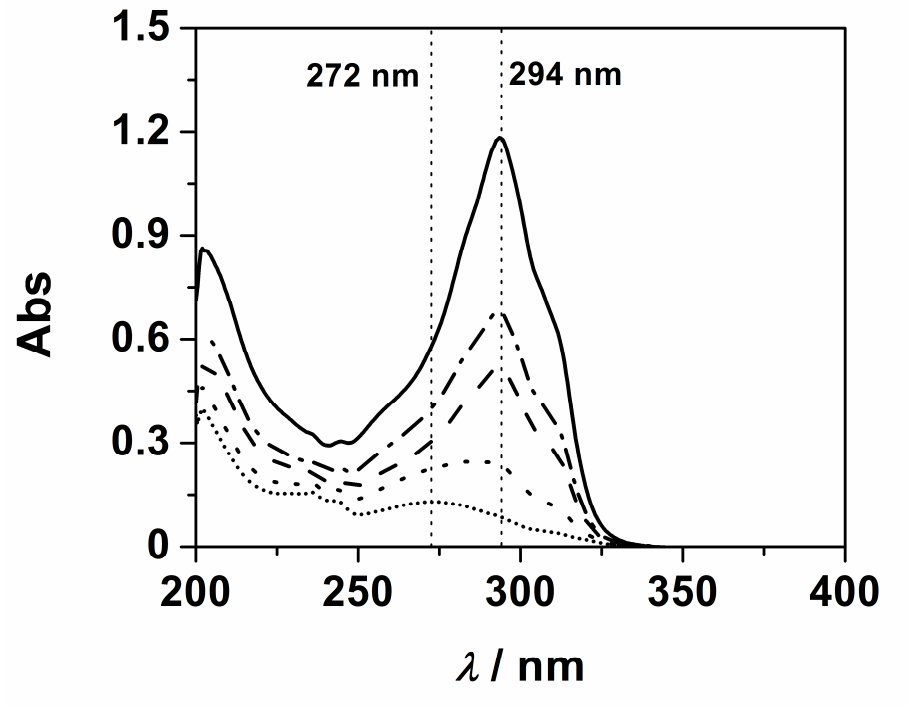

Fig. S2 UV absorption spectral change of the $Ni(acac)_2(H_2O)_2$ solution with adsorption on P-25.

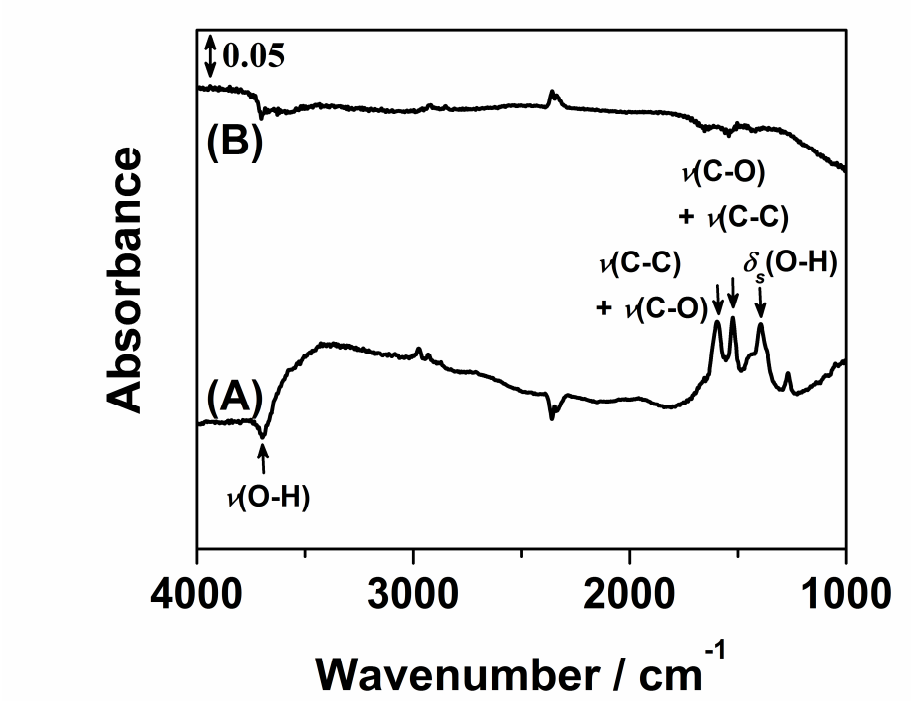

Fig. S3 Difference reflectance Fourier-Transform infrared (DRIFT) spectra: (a) the spectrum subtracting the spectrum of P-25 from that of complex-adsorbed P-25, (b) the spectrum subtracting the spectrum of P-25 from that of the complex-adsorbed P-25 after heating at 773 K (NiO/TiO_2).

