Supporting Information for

Efficient Polyalcohol Oxidation Electrocatalysts Enabled by PtM (M=Fe, Co, Ni) Nanocubes Surrounded by (200) Crystal Facet

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Experimental section

Chemicals and Materials

Platinum (II) acetylacetonate ($Pt(acac)_2$, reagent grade, 97%), Nickel (II) acetylacetonate ($Ni(acac)_2$, 97%), Tungsten carbonyl ($W(CO)_6$, reagent grade, 98%) Oleylamine (OAm, 80%) and 1-octadecylene (ODE, reagent grade, 90%) were purchased from Sigma-Aldrich. Cobalt acetylacetonate ($Co(acac)_3$, 98%) was obtained from Aladdin Industrial Corporation. Iron acetylacetonate ($Fe(acac)_2$, 97%) and citric acid (CA, Analytical Reagent, ≥99.5%) were acquired from Shanghai Macklin Biochemical Co., Ltd. Commercial Pt/C catalyst (20 wt%) was obtained from Shanghai Hesen Electric Co., Ltd. The average particle size was 2.8 nm. All chemicals were used directly without further purification.

Preparation of Pt_4M (M=Fe, Co, Ni) NCs

In the synthesis of Pt_4Ni NCs, $Pt(acac)_2$ (10 mg), $Ni(acac)_2$ (3.3 mg), $W(CO)_6$ (5 mg) and CA (10 mg) were introduced into a glass vessel containing 3 mL of OAm, 2 mL of ODE and 0.1 mL of H_2O. After the mixture has undergone ultrasonic treatment for 1 h, the vessel was sealed and heated in oil bath at 160 ℃ and held for 5 h. Until cooling naturally, the product was centrifuged and washed with a mixture of cyclohexane and ethanol for three times. The Pt_4Fe NCs and Pt_4Co NCs were obtained by changing the 3.3 mg of $Ni(acac)_2$ into 3.3 mg of $Fe(acac)_2$ and 4.5 mg of $Co(acac)_3$.

Physical characterizations

The structure of product was observed on HITACHI HT7700 transmission electron microscope (TEM). The high-resolution TEM, STEM-EDS mapping, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), and the EDS line-scanning profile were performed on FEI Tecnai F20 TEM. The composition of element was detected on EVO 18 scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM-EDS). The crystal property was obtained on X'Pert-Pro MPD diffractometer (PANalytical, Netherlands) with a Cu Kα X-ray source (λ=1.540598 Å). And the X-ray photoelectron spectroscopy (XPS) was conducted on Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer.

Electrooxidation measurements

Before electrochemical tests, the collected Pt_4M NCs were supported on Vulcan XC72R carbon black, which was labeled as Pt_4M NCs/C, then were made into 0.4 $mg_{Pt}mL^{-1}$ catalysts suspension (containing 5% of Nafion). All measurements were performed on three-electrode CHI 660e electrochemical workstation. The glassy carbon electrode (GCE, diameter: 5 mm) covered with 5 μL of catalysts ink was used as the working electrode, the Pt wire as counter electrode and the saturated calomel electrode (SCE) as reference electrode. We scanned the cyclic voltammetry (CV) curves at a scanning rate of 0.05 V s^{-1} in 0.1 M $HClO_4$ solution with the potential range of -0.3~0.9 V. Then we conducted the GOR in 1 M KOH + 1 M glycerol mixed solution and the EGOR in 1 M KOH + 1 M EG solution with the range of -0.9~0.3 V. The chronoamperometry (CA) test was performed in the same mixed solution at -0.25 V for 3600 s. And the continuous CVs was carried out for 250 cycles. Furthermore, the electrochemical impedance spectroscopy (EIS) was tested to evaluate the electronic conductivity.

