Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Composition Tunable Ternary Pt-Ni-Co Octahedra for Optimized Oxygen Reduction Activity

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Materials

Platinum(II) acetylacetonate [Pt(acac)$_2$, Pt 48.0% min], nickle(II) acetylacetonate [Ni(acac)$_2$, 95%], cobalt(II) acetylacetonate [Co(acac)$_2$, Crystalline], citric acid (> 99%), dicobalt octacarbonyl [Co$_2$(CO)$_8$, > 90%], tungsten hexacarbonyl [W(CO)$_6$], Commercial Pt/C catalyst (20 wt% Pt, and particle size 2 to 5 nm) were purchased from Alfa Aesar. *N, N*-dimethylformamide (DMF, ≥99.8%), ethanol (200 proof) were obtained from EMD Millipore, and Decon, respectively. Acetone (≥99.5%) and isopropanol (≥99.5%) were purchased from Fisher Scientific. All reagents were used as received without further purification. Carbon black (Vulcan XC-72) was received from Carbot Corporation, and annealed (2 h/300 ^{o}C/air) before used. The deionized water (18 MΩ/cm) was obtained from an ultra-pure purification system (Milli-Q advantage A10).

Synthesis of carbon-supported dispersive Pt-Ni-Co alloy nano octahedra

Highly dispersive Pt-Ni-Co octahedra on carbon black was prepared as following conditions: firstly, 10 mg of Pt(acac)$_2$, 8 mg of Ni(acac)$_2$, 1.5 mg of Co$_2$(CO)$_8$, 3 mg of Co(acac)$_2$ and 60 mg of citric acid were added to a 11 mL of carbon black suspended DMF solution (total 35 mg carbon black) in a 25 mL glass vial. The vial was then capped and ultrasonic processed for 5 minutes, followed by heating with magnetic stirring in an oil bath at 165 ^{o}C for 24 h. After being cooled to room temperature, the carbon supported dispersive Pt-Ni-Co alloy octahedra were obtained by centrifugation and washed with isopropanol/acetone mixture several times to remove the organic impurities and precursor residues. This synthesis yielded octahedral $PtNi_{0.55}Co_{0.1}$/C, which could be re-dispersed in ethanol for future application.

By changing the precursors' amount, we can tune the composition of alloy Pt-Ni-Co nano octahedra. First we tuned Pt:(Ni+Co) ratio by changing Pt:Ni precursor ratio while keeping Pt:Co precursor ratio the same (Table S1). Then we tuned Ni:Co composition ratio by replacing part of Ni(acac)$_2$ with Co(acac)$_2$ (Table S2). Detailed recipe was noted as following in Tables S1 and S2.

Synthesis of $PtNi_{0.9}Co_{0.05}$ octahedra

10 mg of Pt(acac)$_2$, 15 mg of Ni(acac)$_2$, 1.5 mg of Co$_2$(CO)$_8$, and 60 mg of citric acid were added to a 11 mL of carbon black suspended DMF solution (total 35 mg carbon black) in a 25 mL glass vial. The vial was then capped and ultrasonic processed for 5 minutes. The vial was then heated with magnetic stirring in an oil bath at 165 ^{o}C for 24 hrs. Post reaction process was kept the same as above noted typical method.

Synthesis of $PtNi_{0.6}Co_{0.05}$ octahedra

10 mg of Pt(acac)$_2$, 9 mg of Ni(acac)$_2$, 1.5 mg of Co$_2$(CO)$_8$, and 60 mg of citric acid were added to a 11 mL of carbon black suspended DMF solution (total 35 mg carbon black) in a 25 mL glass vial. The vial was then capped and ultrasonic processed for 5

minutes. The vial was then heated with magnetic stirring in an oil bath at 165 ^oC for 24 hrs. Post reaction process was kept the same as above noted typical method.

Synthesis of $PtNi_{0.4}Co_{0.05}$ octahedra

10 mg of $Pt(acac)_2$, 6 mg of $Ni(acac)_2$, 1.5 mg of $Co_2(CO)_8$, and 60 mg of citric acid were added to a 11 mL of carbon black suspended DMF solution (total 35 mg carbon black) in a 25 mL glass vial. The vial was then capped and ultrasonic processed for 5 minutes. The vial was then heated with magnetic stirring in an oil bath at 165 ^oC for 24 hrs. Post reaction process was kept the same as above noted typical method.

Synthesis of $PtNi_{0.55}Co_{0.1}$ octahedra

10 mg of $Pt(acac)_2$, 8 mg of $Ni(acac)_2$, 1.5 mg of $Co_2(CO)_8$, 3 mg of $Co(acac)_2$ and 60 mg of citric acid were added to a 11 mL of carbon black suspended DMF solution (total 35 mg carbon black) in a 25 mL glass vial. The vial was then capped and ultrasonic processed for 5 minutes. The vial was then heated with magnetic stirring in an oil bath at 165 ^oC for 24 hrs. Post reaction process was kept the same as above noted typical method.