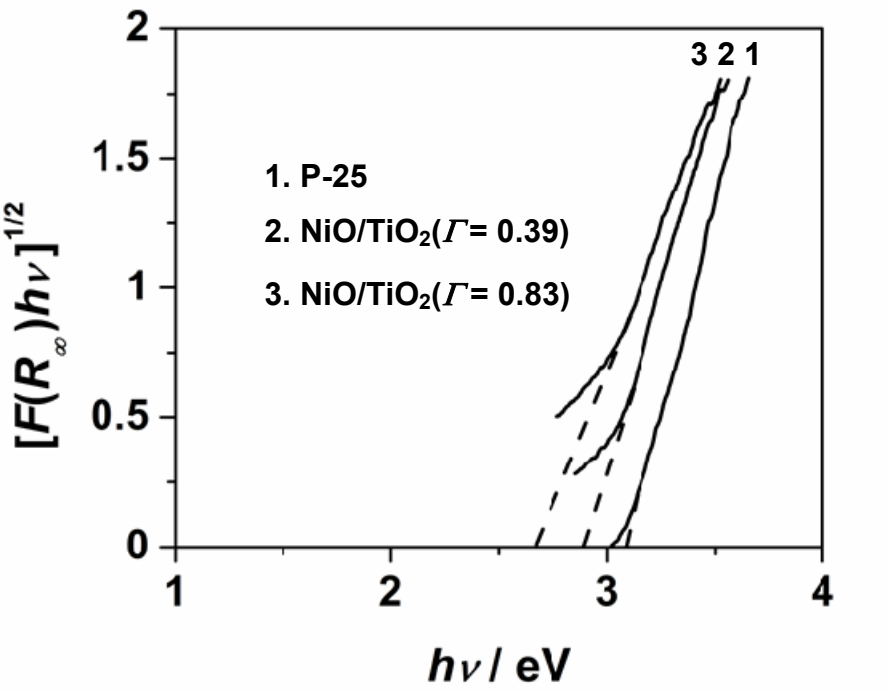

Fig. S4 Plots of $[F(R_\infty)h\nu]^{1/2}$ vs. $(h\nu - E_g)$ plot: $F(R_\infty)$ and $h\nu$ denote the Kubelka-Munk function and the photon energy, respectively. R_∞ was calculated from the reflectance R using the equation of $(1 - R_\infty)^2/2\,R_\infty$.

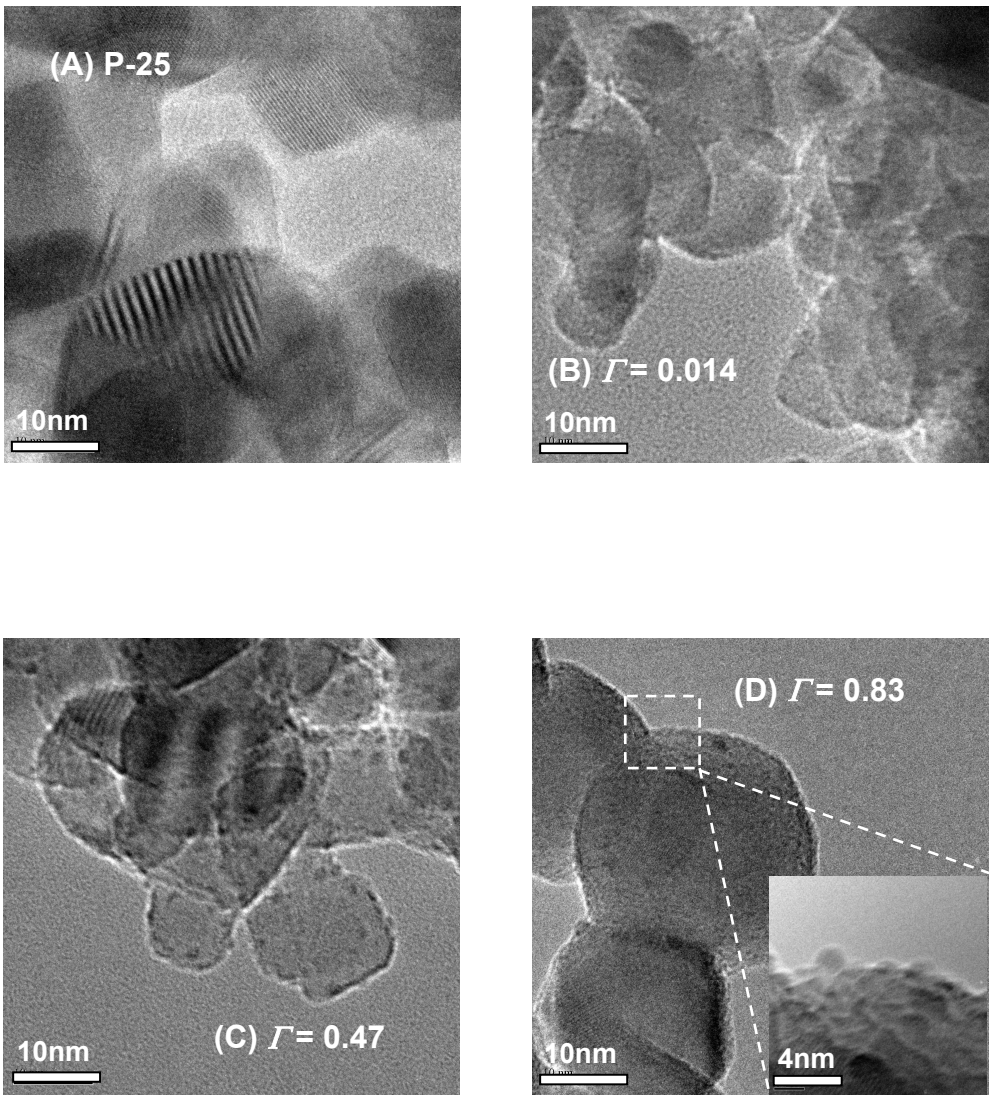

Fig. S5 HRTEM images of NiO/P-25: (A) $\Gamma = 0$; (B) $\Gamma = 0.014$; (C) $\Gamma = 0.47$; (D) $\Gamma = 0.83$.