Supporting Information

Selective Surface Engineering of Heterogeneous Nanostructures: In-Situ Unravelling the Catalytic Mechanism on Pt-Au Catalyst

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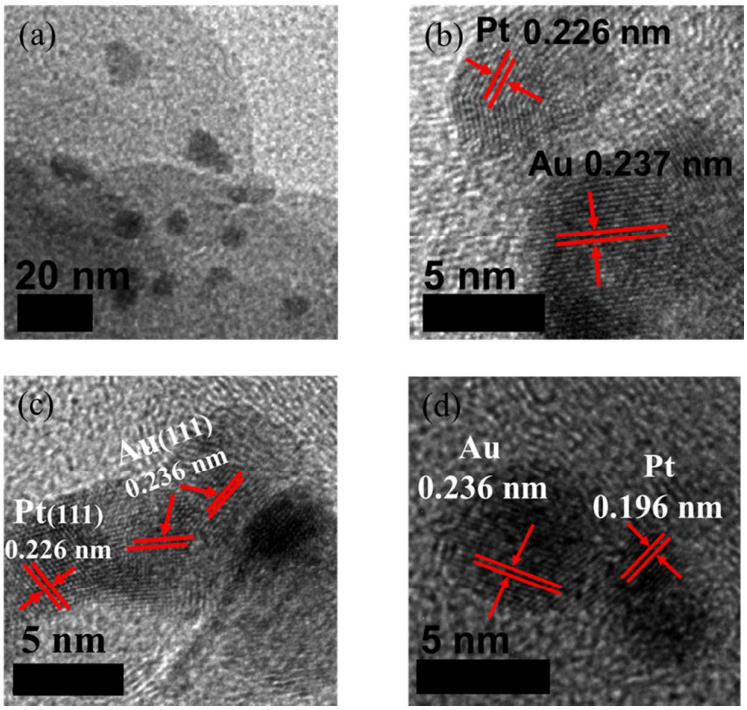

Figure S1. (a) TEM and (b)-(d) HR-TEM images of Pt_1-Au_1/C catalyst.

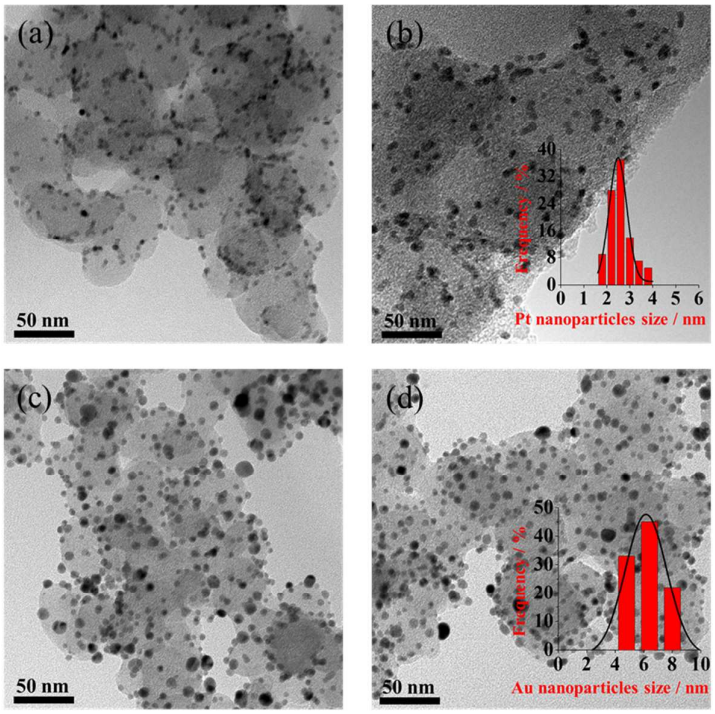

Figure S2. TEM images of Pt (a, b) and Au (c, d) nanoparticles on carbon support. The insets in Figure S2b and S2d are the size distribution of Pt and Au nanoparticles.

