

Electronic Supporting Information

Weakened CO adsorption and enhanced structural integrity of stabilized Pt skin/PtCo hydrogen oxidation catalyst analysed by in situ X-ray absorption spectroscopy

*Guoyu Shi,^a Hiroshi Yano,^b Donald A. Tryk,^b Masashi Matsumoto,^c Hajime Tanida,^c Masazumi Arao,^c Hideto Imai,^c Junji Inukai,^{b,d} Akihiro Iiyama,^b and Hiroyuki Uchida^{*b, c}*

^aInterdisciplinary Graduate School of Medicine, Engineering, and Agricultural Science, University of Yamanashi, 4 Takeda, Kofu, 400-8510, Japan

^bFuel Cell Nanomaterials Center, University of Yamanashi, 4 Takeda, Kofu, 400-8510, Japan

^cDevice-Functional Analysis Department, NISSAN ARC Ltd, Kashima-cho, Yokosuka, 237-0061, Japan

^dClean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu, 400-8510, Japan

E-mail: h-uchida@yamanashi.ac.jp; Fax: +81-55-220-8618; Tel: +81-55-220-8619

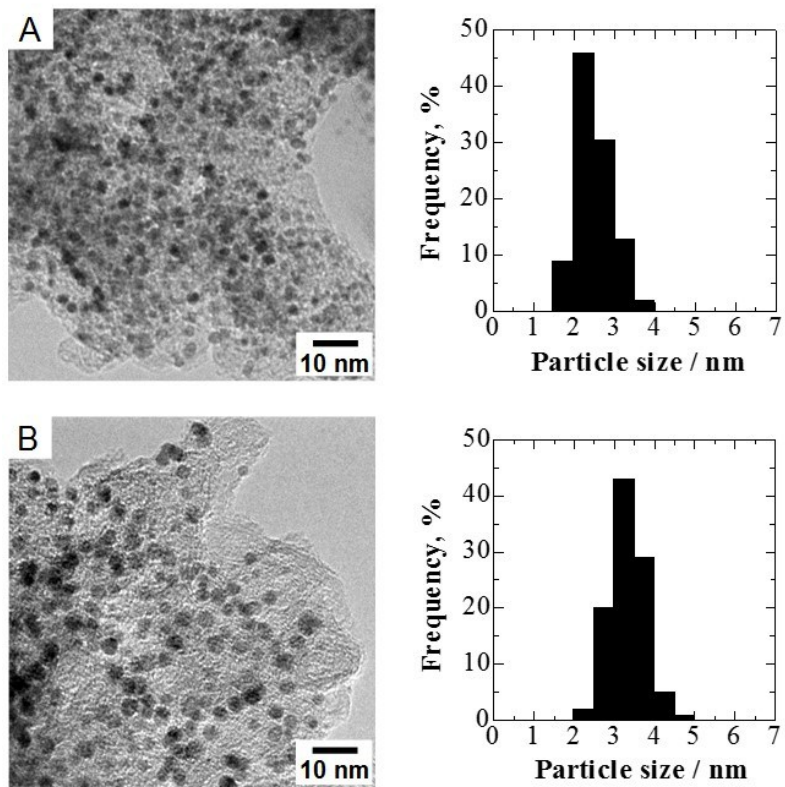


Figure S1. TEM images and particle size distribution histograms of Pt/C and Pt_{xAL}-PtCo/C catalysts after the electrochemical cleaning.

