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Supplementary Information

Platinum-cobalt nanocrystals synthesized under different atmosphere for high catalytic performance of the methanol electro-oxidation

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Experimental section

Synthesis of Pt–Co alloy nanocrystals under air

For the synthesis of Pt–Co alloy NCs under air, PVP (MW = 30000, 220 mg), glycine (88 mg), 4 mL $CoCl_2$ solution (1.66 mM/L) and 1 mL H_2PtCl_6 solution (20 mM/L) were mixed and stirred for 30 minutes, and then sonicated in an ultrasonic bath for 5 min at room temperature. The resulting homogeneous yellow solution was transferred to a 30 mL autoclave.(the sealed autoclave was fed 1 MPa air gas when synthesized the Pt–Co alloy nanoparticles in air at 1 MPa conduction) The sealed vessel was heated at 200 ^{o}C for 7 h before it was cooled to room temperature. The products were separated via centrifugation at 9900 rpm for 15 minutes and further purified by ethanol solution for three times.

Synthesis of Pt–Co alloy nanocrystals under nitrogen

For the synthesis of Pt–Co alloy nanoparticles under nitrogen, PVP (MW = 30000, 220 mg), glycine (88 mg), 4 mL $CoCl_2$ solution (1.66 mM/L) and 1 mL H_2PtCl_6 solution (20 mM/L) were mixed and stirred for 30 minutes, and then sonicated in an ultrasonic bath for 5 min at room temperature. The resulting homogeneous yellow solution was transferred to a 30 mL autoclave. The sealed vessel was eliminated air with nitrogen for three times (the sealed autoclave was fed 1 MPa nitrogen when synthesized the Pt–Co alloy NCs under the 1 MPa nitrogen conduction) and then heated at 200 ^{o}C for 7 h before it was cooled to room temperature. The products were separated via centrifugation at 9900 rpm for 15 minutes and further purified by ethanol solution for three times.

Synthesis of Pt–Co alloy nanocrystals under hydrogen

For the synthesis of Pt–Co alloy nanoparticles under hydrogen , PVP (MW = 30000, 220 mg), glycine (88 mg), 4 mL $CoCl_2$ solution (1.66 mM/L) and 1 mL H_2PtCl_6 solution (20 mM/L) were mixed and stirred for 30 minutes, and then sonicated in an ultrasonic bath for 5 min at room temperature. The resulting homogeneous yellow solution was transferred to a 30 mL autoclave. The sealed vessel was eliminated air with hydrogen for three times (the sealed autoclave was fed 1 MPa hydrogen when synthesized the Pt–Co alloy nanoparticles under the 1 MPa hydrogen conduction) and then heated at 200 ^{o}C for 7 h before it was cooled to room temperature. The products were separated via centrifugation at 9900 rpm for 15 minutes and further purified by ethanol solution for three times.

Characterization

The size and morphology of the NCs were determined by JEM 2100 transmission electron microscope (TEM) at 200 kV, and a Tecnai G2 F20 S-Twin high-resolution transmission electron microscope (HRTEM) operating at 200 kV. The samples were prepared by dropping ethanol dispersion onto carbon-coated copper grids with a pitettor, and the solvent was allowed to evaporate for TEM detection. The high-angle annular dark-field scanning TEM (HAADF-STEM) was determined by Tecnai G2 F20 S-Twin high-resolution transmission electron microscope (HRTEM) operating at 200 kV.

The X-ray diffraction (XRD) patterns of samples were recorded on a Bruker D8-advance X-ray powder diffractometer operated at voltage of 40 kV and current of 40 mA with CuK radiation (λ = 1.5406 Å).

Inductively coupled plasma optical emission spectrometry (ICP-OES): The ICP-OES of samples was performed on IRIS Intrepid II XSP (ThermoFisher). Working parameters: RF Power: 1150 W, Nebulizer Flow: 26.0 PSI, Auxiliary gas: 1.0 LPM.

Reagents and Chemicals

Hexachloroplatinic acid (H_2PtCl_6) and Cobalt chloride ($CoCl_2$) were analysis reagent (A.R.) and purchased from Sinopharm Chemical Reagent Co. Ltd. Poly(vinyl pyrrolidone) (PVP; MW= 30000) and glycine were A. R. and purchased from Sinopharm Chemical Reagent Co. Ltd. Methanol, sulfuric acid and ethanol were A.R. and purchased from Beijing Chemical Reagent Company. Commercial Pt black purchased from Alfa Aesar. All reagents were used as received without further purification. Deionized water was used for the synthesis of Pt nanocrystals.

