

Electronic Supplementary Information

S1. Experimental Section

1.1 Materials

Vulcan XC-72 carbon black was purchased from the Cabot Corporation. The chloroplatinic acid hydrate and the 5 wt% Nafion solution were from the Aldrich Chemical Co. The Pt/C catalysts were purchased from Johnson Matthey Company. Other chemicals were all obtained from Beijing Chemical Reagent Company (Beijing, China). De-ionized water ($18.23\text{M } \Omega$) produced by with the Millipore system (Millipore Ltd., USA) was used throughout all experiments.

1.2 The synthesis of electrocatalysts

Synthesis of $\text{Pt}_x\text{Pb}_{100-x}/\text{C}$ electrocatalysts: 50 mg Vulcan-72 carbon black, 1.428 mL H_2PtCl_6 solution (14 mg Pt mL^{-1}), various content of $\text{Pb}(\text{NO}_3)_2$ (17, 34, 68 and 136 mg corresponding to $\text{Pt}_{67}\text{Pb}_{33}$, $\text{Pt}_{50}\text{Pb}_{50}$, $\text{Pt}_{33}\text{Pb}_{67}$ and $\text{Pt}_{20}\text{Pb}_{80}$, respectively) and 151 mg sodium citrate were added into the solution of 80 mL de-ionic H_2O and 20 mL glycol. This resulting mixture was ultra-sonically dispersed to form uniform ink and deaerated by high-purity nitrogen to remove the oxygen. Subsequently, under the condition of stirring, the as-obtained ink was poured into the freshly-prepared and deaerated 40 mL NaBH_4 solution (1 mg mL^{-1}). The reactive solution was stirred for 8 h, filtered, washed, and dried in a vacuum oven to obtain $\text{Pt}_x\text{Pb}_{100-x}/\text{C}$ electrocatalysts.

1.2 Physical characterizations

The transmission electron microscope (TEM) and high resolution TEM measurements were conducted on a TECNAI G2 operating at 200 Kv; meanwhile an equipped energy dispersive X-ray spectroscopy (EDS) detector was used to verify the coexistence of Pt and Pb components. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos XSAM-800 spectrometer with an Mg $\text{K}\alpha$ radiation source. X-ray diffraction (XRD) measurements were performed with a PW1700 diffractometer (Philips Co.) using a Cu $\text{K}\alpha$ ($\lambda = 1.5405\text{ \AA}$) radiation source.

The obtained XRD patterns were analyzed with Jade 5.0 software to remove the background radiation. The bulk composition of electro-catalysts were evaluated by both inductively coupled plasma optical emission spectrometer (X Series 2, Thermo Scientific USA) and the EDS detector on a JEOL JAX-840 scanning electron microscope operating at 20 kV. The final EDS result was the averaged one of measuring values from at least five different zone of sample.

1.3 Electrochemical measurements

Electrochemical measurements were carried out with an EG&G mode 273 potentiostat/galvanostat and a conventional three-electrode test cell. The catalyst ink was prepared by ultrasonically dispersing a mixture containing 5 mg of catalyst, 950 μL of ethanol and 50 μL of a 5 wt% Nafion solution. Next, 5 μL of the catalyst ink was pipetted onto a pre-cleaned glassy carbon disk (diameter = 3 mm) as the working electrode. A Pt foil and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. All of the potentials are relative to the SCE electrode, unless otherwise noted. The electrochemical testing history is as follows. Firstly, to activate and clean the catalyst surface, the working electrodes were potentially cycled from -0.242 V and 0.958 V vs. SCE at a scan rate of 50 mV s^{-1} in a 0.5 M H_2SO_4 solution until a stable response was obtained. And then, to evaluate the activity of the catalysts for formic acid electrooxidation, the cyclic voltammetry (CV) experiments were carried out in 0.5 M H_2SO_4 + 0.5 M HCOOH solution at a scan rate of 50 mVs^{-1} . Lastly, to estimate the stability of the catalysts, the current-time experiments were performed in the same solution with a potential of 0.2 V vs. SCE. All electrolyte solutions were deaerated by high-purity nitrogen for at least 10 min prior to each measurement.

