

Supporting Information

In Situ ATR-FTIR Analysis of the CO-Tolerance Mechanism on Pt₂Ru₃/C Catalysts Prepared by the Nanocapsule Method

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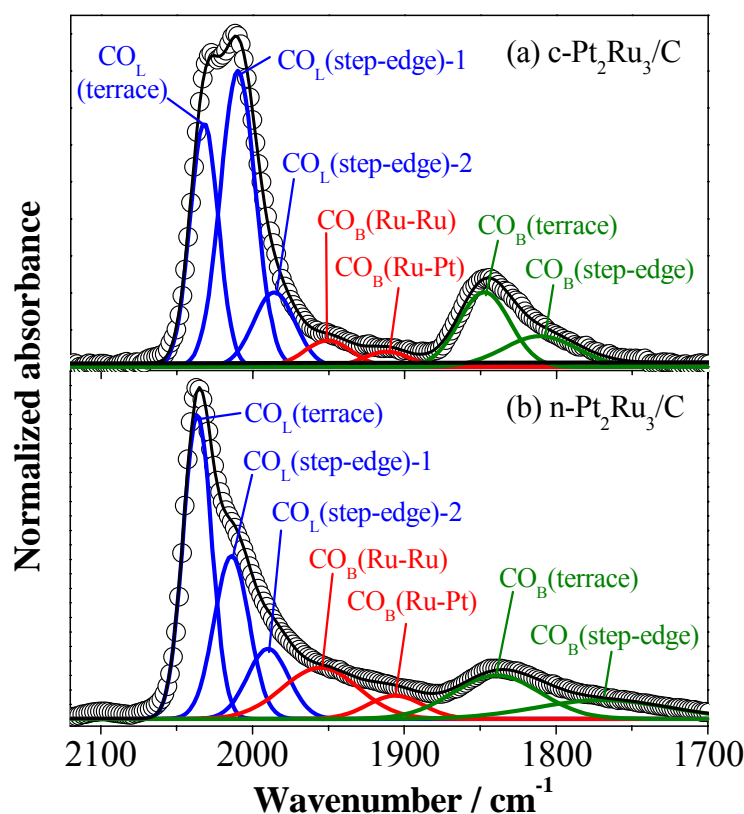


Figure S1. Deconvolution of FTIR spectra of (a) c-Pt₂Ru₃/C and (b) n-Pt₂Ru₃/C electrodes observed at 0.02 V and 25°C in 1% CO (H₂ balance)-saturated 0.1 M HClO₄ solution after 20 min of the CO adsorption. Curve fitting was performed for all spectra with the full width at half maximum (FWHM) fixed as a constant while allowing the peak wavenumbers and areas to vary, based on data in literature.¹⁻⁵ The CO_L band around 2035-1990 cm⁻¹ was deconvoluted into three components, 2035, 2010, and 1990 cm⁻¹. The band at 2035 cm⁻¹ was assigned to the CO_L on Pt terrace site. The bands around 2010 and 1990 cm⁻¹ were assigned to the CO_Ls on Pt step-edge sites, respectively. The peak wavenumber of CO_L(terrace) of Pt₂Ru₃ was similar to the case of Pt/C.¹ However, the peak wavenumber of CO_L(step-edge)-1 and -2 of Pt₂Ru₃ were lower than these of Pt/C, it was interpreted in terms of electronic modification by Ru. The peak wavenumbers of these COs of Pt₂Ru₃ or Pt¹ nanoparticles were lower than those of bulk Pt electrode, because CO_{ad} adsorbed strongly on nanoparticles than the case of bulk electrode. The CO-Ru bands around 1960-1910 cm⁻¹ were deconvoluted into two components, 1955 and 1920 cm⁻¹, which were assigned to the CO_B on Ru-Ru and Ru-Pt sites, respectively.²⁻⁵ The CO_Bs bands around 1850-1790 cm⁻¹ were also deconvoluted into two components, which could be assigned to the CO_Bs on terrace and step-edge sites, respectively. These spectra were normalized with respect to the total intensities of peaks assigned to CO_L, $I[\text{CO}_L]$; (○) experimental spectrum, (—) sum of seven peaks, (—) CO_L peaks, (—) CO-Ru peaks, and (—) CO_B peaks.