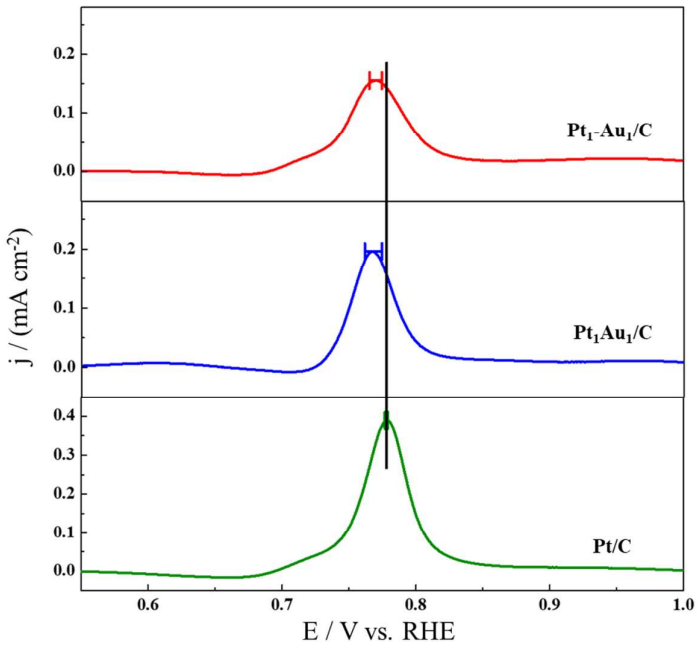

Figure S3. CO stripping voltammetry of Pt_1-Au_1/C, Pt_1Au_1/C and Pt/C in 0.1 M $HClO_4$ at a scan rate of 10 mV s^{-1}.