1.4 Single cell performance tests

The electrocatalytic activity of $\text{Pt}_{33}\text{Pb}_{67}$ HN /C electrocatalyst was also evaluated in the anode of a direct formic acid fuel cell (DFAFC). A home-made catalyzed-gas

diffusion layer was used as the cathode for the single cell testing. The cathode electrocatalyst loading was $2.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. The anode catalyst ink was prepared by ultrasonically mixing the $\text{Pt}_{33}\text{Pb}_{67}$ HN /C catalyst with a 5 wt% Nafion solution, de-ionized water and 2-propanol. To facilitate the transportation of formic acid fuel in the anode, the anodic catalyst ink was sprayed onto a prefabricated carbon cloth instead of water-proofed gas diffusion layer with a loading of $1.6 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. Similarly, a commercial 40wt% Pt/C anodic catalyst with the same loading was also prepared for comparison. The membrane electrode assembly is fabricated by hot-pressing anode and cathode electrodes together with a Nafion 117 membrane. The single cell tests were conducted in a 9 cm^{-2} DFAFC at 25°C with the fuel of 10 M HCOOH solution and the oxidant of oxygen at 1 atm. The single cell performance measurement was carried out by the Fuel Cell Test System (Arbin Instruments Co.) and the polarization curves were recorded in galvanostatic mode.

S2. Figures

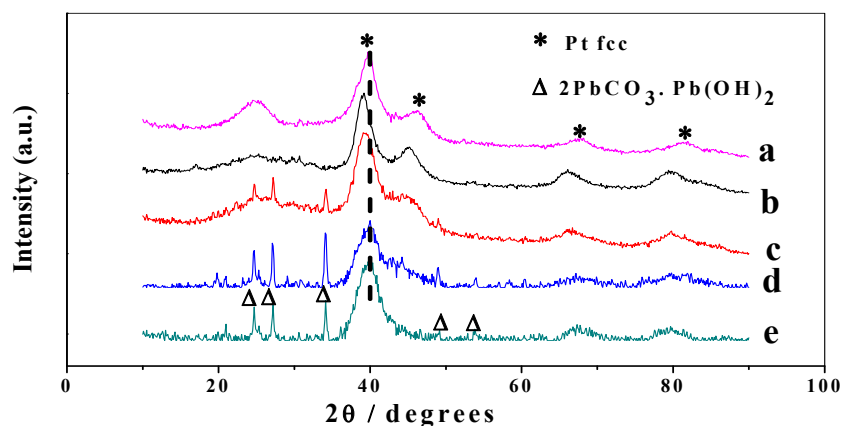


Fig.S1 XRD patterns of 20 wt% commercial Pt/C (a), Pt₆₇Pb₃₃/C (b), Pt₅₀Pb₅₀/C (c) and Pt₃₃Pb₆₇ HN/C (d) and Pt₂₀Pb₈₀/C (e) catalysts. The Pt/C catalyst displays the typical Pt fcc structure. For Pt₃₃Pb₆₇ HN/C and Pt₂₀Pb₈₀/C catalysts, there is co-existence of 2PbCO₃·Pb(OH)₂ phase (ICDD PDF2 File #00-001-0687) and Pt fcc crystal phase indicating the phases separation for Pt and Pb components. The XRD patterns of Pt₆₇Pb₃₃/C displays the typical Pt fcc structure, while the Pt diffraction peaks are shifted to small angle direction demonstrating the Pt alloying with 2PbCO₃·Pb(OH)₂. In contrast, the XRD pattern of Pt₅₀Pb₅₀/C exhibits the mixed phases comprised of the Pt alloy and 2PbCO₃·Pb(OH)₂ phases, that is, a intermediate state between Pt₆₇Pb₃₃/C and Pt₃₃Pb₆₇ HN/C.

