Revealing Surface fine Structure on PtAu catalysts by In-situ ATR-SEIRAS CO-probe method

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Figure S1. (a) Cyclic voltammetry curve in 0.1 M $HClO_4$ and characterization of secondary electroless gold plating on silicon prism/wafer (b) Observation of oxidation peaks of Au from 1.2 to 1.7 V, the electroless Au is polycrystalline electrode. Meanwhile, the Au film is consist of nanoparticles without special fine structure.



Figure S2. (a) XRD pattern of PtAu films and Si substrate (b) The amplified fine XRD patterns from 37° to 41° of PtAu film model catalysts, low angle diffraction peak (black five-pointed star), high angle diffraction peak (black spot) (c) The calculated lattice constant of high angle diffraction peak (d) The calculated lattice constant of low angle diffraction peak, the red dotted line is the theoretical lattice constant of PtAu catalyst calculated by Vegard Law.

Comparing with Si substrate, the diffraction peak at 37°- 42° was obvious and different. It could be attributed to PtAu alloy on PtAu films. The amplifying data and detail analysis show in Fig S2b, which shows phase change of PtAu films. Moreover, based on Bragg's Law (eq 1) and lattice constant calculation equation (eq 2). The calculated lattice constant of different angle diffraction peak and Vegard's Law (eq 3) were shown in Figure S2c and S2d:

$$2dsin\theta = n\lambda \tag{1}$$

$$d = \frac{a}{\sqrt[2]{h^2 + k^2 + l^2}}$$

(2)
$$a_{Pt}_{(1-x)}Au_{x} = (1-x)a_{Pt} + xa_{Au}$$
(3)

d is the interplanar spacing and θ is diffraction angle of crystal plane. λ represents the wavelength of the X-ray and n is the diffraction order. In the paper, the value of λ and n are 1.54 Å and 1, respectively. a is lattice constant and (hkl) represents indices of crystal face. The lattice constants calculated by diffraction peak of Pt (111) crystal plane and the values of (hkl) are (111). $a_{Pt}(1-x)^{Au}x$, a_{Pt} and a_{Au} are lattice constant of PtAu alloy, lattice constant of Pt and lattice constant of Au, respectively. x is the composition fraction percentage.



Figure S3. The Au binding energy shift of PtAu films and Si substrate in XPS. Comparing with Au film, the binding energy of Au of PtAu model films positively shifted, which was consistent with Pt binding energy.



Figure S4. CO adsorption and deposition experiment on Au film coated Si prism in 0.1 M HClO₄ at 0.1 V (vs RHE). The time resolved spectra and the intensity of adsorbed CO were shown in (a) and (b), respectively.

After Ar was introduced in the solution for 168s, CO was introduced for 336s to adsorb on Au film (Au-CO). Then, for excepting CO dissolved in solution, Ar was introduced again until the intensity of adsorbed Au-CO was stably. The reference spectrum was collected in Ar-saturated solution at 0.1 V. It was obvious to observe that the intensity of Au-CO gradually decreased with Ar introducing until closed to 0. It could be attributed to CO weak adsorption effect on Au surface and reported in previous others work. In this work, there were not obvious Au-CO peak in the CO oxidation spectra of Au electrode and all PtAu films, which were consistent with the above results.



Figure S5. (a) The spectra of COR in the $Pt_{0.2}Au_{1.8}$ model film (b) The spectra of COR in the Pt_1Au_1 model film (c) The spectra of COR in the $Pt_{1.8}Au_{0.2}$ model film



Figure S6. CO oxidation spectra and second derivative spectrogram (SDP) of $Pt_{1.5}Au_{0.5}$ (a)(c) and $Pt_{0.5}Au_{1.5}$ (b)(d) with ref



Figure S7. The CO_L peak fitting of $Pt_{1.5}Au_{0.5}$ (a) and $Pt_{0.5}Au_{1.5}$ (b) at 0.1 V.

In (a)-(b), the highest wavenumber CO_L peak (red line), the lowest wavenumber CO_L peak (blue line), sum fitting spectrum (red dash dot line), original spectrum (black line). It's obvious to observe two types CO_L peak, similar with Pt_1Au_1 sample. The number of CO_L peak gradually decreases from 3 types to 1 type with Pt content decreasing. It means that there exist multiple CO active sites in different PtAu films and the number of active sites rely on Pt content.



Figure S8. (a) The electro-oxidation curves of $Pt_{0.2}Au_{1.8}$, Pt_1Au_1 and $Pt_{1.8}Au_{0.2}$ model films in the 0.1 M HClO₄+0.01 M HCOOH solution (b) Summarized the current density of the first oxidation peak (peak 1, green), the second oxidation peak (peak 2, light blue).



Figure S9. The CO_L peak fitting of $Pt_{0.2}Au_{1.8}$ (a)-(h) 0.2 V - 0.9 V with interval 0.1 V. (i) the integrated intensity of CO_L peak. The $Pt_{iso}Au$ -CO_L peak (blue line), sum fitting spectrum (red dash dot line), original spectrum (black line).



Figure S10. The CO_L peak fitting of Pt_1Au_1 (a)-(h) 0.2 V - 0.9 V with interval 0.1 V. (i) the integrated intensity of different types CO_L peak. The $Pt_{adj}Au$ -CO_L peak (red line), the $Pt_{iso}Au$ -CO_L peak (blue line), sum fitting spectrum (red dash dot line), original spectrum (black line).



Figure S11. The CO_L peak fitting of $Pt_{1.8}Au_{0.2}$ (a)-(h) 0.2 V - 0.9 V with interval 0.1 V. (i) the integrated intensity of different types CO_L peak. The $Pt_{iso}Au$ -CO_L peak (blue line), $Pt_{adj}Au$ -CO_L peak (red line), $Pt_{rich}Au$ -CO_L peak (dark yellow line), sum fitting spectrum (red dash dot line), original spectrum (black line).



Figure S12. The electrochemist test and structure characterization of PtAu nanocatalyst (a) XRD pattern; (b) Transmission electron microscope image; (c) Cyclic voltammetry test; (d) CO oxidation curve.



Figure S13. The CO_L peak fitting of PtAu nanocatalyst (a)-(k) 0.1 V - 1.0 V with interval 0.1 V. (i) the wavenumber change of different types CO_L peak. The Pt_{rich}Au-CO_L peak (dark yellow line), the Pt_{adj}Au-CO_L peak (red line), the Pt_{iso}Au-CO_L peak (blue line), sum fitting spectrum (red dash dot line), original spectrum (black line).

Sample	Q _{H-area} (210 mC/cm ²)	Q _{Au-O} (340 mC/cm ²)	Surface Pt ratio	Pt ratio (XPS)
Pt _{1.8} Au _{0.2}	907	146	0.92	0.91
Pt _{1.5} Au _{0.5}	714	220	0.86	0.84
Pt ₁ Au ₁	391	332	0.68	0.66
Pt _{0.5} Au _{1.5}	140	281	0.48	0.44
Pt _{0.2} Au _{1.8}	49	452	0.16	0.14

Table S1. The surface Pt% ratio of PtAu films, calculating by H-area and Au-O peak area to

calculated surface ratio of Pt.