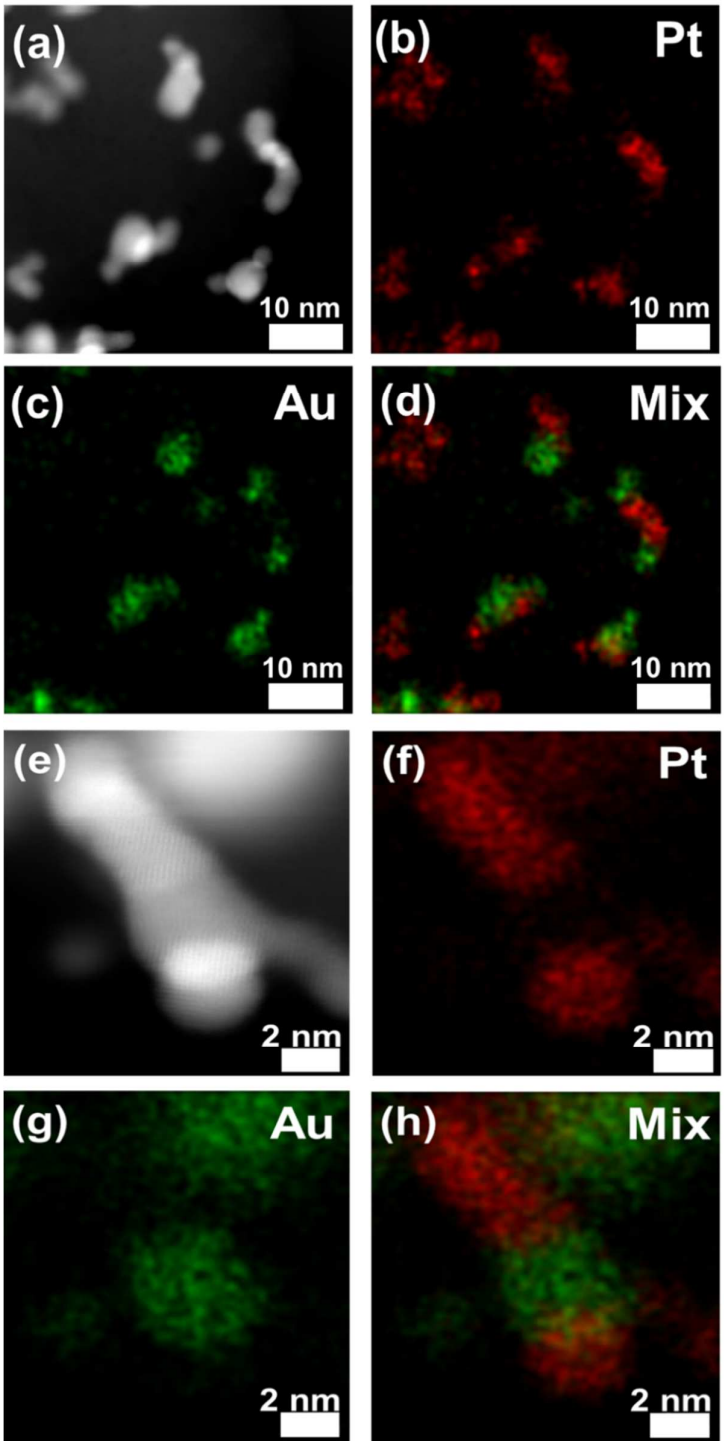

Figure S4. (a, e) HAADF/STEM image and (b-d, f-h) EDS elemental maps of Pt_1-Au_1/C.

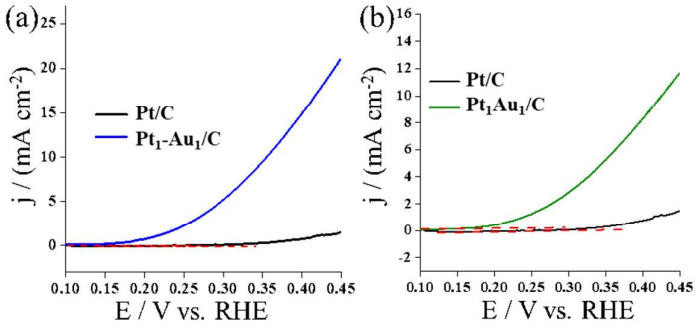

Figure S5. Partial enlargement of the CV curves for Pt_1-Au_1/C and Pt/C (a), Pt_1Au_1/C and Pt/C (b) in Ar saturated 0.5 M HCOOH + 0.1 M $HClO_4$ at a rotation rate of 1600 rpm (scan rate: 50 mV s^{-1}). (The intersection of the formic acid oxidation curves and the horizontal line at j=0 is chosen as the onset potential)

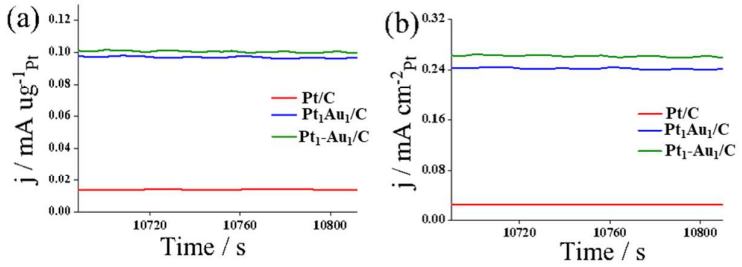

Figure S6. Chronoamperometry curves of HCOOH electrooxidation on Pt/C, Pt_1Au_1/C and Pt_1-Au_1/C in Ar saturated solution of 0.5 M HCOOH + 0.1 M $HClO_4$ at 0.4 V.

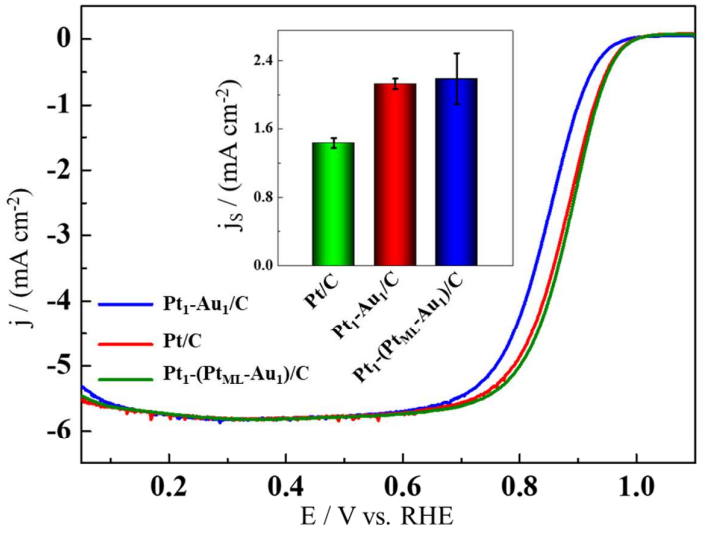

Figure S7. Polarization curves of oxygen reduction and specific activity at 0.85 V of Pt/C, Pt_1-Au_1/C and Pt_1-(Pt_{ML}-Au_1)/C.