Synthesis of $PtNi_{0.5}Co_{0.15}$ octahedra

10 mg of $Pt(acac)_2$, 7 mg of $Ni(acac)_2$, 1.5 mg of $Co_2(CO)_8$, 6.5 mg of $Co(acac)_2$ and 60 mg of citric acid were added to a 11 mL of carbon black suspended DMF solution (total 35 mg carbon black) in a 25 mL glass vial. The vial was then capped and ultrasonic processed for 5 minutes. The vial was then heated with magnetic stirring in an oil bath at 165 ^oC for 24 hrs. Post reaction process was kept the same as above noted typical method.

Synthesis of $PtNi_{0.65}$ octahedra

Pt-Ni octahedra on carbon black was prepared as following conditions: Firstly, 10 mg of $Pt(acac)_2$, 10 mg of $Ni(acac)_2$, 60 mg of citric acid, 0.5 mg $W(CO)_6$ were added to a 10 mL of carbon black suspended DMF solution (3.5 mg/mL) in a 25 mL glass vial. The vial was then capped and ultrasonic processed for 5 minutes. Then the vial was heated with magnetic stirring in an oil bath at 165 ^oC for 24 hrs. After being cooled to room temperature, the carbon supported dispersive Pt-Ni alloy octahedra was obtained by centrifugation and washed with isopropanol/acetone several times to remove the organic impurities and precursor residues. This synthesis yielded octahedra $PtNi_{0.65}/C$, which could be re-dispersed in ethanol for future application.

Characterization

Transmission electron microscopy (TEM) images were taken on a FEI T12 operated at 120 kV. High resolution TEM images was taken on a FEI TITAN operated at 300 kV. Energy-dispersive X-ray spectroscopy (EDS) mapping and high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) image was taken on a TitanX operated at 200 kV. Samples for TEM measurements were prepared by dropping 10 μL octahedral Pt-Ni-Co/C ethanol dispersion onto a carbon-coated copper grids (Ted Pella, Redding, CA) using pipettes and then drying under ambient conditions. Al grid (Ted Pella, Redding, CA) was used for EDS mapping sample preparation. Powder X-ray diffraction patterns (PXRD) were collected on a Panalytical X'Pert Pro X-ray Powder Diffractometer with Cu-K_α radiation. The concentration of catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu ICPE-9000) as well as EDS coupled in ZEISS Supra 40VP scanning electron microscope (SEM).

Electrode preparation and electrochemistry test

The catalyst ink was prepared by mixing 1.3 mg of catalyst Pt-Ni-Co/C powder with 2 mL of ethanol solution containing 20 μL of Nafion (5 wt%) with 5 min ultrasonication time. Then, 10 μL of catalyst ink was dropped onto a 5 mm diameter glassy-carbon electrode (Pine Research Instrumentation) two times, resulting in a total volume of 20 μL. Estimation of Pt loading is based on overall Pt ratio within catalyst determined by ICP-AES, and Pt loading is about 1.2 μg for all tested Pt based alloy samples. The ink was dried under an infrared lamp, then the electrode was ready for electrochemical test. Commercial Pt/C catalyst was used as the baseline catalysts, and similar procedure as described above was used to conduct the electrochemical measurement. Pt loading is about 1.0 μg for commercial Pt/C.

A three-electrode cell was used to carry out the electrochemical measurements. The working electrode was a catalyst coated glassy carbon electrode. Ag/AgCl electrode was used as the reference electrode. Pt wire was used as the counter electrode. Cyclic Voltammetry (CV) measurements was conducted in a N_2 saturated 0.1 M $HClO_4$ solution between 0.05 to 1.1 V vs. reverse hydrogen electrode (RHE) at a sweep rate of 100 mV/s. Oxygen reduction reaction (ORR) measurements were conducted in an O_2 saturated 0.1 M $HClO_4$ solution between 0.05 to 1.1 V vs. RHE at a sweep rate of 20 mV/s. Accelerated degradation test (ADT) was performed in oxygen saturated 0.1 M $HClO_4$ solution by applying cyclic potential sweeps between 0.6 to 1.1 V vs. RHE at a sweep rate of 50 mV/s. For the CO stripping voltammetry measurements, working electrodes coated with different catalysts were firstly immersed in a CO saturated 0.1 M $HClO_4$ solution for 15 min, and then the CO stripping voltammetry was recorded respectively between 0.3 to 1.1 V vs. RHE at a sweep rate of 5 mV/s.

Table S1. Tuning Pt:(Ni+Co) composition ratio of Pt-Ni-Co octahedra by changing Pt:Ni precursor ratio, while fixing Pt:Co precursor ratio.

Experiment	Precursor Ratio					Composition Ratio
	$Pt(acac)_2$ mg	$Ni(acac)_2$ mg	$Co_2(CO)_8$ mg	$Co(acac)_2$ mg	Pt:Ni:Co atomic	Pt:Ni:Co atomic
(i)	10	15	1.5	0	1:2.30:0.34	1:0.9:0.05
(ii)	10	9	1.5	0	1:1.38:0.34	1:0.6:0.05
(iii)	10	6	1.5	0	1:0.92:0.34	1:0.4:0.05

Table S2. Tuning Ni:Co composition ratio of Pt-Ni-Co octahedra by replacing part of $Ni(acac)_2$ with $Co(acac)_2$, while fixing Pt:(Ni+Co) ratio within alloy octahedra.