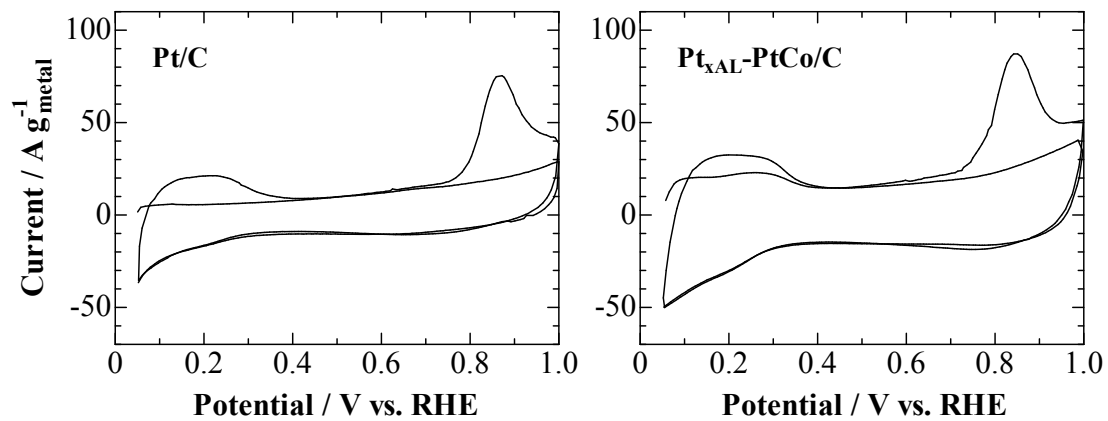


Figure S2. CO stripping voltammograms in N_2 -saturated 0.1 M $HClO_4$ at Pt/C and Pt_{xAL} -PtCo/C catalysts. Potential scan rate: 50 mV s^{-1} .

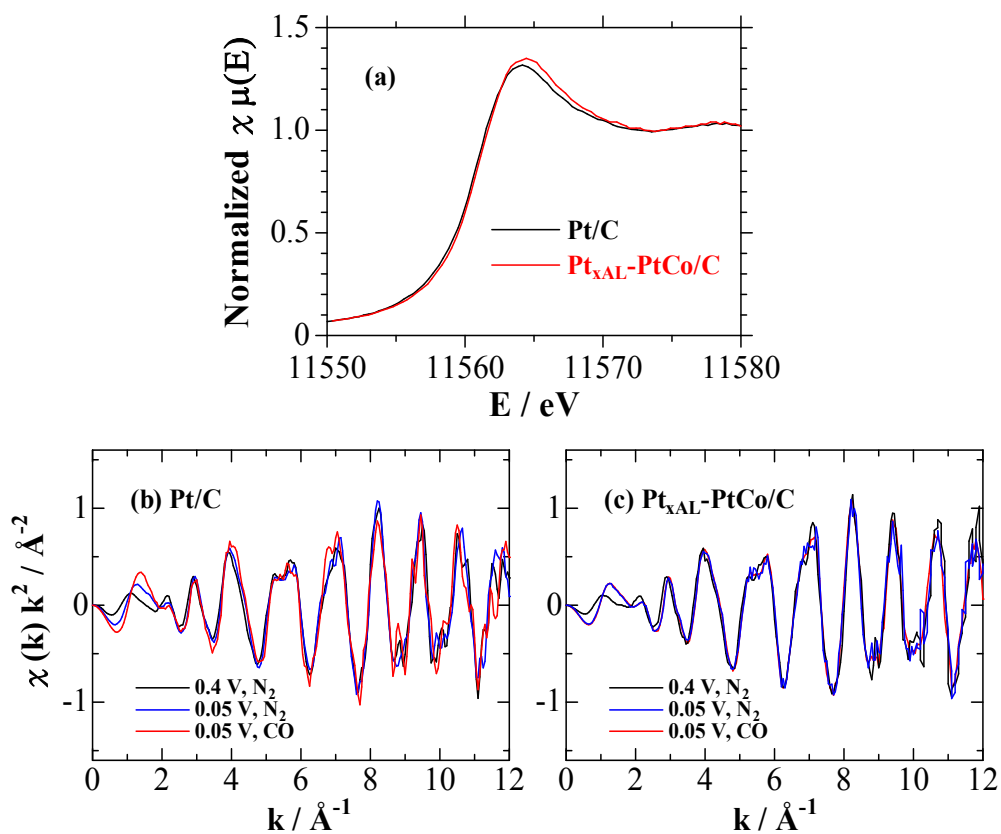


Figure S3. In situ XANES spectra (upper figure) at Pt L₃ edges of the Pt/C and Pt_{xAL}-PtCo/C catalysts held at 0.40 V in N₂ saturated 0.1 M HClO₄ electrolyte solution (a) and the k²-weighted $\chi(k)$ EXAFS spectra (two bottom figures) for Pt L₃-edge of Pt/C (b) and Pt_{xAL}-PtCo/C (c) under three operating conditions.