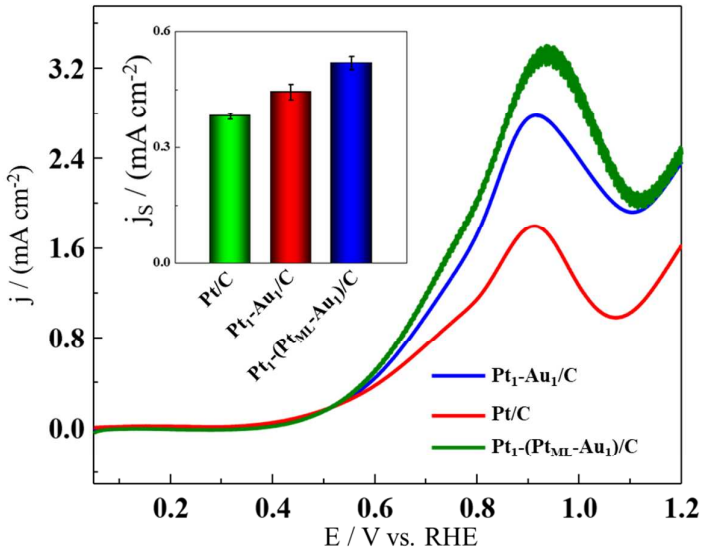

Figure S8. Cyclic voltammetry and specific activity at 0.6 V of Pt/C, Pt_1-Au_1/C and Pt_1-(Pt_{ML}-Au_1)/C in Ar saturated 0.5 M ethanol + 0.1 M $HClO_4$ at a scan rate of 50 mV/s.

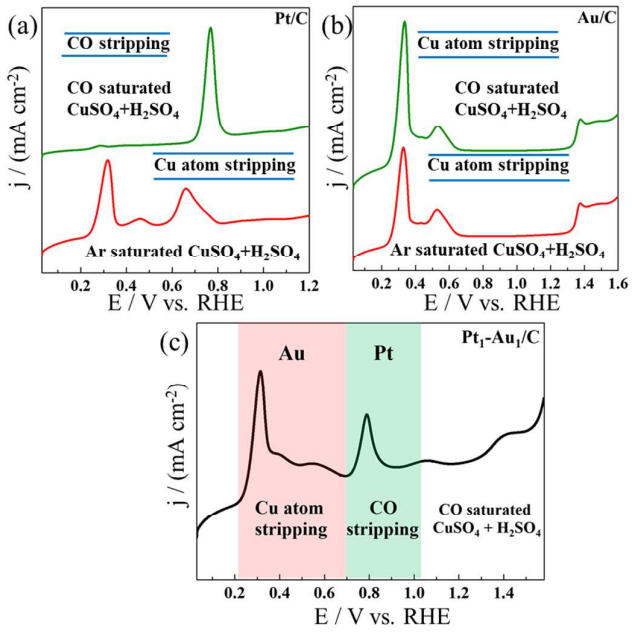

Figure S9. LSV of Pt/C (a) and Au/C (b) in Ar saturated 0.1 M $HClO_4$ solution after Cu UPD in Ar and CO saturated 50 mM $CuSO_4$ + 50 mM H_2SO_4 solution. LSV of Pt_1-Au_1/C (c) in Ar saturated 0.1 M $HClO_4$ solution after Cu deposition in CO saturated 50 mM $CuSO_4$ + 50 mM H_2SO_4 solution. Interestingly, the CO stripping peak on Pt_1-Au_1/C is more positive than that of Pt/C in this figure, which is contrary to Figure S3. The different shifts should be ascribed to the presence of Cu^{2+} ions, whose competitive adsorption has severe impact on the CO stripping on Pt.