Supplementary Figures and Tables

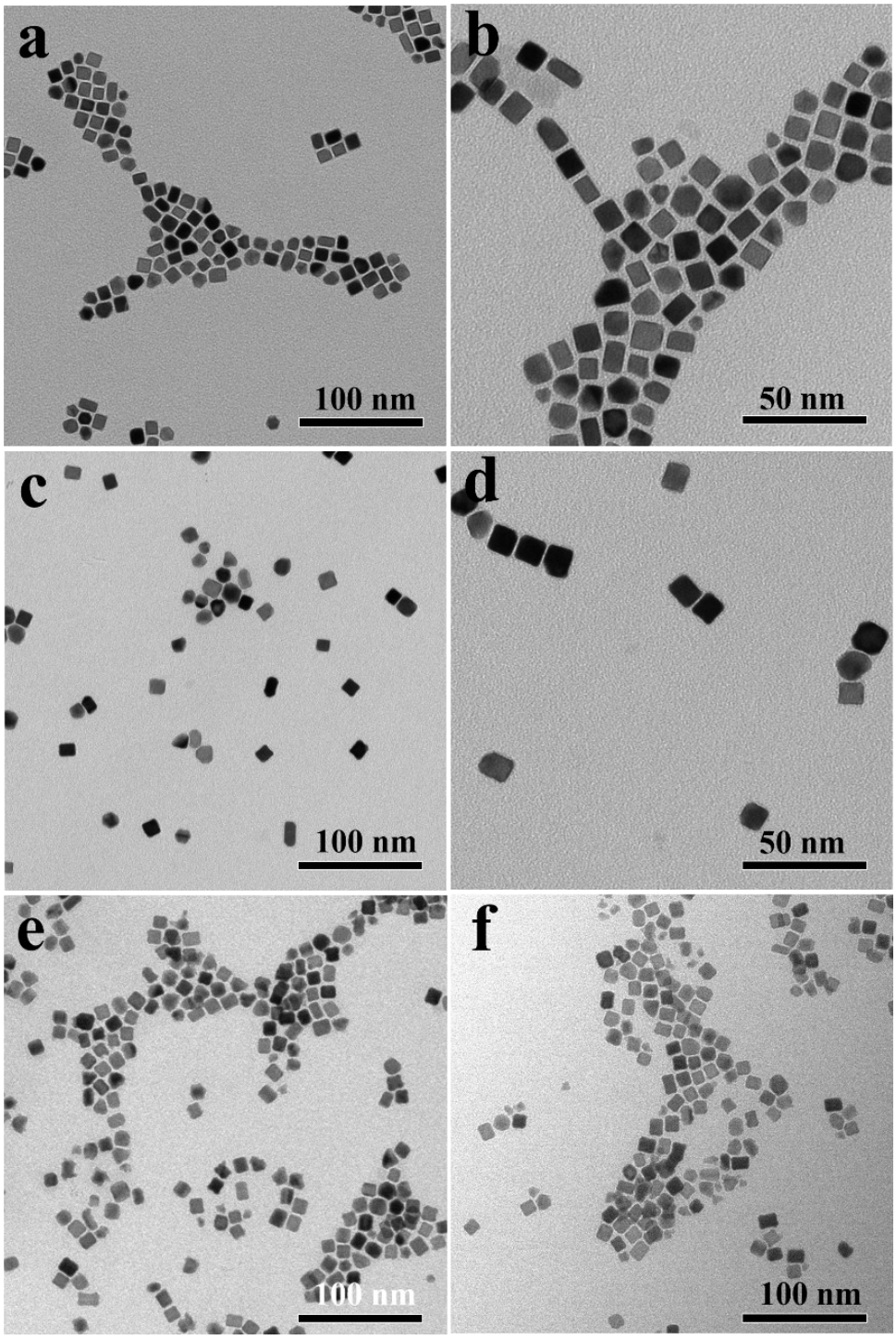

Fig. S1 Representative TEM images of the products with the same reaction conditions as that of Pt_4Ni NCs but changing the temperature: (a, b) 150 ℃, (c, d) 170 ℃, and (e, f) 180 ℃.

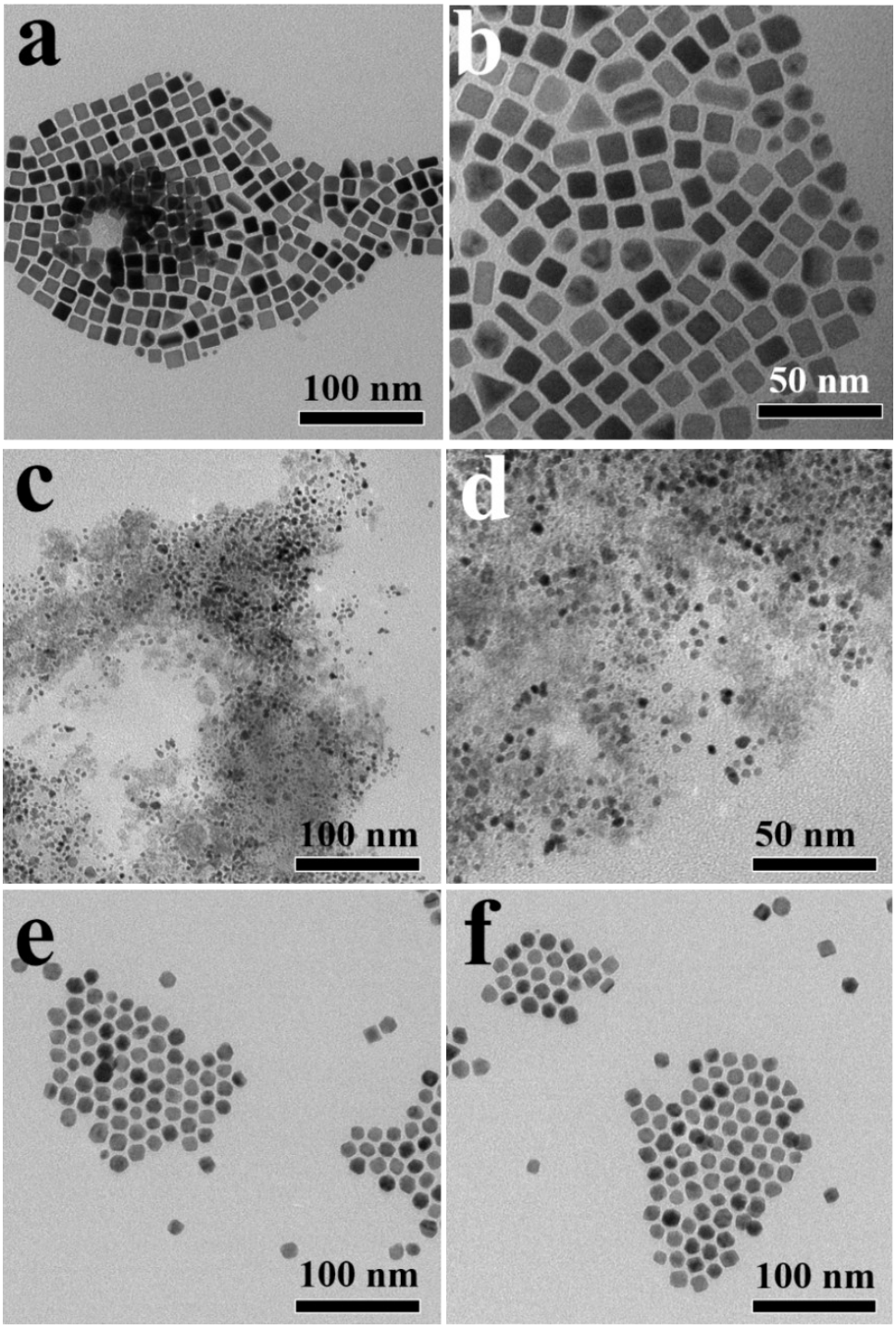

Fig. S2 Representative TEM images of the products with the same reaction conditions as that of Pt_4Ni NCs but changing the solvent: (a, b) 5 mL OAm, (c, d) 5 mL ODE, and (e, f) 4 mL OAm and 1 mL OA.