Experiment	Precursor Ratio					Composition Ratio
	$Pt(acac)_2$ mg	$Ni(acac)_2$ mg	$Co_2(CO)_8$ mg	$Co(acac)_2$ mg	Pt:Ni:Co atomic	Pt:Ni:Co atomic
(ii)	10	9	1.5	0	1:1.38:0.34	1:0.6:0.05
(iv)	10	8	1.5	3	1:1.22:0.80	1:0.55:0.10
(v)	10	7	1.5	6.5	1:1.07:1.34	1:0.5:0.15

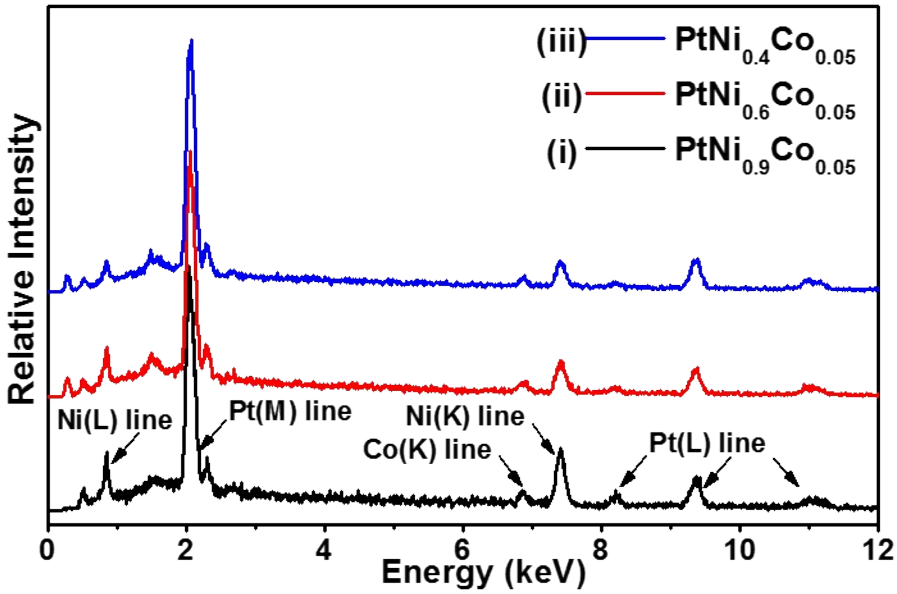

Fig. S1 EDS spectra of octahedral sample (i) $PtNi_{0.9}C0_{0.05}$, (ii) $PtNi_{0.6}Co_{0.05}$, (iii) $PtNi_{0.4}Co_{0.05}$.

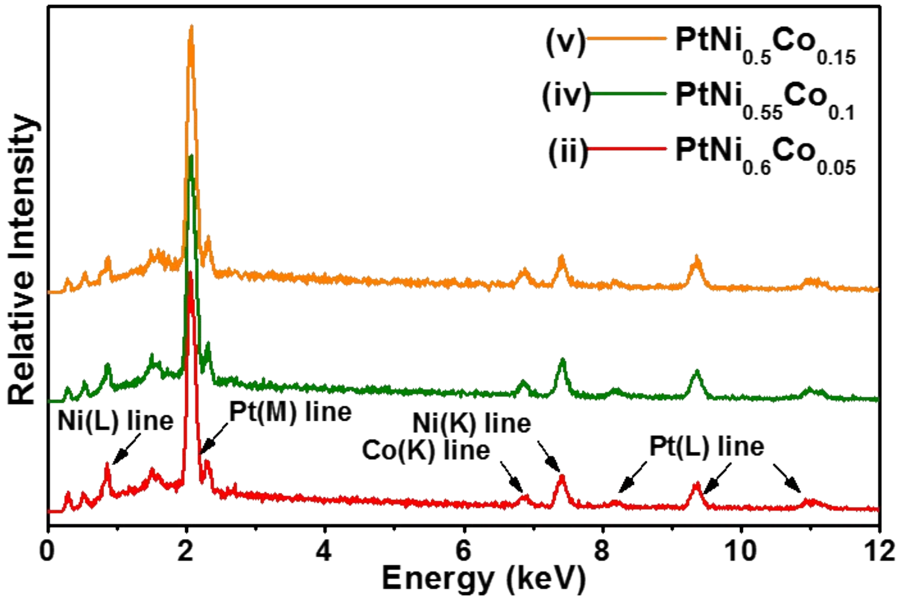

Fig. S2 EDS spectra of octahedral sample (ii) $PtNi_{0.6}Co_{0.05}$, (iv) $PtNi_{0.55}Co_{0.1}$, and (v) $PtNi_{0.5}Co_{0.15}$.