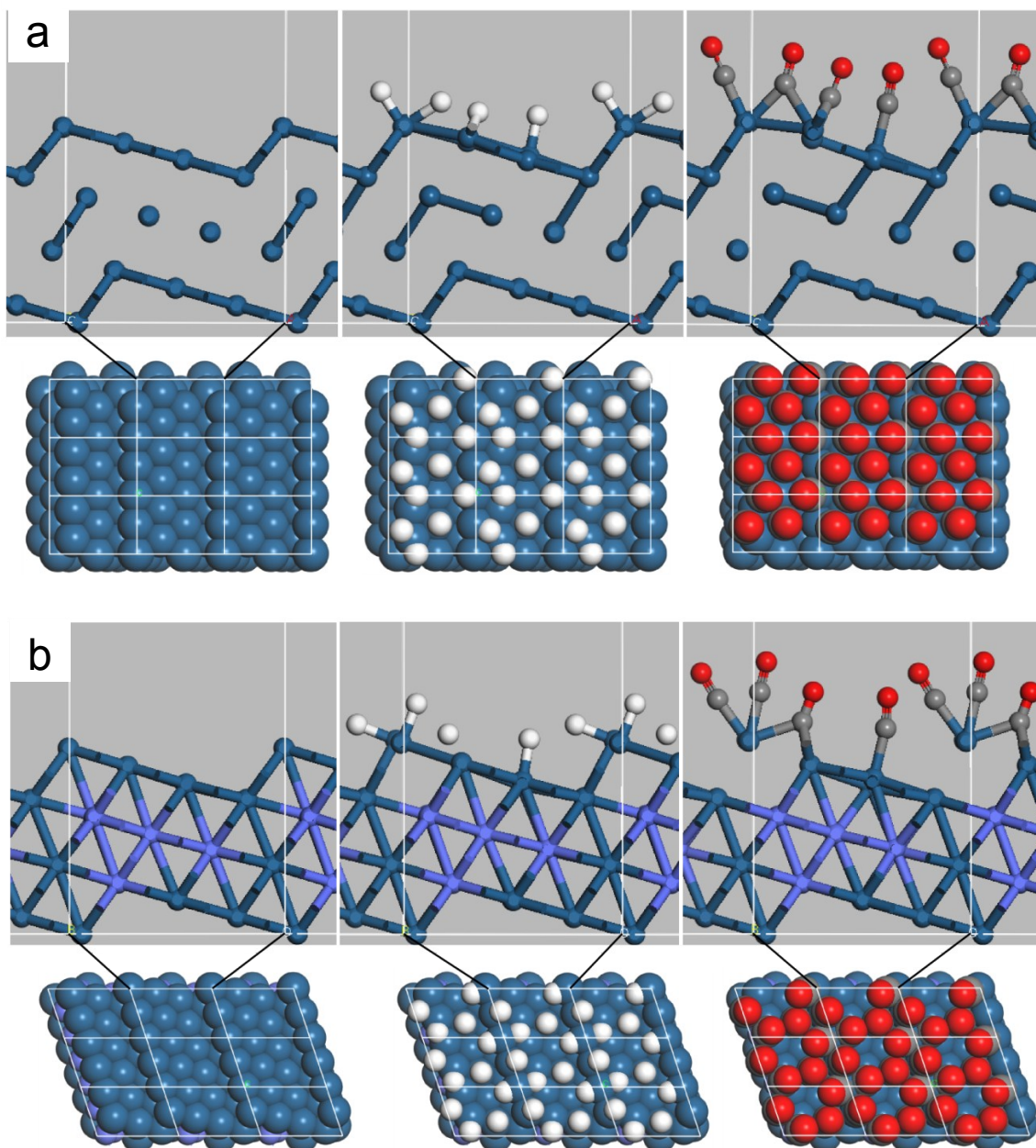


Figure S4. Atomic models, side views (upper) and top views (lower) of (a) Pt(221) and (b) Pt_{1AL}-PtCo(221) based on unit cell of Pt₂₄ and Pt₁₆Co₈. From left to right: bare surface, 4H-adsorbed surface and 4CO-adsorbed surface.