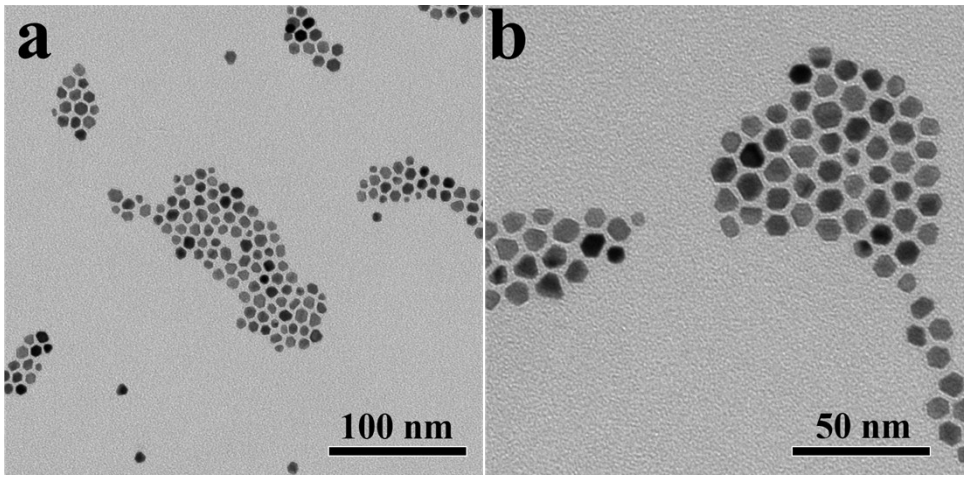

Fig. S3 Representative TEM images of the products with the same reaction conditions as that of Pt_4Ni NCs but without the water.

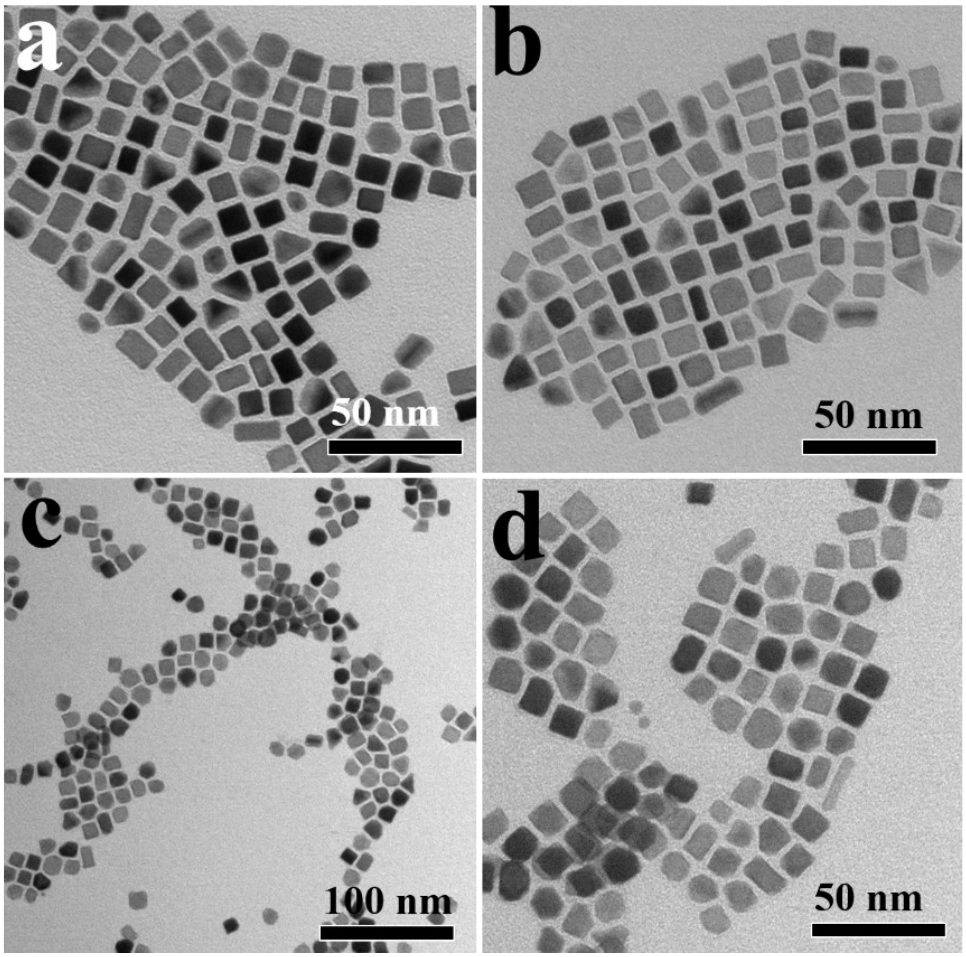

Fig. S4 Representative TEM images of the products with the same reaction conditions as that of Pt_4Ni NCs but changing the ratio of OAm to ODE: (a, b) 4 mL OAm and 1 mL ODE, and (c, d) 2 mL OAm and 3 mL ODE.

