

Electronic Supporting Information:

PtCu/C synthesized with citric acid using galvanic displacement with high electrocatalytic activity toward methanol oxidation

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Methods

Materials. Commercial state-of-the-art 20 wt% Pt/C (Johnson Matthey Company, HiSPEC™ 3000) was used as the benchmark for comparison and was denoted as Pt/C-C. Sodium borohydride (NaBH_4 , 96%) and Copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) were obtained from Slonopharm Chemical Reagent Co. Ltd., Shanghai, China. Citric acid monohydrate was purchased from Beijing Chemical works. Chloroplatinic(IV) acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 37% Pt) was bought from Shanghai Reagent Factory. Vulcan carbon powder XC-72R was purchased from Cabot Co. (USA). Nafion solution (5%) was purchased from Dupont Co. (USA). All chemicals were used without further purification. Highly purified nitrogen ($\geq 99.99\%$), oxygen ($\geq 99.99\%$) and carbon monoxide ($\geq 99.99\%$) were supplied by Changchun Juyang Co Ltd. Ultrapure water (resistivity: $\rho \geq 18 \text{ M}\Omega\text{cm}^{-1}$) was used to prepare the solutions.

Catalyst synthesis. PtCu/C catalysts were synthesized by galvanic placement reaction from Cu/C. Briefly, 96 mg Vulcan XC-72R was dispersed into 120 mL DI water in a beaker under ultrasonic treatment for 1 h to form a uniform ink. Then 24 mL 0.01 M CuCl_2 aqueous solution was added with mechanical stirring. The stirring solutions were purged with Ar to eliminate O_2 from the

solution for 1 h previously; pre-prepared NaBH₄ solution (18.62 mg NaBH₄ with 12 mL DI water) were poured to the mixed suspension. After 3 h, proper amount of citric acid aqueous solution and 24 mL 0.005 M H₂PtCl₆ aqueous solution were added to the suspension successively and maintained stirring for another 12 h. During all the process, the beaker was maintained in water bath at 30 °C and Ar was purged to eliminate O₂. Finally, the suspension was filtered with filter paper, washed with excess DI water, and dried in air at 60 °C. Pt/C-H catalyst was prepared by the same process without the addition of CuCl₂ aqueous solution.

Physical characterizations. The metal loading was determined by inductively coupled plasma mass spectrometry (ICP-MS) (XSeries II ICP-MS, Thermo Electro). The X-ray diffraction (XRD) patterns were obtained using a PW1700 diffractometer (Philips Co.) with a Cu K α ($\lambda=1.5405\text{\AA}$) radiation source operating at 40 kV and 200 mA. The particle size and dispersion of the catalysts were analyzed by transmission electron microscopy (TEM) operating at 200kV (Philips TECNAI G2). X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB MK II photoelectron spectrometer (VG Scientific). The XPS experiments were performed in a spectroscopy chamber using a standard Al anode X-ray source. The C 1s electron binding energy was referenced at 284.6 eV.

Electrochemical measurements. The electrochemical measurements were performed with an EG&G Par potentiostat/galvanostat (Model 273A Princeton Applied Research Co. USA) and a conventional three-electrode electrochemical cell at the ambient temperature. A Pt foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All the potentials were quoted against the reference SCE. The working electrode was prepared as follows. First, 5mg of the catalyst was dispersed ultrasonically in 1mL alcohol and 50 μ L Nafion

solution (5wt%, Aldrich Co. USA) to obtain catalyst ink. Second, 10^μL of the as-prepared catalyst ink was pipetted and spread on the 5 mm diameter pre-cleaned glassy carbon electrode. At last, it was dried at room temperature for 30 min. The glass carbon electrode was polished with alumina slurry of 0.5 and 0.03^μm successively before use. N₂ was purged for 20min before starting the electrochemical experiments. To evaluate the activity of catalysts for methanol oxidation, the cyclic voltammetric experiments were performed in 0.5 M H₂SO₄+1.0 M CH₃OH solution at a scan rate of 50 mV s⁻¹. To estimate the stability of the catalysts, the chronoamperometric (CA) experiments were performed in the same solution at a potential of 0.5 V. The electrochemical surface areas (ESA) and the tolerance to CO poisoning were calculated by the CO stripping test, assuming that the Coulombic charge required for the oxidation of the CO monolayer is 420^μC cm⁻². All the measurements were carried out at room temperature and stable results were reported.

