Supplementary Information

Distribution of Oxygen Vacancies and Their Impact on the Charge State of Pt on TiO_2

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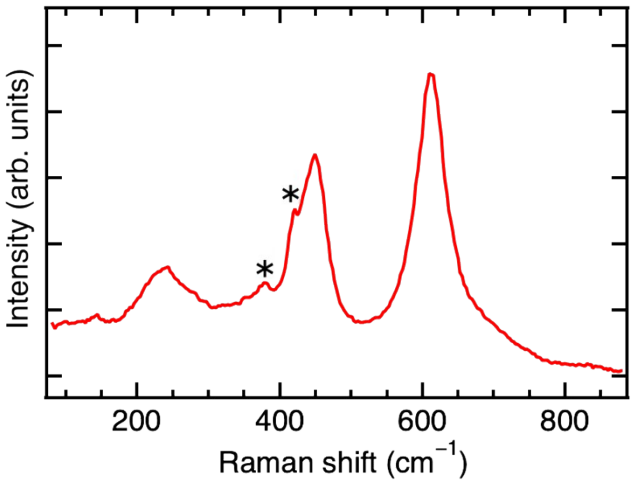

Figure S1. Raman spectrum of the TiO_2 film grown on the *r*-plane Al_2O_3 substrate. Peaks marked with an asterisk are from Al_2O_3 substrate.

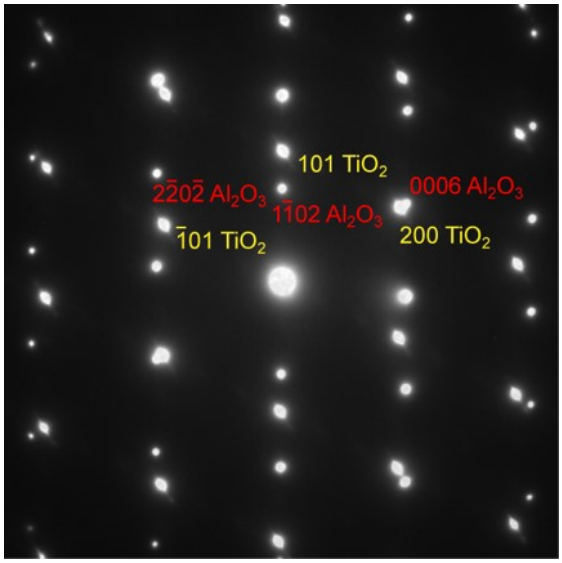

Figure S2. SAED pattern of the TiO_2 film on the *r*-plane Al_2O_3 substrate taken at the TiO_2/Al_2O_3 interface along the $[\bar{1}\bar{1}20]$ zone axis of Al_2O_3.

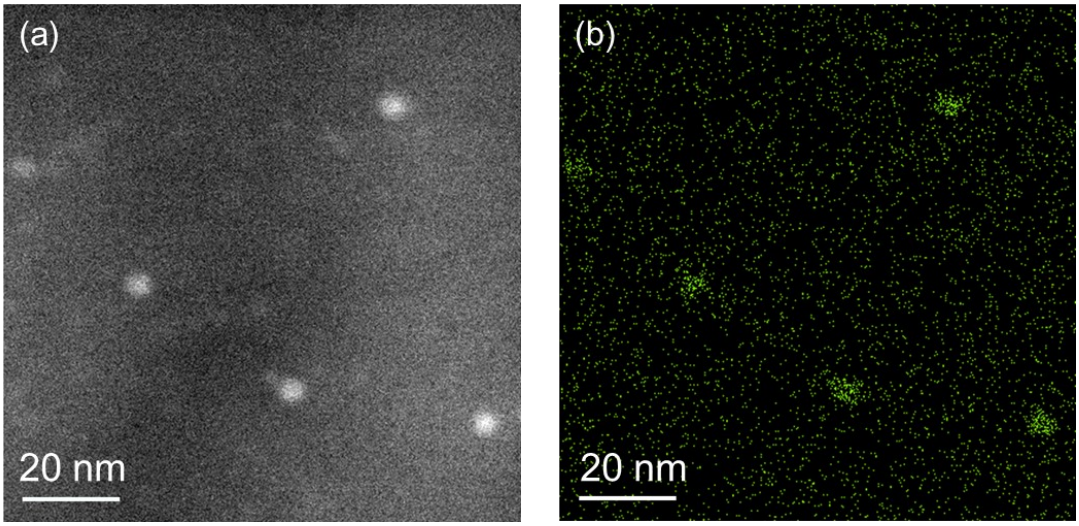

Figure S3. (a) Plan-view ADF-STEM image and (b) Pt EDS map of the Pt/TiO_2 model catalyst. The white particles in the ADF image are confirmed to be Pt nanoparticles. The weak Pt signal observed in regions where no nanoparticles are visible can be attributed to background noise and statistical fluctuations in the EDS signal, rather than to atomically dispersed Pt species.