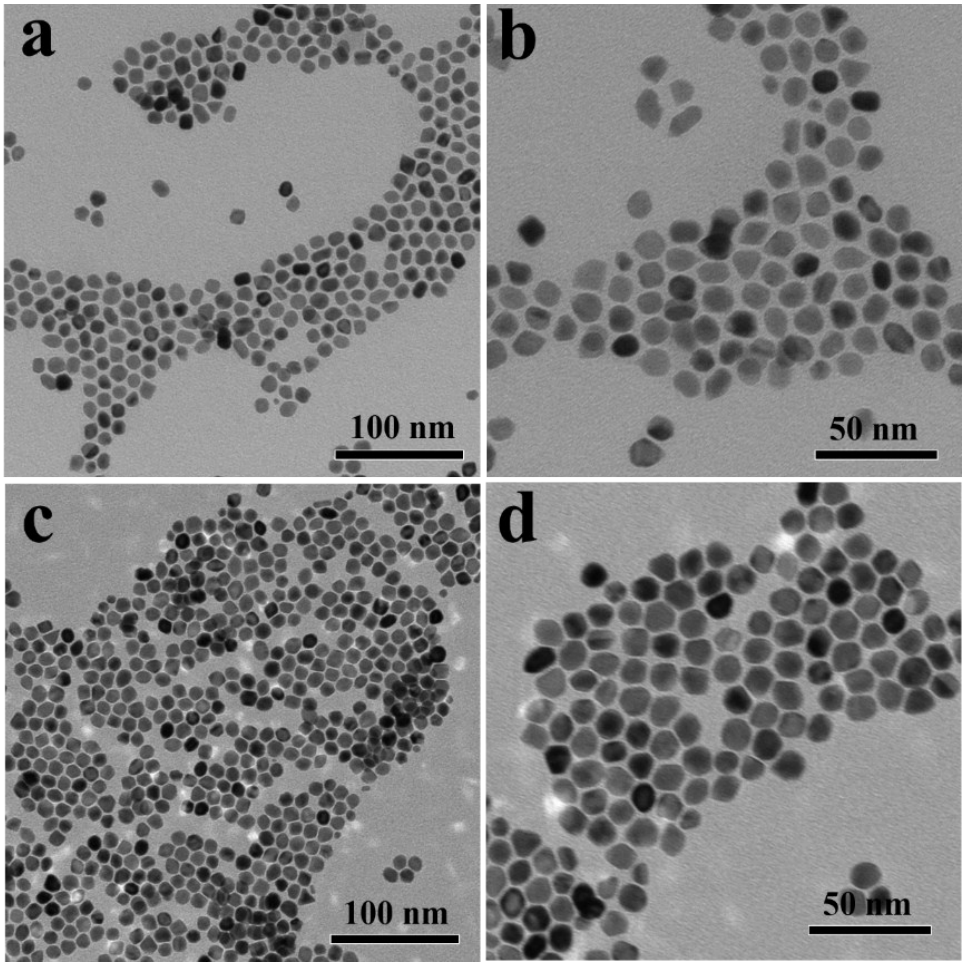

Fig. S5 Representative TEM images of the products with the same reaction conditions as that of Pt_4Ni NCs but varying amounts of $W(CO)_6$: (a, b) 10 mg, and (c, d) 20 mg. In the absence of $W(CO)_6$, the system has no products.

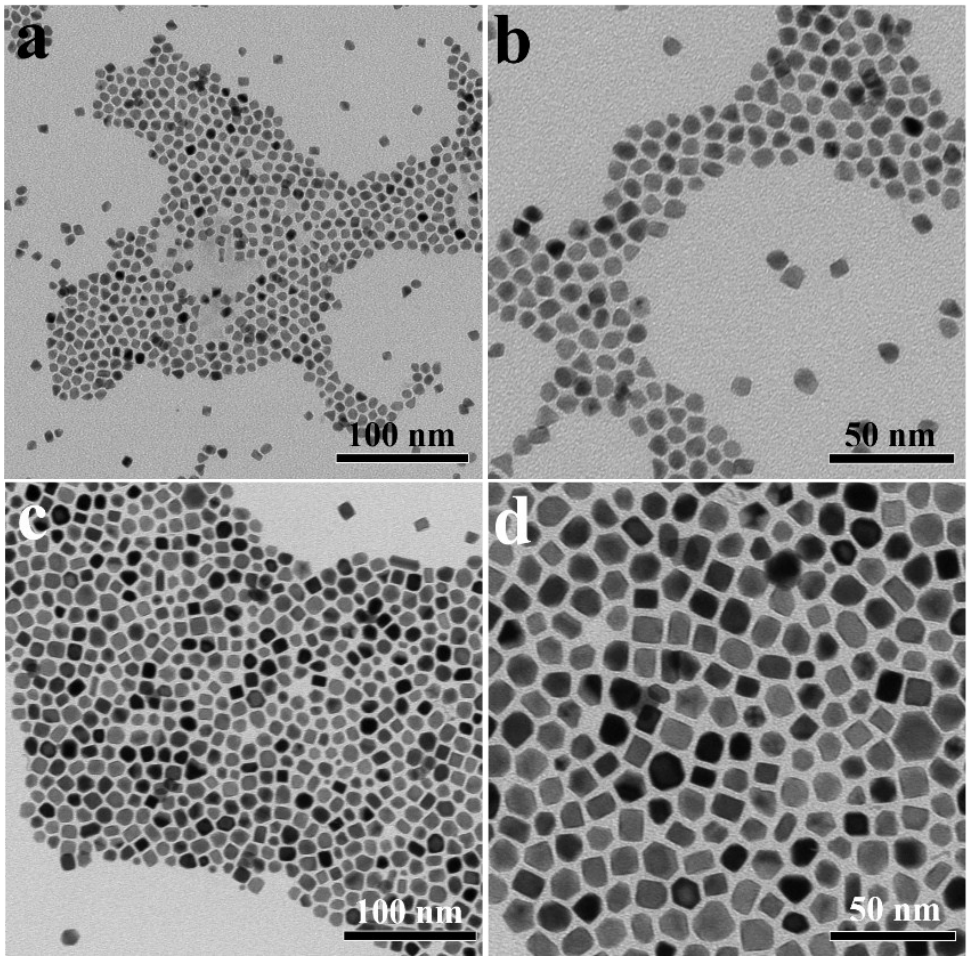

Fig. S6 Representative TEM images of the products with the same reaction conditions as that of Pt_4Ni NCs but varying amounts of CA: (a, b) 0 mg, and (c, d) 40 mg.