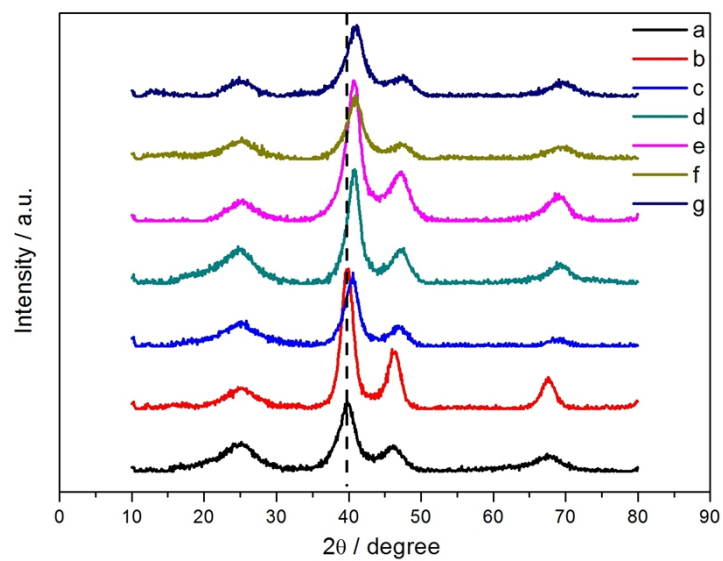


Fig. S1 XRD patterns of Pt/C-C (a), Pt/C-H (b), PtCu/C-1 (c), PtCu/C-2 (d), PtCu/C-3 (e), PtCu/C-4 (f) and PtCu/C-5 (g).

Table S1 The metal loading determined by ICP-MS for all the catalysts.

Catalysts	Cu / %	Pt / %
Pt/C-C	\	22.28
Pt/C-H	\	20.47
PtCu/C-1	1.789	20.49
PtCu/C-2	1.589	18.39
PtCu/C-3	1.683	19.33
PtCu/C-4	1.583	21.42
PtCu/C-5	1.755	20.54

