Supporting Information

In Situ ATR-FTIR Analysis of the CO-Tolerance Mechanism on Pt$_2$Ru$_3$/C Catalysts Prepared by the Nanocapsule Method

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**Figure S1.** Deconvolution of FTIR spectra of (a) c-Pt\textsubscript{2}Ru\textsubscript{3}/C and (b) n-Pt\textsubscript{2}Ru\textsubscript{3}/C electrodes observed at 0.02 V and 25°C in 1% CO (H\textsubscript{2} balance)-saturated 0.1 M HClO\textsubscript{4} 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.\textsuperscript{1-5} The CO\textsubscript{L} band around 2035-1990 cm\textsuperscript{-1} was deconvoluted into three components, 2035, 2010, and 1990 cm\textsuperscript{-1}. The band at 2035 cm\textsuperscript{-1} was assigned to the CO\textsubscript{L} on Pt terrace site. The bands around 2010 and 1990 cm\textsuperscript{-1} were assigned to the CO\textsubscript{L} on Pt step-edge sites, respectively. The peak wavenumber of CO\textsubscript{L}(terrace) of Pt\textsubscript{2}Ru\textsubscript{3} was similar to the case of Pt/C.\textsuperscript{1} However, the peak wavenumber of CO\textsubscript{L}(step-edge)-1 and -2 of Pt\textsubscript{2}Ru\textsubscript{3} were lower than those of Pt/C, it was interpreted in terms of electronic modification by Ru. The peak wavenumbers of these COs of Pt\textsubscript{2}Ru\textsubscript{3} or Pt\textsuperscript{1} nanoparticles were lower than those of bulk Pt electrode, because CO\textsubscript{ad} adsorbed strongly on nanoparticles than the case of bulk electrode. The CO-Ru bands around 1960-1910 cm\textsuperscript{-1} were deconvoluted into two components, 1955 and 1920 cm\textsuperscript{-1}, which were assigned to the CO\textsubscript{B} on Ru-Ru and Ru-Pt sites, respectively.\textsuperscript{2-5} The CO\textsubscript{B}s bands around 1850-1790 cm\textsuperscript{-1} were also deconvoluted into two components, which could be assigned to the CO\textsubscript{B}s on terrace and step-edge sites, respectively. These spectra were normalized with respect to the total intensities of peaks assigned to CO\textsubscript{L}, I[CO\textsubscript{L}]; (O) experimental spectrum, ()—sum of seven peaks, ( ) CO\textsubscript{L} peaks, ( ) CO-Ru peaks, and ( ) CO\textsubscript{B} peaks.
Figure S2. (a) TEM images (by Hitachi H-9500) and (b) particle size distribution histograms of n-Pt$_2$Ru$_3$/C (H$_2$). The histogram was obtained among 500 particles in the TEM images. The particle size distribution after H$_2$-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-Pt$_2$Ru$_3$/C (H$_2$), (---) n-Pt$_2$Ru$_3$/C (without H$_2$ treatment).

Figure S3. Cyclic voltammograms of ( —— ) n-Pt$_2$Ru$_3$/C (H$_2$) and ( - - - - ) n-Pt$_2$Ru$_3$/C electrodes measured in N$_2$-purged 0.1 M HClO$_4$ 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 m$^2$ g$_{metal}^{-1}$ and 37 m$^2$ g$_{metal}^{-1}$ for n-Pt$_2$Ru$_3$/C (H$_2$) and n-Pt$_2$Ru$_3$/C, respectively.
References