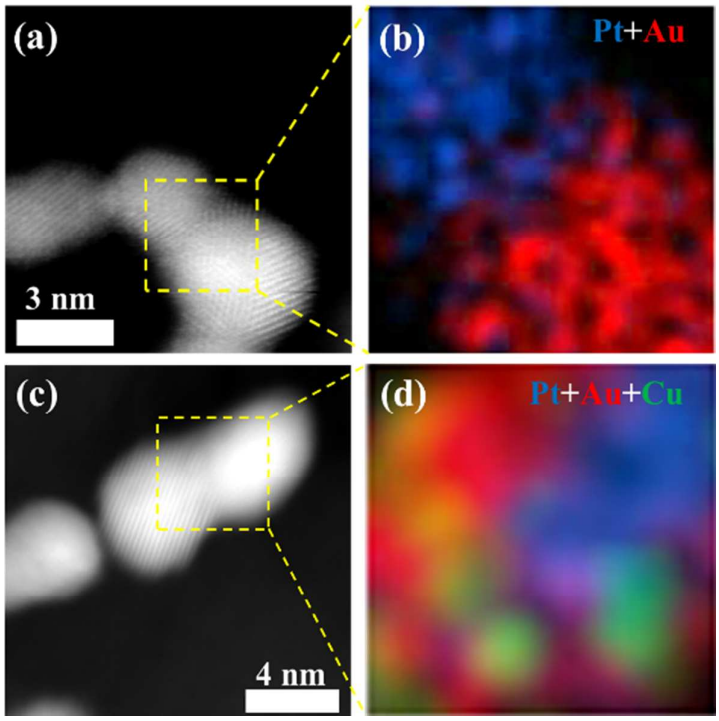

Figure S10. (a) HAADF/STEM image of Pt_1-Au_1/C and (b) EDS elemental map overlapping Pt (blue) and Au (red). (c) HAADF/STEM image of Pt_1-(Cu-Au_1)/C and (d) EDS elemental map overlapping Pt (blue), Au (red) and Cu (green). In order to guarantee that the Au signal is not masked by Cu, the Au surface is partially covered by Cu atoms.

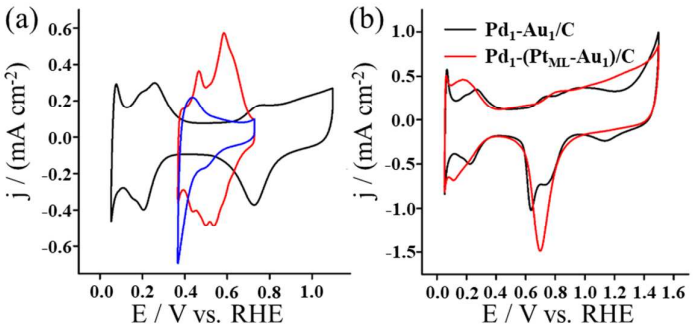

Figure S11. (a) Cyclic voltammetry for under potential deposition of Cu on Pd/C in Ar (red line) and CO (blue line) saturated 50 mM H_2SO_4 and 50 mM $CuSO_4$, and for Pd/C in Ar saturated 0.1 M $HClO_4$ (black line) at the scan rate of 50 mV s^{-1}. (b) Cyclic voltammetry for Pd_1-Au_1/C and Pd_1-(Pt_{ML}-Au_1)/C in Ar saturated 0.1 M $HClO_4$ at the scan rate of 50 mV s^{-1}.