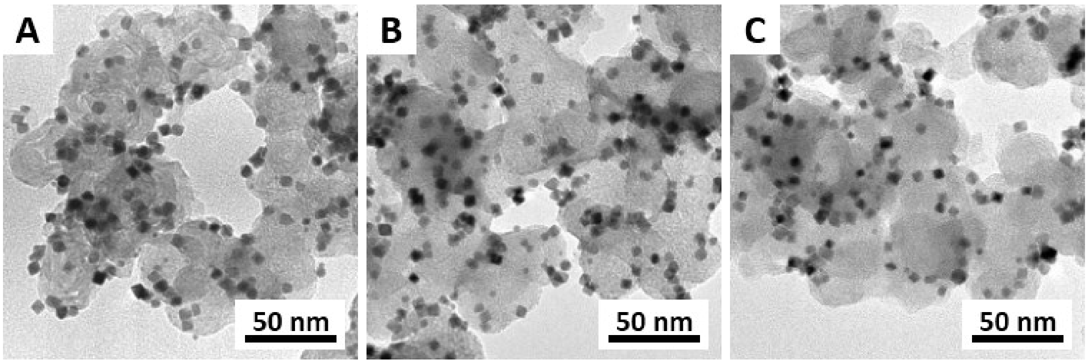

Fig. S3 TEM images of octahedral sample (A) $PtNi_{0.9}C0_{0.05}$, (B) $PtNi_{0.6}Co_{0.05}$, (C) $PtNi_{0.4}Co_{0.05}$

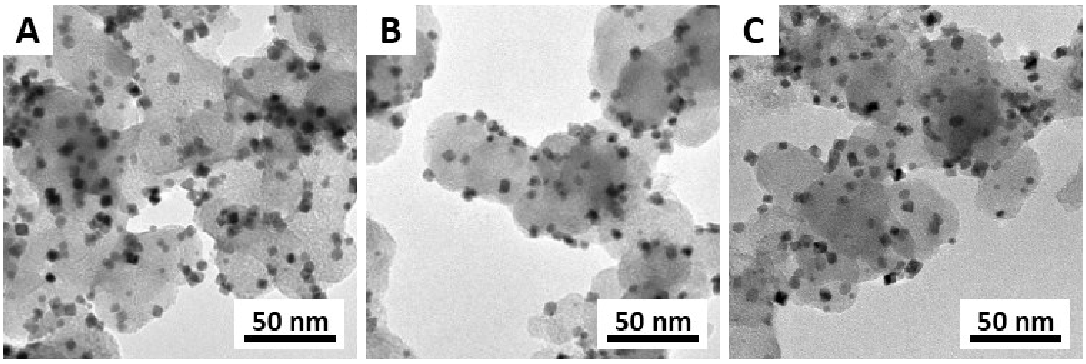

Fig. S4 TEM images of octahedral sample (A) $PtNi_{0.6}Co_{0.05}$, (B) $PtNi_{0.55}Co_{0.1}$, and (C) $PtNi_{0.50}Co_{0.15}$.

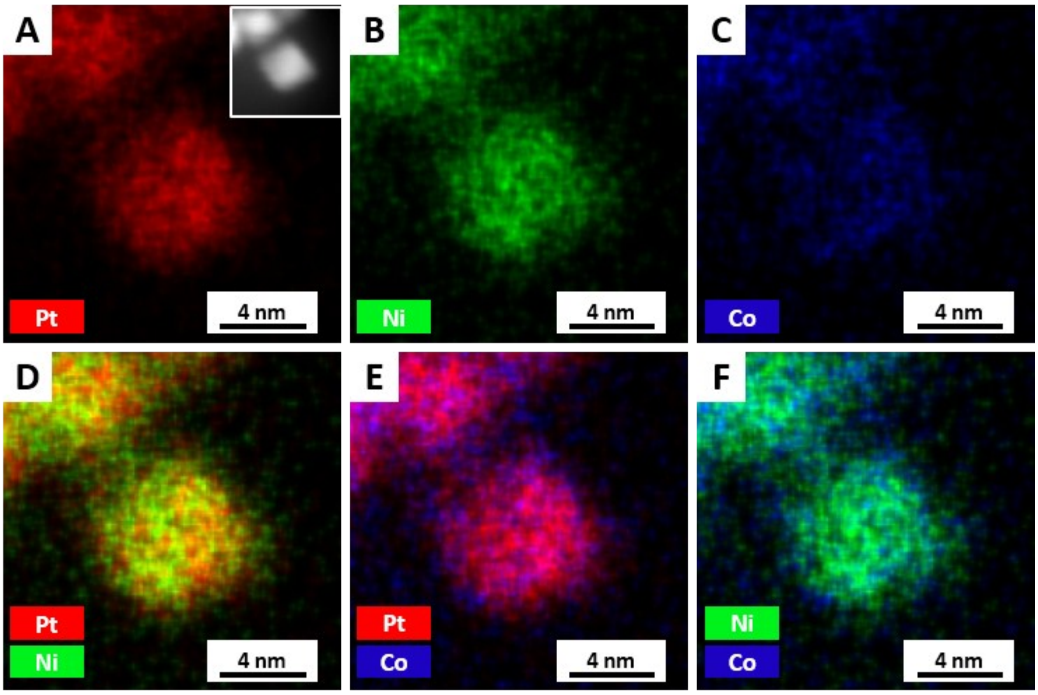

Fig. S5 Corresponded EDS mapping in Figure 3, EDS mapping only show (A) Pt distribution, insert: STEM of mapping area (B) Ni distribution, (C) Co distribution, (D) Pt, Ni overlap, (E) Pt, Co overlap, (F) Ni, Co overlap.

