

## Supporting Information

### Two typical crystal growth modes to endow Pt-M (M = Cu, Fe, Zn, etc) bimetallic nanomaterials with abundant surface defects and robust catalytic properties

#### Experimental Section

**Chemicals and Materials:** Reagents including Hexachloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), Ethylene glycol (EG), Octadecylamine (ODA), Oleic acid (OA), Glucose and Heptanol were A. R. grade from Sinopharm Chemical Reagent Co., Ltd. Potassium tetrachloroplatinate ( $\text{K}_2\text{PtCl}_4$ ), Iron acetylacetonate ( $\text{Fe}(\text{acac})_3$ ) and Copper acetylacetonate ( $\text{Cu}(\text{acac})_2$ ) were purchased from Alfa Aesar. All of the chemicals were used without further purification.

**Characterization:** The powder XRD patterns were recorded with a Bruker D8-advance X-ray powder diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). TEM and HRTEM images were recorded by a JEOL JEM-1200EX working at 100 kV and a FEI Titan 80–300 transmission electron microscope equipped with a spherical aberration (Cs) corrector for the objective lens working at 300 kV. The composition of the product was measured by the inductively coupled plasma-mass spectrometry and energy dispersive X-ray spectrometer.

**Electrochemical measurements:** Electrochemical measurements were conducted on a computer-controlled electrochemical analyzer (CHI 660D, Chenhua, China) at room temperature. Pt/C or Pt-Cu modified glassy carbon (GC) electrodes were used as working electrodes, platinum spiral wire as counter electrode and Ag/AgCl (KCl-saturated) electrode as reference electrode. GC substrate electrodes were first polished with 0.3 and 0.05  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  slurry on a polishing cloth and then sonicated in ethanol and water each for several times. After the electrode was dried, 5  $\mu\text{L}$  Nafion dilutes (0.05 wt%) was coated on the catalyst surface. Aqueous solutions of 0.5 M  $\text{H}_2\text{SO}_4$  and 0.5 M  $\text{H}_2\text{SO}_4$  containing 2 M methanol were used for the electrolytes. ORR measurements were conducted in a 0.1 M  $\text{HClO}_4$  solution which was purged with oxygen during the measurement. The ORR polarization curves were collected at 1600 rpm. The accelerated stability tests were performed at room temperature in  $\text{O}_2$ -saturated 0.1 M  $\text{HClO}_4$  solutions by applying cyclic potential sweeps between 0.6 and 1.1 V versus RHE at a sweep rate of 50 mV/s for 8000 cycles. All electrochemical experiments were performed at room temperature.

**Synthesis of Pt-Cu octahedral nanocrystals.**

In a typical synthesis, 10.4 mg  $K_2PtCl_4$ , 6.6 mg  $Cu(acac)_2$  and 0.1 mL of ethylene glycol were mixed with 4.04 g ODA in a 25 mL round-bottom flask equipped with a magnetic stirrer and heated at 80 °C to form a clear solution. After being pumped on a vacuum line for 30 min, the flask was heated up to 160 °C and kept at that temperature for 180 min under a carbon monoxide balloon. Finally, dark brown precipitates could be obtained by cooling down to room temperature and then washed with hexane and ethanol for several times.

#### **Synthesis of Pt-Cu hexameric octahedral nanocrystals.**

In a typical synthesis, 13 mg  $H_2PtCl_6$ , 6.6 mg  $Cu(acac)_2$ , 20 mg glucose and 0.1 mL of ethylene glycol were mixed with 4.04 g ODA in a 25 mL round-bottom flask equipped with a magnetic stirrer and heated at 80 °C to form a clear solution. After being pumped on a vacuum line for 30 min, the flask was heated up to 160 °C and kept at that temperature for 180 min under a carbon monoxide balloon. Finally, dark brown precipitates could be obtained by cooling down to room temperature and then washed with hexane and ethanol for several times.

#### **Synthesis of Pt-Cu multimeric octahedral nanocrystals.**

In a typical synthesis, 13 mg  $H_2PtCl_6$ , 6.6 mg  $Cu(acac)_2$ , 20 mg glucose and 0.5 mL of heptanol were mixed with 4.04 g ODA in a 25 mL round-bottom flask equipped with a magnetic stirrer and heated at 80 °C to form a clear solution. After being pumped on a vacuum line for 30 min, the flask was heated up to 160 °C and kept at that temperature for 180 min under a carbon monoxide balloon. Finally, dark brown precipitates could be obtained by cooling down to room temperature and then washed with hexane and ethanol for several times.