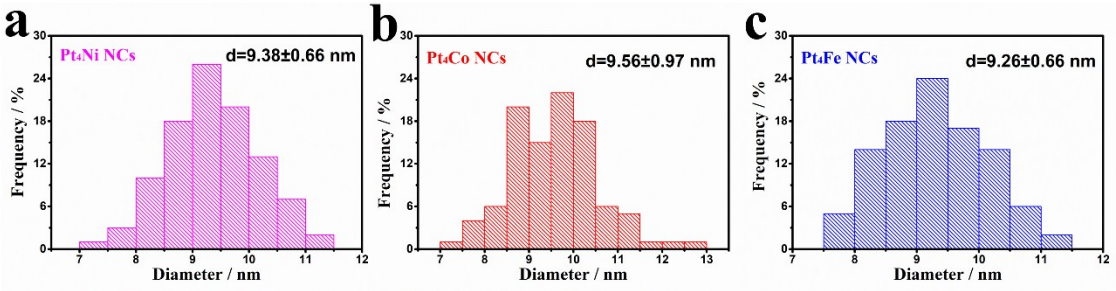

Fig. S7 The size distribution of (a) Pt_4Ni NCs, (b) Pt_4Co NCs, and (c) Pt_4Fe NCs.

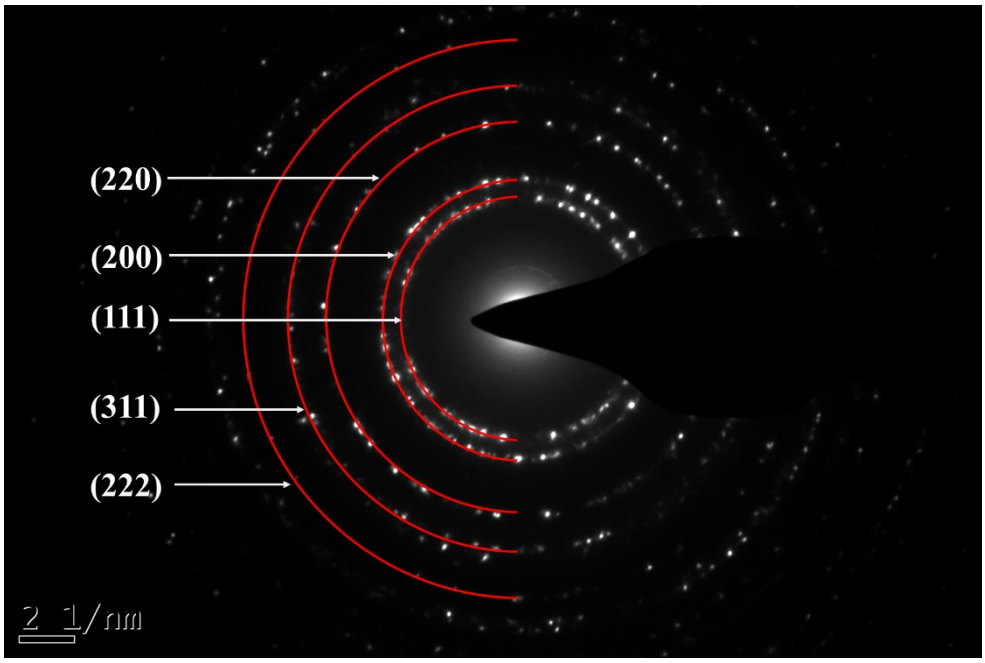

Fig. S8 The selected area electron diffraction pattern of the Pt_4Ni NCs.

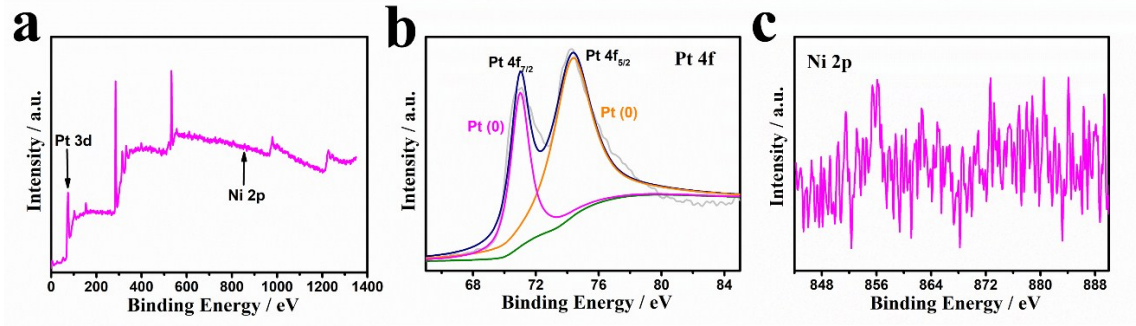

Fig. S9 The XPS analysis of (a) survey spectrum, (b) Pt 4f, and (c) Ni 2p in the Pt_4Ni NCs electrocatalysts.