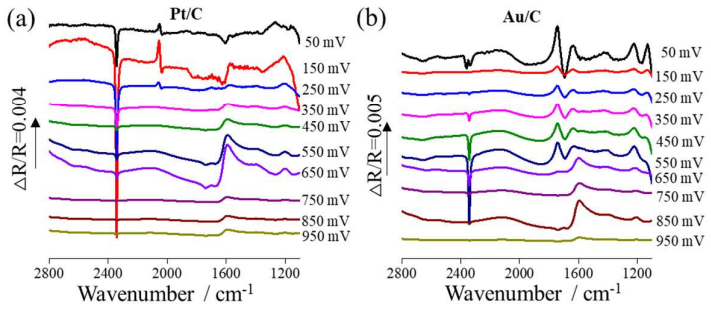

Figure S12. In-situ FTIR spectra on Pt/C (a) and Au/C (b) at different potentials in 0.5 M HCOOH + 0.1 M $HClO_4$ solution.

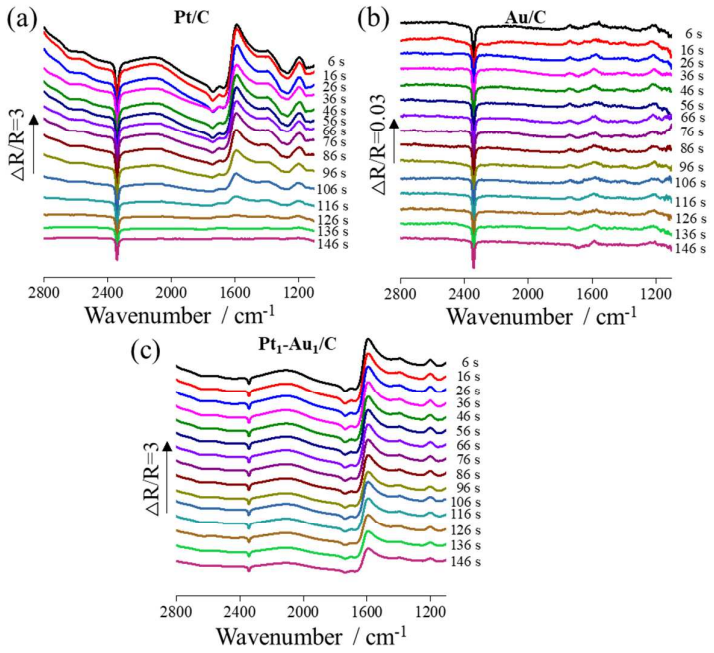

Figure S13. Time resolved in-situ FTIR spectra of Pt/C (a), Au/C (b) and Pt_1-Au_1/C (c) at 350 mV in 0.1 M $HClO_4$ mixed solution recorded after the addition of HCOOH.

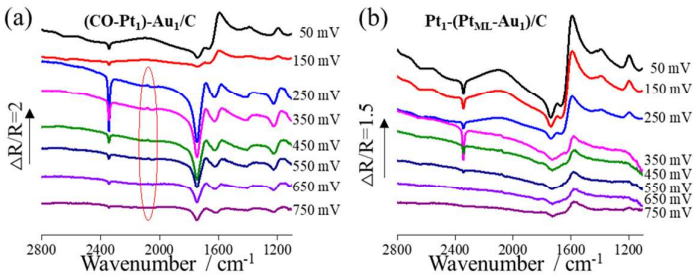

Figure S14. In-situ FTIR spectra on (CO-Pt_1)-Au_1/C (a) and Pt_1-(Pt-Au_1)/C (b) at different potentials in 0.5 M HCOOH + 0.1 M $HClO_4$ solution.

Table S1. Measured bulk and surface composition of different catalysts by ICP and XPS.

	Pt loading (%)	Au loading (%)	Pt/Au molar ratio	Surface Pt/Au molar ratio
Pt/C	16.5			
Au/C		19.2		
Pt_1Au_1/C	8.9	9.53	0.94	1.08
Pt_1-Au_1/C	13.6	15.8	0.87	1.18

Table S2. The Cu content of Cu/Pt and Cu/Au surface after Cu deposition in Ar and CO saturated 50 mM $CuSO_4$ + 50 mM H_2SO_4. (Cu content was measured by ICP and the detection limit is 0.005 ppm.)

	Cu ion content (ppm)
Pt (Cu UPD in Ar saturated solution)	0.027
Pt (Cu UPD in CO saturated solution)	0.003
Au (Cu UPD in Ar saturated solution)	0.021
Au (Cu UPD in CO saturated solution)	0.028