#### **Synthesis of Pt-Fe nanocubes.**

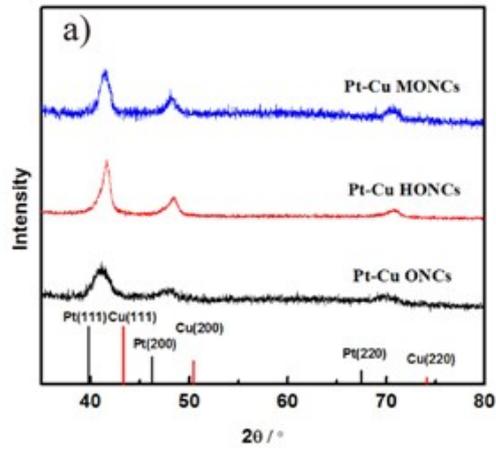
In a typical synthesis, 13 mg  $H_2PtCl_6$ , 8.8 mg  $Fe(acac)_3$ , 50 mg glucose and 0.5 mL of oleic acid were mixed with 4.04 g ODA in a 25 mL round-bottom flask equipped with a magnetic stirrer and heated at 80 °C to form a clear solution. After being pumped on a vacuum line for 30 min, the flask was heated up to 200 °C and kept at that temperature for 300 min under a carbon monoxide balloon. Finally, dark brown precipitates could be obtained by cooling down to room temperature and then washed with hexane and ethanol for several times.

#### **Synthesis of Pt-Fe concave nanocubes.**

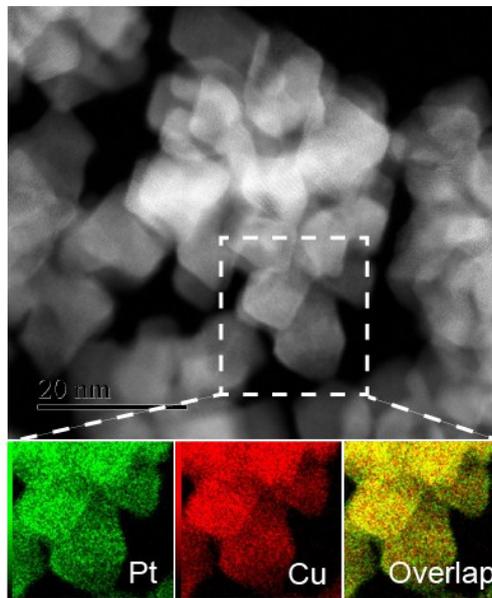
In a typical synthesis, 13 mg  $H_2PtCl_6$ , 8.8 mg  $Fe(acac)_3$ , and 50 mg glucose were mixed with 4.04 g ODA in a 25 mL round-bottom flask equipped with a magnetic stirrer and heated at 80 °C to form a clear solution. After being pumped on a vacuum line for 30 min, the flask was heated up to 180 °C and kept at that temperature for 300 min under a carbon monoxide balloon. Finally, dark brown precipitates could be obtained by cooling down to room temperature and then washed with hexane and ethanol for several times.

#### **Synthesis of Pt-Fe nanodendrites.**

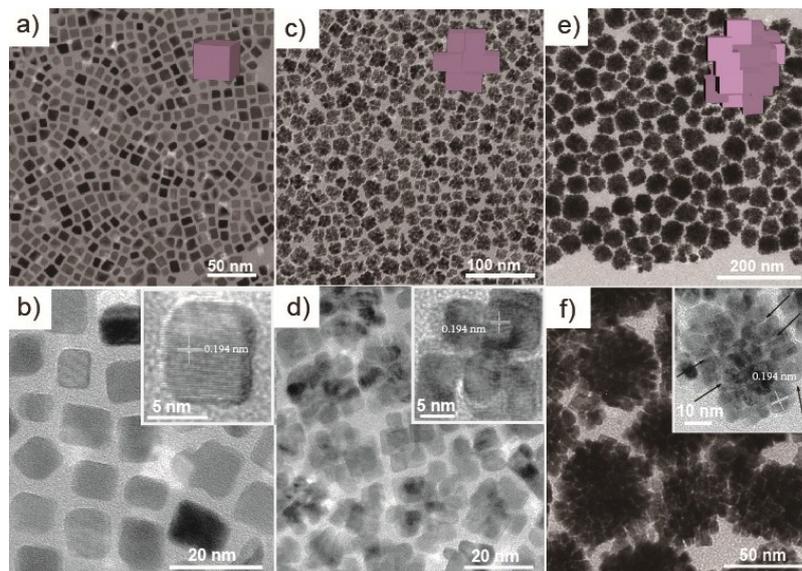
In a typical synthesis, 10.4 mg  $K_2PtCl_4$ , 8.8 mg  $Fe(acac)_3$ , 50 mg glucose and 0.5 mL of heptanol were mixed with 4.04 g ODA in a 25 mL round-bottom flask equipped with a magnetic stirrer and heated at 80 °C to form a clear solution. After being pumped on a vacuum line for 30 min, the flask was heated up to 180 °C and kept at that temperature for 300 min under a carbon monoxide balloon. Finally, dark brown precipitates could be obtained by cooling down to room temperature and then washed with hexane and ethanol for several times.