Electrochemical measurements

Electrochemical experiments were carried out using CHI 650D electrochemical analyzer (CHI Instrument, CHN). A conventional three-electrode cell was used, including a saturated calomel electrode (SCE) as reference electrode, a Pt wire as counter electrode, and a glassy carbon (GC) electrode (3 mm in diameter) as working electrode. The electrode potentials presented in this paper are quoted versus the SCE.

A GC electrode was carefully polished with Al_2O_3 paste, and washed with deionized water before each experiment. After the electrode was dried, the solution mixed with water and ethanol dispersion of Pt–Co alloy NCs was dropped onto the GC electrode with the same loading of 6 μL. After evaporation of solvent under an IR lamp, the electrode was illuminated by a UV lamp (10 W, with 185 nm and 254 nm emissions) at the distance of about 3 mm for 12 h to remove the organic capping agents before electrochemical measurements. The electrode was then covered with 0.5 μL of 0.5 wt% Nafion (Alfa Aesar) in ethanol and dried in air. For comparison, the concentrations of commercial Pt black are equal to that of Pt–Co alloy NCs.

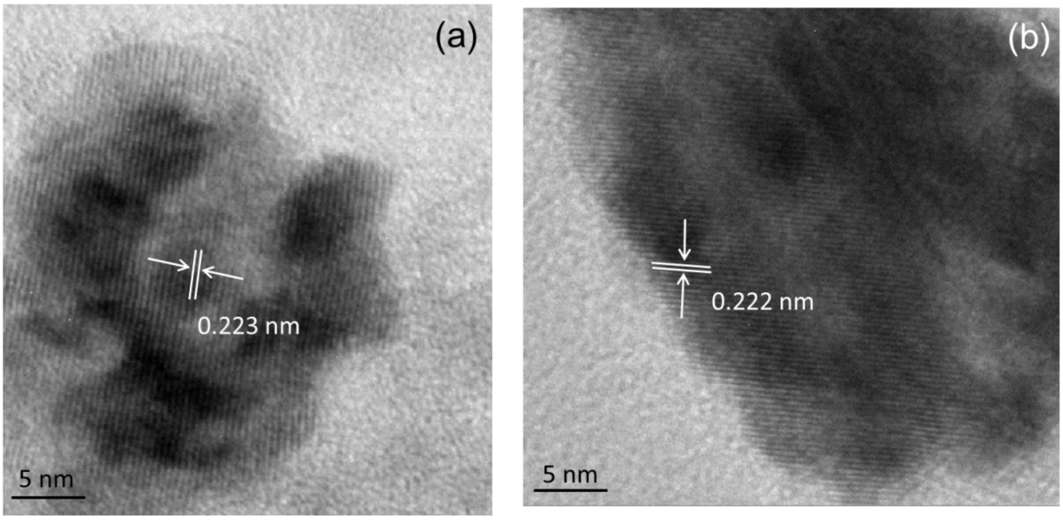

Fig. S1 HRTEM images of (a) Pt–Co (HAP) and (b) Pt–Co (NAP).

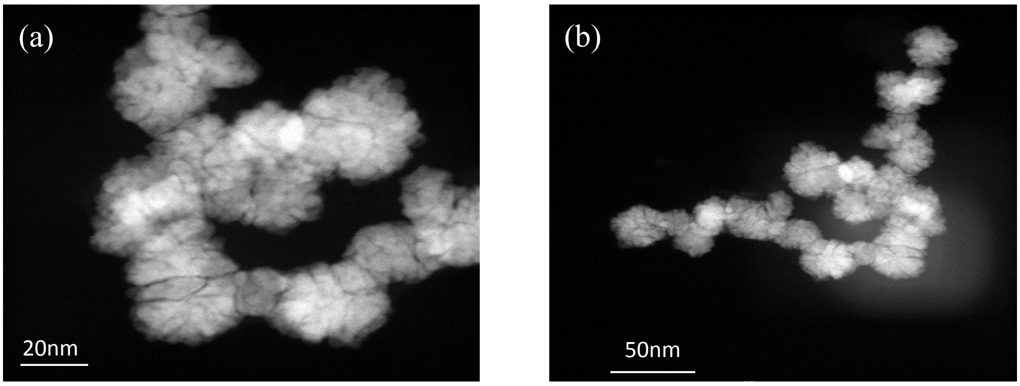

Fig. S2 The HAADF-STEM images images of products synthesized in nitrogen at 1 MPa

