Supporting Information

A New Indicator for Single Metal Dispersion on a TiO_2(110) Surface Premodified with a Mercapto Compound

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Supporting information contains XPS and XANES results for Ni/*o*-MBA/TiO_2(110) and Pt/*o*-MBA/TiO_2(110) (Figures S1-S4)

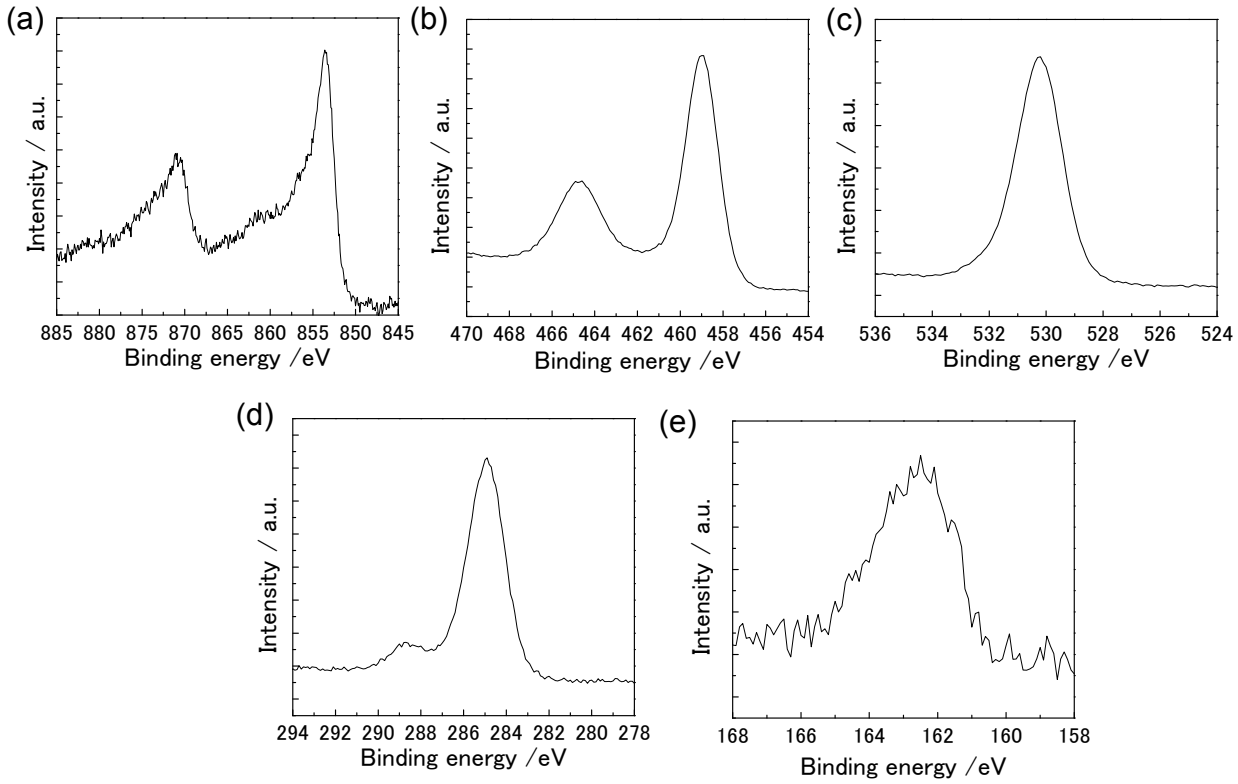

Figure S1 (a) Ni2p, (b) Ti2p, (c) O1s, (d) C1s and (d) S2p XPS spectra of Ni/*o*-MBA/TiO_2(110). The spectra were calibrated so that $Ti2p_{3/2}$ peak appeared at 459.0 eV of the binding energy expected for bulk TiO_2.[(1)] In (e), the peak energy was 162.6 eV which was shifted by -1.4 eV after Ni deposition, indicating Ni-S bond formation.

