

## Supplementary Information

### Inhibiting CO formation by adjusting surface composition in PtAu alloys for methanol electrooxidation

Min Yin,<sup>a,c</sup> Yunjie Huang,<sup>b</sup> Liang Liang,<sup>b</sup> Jianhui Liao,<sup>b</sup> Changpeng Liu<sup>\*b</sup> and Wei Xing<sup>\*a</sup>

<sup>a</sup> State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, 5625 Renmin Street, Changchun, China.

<sup>b</sup> Laboratory of Advanced Power Sources, Changchun Institute of Applied Chemistry, 5625 Renmin Street, Changchun, China.

<sup>c</sup> Graduate University of Chinese Academy of Sciences, Beijing, China.

#### Experimental Methods

##### Synthesis of PtAu/C materials

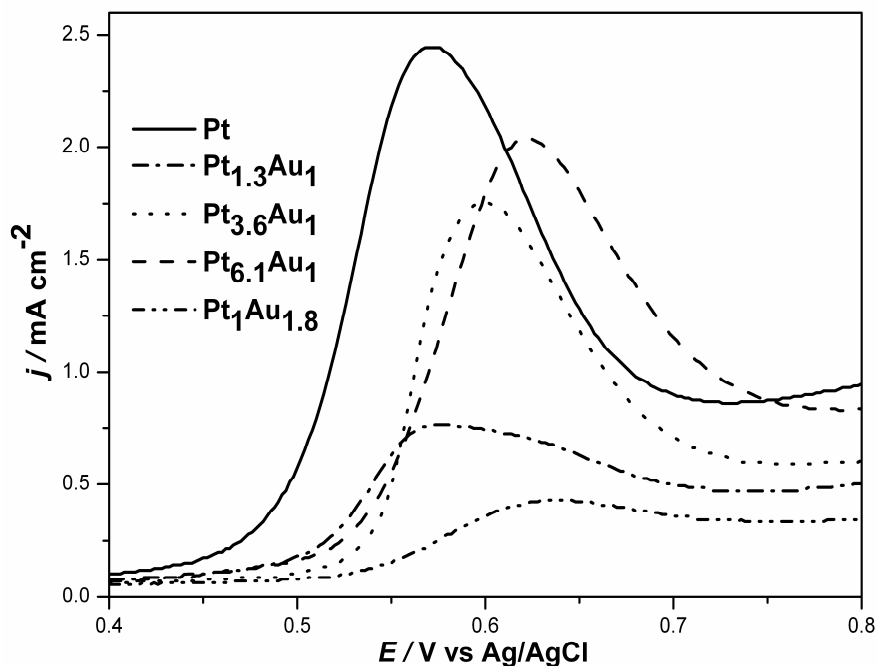
PtAu alloys supported on carbon black were prepared by microwave-assisted polyol reduction method. Firstly, Vulcan XC-72 carbon black was ultrasonically suspended in ethylene glycol for 2 h, following by mixing with a certain proportion of H<sub>2</sub>PtCl<sub>6</sub> and HAuCl<sub>4</sub> solution. The feeding molar ratio of Pt/Au in H<sub>2</sub>PtCl<sub>6</sub> and HAuCl<sub>4</sub> solution is 1/1, 2/3, 1/2, respectively. Then, 100 s microwave operation was performed after pH was adjusted to 10. At last, the suspension was filtered and washed with the hot triply distilled water until no Cl<sup>-</sup> was detected and dried in a vacuum oven overnight. Thermal treatment was performed at 500 °C for 2 h under N<sub>2</sub>/H<sub>2</sub> (9:1 in volume) atmosphere only for the sample with 1/1 PtAu composition.

##### Materials Characterization

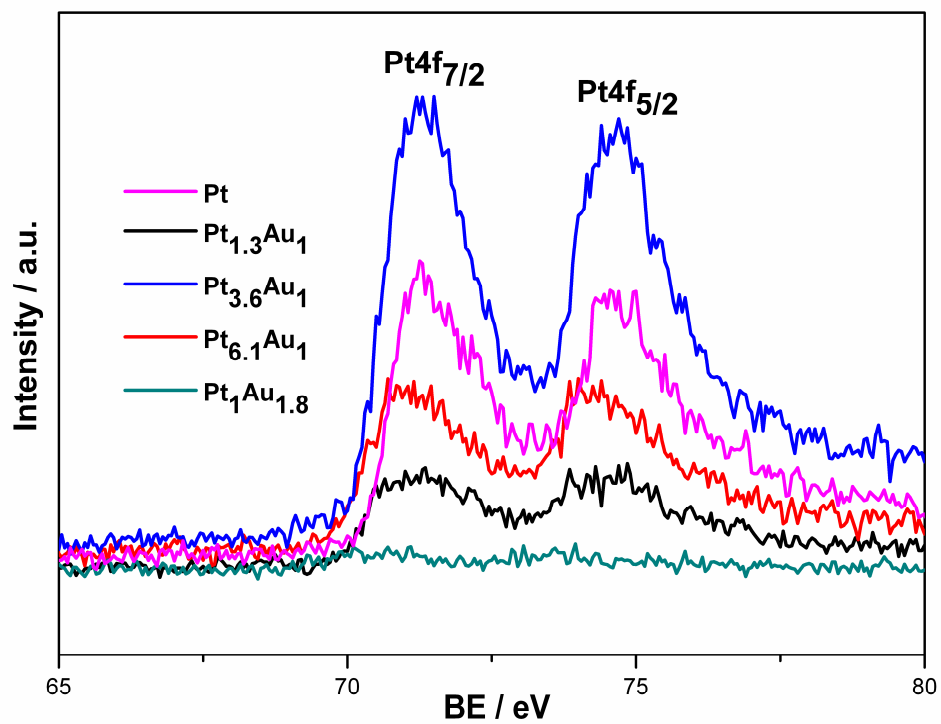
X-ray diffraction patterns were obtained using a Rigaku-D/MAX-PC2500 X-ray diffractometer (Japan) with the Cu K $\alpha$  ( $\lambda=1.5405 \text{ \AA}$ ) as a radiation source operating at 40 kV and 200 mA. X-ray photoelectron spectroscopy was recorded on a Kratos XSAM-800 spectrometer with an Al K $\alpha$  monochromatic source. The surface content ratio of Pt and Au was determined by integrating the surface area under the Pt and Au 4f core-level peaks. The C 1s peak was used as a reference.

##### Electrochemical measurements

Electrochemical measurements were carried out with a Princeton Applied Research Model 273A Potentiostat/Galvanostat with a Pt coil as the counter electrode and Ag/AgCl as the reference electrode. For the working electrode preparation, a 5 mg of the PtAu/C catalyst was dispersed ultrasonically in 1 ml of ethanol with 50  $\mu$ l of 5 % Nafion solution. Then, 10  $\mu$ l of the dispersion was pipetted on a polished glassy carbon electrode. Finally, the electrode was obtained after the solvent volatilized.



**Fig. S1.** CO-stripping voltammogram: first cyclic scan (scan rate: 20mV s<sup>-1</sup>) at the CO-adsorbed PtAu alloy catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions.



**Fig. S2.** XPS spectra of Pt 4f regions for PtAu alloy catalysts.