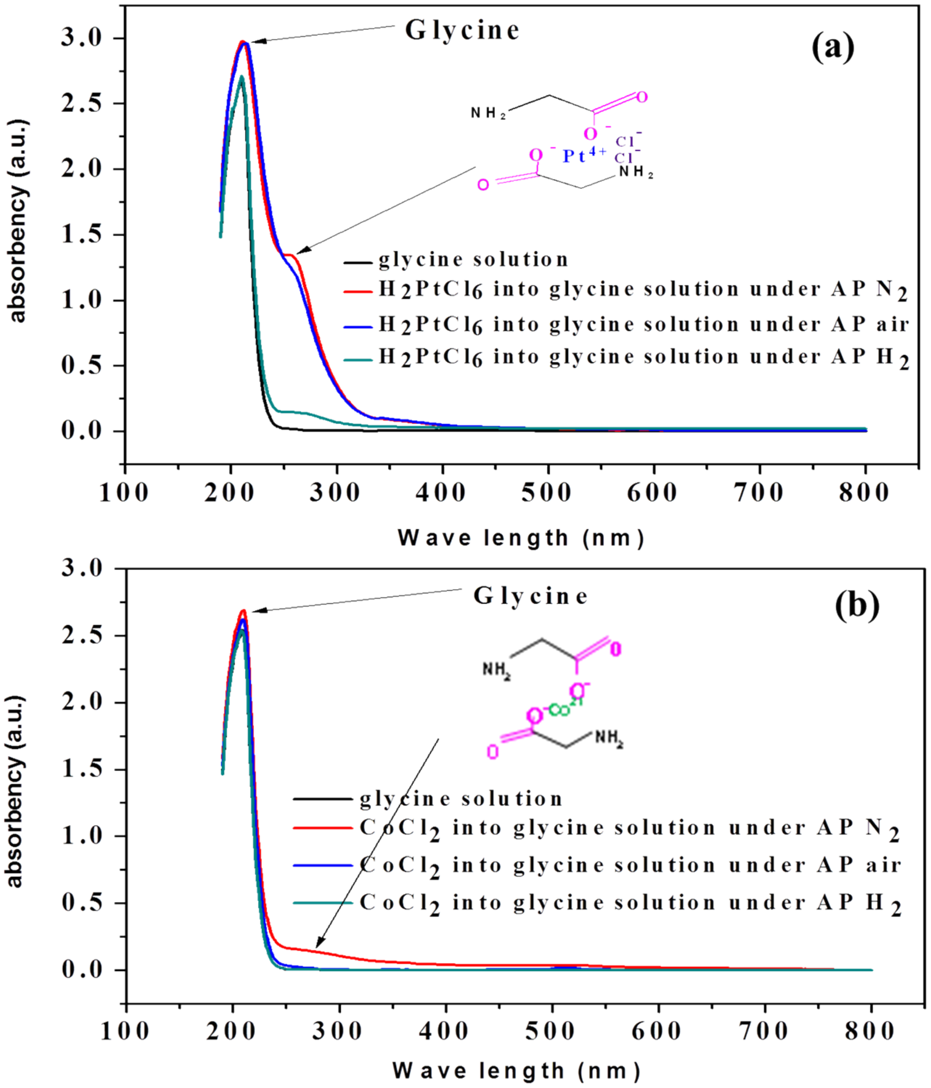

Fig. S3 Study of the interaction between the glycine and (a) H_2PtCl_6, (b)$CoCl_2$ in different atmosphere by UV-vis spectra at room temperature .

Air condition

The glycine solution was prepared with 88mg glycine added in 4 mL H_2O. 1 mL H_2PtCl_6 (20 mM/L) solution was added into the glycine solution and stirred for 30 min at room temperature and sonicated in an ultrasonic bath for 5 min. Then the solution was detected by UV-Vis spectrum.

The glycine solution was prepared with 88mg glycine added in 4 mL H_2O. 4 mL $CoCl_2$ (1.66 mM/L) solution was added into the glycine solution and stirred for 30min at room temperature and sonicated in an ultrasonic bath for 5 min. Then the solution was detected by UV-Vis spectrum.

Hydrogen condition

The glycine solution was prepared with 88mg glycine added in 4mL H_2O. 1mL H_2PtCl_6 (20mM/L) solution was added into the glycine solution. The air in sealed vessel was eliminated with hydrogen for three times. After that the solution was stirred for 30min at room temperature and sonicated in an ultrasonic bath for 5 min. Then the solution was detected by UV-Vis spectrum.

