

Supporting Information

Pd@Pt/C catalysts fabricated using chemisorbed CO as in-situ reductant: advanced catalytic behaviour for formic acid oxidation

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Experimental Section

Materials

The chemical reagent $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and sodium ascorbic acid was purchased from Sinopharm Chemical Reagent Co.,Ltd. (Shanghai, China). Nafion solution (5 wt.%) was purchased from Dupont Co. (USA). Sulfuric acid was purchased from Beijing Chemical Co. (China). Distilled water (18.2 M Ω) was used to prepare the solutions. All the chemicals were of analytical grade and used as received unless otherwise noted.

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 the mixture of 5mg catalysts, 1mL ethanol, and 50 μL 5wt.% Nafion solutions. 5 μL catalyst inks was pipetted and spread on the

glassy carbon disk. A Pt foil and a SCE were used as the counter and reference electrodes, respectively. All electrolyte solutions were deaerated by high-purity nitrogen for 20 min prior to any measurement.

Electrochemical CO stripping voltammograms was carried out by oxidation of CO_{ad} in the 0.5 M H_2SO_4 solution at a scan rate of 20 mV s^{-1} . CO was bubbled into the 0.5 M H_2SO_4 solution for 30 min to allow the complete adsorption of CO onto the Pt when the working electrode was kept at open circuit, and excess CO in the electrolyte was then purged out with N_2 for 30 min. To investigate the stability of the chemisorbed CO, the excess CO were purged out with N_2 for different time and the following electrochemical CO stripping voltammograms were performed in another deaerated test cell.

Synthesis of shaped Pt nanoparticle

The Shaped Pt nanoparticles (Pt-S) synthesized according to the lecture.¹ Briefly, A total of 0.05 mmol of Pt ions H_2PtCl_6 , 0.75 mmol of tetramethylammonium bromide, and 1.00 mmol of poly(vinylpyrrolidone) (in terms of the repeating unit; M_w 29 000) were dissolved into 10 mL of ethylene glycol in a 25 mL round-bottom flask at room temperature. The mixed solution was heated to 180°C in an oil bath and held at 180°C for 20 min under argon protection and magnetic stirring, resulting in a dark brown solution. After the solution was cooled to room temperature, acetone (90 mL) was then added to form a cloudy black suspension, which was separated by centrifugation.

The product was collected and further washed three times by precipitation/dissolution.

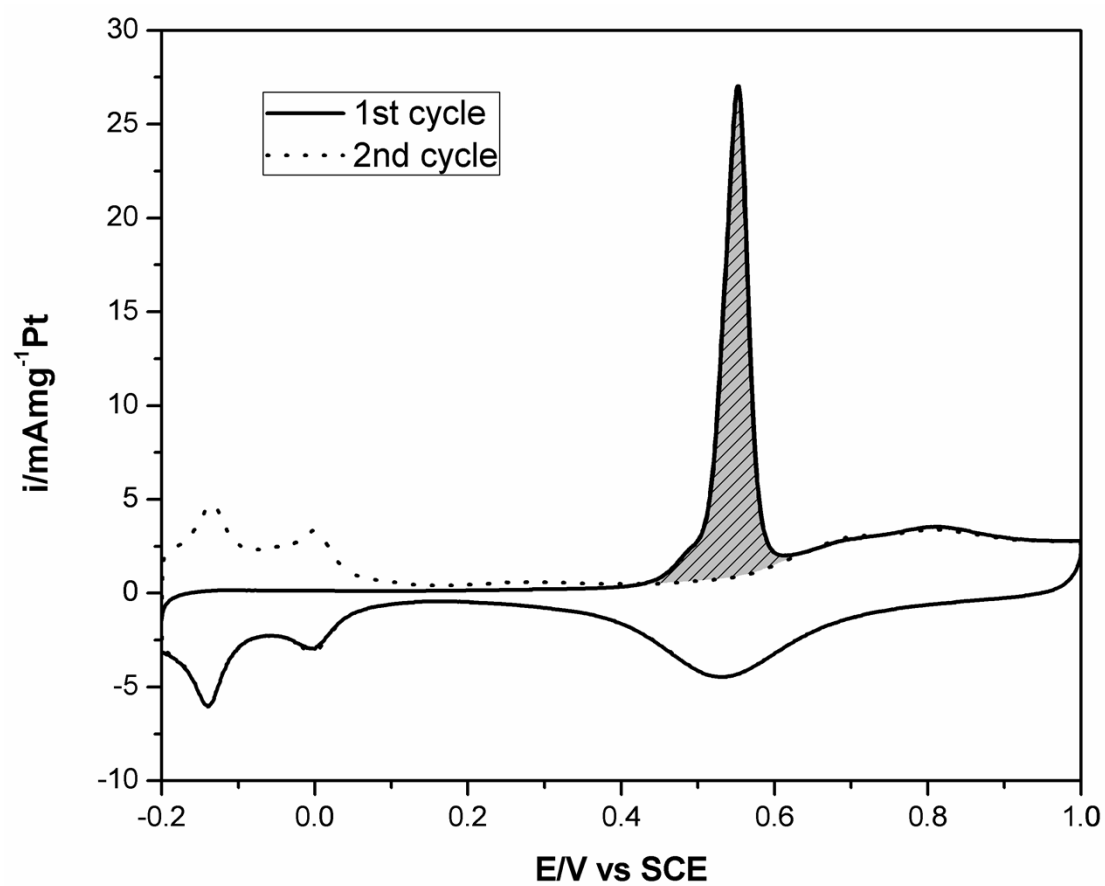
The nanocrystals were then redispersed in 10 mL of ethanol for characterization.