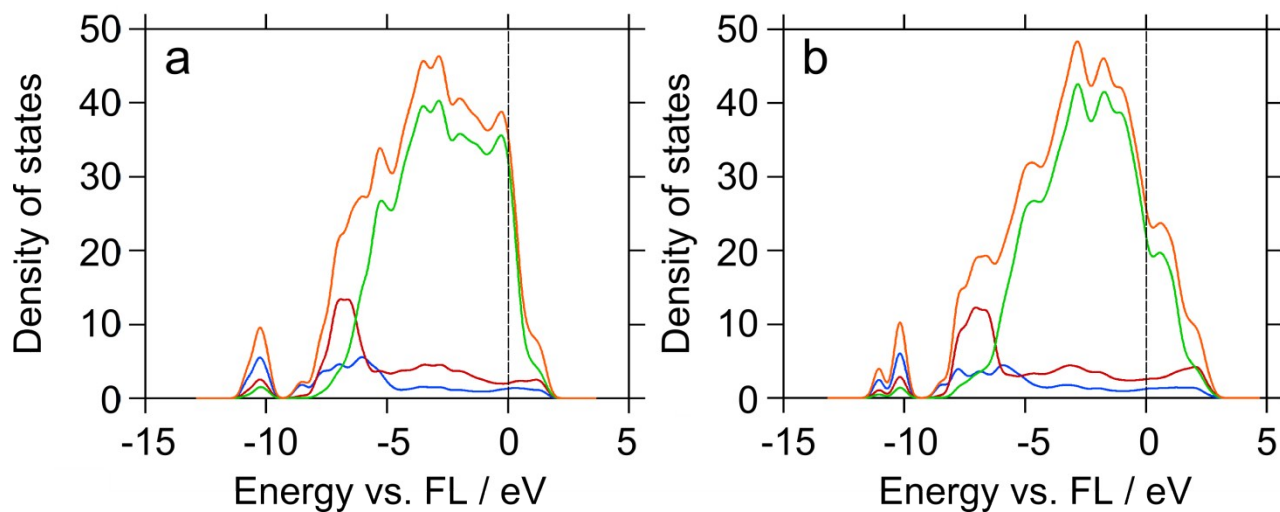


Figure S5. Density of states for (a) Pt(221)-4CO and (b) Pt_{1AL}-PtCo(221)-4CO; s-projected DOS (blue), p-projected DOS (red), d-projected DOS (green), total DOS (orange).