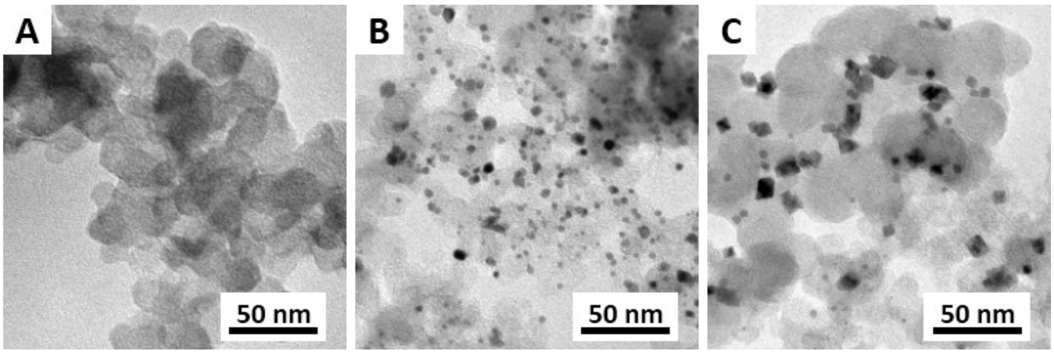

Fig. S6 TEM images of the products collected from control experiments with the same condition used in the synthesis of octahedral $PtNi_{0.55}Co_{0.1}$ but in the absence of (A) $Pt(acac)_2$, (B) $Ni(acac)_2$, (C) $Co(acac)_2$ and $Co_2(CO)_8$.

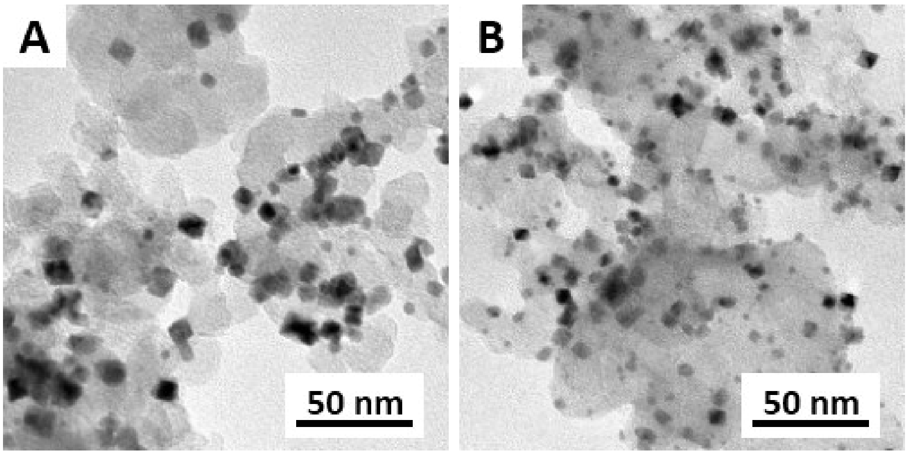

Fig. S7 TEM images of the products collected from control experiments with the same condition used in the synthesis of octahedral $PtNi_{0.55}Co_{0.1}$ but (A) without $Co_2(CO)_8$, (B) with double amount of $Co_2(CO)_8$ (3 mg).

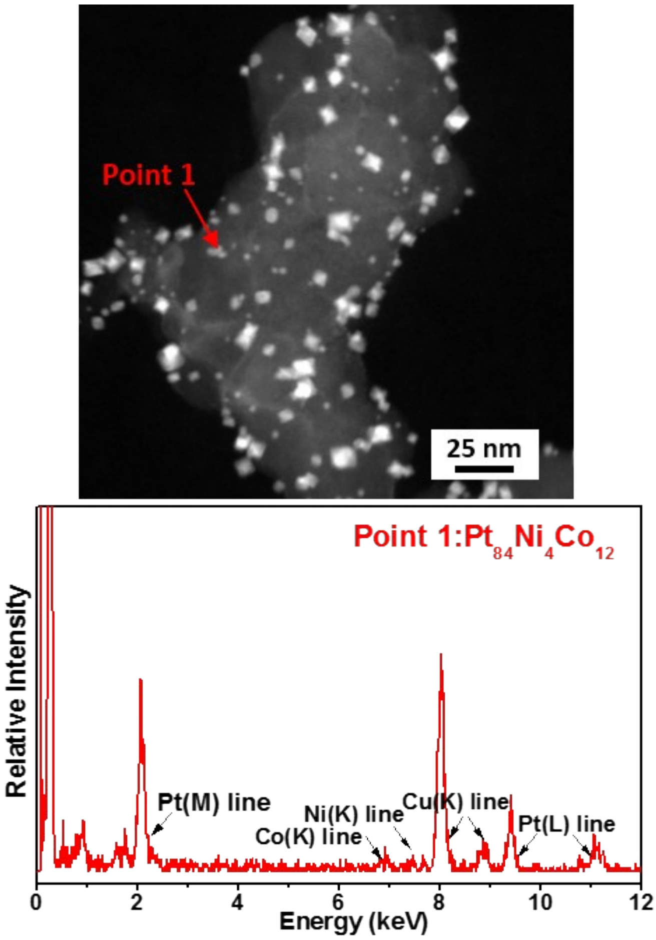

Fig. S8 STEM image of control experiments showed in Figure S7B, and corresponded point EDS. EDS focused on point 1, which are representative small particles, showed a Pt rich composition around $Pt_{84}Ni_4Co_{12}$. The Cu lines showed in EDS were from Cu TEM grid.

