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

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Figure S1. TEM images and particle size distribution histograms of Pt/C and Pt$_{x}$AL–PtCo/C catalysts after the electrochemical cleaning.
**Figure S2.** CO stripping voltammograms in N₂-saturated 0.1 M HClO₄ at Pt/C and PtₓAL–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 PtₓAL–PtCo/C catalysts held at 0.40 V in N₂ saturated 0.1 M HClO₄ electrolyte solution (a) and the k²-weighted χ(k) EXAFS spectra (two bottom figures) for Pt L₃-edge of Pt/C (b) and PtₓAL–PtCo/C (c) under three operating conditions.
Figure S4. Atomic models, side views (upper) and top views (lower) of (a) Pt(221) and (b) Pt1AL-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$_{1/2}$-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$_{1\text{AL}}$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$_{16}$-PtCo(221) (lower) for unit cells of Pt$_{24}$ and Pt$_{16}$Co$_8$. 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.