Supplementary Information

Tuning the surface structure of supported PtNi_x bimetallic electrocatalysts for methanol electro-oxidation reaction

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Experimental Section

Synthesis of bimetalic PtNi₂ NPs

The polyhedral PtNi₂ NPs were synthesized by solvothermal method. Platinum (II) acetylacetonate (\geq 98.0%; purchased from Yangzhou Additive Chemicals Company) and Nickel (II) acetylacetonate (\geq 99.0%; purchased from Yangzhou Additive Chemicals Company) were used as metal precursors. Benzyl alcohol (purchased from Sinopharm Chemical Reagent Co., Ltd) was used as solvent. The general procedure was as follows: the mixture with Pt(acac)₂ 62.7 mg, Ni(acac)₂ 48 mg and polyvinylpyrrolidone 480 mg (high

purity; Alfa Aesar) were dissolved in 30 ml benzyl alcohol and 0.6 ml aniline (purchased from Sinopharm Chemical Reagent Co., Ltd) by magnetic stirring for 30 min at room temperature (RT) to ensure that the powders were completely dissolved. Then the solution was moved to a sealed hydrothermal reactor and thermally treated at 150 °C for 12 h in an oven. After the reaction, the solution was cooled to RT, the PtNi₂ NPs were washed by acetone (purchased from Sinopharm Chemical Reagent Co., Ltd) and isolated by centrifugation (10000 rpm, 5 min).

Preparation of the supported electrocatalysts

PtNi₂ NPs were washed twice with the mixture of 15 ml ethanol and 15 ml acetone, after sonication the solid content was recovered by centrifugation. The obtained NPs were refluxed at 80 °C for 1 h in 10 ml chloroform (purchased from Sinopharm Chemical Reagent Co., Ltd) and 0.2 ml aniline, and then cool down and washed again. The NPs was sonicated for 2 h with 45 mg multilayer graphene (>98%, supplied by Shanxi Institute of Coal Chemistry, Chinese Academy of Sciences, and deal with HCl aquous before use) in 10 ml cyclohexane (purchased from Sinopharm Chemical Reagent Co., Ltd), then washed by ethanol and cyclohexane. After centrifugation, the sample was kept at 70 °C in 40 ml acetic acid (purchased from Sinopharm Chemical Reagent Co., Ltd) for 10 h. The obtained powders were washed with ethanol and dried at 80 °C in vacuum oven.

Surface reconstruction of PtNi₂ NPs induced by thermal annealing in different atmosphere

This process was processed in tube furnace. The furnace was fed 50 ml/min CO or Ar gas respectively, and heated from RT to 300 °C at the speed of 10 °C/min and kept at 300 °C for 4 h, and then it was naturally cooled down to RT. The CO thermal treatment condition should feed 10 min inert gas after experiment to reduce the CO density at the surface of sample.

Methanol electro-oxidation reaction

All the electrochemical measurements were carried out by Epsilon Electrochemical Station (PAR2273) at 25 °C with a graphite rod as counter electrode and Ag/AgCl as reference electrode. The working electrodes were prepared by coating 10 μ L of catalyst ink containing 5 wt % Nafion into glassy carbon electrode. To prepare the catalyst ink, 5 mg catalyst was ultrasonically dispersed into 1 mL of isopropanol. The MOR were conducted from -0.24 V to 1.05 V in N₂-saturated 0.5 M H₂SO₄ + 2.0 M CH₃OH solution at the scan rate of 50 mVs⁻¹. The stability at a constant potential of 0.7 V was studied by chronoamperometry for 1 h. The CO stripping was performed as follows: The CO gas was purged into the 0.5 M H₂SO₄ solution for 20 min while holding the electrode potential at - 0.05 V, and then the voltammogram for CO stripping was recorded from 0 to 1.0 V with scan rate of 50 mV s⁻¹.

Structure Characterization

PtNi₂/Gr, PtNi₂/Gr-CO and PtNi₂/Gr-Ar samples were ultrasonically dispersed in ethanol, and then a drop of the solution was placed on a holey C/Cu TEM grid to be used for the TEM characterization. FEI Tecnai G² F20 microscope and FEI Titan 80-300 Cs corrected microscope equipped with EDAX and HAADF detectors were used to perform structural investigations of the serials of PtNi₂ samples in both TEM and STEM modes. XRD patterns were measured on an X-ray diffractometer (Rigaku D/max 2400, Cu K α radiation, λ = 0.15418 nm) by depositing the sample on glass.



Fig. S1 XRD patterns of unsupported PtNi₂ (black), PtNi₂/Gr (red), PtNi₂/Gr-Ar (blue) and PtNi₂/Gr-CO (Magenta) samples. The dashed lines are the diffraction-peak positions of Pt (royal) and Ni (orange), referring to JCPDS cards of Pt (No.04-0802) and Ni (No.04-0850).



Fig. S2 Original high-resolution TEM images of Figures 2c and 2d (PtNi2/Gr sample).



Fig. S3 Low-magnification TEM image (a), HRTEM image (b), and EDS elemental maps (c) of PtNi₂/Gr-Ar sample. The inset in (b) is the corresponding local FFT.



Fig. S4 Low-magnification TEM image (a), HRTEM image (b), high-resolution STEM image (c), and EDS elemental maps (d) of PtNi₂/Gr-CO sample. The insets in (b) are the corresponding local FFT and shape of PtNi₂ NP.



Fig. S5 STEM images and corresponding EDS elemental maps of PtNi₂/Gr-Ar (a) and PtNi₂/Gr-CO (b) NPs.

Supporting Table

Table S1. ICP-MS results of Pt and Ni contents in PtNi₂/Gr, PtNi₂/Gr-Ar and PtNi₂/Gr-CO samples.

Samples	Pt wt%	Ni wt%	Х
PtNi ₂ /Gr	12.5	8.7	2.1
PtNi ₂ /Gr-Ar	13.8	8.8	2.1
PtNi ₂ /Gr-CO	14.6	8.9	2.0