

[Electronic Supplementary Information]

Consistent changes of electronic states and photocatalytic activities of metal (Au, Pd, Pt)-modified TiO₂ studied by far-ultraviolet spectroscopy

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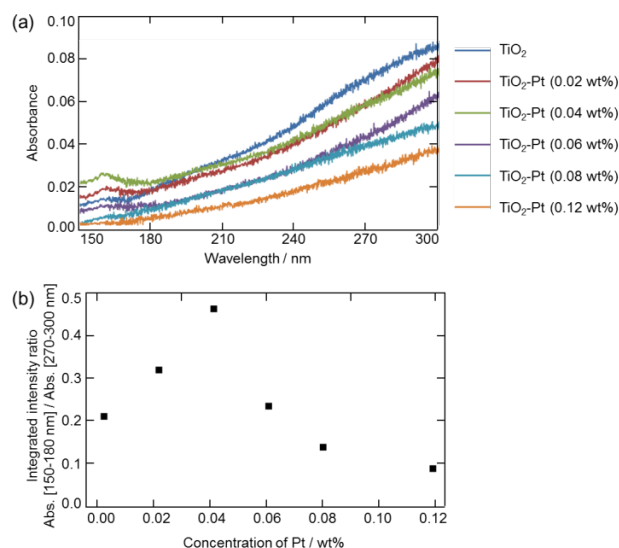


Fig. S1. ATR-FUV spectral changes of TiO₂ with various concentrations of Pt nanoparticles. (a) ATR-FUV spectra of TiO₂ with various concentrations (0.00–0.12 wt%) Pt nanoparticles. (b) Integrated intensity ratio of absorption in the 150–180 nm region to that in the 270–300 nm region plotted against the concentrations of Pt nanoparticles.

The content of mixed Pt nanoparticle colloid was varied from 0 to 600 μ L (0, 100, 200, 300, 400, and 600 μ L, corresponding to ~0, 0.02, 0.04, 0.06, 0.08, and 0.12 wt%) per 1 g of TiO₂. The spectrum of pure TiO₂ was measured after the mixing with the solution without Pt nanoparticles in an agate mortar until the solution completely dried off in the atmosphere. The absorption spectrum of TiO₂ mixed with 200 μ L Pt nanoparticle colloid showed the largest increase in the shorter wavelength region, while the absorption intensity of the entire wavelength range was suppressed when greater than 400 μ L of Pt nanoparticle colloid was utilized, as shown in Fig. S1. The deposition of too many Pt nanoparticles separates TiO₂ from the sapphire IRE surface, decreasing the content of TiO₂ in the evanescent wave range. The suppression of the absorption intensity over the entire wavelength range indicates that the increase in the shorter wavelength region is not due to the absorption of Pt nanoparticles or the protecting agent.

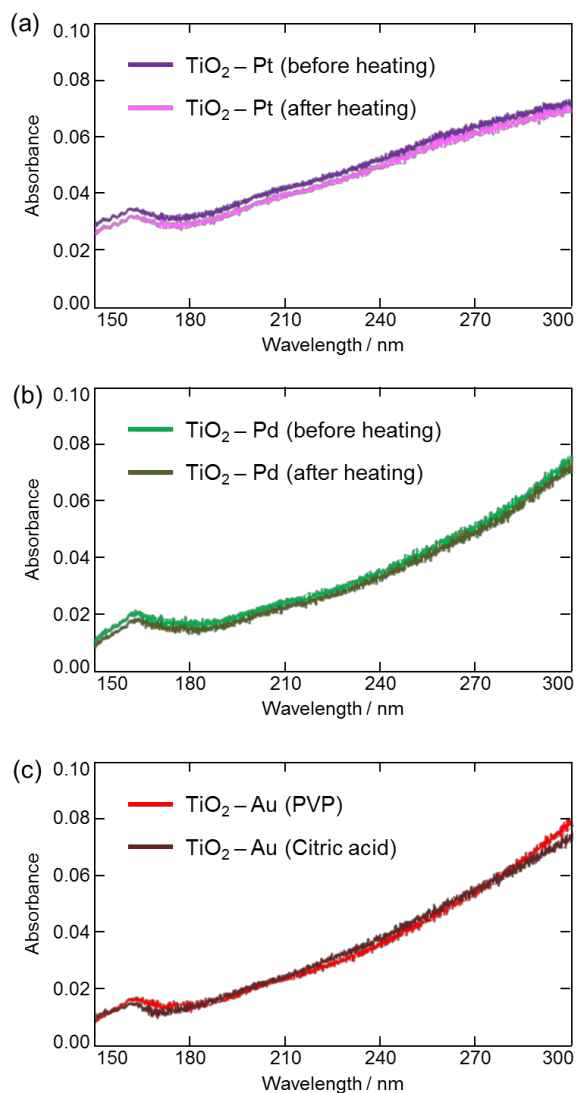


Figure S2. Estimation of effects of protecting agents of Pt, Pd and Au nanoparticles. (a) ATR-FUV spectra of TiO₂-Pt nanoparticles before (purple) and after (pink) heating (200 °C, 1 h) in order to remove protecting agent (PVP). (b) ATR-FUV spectra of TiO₂-Pd nanoparticles before (green) and after (deep green) heating (200 °C, 1 h) in order to remove protecting agent (PVP). (c) ATR-FUV spectra of TiO₂-Au protected by PVP (red) and TiO₂-Au protected by citric acid (brown) nanoparticles.

These spectra show no substantial changes upon removing or changing the protecting agents, which means that protecting agents have no substantial effects on ATR-FUV spectra. Metal nanoparticle colloids of Pt (10 mM in a water/ethanol solution, 1–6 nm diameter, protected by PVP), Pd (10 mM in a water/ethanol solution, 2–7 nm diameter, protected by PVP) and Au (10 mM in water, 6–9 nm diameter, protected by polyethylenimine) were purchased from Wako Pure Chemical Industries, Ltd. Au (3 mM in water, 5 nm, protected by citric acid) was purchased from Tanaka Holdings Co., Ltd.