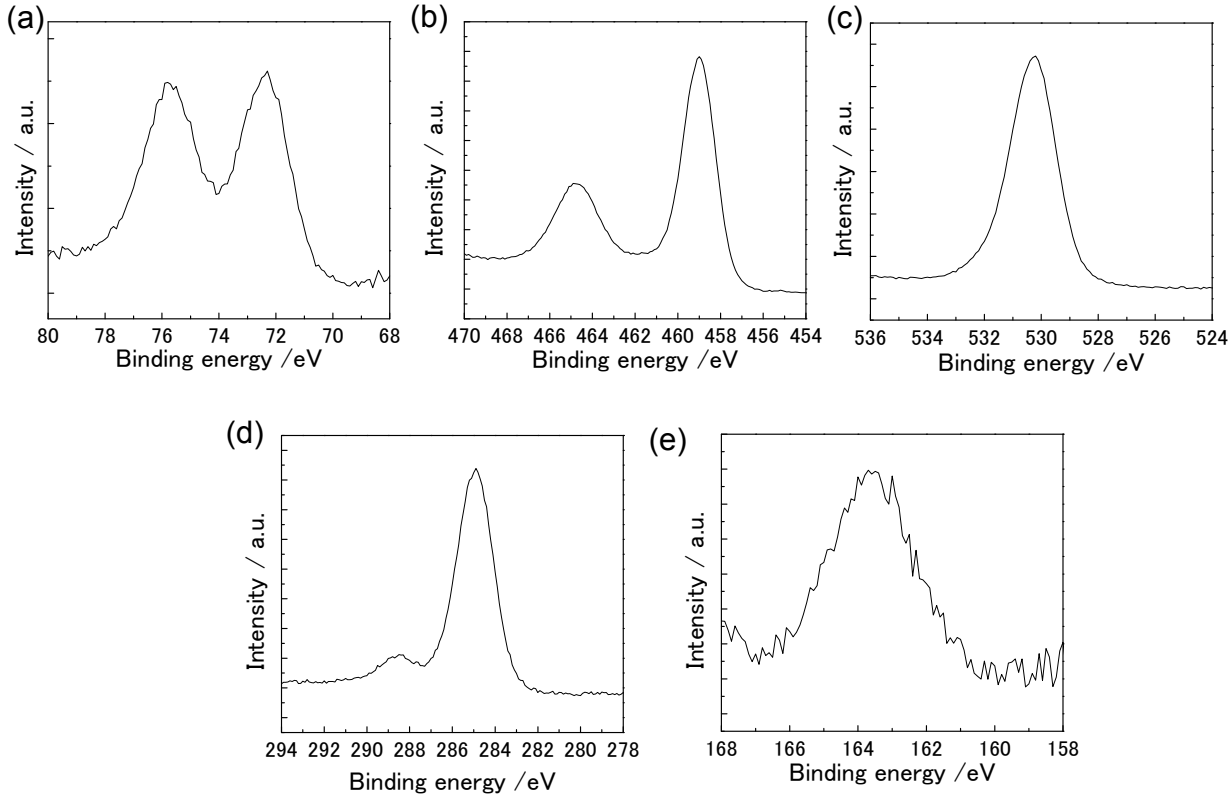

Figure S2 (a) Pt4f, (b) Ti2p, (c) O1s, (d) C1s and (d) S2p XPS spectra of Pt/*o*-MBA/TiO_2(110). The spectra were calibrated so that $Ti2p_{3/2}$ peak appeared at 459.0 eV of the binding energy expected for bulk TiO_2.[(1)] In (e), the peak energy was 163.6 eV which was shifted by -0.4 eV after Pt deposition, indicating Pt-S bond formation.