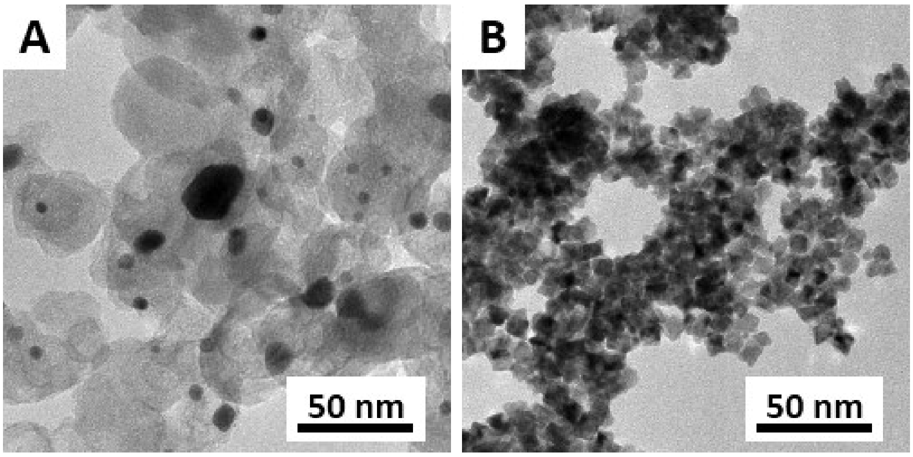

Fig. S9 TEM images of the products collected from control experiments with the same condition used in the synthesis of octahedral $PtNi_{0.55}Co_{0.1}$ but in the absence of (A) citric acid, (B) carbon support.

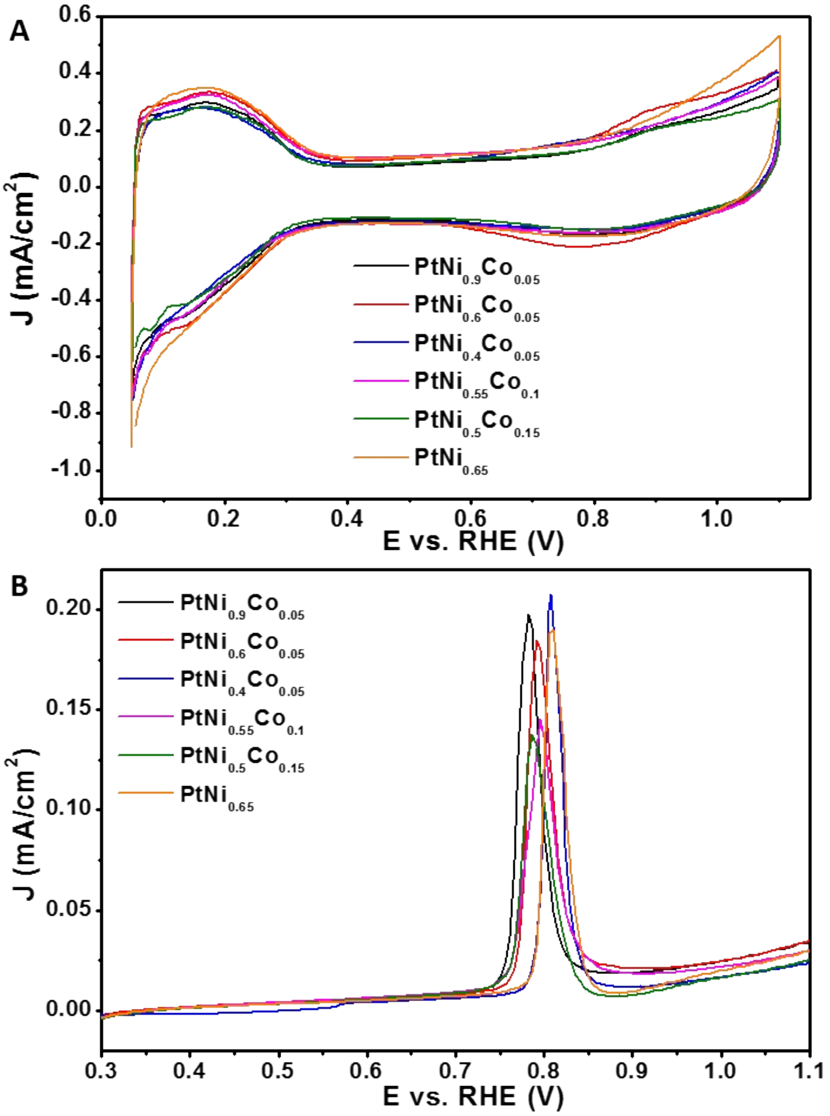

Fig. S10 (A) CV curves of octahedral (i) $PtNi_{0.9}C0_{0.05}$, (ii) $PtNi_{0.6}Co_{0.05}$, (iii) $PtNi_{0.4}Co_{0.05}$, (iv) $PtNi_{0.55}Co_{0.1}$, (v) $PtNi_{0.5}Co_{0.15}$ and $PtNi_{0.65}$ on carbon. The electrochemical active process was carried out in a 0.1 M $HClO_4$ solution between 0.05 to 1.1 V vs. RHE at a sweep rate of 100 mV/s. (B) CO stripping voltammetric curves of octahedral (i) $PtNi_{0.9}C0_{0.05}$, (ii) $PtNi_{0.6}Co_{0.05}$, (iii) $PtNi_{0.4}Co_{0.05}$, (iv) $PtNi_{0.55}Co_{0.1}$, (v) $PtNi_{0.5}Co_{0.15}$ and $PtNi_{0.65}$ on carbon. CO stripping voltammetry measurements were conducted in a 0.1 M $HClO_4$ solution between 0.3 to 1.1 V vs. RHE at a sweep rate of 5 mV/s.