**Figure S1.** XRD patterns of Pt-Cu NCs.

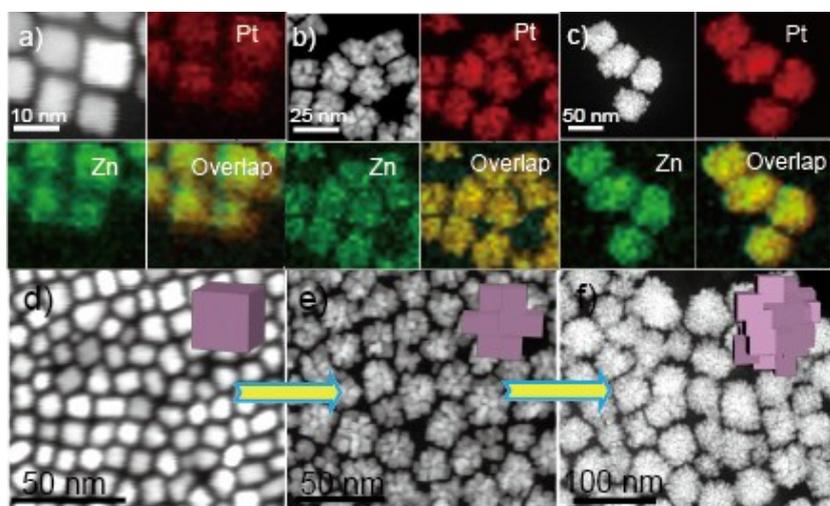


**Figure S2.** (e) HAADF-STEM images, and magnified EDX mapping of Pt-Cu MONCs.

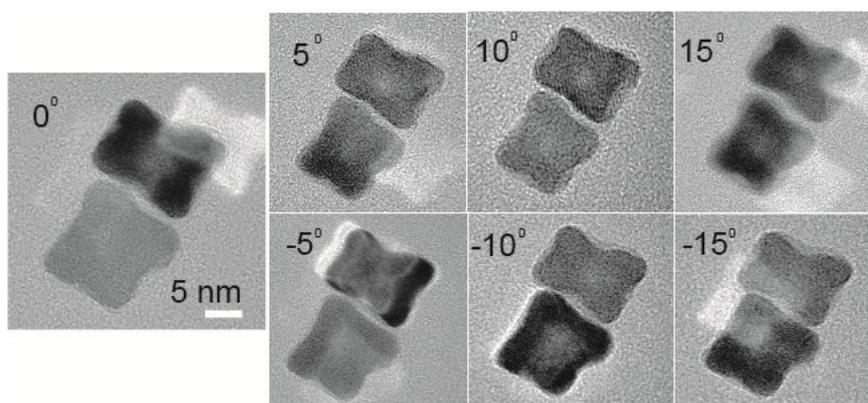


**Figure S3** (a) TEM (Top-right inset shows the ideal structure model), and (b) enlarged TEM (Top-right inset

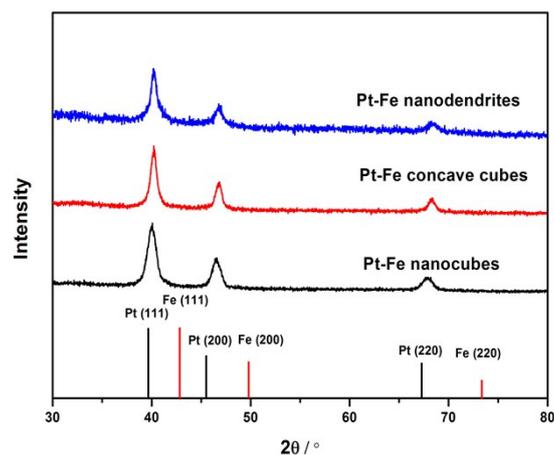
shows HRTEM image) images of Pt-Zn cubic NCs. (c) TEM and (d) enlarged TEM images of Pt-Zn dodecimeric cubic NCs. (e) TEM, and (f) enlarged TEM images of Pt-Zn multimeric cubic NCs. The black arrows indicate defects on the nanocrystals surface.