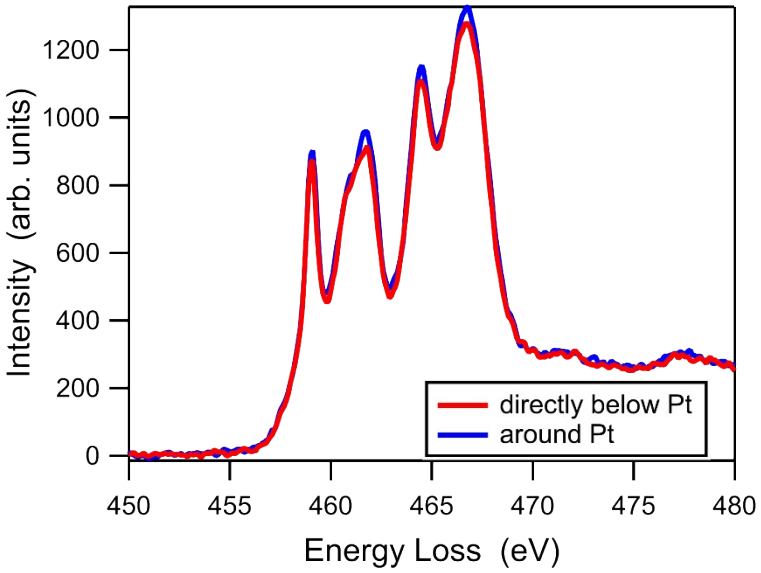

Figure S4. Typical EEL spectra of the Ti-$L_{2,3}$ edge directly below Pt and around Pt. Unlike the EEL spectra at the O K-edge shown in Figure 2, these spectra were similar in both regions.

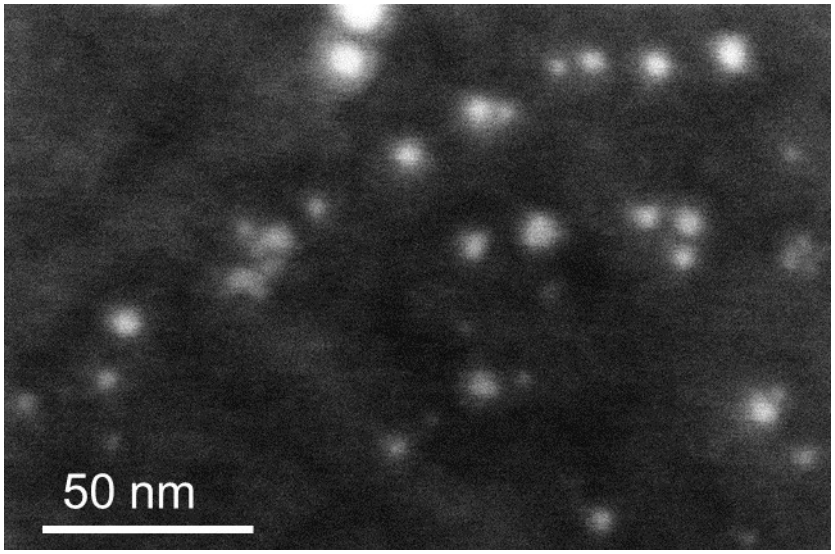

Figure S5. SEM image of the Pt(TEM)–TiO_2 sample at a high magnification. Due to the magnification limitation, Pt nanoparticles with a diameter of a few nanometers are only slightly visible. We confirmed that larger Pt nanoparticles are aggregations of smaller Pt nanoparticles.

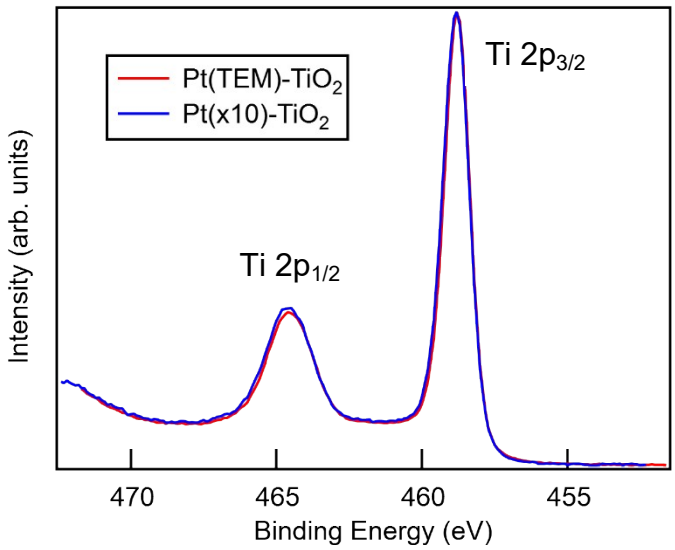

Figure S6. Ti 2p XPS spectra of Pt(TEM)–TiO_2 and Pt(×10)–TiO_2.