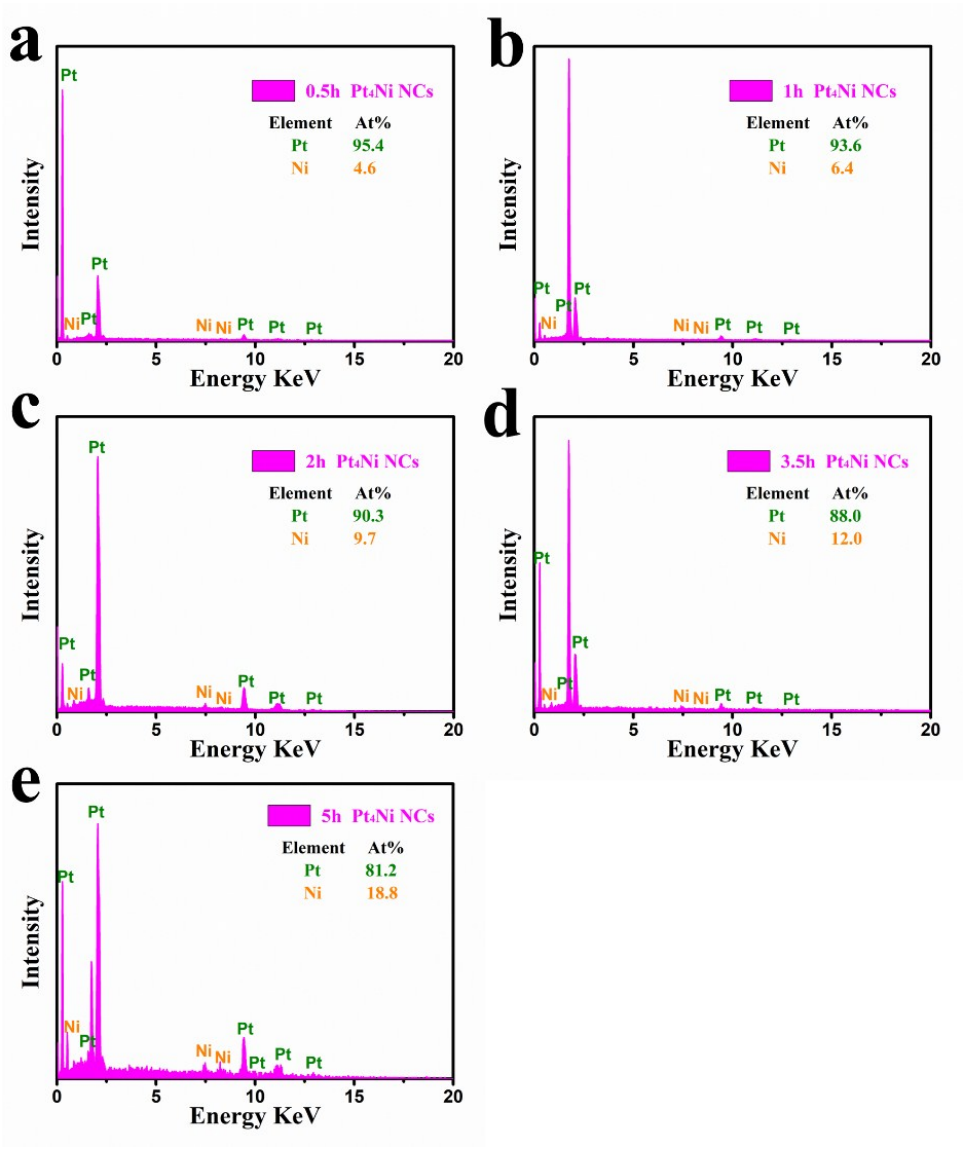

Fig. S10 The EDS spectrum of Pt_4Ni NCs intermediates obtained after the reaction have processed for (a) 30 min, (b) 1 h, (c) 2 h, (d) 3.5 h, and (e) 5h.

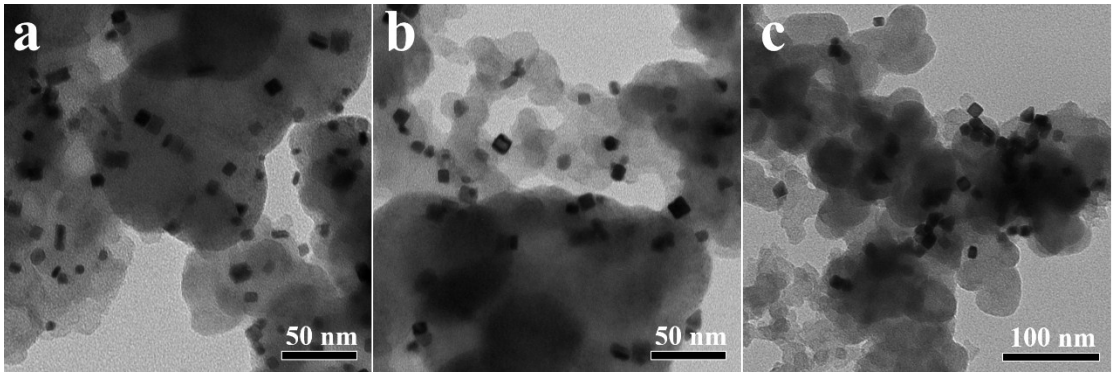

Fig. S11 The TEM images of (a) Pt_4Co NCs/C, (b) Pt_4Fe NCs/C, and (c) Pt_4Ni NCs/C.

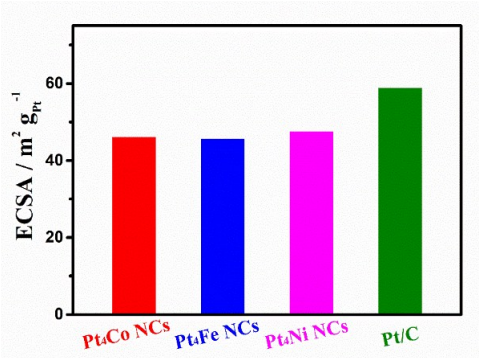

Fig. S12 The histograms of ECSA values of the four different electrocatalysts.

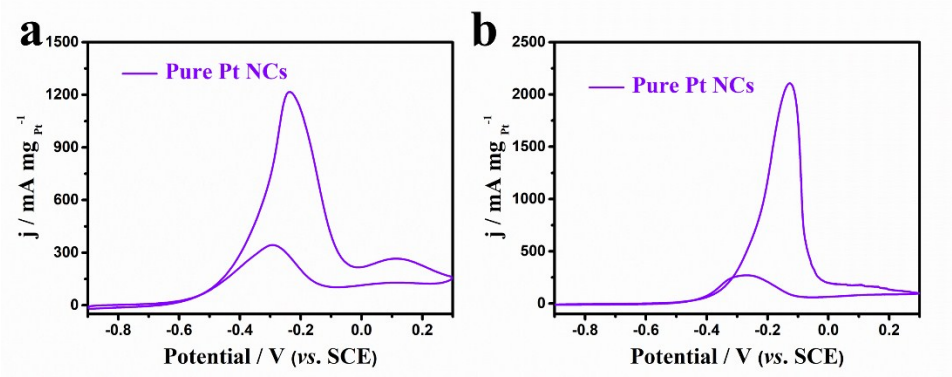

Fig. S13 The CV curves of pure Pt NCs towards (a) GOR in 1 M KOH+1 M glycerol at 0.05 V s^{-1}, and (b) EGOR in 1 M KOH+1 M EG at 0.05 V s^{-1}.

