

Supplementary Information

A non-intermetallic PtPb/C catalyst of hollow structure with high activity and stability for electrooxidation of formic acid

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1. Synthesis of PtPb/C Catalyst

K_2PtCl_6 (7.5 mg), $Pb(NO_3)_2$ (10.2 mg), and Vulcan XC-72 carbon black (12.5 mg) were added into 10 mL deionized water. Under vigorous sonication, $NaBH_4$ (60 mg, dissolved in 10 mL water) solution was gradually dropped into the suspension to co-reduce K_2PtCl_6 and $Pb(NO_3)_2$. (2) After centrifugal separation and re-suspending of pre-formed PtPb/C in water, 5.1 mg K_2PtCl_6 was added, and reduced again by $NaBH_4$. The resulting PtPb/C catalyst was centrifugally separated and washed by water several times.

The size, morphology, composition and structure of the PtPb/C catalyst were characterized by HRTEM (JEM-2100), EDX (INCA Energy, Oxford Instruments, UK), XRD (P.A. Nalytical X-pert), and XPS (PHI Quantum 2000).

2. XPS analysis of PtPb/C catalyst

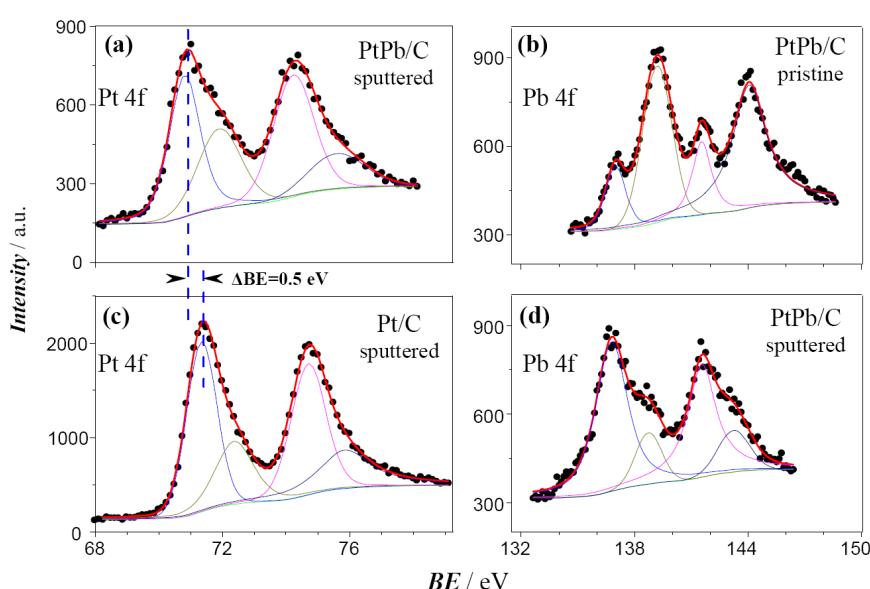


Fig. S1 XPS spectra of (a) sputtered PtPb/C and (c) commercial Pt/C catalyst in Pt4f regions, and of PtPb/C in Pb4f regions (b) before and (d) after sputtering

Surface composition and chemical state of the PtPb/C catalyst were analyzed by XPS. Fig. S1a shows the Pt 4f core region spectra for the sputtered surface of the PtPb/C. The $4f_{7/2}$ and $4f_{5/2}$ peaks at 70.9, 74.3 eV, can be attributed to metallic Pt, i.e., Pt(0). Several satellite peaks indicate the presence of higher oxidation states of Pt, such as PtO , PtO_2 ^{s1-s3}. It is interesting to note that the Pt4f binding energy (BE) of the PtPb/C is negatively shifted by 0.5 eV in comparison with that of the Pt/C (Fig. 2c)^{s3}, suggesting that the electronic environment surrounding the Pt atom is significantly changed due to the doping of Pb. Fig. S2b shows the Pb 4f spectra of the PtPb/C catalyst before sputtering. A couple of weak peaks at 137.0 and 141.5 eV are the $4f_{7/2}$ and $4f_{5/2}$ of metallic lead Pb(0), and the other couple of strong peaks at 139.2 and 144.1 eV correspond to Pb(II)^{s2, s4}. Clearly, the dominant Pb species is Pb(II) on the pristine surface, which may be attributed to the carbonate and/or hydroxyl species ($\text{PbCO}_3/\text{Pb(OH)}_2$)^{s2}. After sputtering the surface with Ar^+ ions, the Pb(0) peaks increases significantly (Fig. 2d).

