Supplementary Information

Chemicals: Al(NO₃)₃, HClO₄, PVP (K 30), methanol and DMF were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Pt(acac)₂, Co(acac)₃, Ni(acac)₂ and Fe(acac)₃ were purchased from Alfa Aesar Chemical Co. Ltd.(USA). Formic acid was purchased from Acros organics (Belgium). Carbon black (Vulcan XC-72) was purchased from Carbot Corporation.

Characterizations: Powder X-ray diffraction patterns (XRD) were recorded with a Rigaku D/max 2500Pc X-ray powder diffractometer with monochromatized Cu K α radiation (λ = 1.5406 Å). Transmission electron microscopy (TEM) and high-resolution (HRTEM) images were recorded by a Hitachi HT7700 working at 100 kV and a FEI Tecnai G2 F20 S-Twin working at 200 kV. High-angle annular dark-field (HAADF) images were taken on a JEM-ARM200F atomic resolution analytical microscope operated at 300 kV. Inductively coupled plasma-optical emission spectrometer (ICP-OES) was measured by a Thermo fisher X2.

Method:

Preparation of PtAl truncated octahedron nanocrystals. 19.6 mg Pt(acac)₂ (0.050 mmol), 4.7 mg Al(NO₃)₃·9H₂O, 80 mg PVP (30 K) and 5 mL DMF were added into a 10 mL Teflon-lined stainless-steel autoclave. After vigorous stirring at room temperature, the solution was heated at 200 °C for 12 h. Then the sealed autoclave cooled down to room temperature. The black products were precipitated by acetone, separated via centrifugation, and further purified by an ethanol–acetone mixture. PtFe, PtCo, PtNi NCs were prepared using the same method, except the metal precursor dosages are 4.7 mg Al(NO₃)₃·9H₂O to 4.4 mg Fe(acac)₃, 4.5 mg Co(acac)₃ and 3.2 mg Ni(acac)₂ respectivly.

XPS Measurements:

XPS experiments were performed at the Photoemission Endstation at the BL10B beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The samples were deposited onto double-sided carbon tape for XPS spectrascopy.

EXAFS Measurements:

All of the XAFS measurements were carried out at the BL14W1 station in Shanghai Synchrotron Radiation Facility (SSRF, 3.5 GeV, 250 mA in maximum, Si (311) doublecrystals). The Pt L-edge spectra of PtAl NCs and Pt foil were recorded in transmission mode using ionization chamber. The acquired XAFS data were analyzed by Athena software, according to the standard procedures. The k²-weighted EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. χ (k) data of Pt L-edge in the k-space from 2.7-14.4 Å⁻¹ were Fourier transformed to real (R) space using a hanning windows (dk=1.0 Å⁻¹) to separate the EXAFS contributions from different coordination shells.

Electrochemical Measurements:

A three-electrode cell was used to do the electrochemical measurements. The 3 mmdiameter working electrode was prepared according to the reported method¹. Initially, 5 mg Carbon black (Vulcan XC-72) was dispersed in ethanol and sonicated for 1 h. After cooling to room temperature, as-prepared PtAl NCs dispersed in ethanol was added and mixed. Then the slurry was stirred for 24 h and ethanol was removed under reduced pressure. The solids were used for the electrochemical measurement without further pre-treatment and were dispersed in mixed solvent (H₂O: ethanol: 5% Nafion = 1: 1: 0.025) at a concentration of 2 mg/mL. For electrochemical measurement, 4 µL suspension of this PtAI/C catalyst was dropped on a glassy carbon electrode. The electrode was dried under ambient condition. Saturated Ag/AgCl was used as reference electrode and Pt wire was used as counter electrode. All electrochemical measurements were conducted at room temperature. Before the electrochemical surface area (ECSA) measurements, the electrode was immersed in argon saturated 0.1 M HClO₄ solution for 100 segments of cyclic voltammetry (CV) tests from 0.03 to 1.23 V vs reversible hydrogen electrode (RHE) at a scan rate of 100 mV/s. ECSA were determined by integrating the hydrogen adsorption charge on the CV at room temperature in argon saturated 0.1 M HClO₄ solution at a scan rate of 50 mV/s. Formic acid oxidation measurements were conducted in argon saturated mixed solution of 0.1 M HClO₄ and 1 M formic acid from 0.03 to 1.23 V (vs. RHE) at a scan rate of 50 mV/s. The stability tests were performed at room temperature in argon saturated mixed solution of 0.1 M HClO₄ and 1 M formic acid by applying cyclic potential sweeps between -0.03 and 1.23 V (vs. RHE) at a scan rate of 50 mV/s for 2000 cycles. For comparison, commercial Pt/C catalyst (Alfa Aesar, 20 wt. % Pt, Pt particle size: 3.4 ±1.4 nm) were used as the baseline catalysts, and the same procedure as described above was used to conduct the electrochemical measurement.





Table S1 | Relative content of different Al speciesAl speciespositonFWHMPeak areaAl³⁺119.521.32438.734Al⁰118.172.573298.857ratio:20:27





Fig. S4 Atomic-resolution STEM-BF (a) and HAADF-STEM (b) images of PtAl NCs, where the darker spots in the red cycle is Al atoms and other bright spots are Pt atoms. (c) The Z-contrast analysis of corresponding area (marked with blue arrow in (b)).



Fig. S5 | The EXAFS oscillation functions at the Pt L-edge of PtAl NCs and Pt foil.



Fig. S6] The cylic voltammograms curves (CVs) in 0.1 M HClO₄, room temperature, scan rate: 50 mV/s.





Fig. S8| The XRD pattern of PtCo NCs.





 $\label{eq:Fig. S10| (a) The CV curves of PtAl/C, Pt/C and PtCo/C. (b) The specific J_f values of PtAl/C, Pt/C, PtCo/C, PtNi/C and PtFe/C respectivly.$

Reference

1. H. Rong, J. Mao, P. Xin, D. He, Y. Chen, D. Wang, Z. Niu, Y. Wu and Y. Li, *Advanced Materials*, 2016, **28**, 2540-2546.