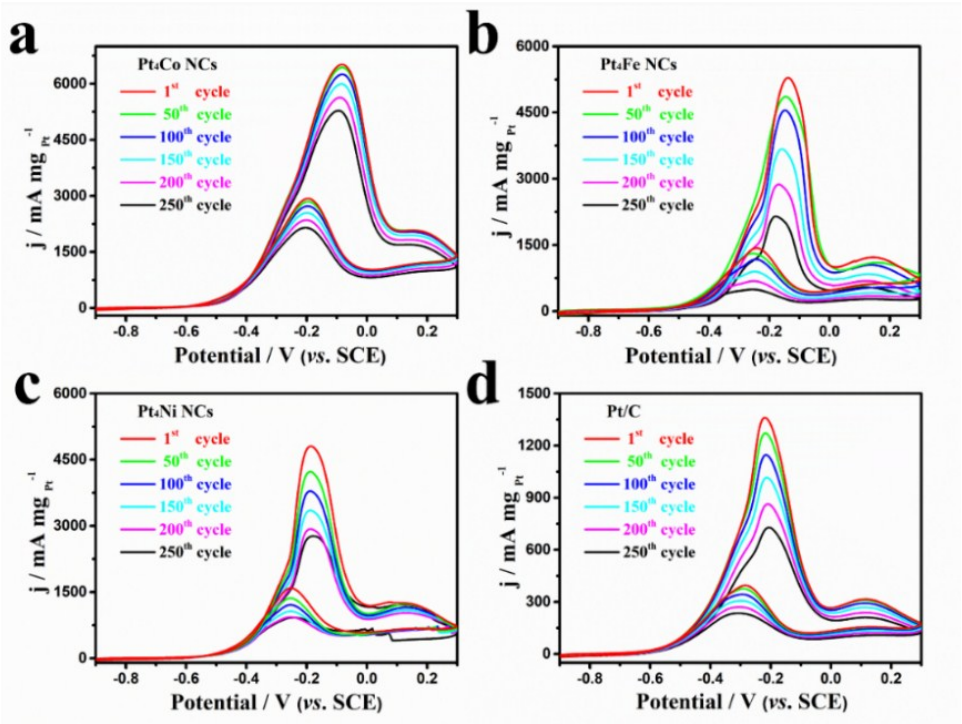

Fig. S14 The CV curves of (a) Pt_4Co NCs, (b) Pt_4Fe NCs, (c) Pt_4Ni NCs, and (d) commercial Pt/C catalysts towards GOR applying the successive CVs for 250 cycles.

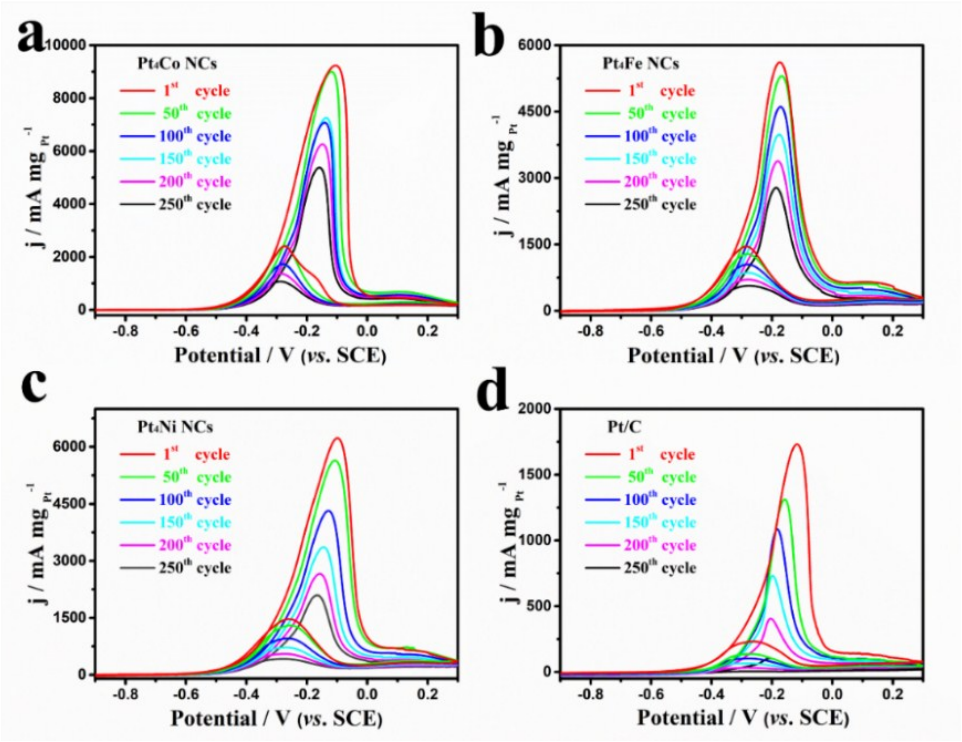

Fig. S15 The CV curves of (a) Pt_4Co NCs, (b) Pt_4Fe NCs, (c) Pt_4Ni NCs, and (d) commercial Pt/C catalysts towards EGOR applying the successive CVs for 250 cycles.