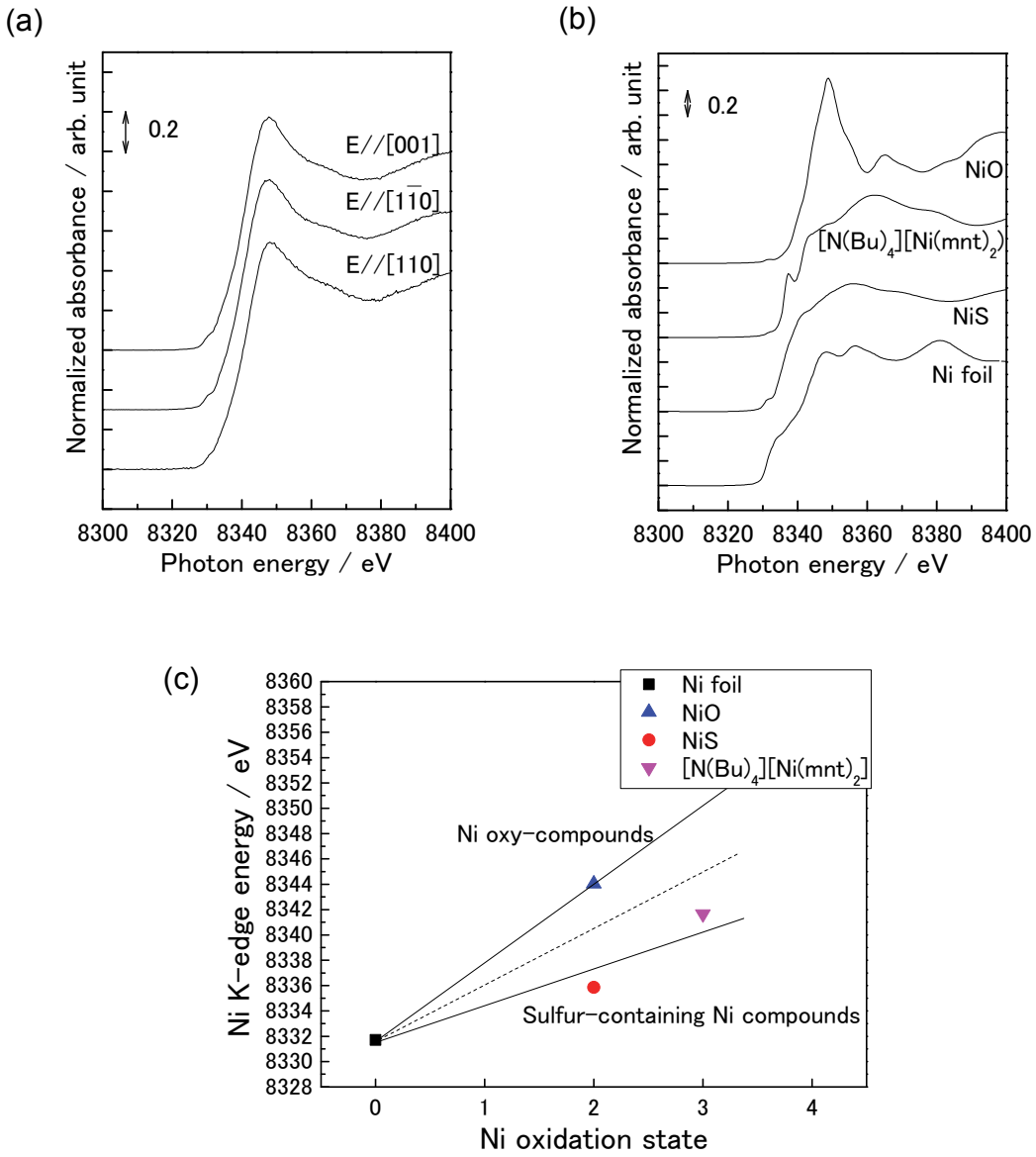

Figure S3 (a) Ni K-edge XANES spectra of Ni/*o*-MBA/TiO_2(110) in three different polarization directions. (b) Ni K-edge XANES spectra of reference compounds which are Ni metal (Ni foil), oxy-compound with Ni-O bonds (NiO) and sulfur-containing compounds with Ni-S bonds (NiS and $[N(Bu)_4][Ni(mnt)_2]$). (c) Plot of Ni K-edge energies for the reference compounds as a function of oxidation state. The dotted line shows the intermediate one between the lines corresponding to the oxy- and sulfur-containing compounds. The Ni K-edge energies for Ni foil, NiO, NiS and $[N(Bu)_4][Ni(mnt)_2]$ were 8331.7 eV, 8344.0 eV, 8335.9 eV and 8341.7 eV, respectively. They were determined as the first inflection point of the absorption edge for Ni foil, NiO and NiS and as the second inflection point for $[N(Bu)_4][Ni(mnt)_2]$. The XANES spectra were calibrated with the inflection point of Ni foil as 8331.7 eV.