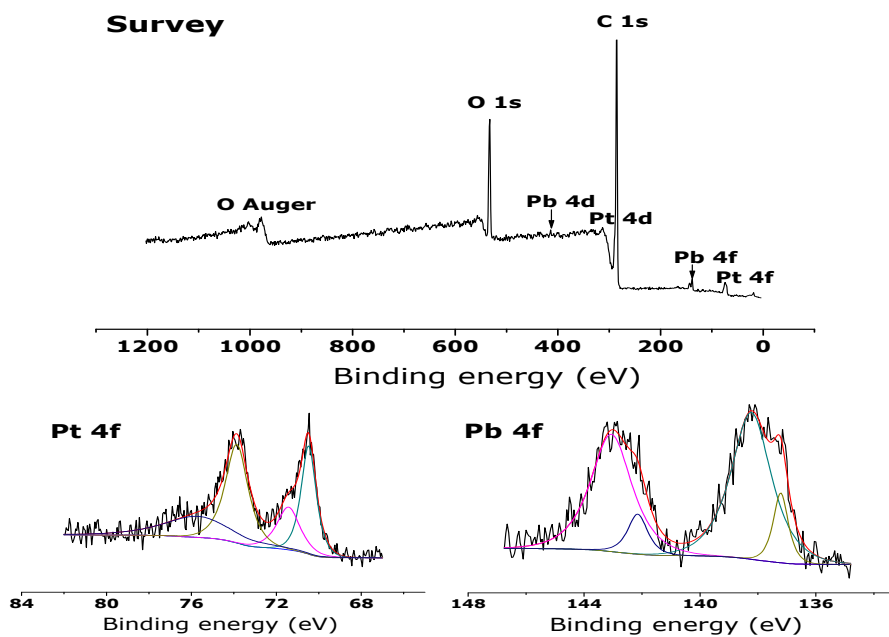


Fig.S2. XPS results for Pt₃₃Pb₆₇ HN/C catalyst. The survey spectra of Pt₃₃Pb₆₇ HN/C show Pt and Pb characteristics peaks. The Pt 4f_{7/2} and Pt 4f_{5/2} regions can be deconvoluted into metallic Pt and Pt (II) species. By deconvolution, Pb 4f signal display the characteristics of Pb (II) species at 138.2 and 143.1 eV, and Pb (IV) species at 137.2 and 142.1 eV. The XPS analysis shows that lead in surface layer is easily oxidized to lead oxide at ambient environment, which is in accordance with the XRD pattern of Pt₃₃Pb₆₇ HN/C.

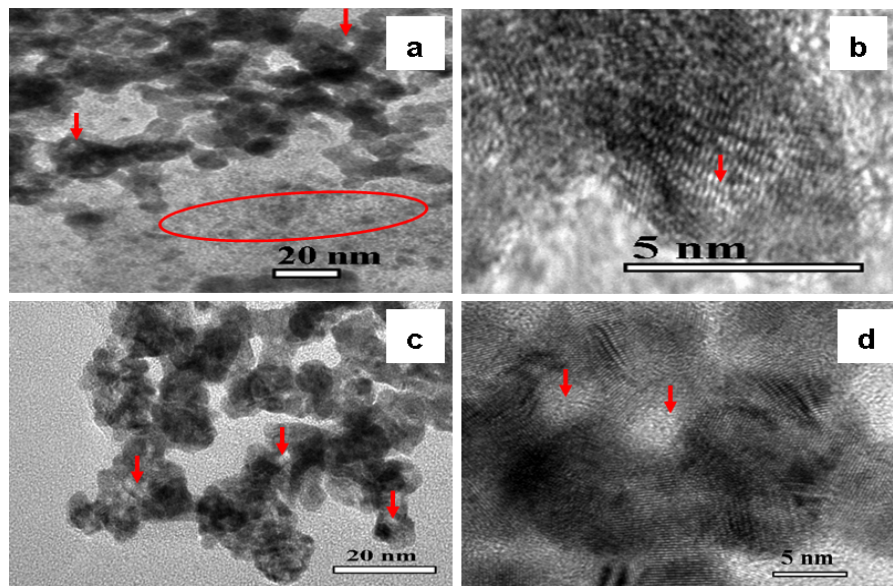


Fig.S3 The effect of concentration of sodium citrate on the morphology of $\text{Pt}_{50}\text{Pb}_{50}/\text{C}$: 0 mM (a-b) and 20 mM (e-f) sodium citrate. The rows indicate the hollow structure and the ring part indicates the presence of nanoparticles.