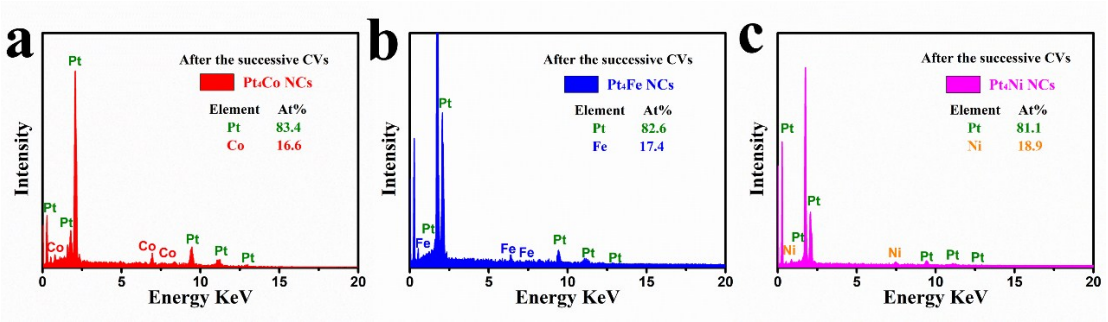

Fig. S16 EDS spectrum of (a) Pt_4Co NCs, (b) Pt_4Fe NCs, and (c) Pt_4Ni NCs catalysts after electrochemical durability test.

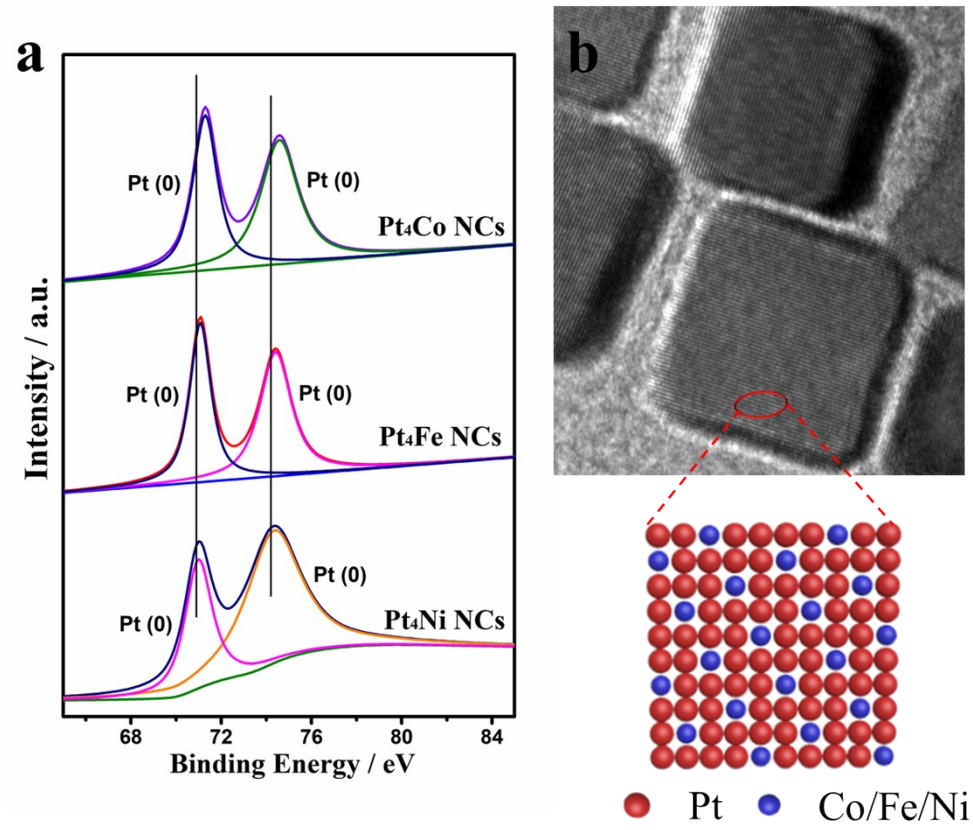

Fig. S17 (a) XPS spectra of Pt 4f in Pt_4M (Co, Fe, and Ni) NCs. (b) The schematic illustration of the improved electrocatalytic performance mechanisms of the Pt_4M (Co, Fe, and Ni) NCs.

Table S1 Other Pt-based electrocatalysts in different morphology for the glycerol electrochemical oxidation reaction in alkaline media.

Catalysts	Morphology	Electrolyte	Mass activity ($mA\ mg^{-1}$)	Reference
Pt_4Co NCs	Nano-cubes	1 M KOH + 1 M glycerol	6320.0	**This work**
Pt_3Ni SNWs	Sinuous Nano-wires	1 M KOH + 1 M glycerol	4250.3	Nanoscale, 2019, **11**, 4831-4836
$Pt_{89}Co$ NWs	Nano-wires	1 M KOH + 1 M glycerol	4573.0	J. Colloid Interf. Sci., 2019, **556**, 441-448
PtCo EDNC/C	Deeply Excavated Nano-cubes	1 M KOH + 0.1 M glycerol	~1200	Appl. Catal. B- Environ., 2019, **258**, 117951
PdPtCu NSs	Nano-sheets	0.1 M KOH + 0.1 M glycerol	~1400	Green Chem., 2019, **21**, 2367-2374
Pt_3Ni NRs	Nano-rods	1 M KOH + 1 M glycerol	4601.5	J. Power Sources, 2019, **425**, 179-185
Pt_2Au NWs	Nano-wires	1 M KOH + 0.1 M glycerol	3400	J. Electroanal. Chem., 2018, **811**, 37-45

Table S2 Other Pt-based electrocatalysts in different morphology for the ethylene glycol electrochemical oxidation reaction in alkaline media.

Catalysts	Morphology	Electrolyte	Mass activity ($mA\ mg^{-1}$)	Reference
Pt_4Co NCs	Nano-cubes	1 M KOH + 1 M EG	9345.0	**This work**
Pt_1Cu_1	Nano-spheres	1 M KOH + 1 M EG	2146.9	J. Colloid Interf. Sci., 2019, **551**, 81-88
Pt-Co EDNC/C	Deeply Excavated Nano-cubes	1 M KOH + 0.1 M EG	~2500	Appl. Catal., B: Environ., 2019, **258**, 117951
PtRu alloy	Nano-crystal	1 M KOH + 1 M EG	3052	Int. J. Hydrogen Energy, 2017, 42, 20720-20728