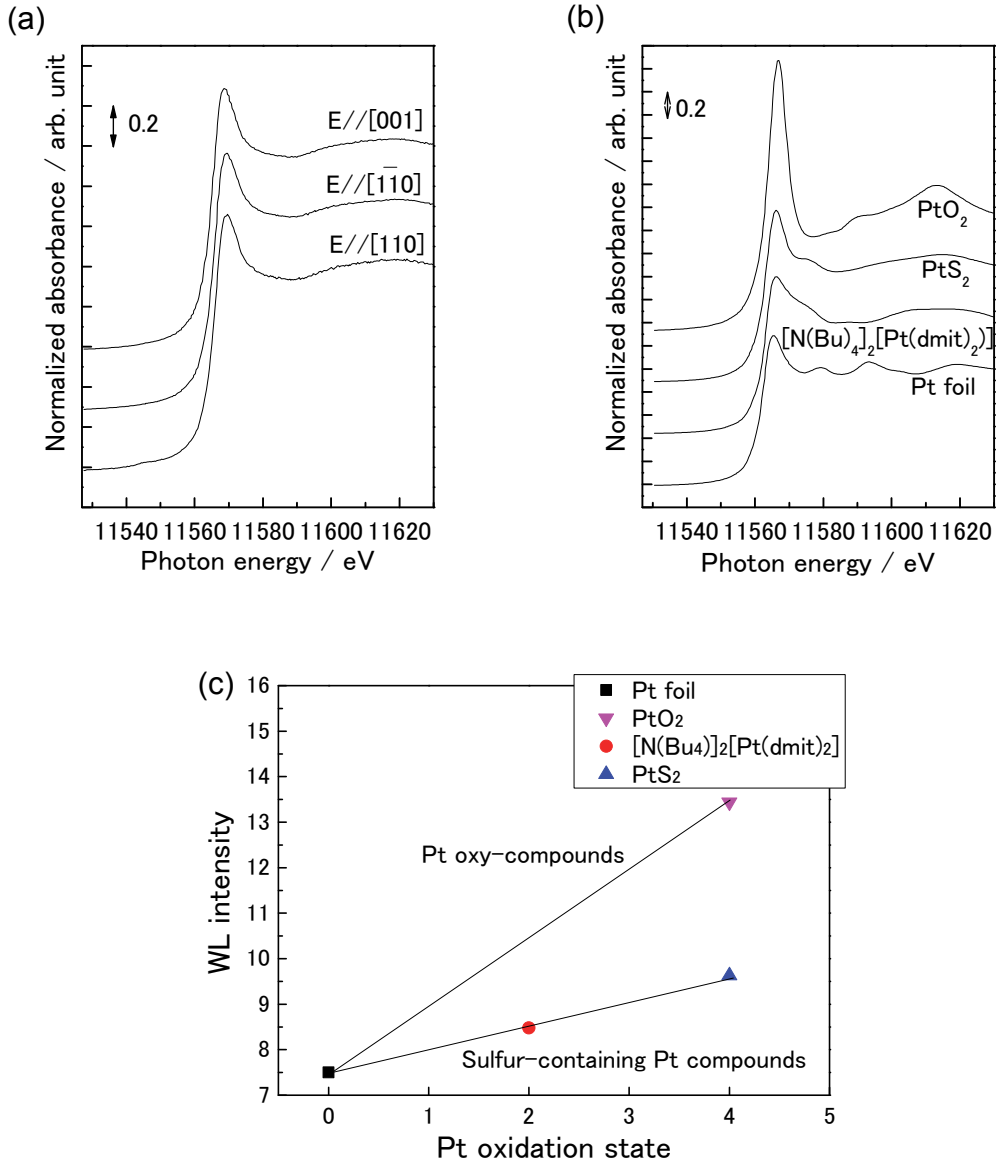

Figure S4 (a) Pt L_3-edge XANES spectra of Pt/*o*-MBA/TiO_2(110) in three different polarization directions. (b) Pt L_3-edge XANES spectra of reference compounds which are Pt metal (Pt foil), oxy-compound with Pt-O bonds (PtO_2) and sulfur-containing compounds with Pt-S bonds ($[N(Bu)_4]_2[Pt(dmit)_2]$ and PtS_2). (c) Plot of white line (WL) intensity (peak areas) for the reference compounds as a function of oxidation state. The WL intensities for Pt foil, PtO_2, $[N(Bu)_4]_2[Pt(dmit)_2]$ and PtS_2 were 7.5, 13.4, 8.5 and 9.6, respectively. They were evaluated by a curve fitting analysis using a set of a Lorentzian and an arctangent function. The XANES spectra were calibrated with the inflection point of Pt foil as 11562 eV.

References

(1) Carley, A.F.; Chalker, P.R.; Riviere, J.C.; Roberts, M.W. The Identification and Characterisation of Mixed Oxidation States at Oxidised Titanium Surfaces by Analysis of X-ray Photoelectron Spectra. *J. Chem. Soc., Faraday Trans. 1*, **1987**, *83*, 351-370