Tuning the CO-tolerance of Pt-Fe Bimetallic Nanoparticle Electro catalysts Through Architectural Control

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Supporting Information

Synthesis of as-prepared PtFe random alloy NPs: PtFe as-prepared NPs were prepared by the diol reduction of Pt(acac)$_2$ and the decomposition of Fe(CO)$_5$ under N$_2$ atmosphere.$^1$ Specifically, 197.0 mg of Pt(acac)$_2$ and 390.0 mg of 1,2 hexadecanediol were added in a three-neck flask with 20 ml diphenyl ether. The flask was equipped with magnetic stirring, a heating mantle, a reflux condenser and a thermometer. The mixture was first heated to 100°C when oleic acid (0.16 ml) and oleylamine (0.17 ml) were introduced. The solution was then heated to 110°C when 75 µl of Fe(CO)$_5$ was quickly injected. Afterwards, the obtained mixture was heated to reflux for 30 minutes, followed by cooling down to room temperature. Finally, the particles were washed with ethanol and precipitated by centrifugation.

Preparation of carbon-supported Pt-Fe bimetallic catalysts: To make carbon-supported PtFe random alloy electrocatalysts with 30 wt.% (total metal) loading, 20 mg as-prepared NPs dispersed in hexane were mixed with 46.6 mg of Vulcan® XC-72 carbon powder by 3-hr of sonication. After sonication, the catalyst was dried in air with the evaporation of hexane. The dried catalyst was then subjected to heat treatment at 500°C in Ar/H$_2$ (5% of H$_2$) atmosphere for 2 hrs. The Pt$_3$Fe@Pt core-shell catalysts were prepared by further heat treating the PtFe random alloy catalyst (500°C) in Ar-H$_2$ atmosphere at 700°C for 2 hrs, then catalyst ink (mixed with Nafion, isopropanol and H$_2$O) was deposited on a glassy carbon electrode and was subject to 200 potential cycles (-0.24 V - 0.6 V vs. SCE, scan rate: 50 mV/s) in Ar-saturated H$_2$SO$_4$ solution. The Pt$_3$Fe intermetallic catalysts was prepared by heat treating the as-prepared random alloy catalysts in Ar-H$_2$ atmosphere at 650°C for 2 hrs, while the Pt@Fe$_x$O$_y$ catalysts were made by further treating the Pt$_3$Fe intermetallic catalysts in air at 185°C for 2 hrs.

Characterizations: TEM and HRTEM images were obtained on a JEM 2100 LaB6 TEM operating at 200 kV. EDX and EDX line scan analysis was performed on a JEOL 2100F Field Emission TEM operating in the STEM mode. XRD patterns of samples were obtained on a Bruker D8 Advance X-ray diffractometer. Electrochemical experiments were performed in a standard three-electrode electrochemical cell. A rotating disk electrode (glassy carbon) with dried catalyst ink on its surface was used as a working electrode. A Pt wire counter electrode and a saturated calomel electrode
(SCE) reference electrode were used. All the potentials are reported with respect to SCE. The electrolyte was a 0.5 M H$_2$SO$_4$ solution. In the CO-stripping experiments, the Pt-Fe catalysts were saturated with CO by bubbling CO in the electrolyte for 15 minutes with the electrode potential held at -0.20 V vs. SCE, followed by argon-purging for 40 minutes. To obtain the polarization curves for electrooxidation of H$_2$ in the presence of CO, the electrolyte was bubbled with CO/H$_2$ mixture (1000 ppm of CO) for 2 hrs with the electrode potential held at -0.20 V vs. SCE, followed by the potential scan at 1 mV/s with rotation rate of 1600 rpm.

**Figure S1.** EDX analysis of the as-prepared PtFe random alloy NPs.

**Figure S2.** STEM-EDX line scan of the PtFe random alloy (left) and Pt$_3$Fe@Pt core-shell (right) NPs.
**Figure S3.** TEM image of Pt$_3$Fe intermetallic NPs. The insert is the lattice fringe image of one particle.

**Figure S4.** Polarization curve of PtFe random alloy catalysts in 0.5 M H$_2$SO$_4$ solution saturated with argon (blue curve) and mixture of H$_2$+1000 ppm CO (green curve). The curves were recorded at 298K with 1 mV/s scan rates and 1600 rpm rotation rates. Electrolyte: 0.5 M H$_2$SO$_4$ solution.
**Figure S5.** CO stripping curves of carbon-supported Pt-Fe bimetallic catalysts in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution. Scan rate: 20 mV/s, and T=298 K.

**References:**