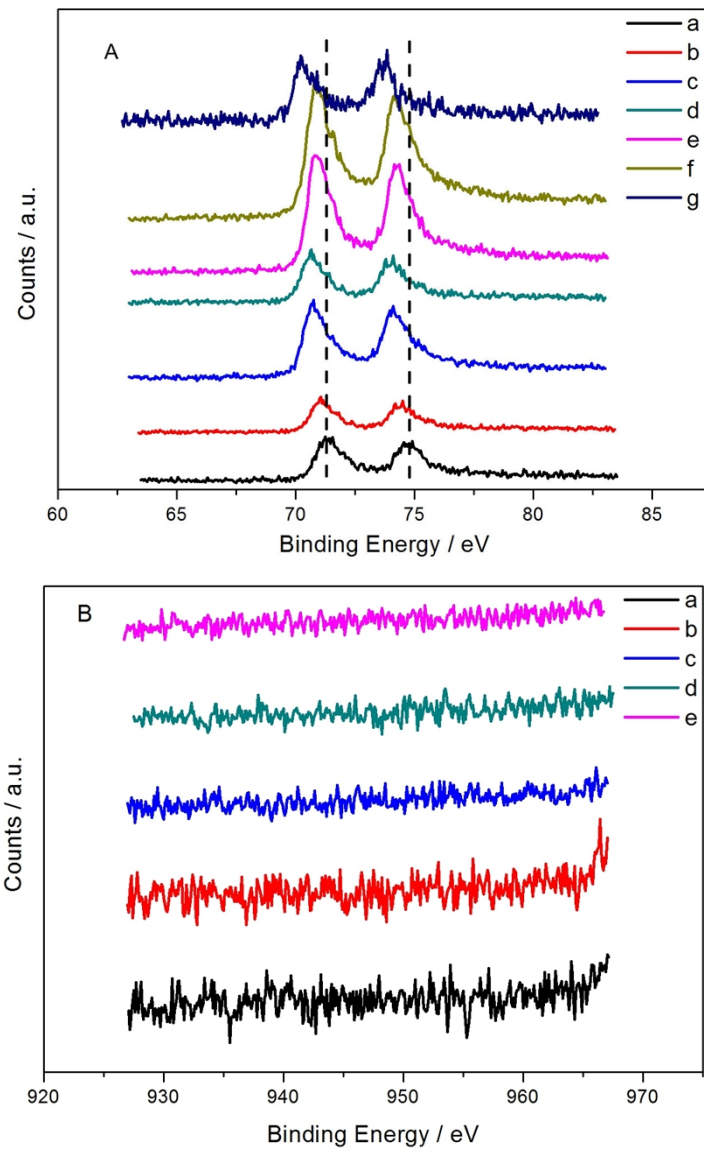


Fig. S2 X-ray photoelectron spectroscopy (XPS) of Pt 4f for Pt/C-C (a), Pt/C-H (b), PtCu/C-1 (c), PtCu/C-2 (d), PtCu/C-3 (e), PtCu/C-4 (f) and PtCu/C-5 (g) catalysts(A); XPS of Cu 2p for PtCu/C-1 (a), PtCu/C-2 (b), PtCu/C-3 (c), PtCu/C-4 (d) and PtCu/C-5 (e) catalysts (B).

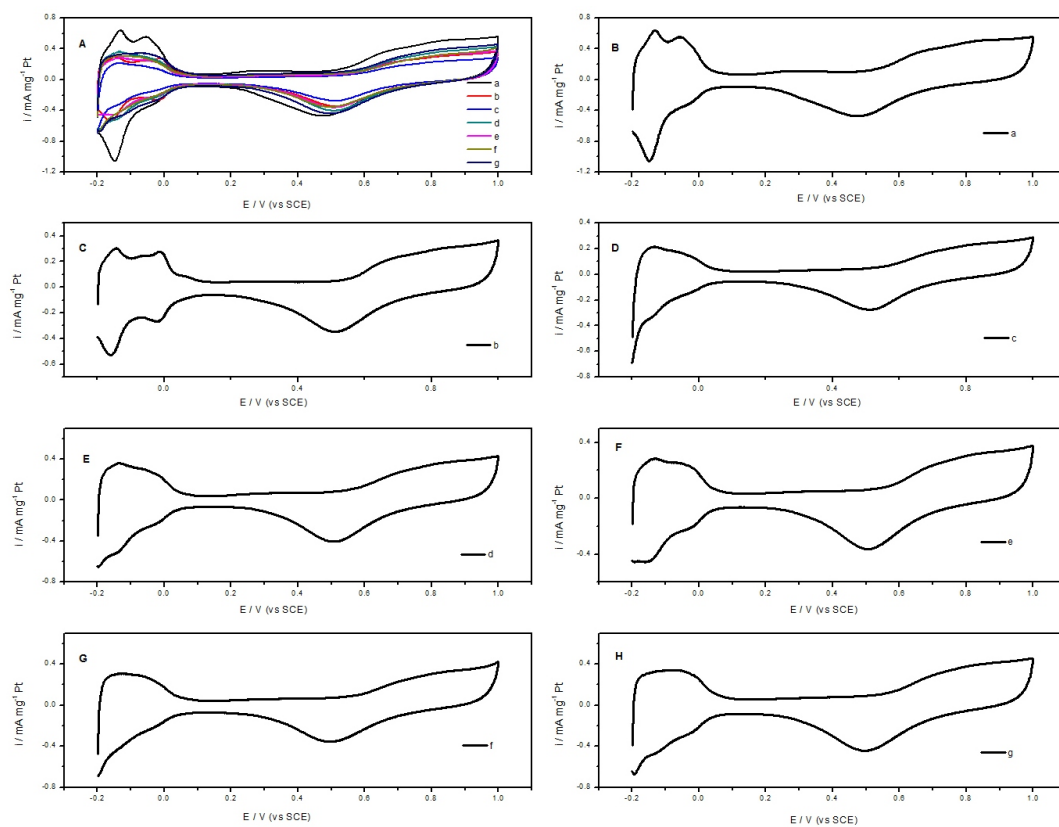


Fig. S3 CV of all the catalysts (A), Pt/C-C (B), Pt/C-H (C), PtCu/C-1 (D), PtCu/C-2 (E), PtCu/C-3 (F), PtCu/C-4 (G) and PtCu/C-5 (H) electrode in 0.5 M H_2SO_4 solution at the scan rate of 50 mV s^{-1} .

s^{-1} .