Synthesis of Pd@Pt samples

The Pd@Pt bimetallic sample (Pd@Pt-CO) was synthesized by the following procedure: 50 mg of commercial Pt black was dispersed in 0.1 molL⁻¹ HCl aqueous solution by ultrasonic to a conical flask with a fitted two-holed rubber stopper. After that CO was bubbled into the obtained mixture through the glass tubes inserted in rubber stopper under magnetic stirring. The bubbling was last for 30 min to allow the complete adsorption of CO onto the Pt black. N₂ was then bubbled for 30 min to purge out both the excess CO in solution and the H₂ generated from the progress of CO adsorption. And then 1.5 mg Pd²⁺ was added. The magnetic stirrering was lasted for another 30 min to allow the complete reduction. Finally, the formed nanoparticle were filtered and washed with hot distilled water until no Cl⁻ was detected. The Pd@Pt/C was prepared by similar procedure except that 7.5 mg Pd²⁺ was added for 50 mg Pt/C substrate. For the preparation of Pd@Pt-S, 5 mL ethanol dispersion of Pt-S was engaged and 4.9 μg Pd²⁺ were added. The Pd@Pt-H is synthesized for comparison based on commercial 60% Pt/C according to literature.²

Table 1. The electrochemically active surface area of commercial Pt black after bubbling N₂ for 0 min, 30 min and 60 min.

time(min)	0	30	60
ECSA(m ² /g)	13.5	12.8	12.1



FigureS1. CO_{ad} stripping voltammograms of JM Pt black in a 0.5 mol L⁻¹ H₂SO₄ solution at a scan rate of 20 mV s⁻¹.

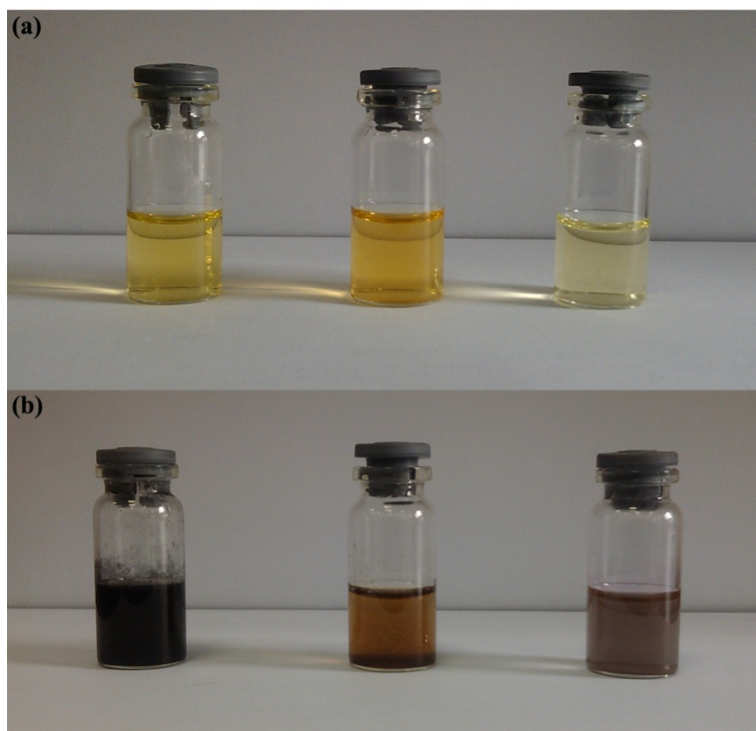


Figure S2. The picture of 5 mmolL⁻¹ PdCl₂, H₂PtCl₆, AuCl₃ before(a) and after(b) bubbling CO for 30 min