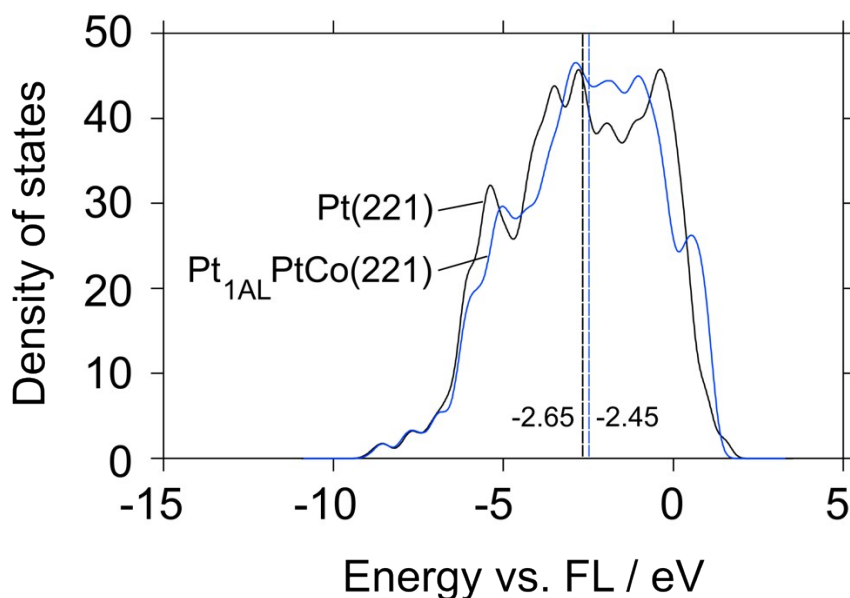


Figure S6. Total density of states for bare Pt(221), with a d-band center at -2.65 eV and bare Pt_{1AL}-PtCo(221), with a d-band center at -2.45 eV. According to T. Hofmann, T. H. Yu, M. Folse, L. Weinhardt, M. Bar, Y. F. Zhang, B. V. Merinov, D. J. Myers, W. A. Goddard and C. Heske, *J. Phys. Chem. C*, 2012, **116**, 24016, the value for Pt falls within the range of reported theoretical and experimental values. However, according to J. R. Kitchin, J. K. Nørskov, M. A. Barteau and J. G. Chen, *J. Chem. Phys.*, 2004, **120**, 10240, the effect of a subsurface layer of Co would shift the d-band center from -2.44 eV for pure Pt to -2.74 eV. Thus, the present results are at variance with the conventional view of the effect of alloying on the d-band structure.

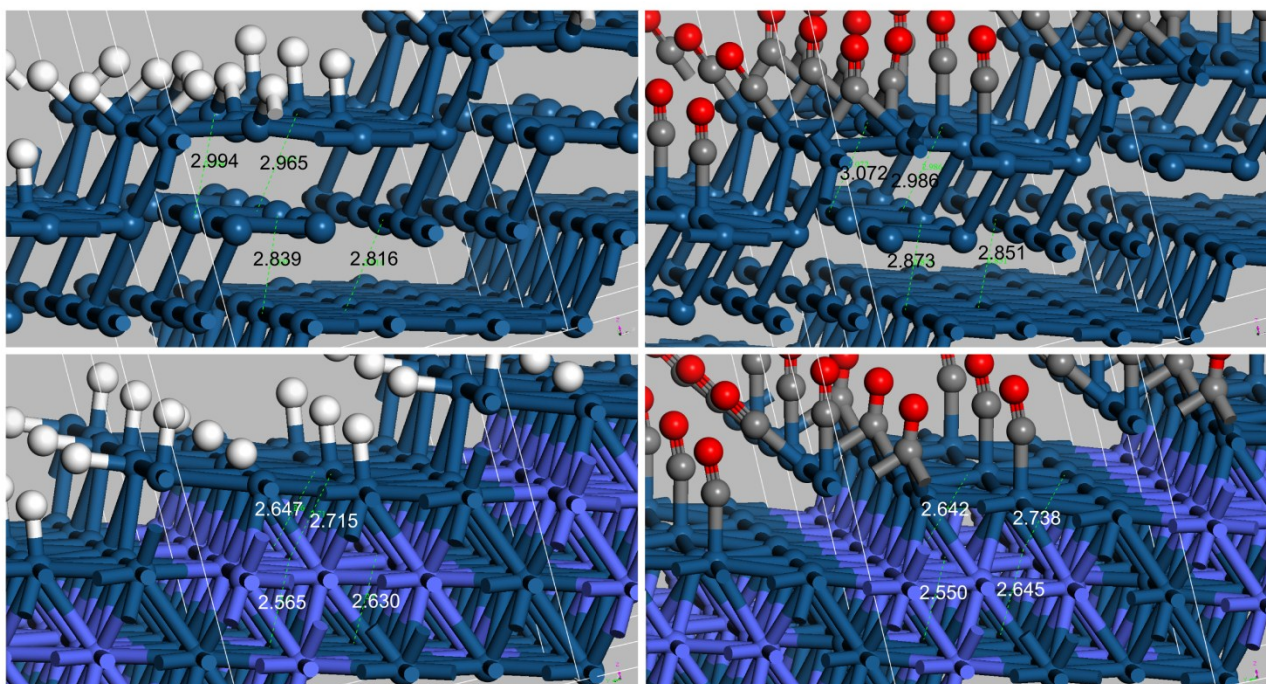


Figure S7. Atomic models, side views of Pt(221) (upper) and (b) Pt_{1AL}-PtCo(221) (lower) for unit cells of Pt₂₄ and Pt₁₆Co₈. Left panels show 4H on 6 Pt sites; right panels show 4CO on 6 Pt sites. Representative distances are shown in Å between nearest neighbor atoms in the lower two layers and in the top and middle layers.