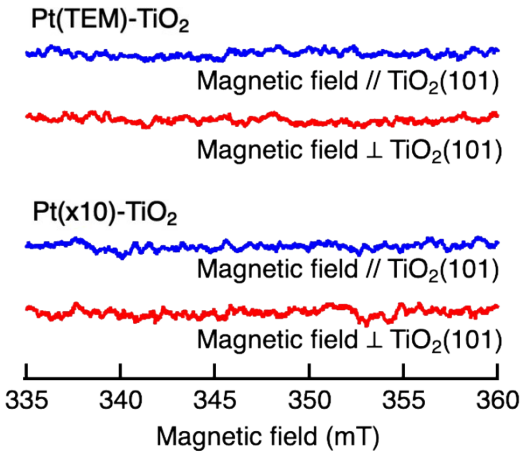

Figure S7. EPR spectra of Pt(TEM)–TiO_2 and Pt(×10)–TiO_2 samples at room temperature in two configurations, where the magnetic field was applied parallel and perpendicular to the TiO_2 (101) plane.

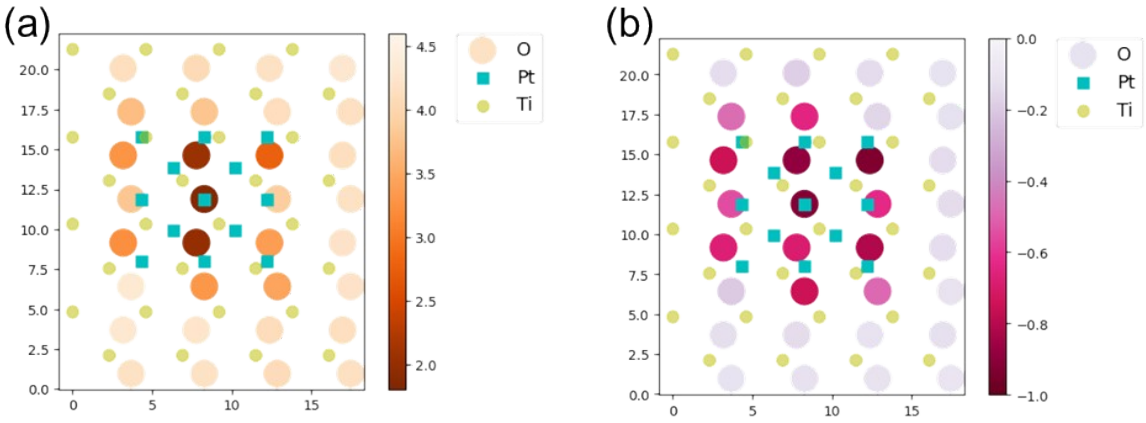

Figure S8. Atomic arrangement near the interface showing (a) the distribution of oxygen vacancy formation energies and (b) Pt charge states after the formation of oxygen vacancies based on DFT calculations.

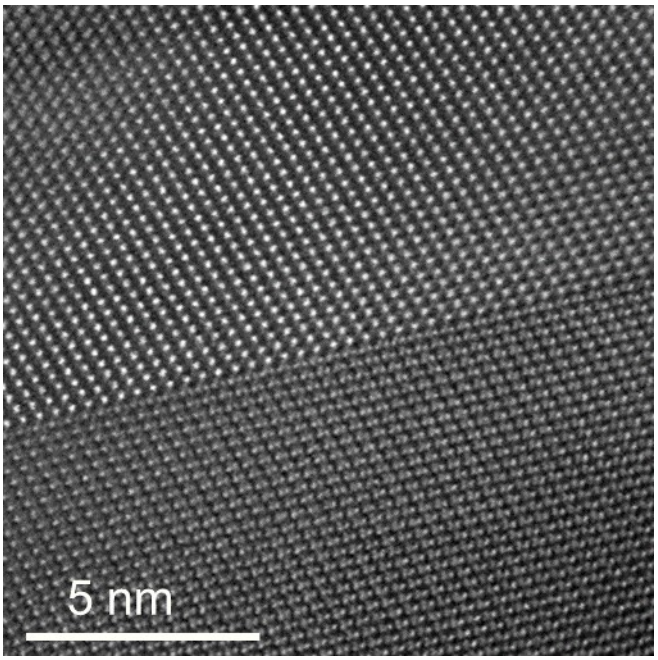

Figure S9. ADF-STEM image of the TiO_2 film in the plan-view direction. Many stacking defects, as shown in this figure, were observed, but no preferential deposition of Pt nanoparticles on such defects was observed.