The glycine solution was prepared with 88mg glycine added in 4mL H_2O. 4mL $CoCl_2$ (1.66mM/L) solution was added into the glycine solution. The air in sealed vessel was eliminated with hydrogen for three times. After that the solution was stirred for 30min at room temperature and sonicated in an ultrasonic bath for 5 min. Then the solution was detected by UV-Vis spectrum.

Nitrogen condition

The glycine solution was prepared with 88mg glycine added in 4mL H_2O. 1mL H_2PtCl_6 (20mM/L) solution was added into the glycine solution. The air in sealed vessel was eliminated with nitrogen for three times. After that the solution was stirred for 30min at room temperature and sonicated in an ultrasonic bath for 5 min. Then the solution was detected by UV-Vis spectrum.

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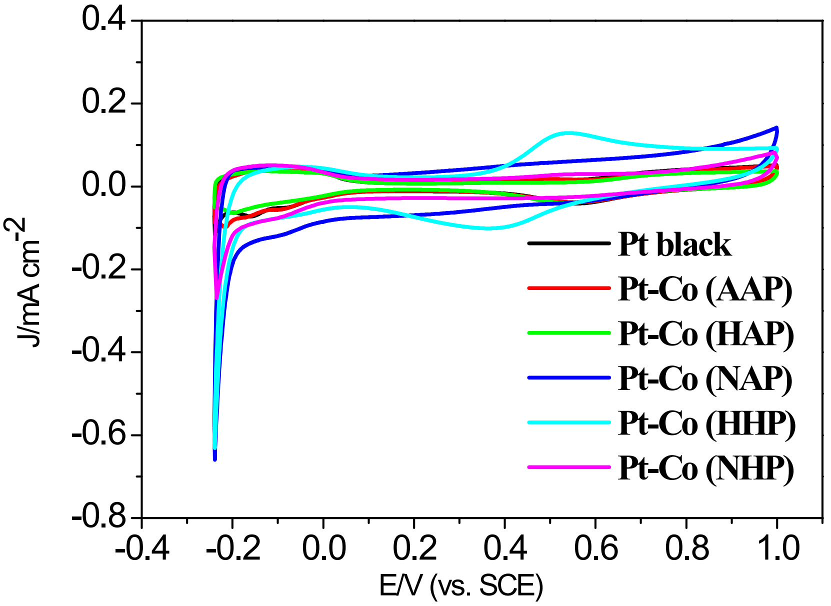

Fig. S4 CV curves of Pt–Co NCs in a N_2-purged 0.5 M H_2SO_4 solutionat a scan rate of 50 mV s^{-1}.

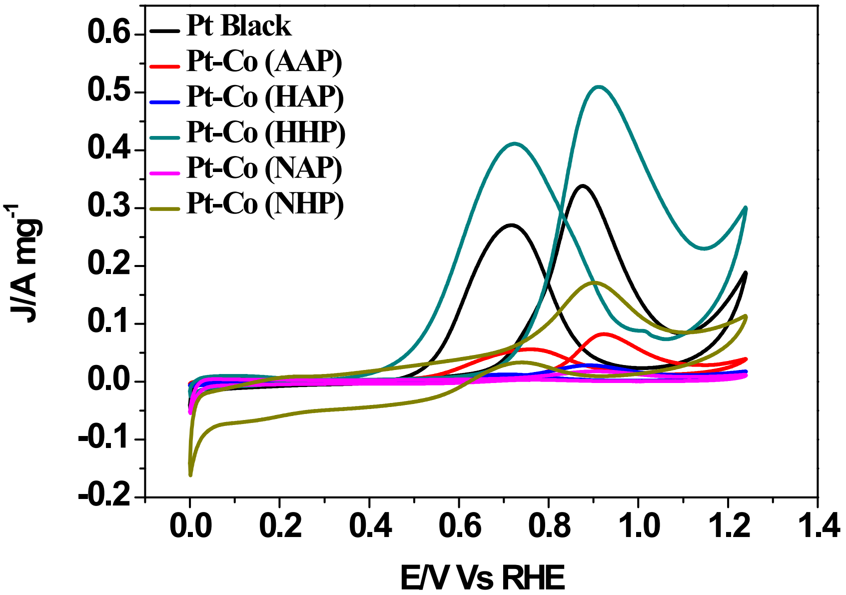

Fig. S5 Mass activity of the as-prepared Pt–Co NCs in 0.5 M H_2SO_4+ 2 M CH_3OH solution at a scan rate of 50 mV s^{-1}. It is seen that, 1 MPa Pt–Co NCs showed higher mass activity toward the electro-oxidation of methanol.