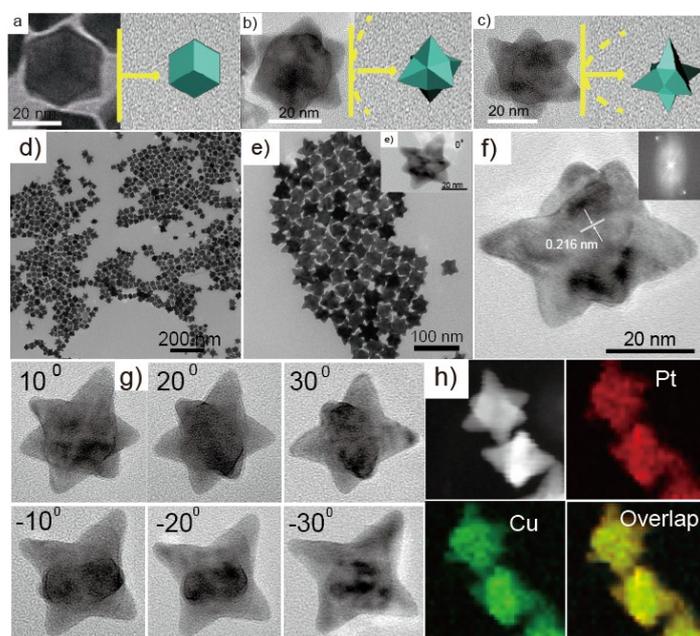
**Figure S4.** Composition and structure analyses for Pt-Zn NCs. EDX mapping and HAADF-STEM images of (a, d) Pt-Zn cubic NCs, (b, e) Pt-Zn dodecimeric cubic NCs, and (c, f) Pt-Zn multimeric cubic NCs.



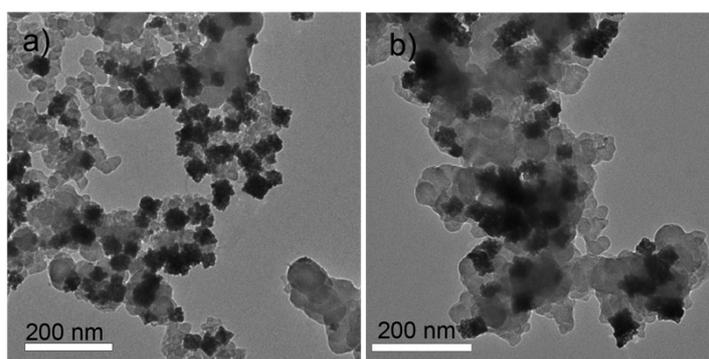
**Figure S5.** Tilted TEM images of the Pt-Fe concave nanocubes.



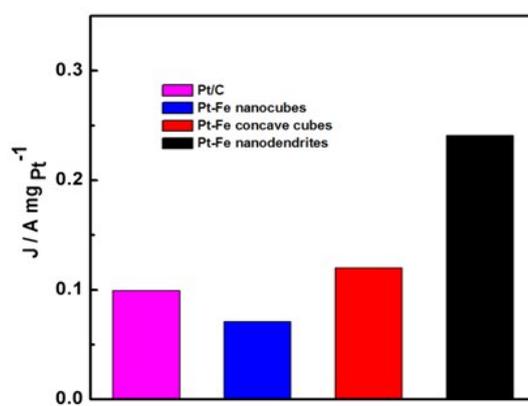
**Figure S6.** XRD patterns of Pt-Fe NCs.



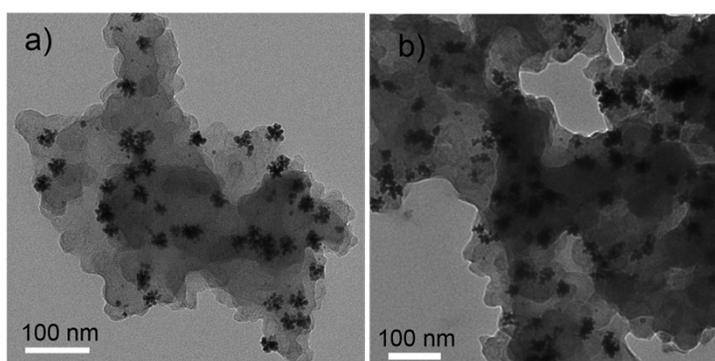
**Figure S7.** TEM images of the Pt-Cu NCs with (a) rhombic dodecahedron, (b) concave rhombic dodecahedron, and (c-e) concave hexapod structures and the corresponding models (the yellow line indicates the different degree of concavity). (f) HRTEM image of concave hexapod Pt-Cu NCs, the inset is the FFT pattern. (g) TEM images of concave hexapod Pt-Cu NCs with different angles. (h) EDS elemental maps of concave hexapod NCs.



**Figure S8.** Representative TEM images of a) fresh and b) the recycled catalyst;



**Figure S9.** ORR mass activity of Pt-Fe NCs.



**Figure S10.** Representative TEM images of a) fresh and b) the recycled catalyst;