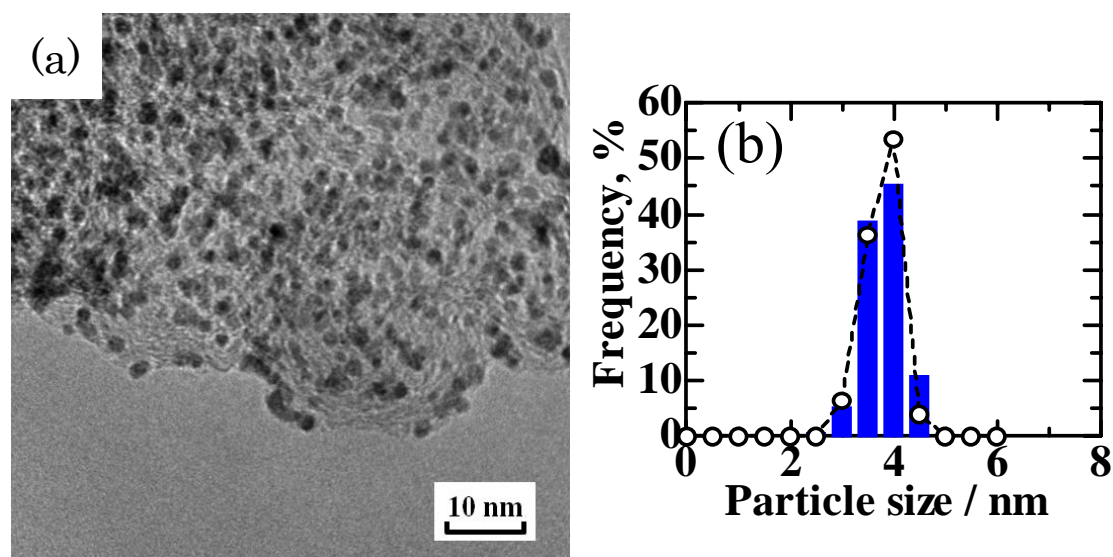


Figure S2. (a) TEM images (by Hitachi H-9500) and (b) particle size distribution histograms of n-Pt₂Ru₃/C (H₂). The histogram was obtained among 500 particles in the TEM images. The particle size distribution after H₂-treatment was 3.6 ± 0.4 nm, which was nearly identical with the value of the catalyst without treatment (3.6 ± 0.3 nm, see Table 1 in the article); (■) n-Pt₂Ru₃/C (H₂), (---○---) n-Pt₂Ru₃/C (without H₂ treatment).

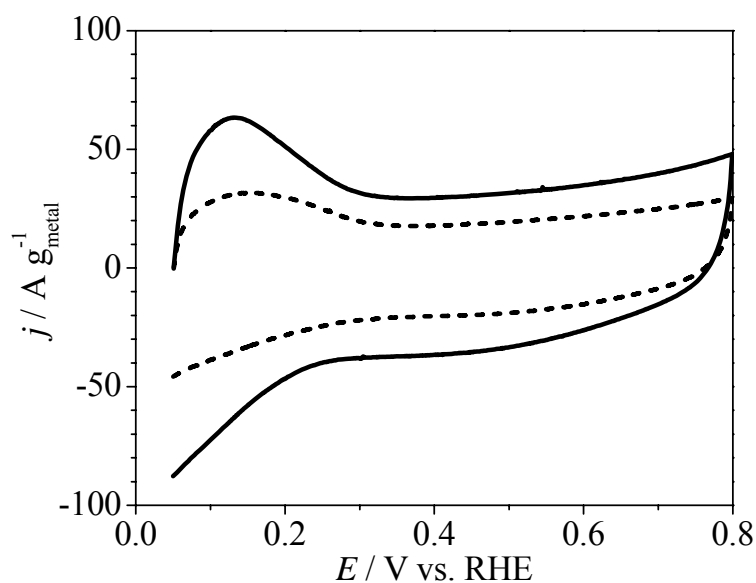


Figure S3. Cyclic voltammograms of (—) n-Pt₂Ru₃/C (H₂) and (---) n-Pt₂Ru₃/C electrodes measured in N₂-purged 0.1 M HClO₄ at 25°C and a potential sweep rate of 0.05 V s⁻¹. The values of electrochemically active area S_H evaluated from the hydrogen desorption charge in the positive-going scan were $49 \text{ m}^2 \text{ g}_{\text{metal}}^{-1}$ and $37 \text{ m}^2 \text{ g}_{\text{metal}}^{-1}$ for n-Pt₂Ru₃/C (H₂) and n-Pt₂Ru₃/C, respectively.

References

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