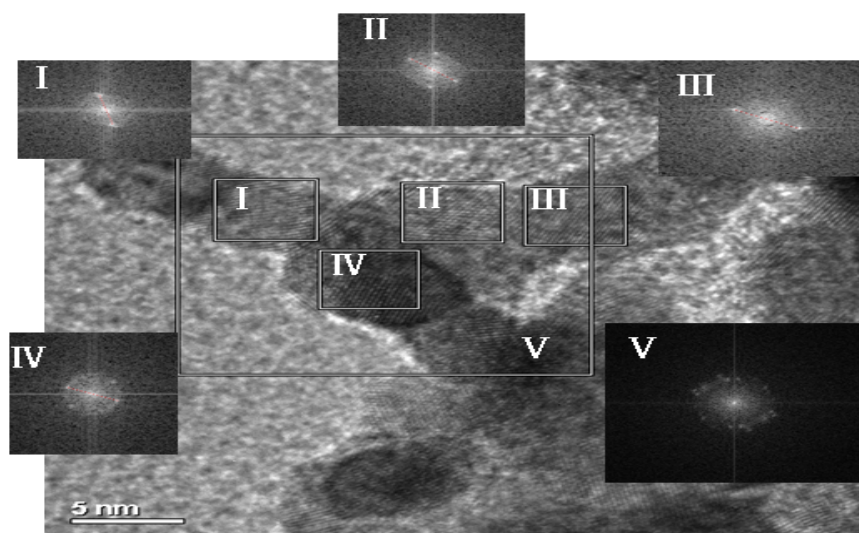


Fig.S4 The corresponding FFT patterns at different particle zones of networks for $\text{Pt}_{67}\text{Pb}_{33}/\text{C}$. From the orientation of Pt {111} plane, it is deduced that the particle attachment adopts a random mode.

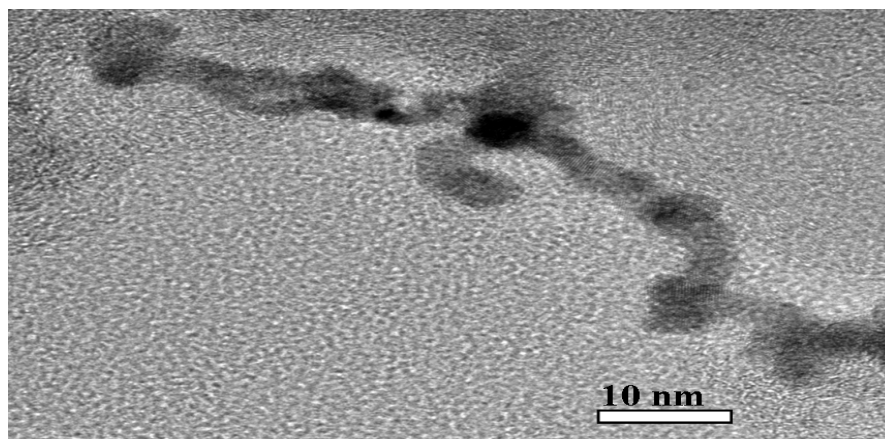


Fig.S5 TEM observation for single nanochain of Pt₅₀Pb₅₀/C

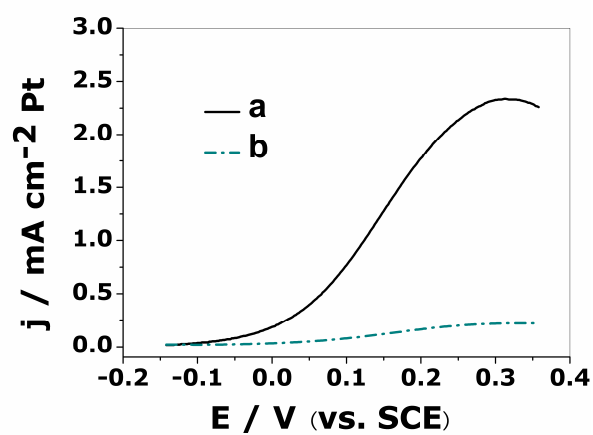


Fig.S6 Specific activity of Pt₃₃Pb₆₇ HN/C (a) and Pt/C (b) catalysts for FAEO evaluated in 0.5 M HCOOH+0.5M H₂SO₄ solution at a scan rate of 50 mV s⁻¹.