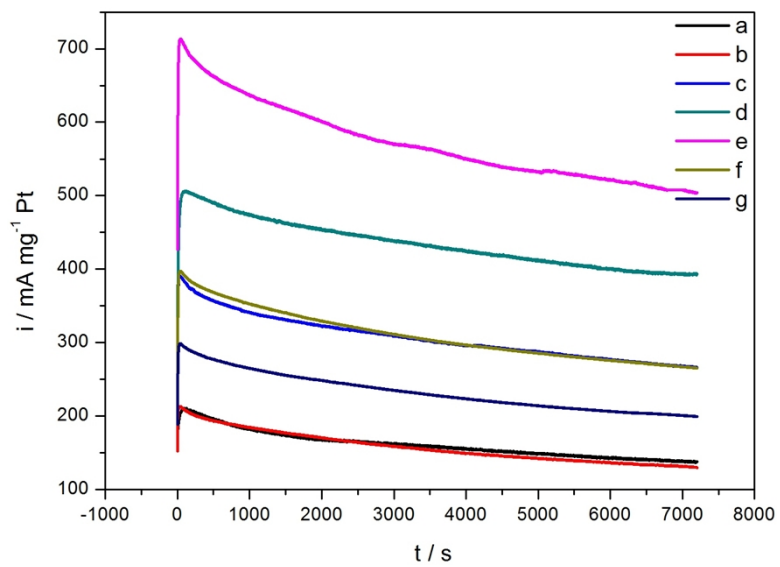


Fig. S4 CA response of methanol electrooxidation under constant potential of 0.5 V at Pt/C-C (a), Pt/C-H (b), PtCu/C-1 (c), PtCu/C-2 (d), PtCu/C-3 (e), PtCu/C-4 (f) and PtCu/C-5 (g) catalysts in 0.5 M H₂SO₄ + 1.0 M CH₃OH solution.

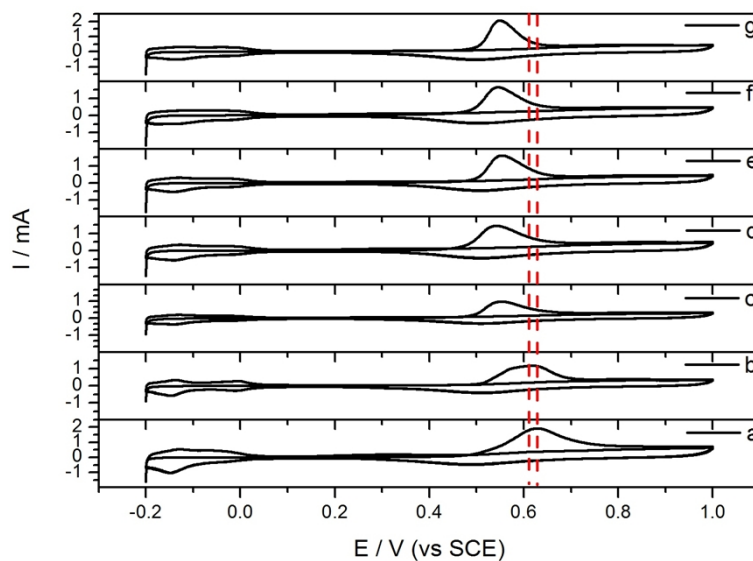


Fig. S5 CO-stripping voltammogram at the CO-adsorbed Pt/C-C (a), Pt/C-H (b), PtCu/C-1 (c), PtCu/C-2 (d), PtCu/C-3 (e), PtCu/C-4 (f) and PtCu/C-5 (g) catalysts in 0.5 M H₂SO₄ solutions at the scan rate of 50 mV s⁻¹.

Table S2 The electrochemical surface area (ECSA) calculated from CO_{ad} stripping voltammetry results for all the catalysts.

Catalysts	Pt/C-C	Pt/C-H	PtCu/C-1	PtCu/C-2	PtCu/C-3	PtCu/C-4	PtCu/C-5
ECSA (m ² g ⁻¹)	126	68.9	54.9	76.5	85.9	84.7	83.4