Table S3. Integrated charge ratio based on CO stripping results and hydrogen underpotential deposition (H_{upd}). Electrochemical active surface area (ECSA) based on CO stripping is calculated by integration of CO striping peak with a conversion constant of 420 μC/cm^2. ECSA based on H_{upd} is calculated by integration from 0.05 to 0.35 V vs. RHE with a conversion constant of 210 μC/cm^2. Q_{CO} / $2Q_H$ represents electrochemical surface area difference estimated by CO stripping and H_{upd} (Q represents the integrated charge).

Sample	Q_{CO} / $2Q_H$
(i) $PtNi_{0.9}Co_{0.05}$	1.24
(ii) $PtNi_{0.6}Co_{0.05}$	1.21
(iii) $PtNi_{0.4}Co_{0.05}$	1.21
(iv) $PtNi_{0.55}Co_{0.1}$	1.19
(v) $PtNi_{0.5}Co_{0.15}$	1.19
$PtNi_{0.65}$	1.17

Table S4. Performance comparison between the as-prepared Pt-Ni-Co catalysts and several published Pt-Ni-Co catalysts.

Catalyst			Specific activity (mA/cm^2)		Mass activity (A/mg_{Pt})
			Based on H_{upd}	Based on CO stripping	
This paper	$Pt_{51}Ni_{46}Co_3$ ($PtNi_{0.9}Co_{0.05}/C$)	octahedral	4.37	3.52	1.97
This paper	$Pt_{61}Ni_{36}Co_3$ ($PtNi_{0.6}Co_{0.05}/C$)	octahedral	5.50	4.54	2.49
This paper	$Pt_{69}Ni_{28}Co_3$ ($PtNi_{0.4}Co_{0.05}/C$)	octahedral	4.85	4.01	2.17
This paper	$Pt_{61}Ni_{33}Co_6$ ($PtNi_{0.55}Co_{0.1}/C$)	octahedral	6.01	5.05	2.80
This paper	$Pt_{61}Ni_{30}Co_9$ ($PtNi_{0.5}Co_{0.15}/C$)	octahedral	4.22	3.54	1.96
Ref. 25	$Pt_{71}Ni_{25}Co_4/C$	octahedral	3.88	NA	2.33
Ref. 26	$Pt_{48}Ni_{27}Co_{25}$ /C	octahedral	3.5*	NA	0.45*
Ref. 26	$Pt_{30}Ni_{51}Co_{19}/C$	octahedral	1.5*	NA	0.50*
Ref. 18	$Pt_{36}Ni_{15}Co_{49}$ /C	spherical	1.85	NA	0.88

(NA: not available; *: extracted from plot in literature)

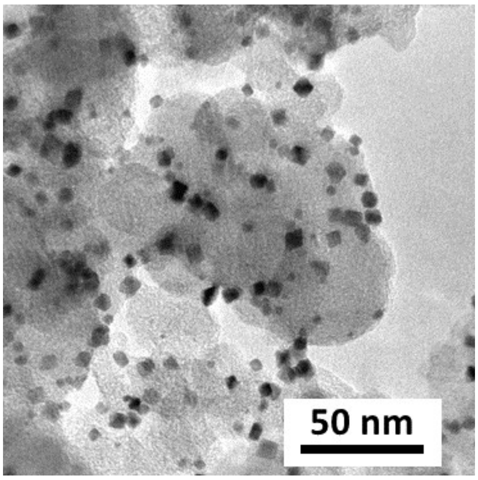

Fig. S11 TEM image of octahedral $PtNi_{0.65}/C$ nano catalyst.