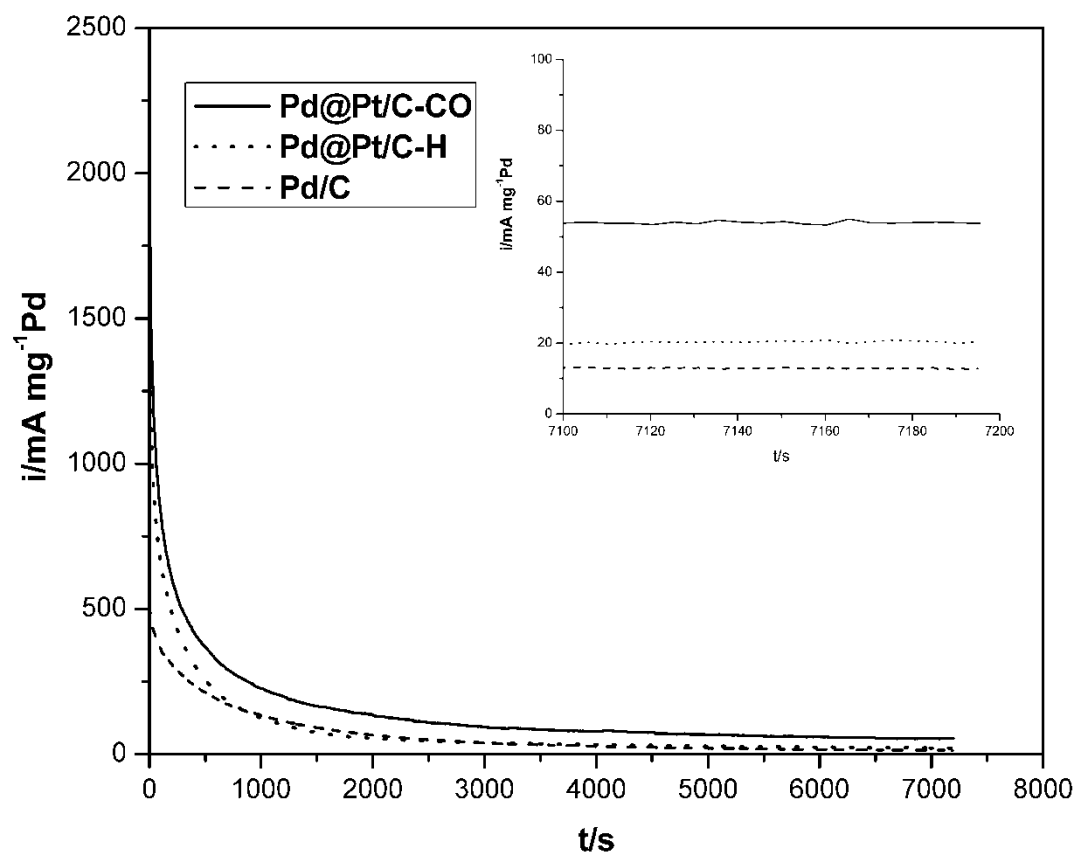


Figure S3. Chronoamperometric curves for **Pd@Pt/C-CO**, **Pd@Pt/C-H** and **Pd/C** catalysts in $0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4 + 0.5 \text{ mol L}^{-1} \text{HCOOH}$ solution at 0.1 V .

References

1. C.-K. Tsung, J. N. Kuhn, W. Huang, C. Aliaga, L.-I. Hung, G. A. Somorjai and P. Yang, *Journal of the American Chemical Society*, 2009, 131, 5816-5822.
2. L. Feng, F. Si, S. Yao, W. Cai, W. Xing and C. Liu, *Catalysis Communications*, 2011, 12, 772-775.