The atomic concentrations were obtained from the XPS core level peak areas of the various components including Pt4f_{7/2}, Pb4f_{7/2} and their satellite peaks. The relative proportion of surface atoms of Pt, Pb, and the different metal oxidation states, presented in Table S1, were calculated using Eq. (1):

$$\frac{c_i}{\sum c_i} = \frac{A_i / S_i}{\sum (A_i / S_i)} \quad \text{Eq. (1)}$$

where c_i , A_i , and S_i are, respectively, the atomic surface concentration, the corresponding core level peak area, and the sensitivity factor of the surface species i .

Based on the XPS spectra shown in Fig. S1, the following composition of PtPb/C catalyst was obtained:

Table S1. Relative proportion of surface atoms for pristine and sputtered surface of PtPb/C catalyst

	Pt	Pb	PtO_x	$\text{PbCO}_3/\text{Pb(OH)}_2$
Pristine surface	30.5%	12.5%	19.2%	37.8%
Sputtered surface	34.4%	38.7%	19.8%	7.2%

3. Electrode preparation and electrochemical measurement

Electrode preparation: 5 or 25 μL suspension (0.20 mg Pt mL⁻¹) of PtPb/C catalyst was spreaded on the glassy carbon electrode. As soon as the electrode was dried under infrared lamp, 2 μL Nafion diluents (0.1 wt. % Nafion® solution) was coated onto the surface of catalyst. Suspensions of Pd black catalyst (Alfa Aesar®, Johnsom Matthey Company, surface area $\sim 20 \text{ m}^2\text{g}^{-1}$) and 20 wt. % Pt/C catalyst (Alfa Aesar®, Johnsom Matthey Company, HiSPEC™ 3000) were also spreaded onto the glassy carbon electrodes using the same method. The precious metal (Pt or Pd) loading on each glassy carbon electrode was 1 μg for cyclic voltammetry test, and 5 μg for chronoamperometry (i.e., current ~ time) test.

Electrochemical measurements: The electrochemical measurements were carried

out in a conventional three-electrode cell using EG&G 273A potentiostat/galvanostats. A platinized Pt foil was used as counter electrode, and a reversible hydrogen electrode (RHE) was used as reference electrode. Cyclic voltammetry for oxidation of formic acid was recorded in a solution of 0.5 M HCOOH + 0.1 M H₂SO₄ at a sweep rate of 50 mV s⁻¹. Chronoamperometry was carried out at 0.30 V in the same solution. Formica acid (88%, Analytical reagent) and sulfuric acid (98%, Guaranteed reagent) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All solutions were prepared with 18 MΩ Millipore water and deaerated with high-purity nitrogen (Linde, purity > 99.99%) for at least 20 min before each experiment. All of the electrochemical measurements were carried out in 30±1 °C water bath.

4. Electrochemical *in situ* FTIR reflection spectroscopy

Electrochemical *in situ* FTIR reflection spectroscopic studies were carried out on a Nexus 870 FTIR spectrometer (Nicolet) equipped with a liquid-nitrogen-cooled MCT-A detector, an EverGlo IR source, which has been detailed previously.^{s5} In this configuration, infrared radiation sequentially passed through a CaF₂ window and a thin-layer solution (~ 10 μm), and then it was reflected by the electrode surface. As a result, both dissolved substances in the thin-layer solution and adsorbed species on electrode surface can be detected. The resulting spectra were reported as relative change in reflectivity, that is,

$$\frac{\Delta R}{R} = \frac{R(E_S) - R(E_R)}{R(E_R)} \quad (1)$$

where $R(E_S)$ and $R(E_R)$ are the single-beam spectra collected at sample potential E_S and reference potential E_R , respectively. By this definition, the downward bands in the resulting spectra indicate the formation of products, while upward bands denote the consumption of reactants. The spectral resolution was 8 cm⁻¹.

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