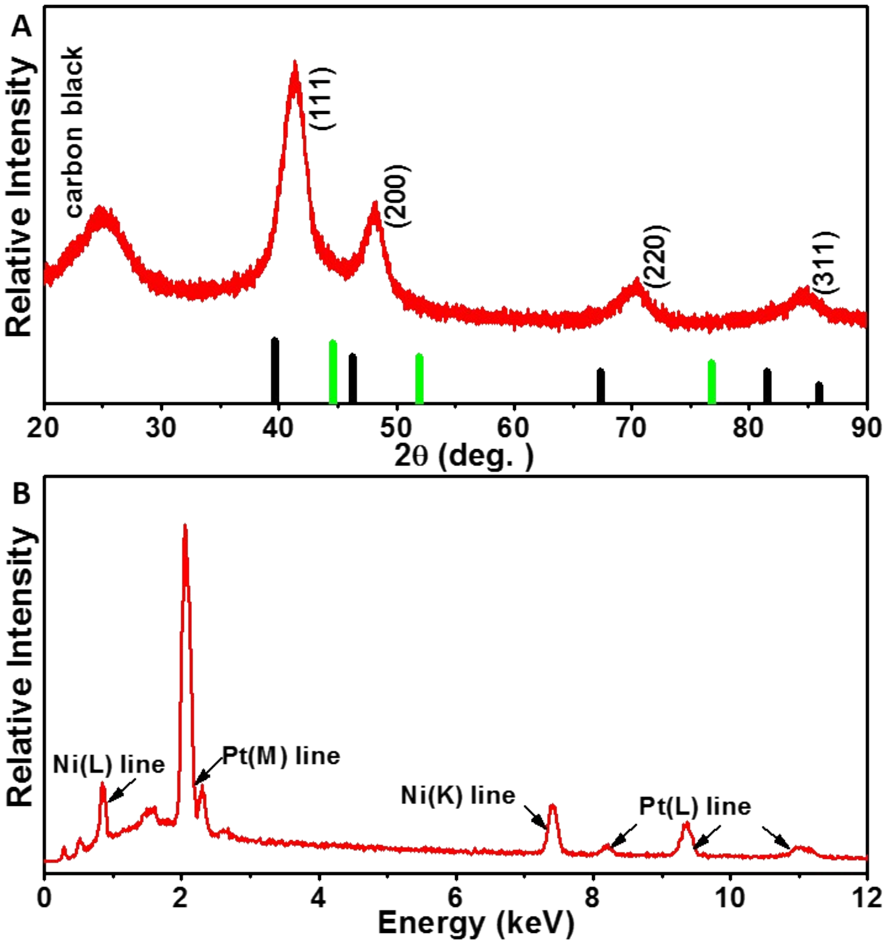

Fig. S12 (A) XRD of sample octahedral $PtNi_{0.65}/C$, black and green perpendicular lines represent standard Pt and Ni peak position, respectively. (B) EDS of sample octahedral $PtNi_{0.65}/C$.

Table S5. Stability comparison of our octahedral $PtNi_{0.55}Co_{0.1}$/C and several Pt-Ni and Pt-Ni-Co catalyst in literature. Comparison was made regarding specific activity (SA) and mass activity (MA) at 0.9 V *vs*. RHE.

Reference	Octahedral Catalyst	Potential Range *vs*. RHE	Purging Gas	ADT Cycles	Initial SA (mA/cm^2)	Decrease Ratio	Initial MA ($mA/\mu g_{Pt}$)	Decrease Ratio
Ref. 14	$Pt_{2.5}Ni$	0.65-1.0 V (square wave)	O_2	5000	NA	NA	3.3	40%
Ref. 15	$Pt_{1.5}Ni$	0.6-1.0 V	NA	4000	3.3*	50%*	1.2*	16%
Ref. 15	PtNi	0.6-1.0 V	NA	4000	3.8*	66%*	1.7*	66%
Ref. 15	$PtNi_{1.5}$	0.6-1.0 V	NA	4000	2.9*	45%*	1.0*	45%
Ref. 26	$Pt_{71}Ni_{25}Co_4$	0.6-1.1 V	O_2	6000	3.88	NA	2.33	57%
Ref. 27	$Pt_{48}Ni_{27}Co_{25}$	0.5-1.0 V	N_2	4000	3.5*	51%	0.45*	51%
Ref. 27	$Pt_{30}Ni_{51}Co_{19}$	0.5-1.0 V	N_2	4000	1.5*	34%	0.50*	47%
This work	$Pt_{61}Ni_{33}Co_6$ ($PtNi_{0.55}Co_{0.1}$)	0.6-1.1 V	O_2	6000	5.05	58%	2.80	51%

(NA: not available; *: extracted from plot in literature)

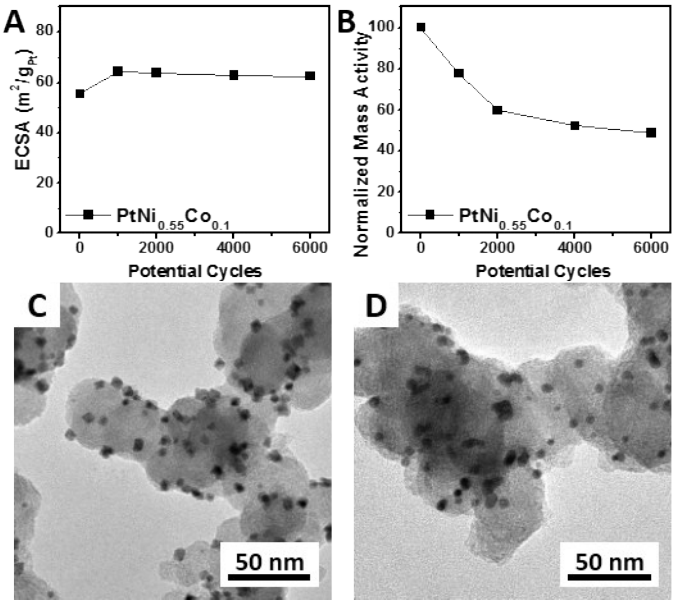

Fig. S13 ADT test of octahedral $PtNi_{0.55}Co_{0.1}/C$ (A) ECSA changing trend, (B) Normalized mass activity changing trend. (C) TEM of octahedral $PtNi_{0.55}Co_{0.1}/C$ before ADT test, (D) TEM of octahedral $PtNi_{0.55}Co_{0.1}/C$ after ADT test.