Supporting Information

Defect-dominated Shape Recovery of Nanocrystal: A New Strategy for Trimetallic

Catalysts

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1. Materials and Methods

Chemicals.

Analytical grade benzyl alcohol, benzoic acid, dimethylglyoxime, chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), silver nitrate (AgNO_3), and acetic acid were obtained from Beijing Chemical Reagents, China. platinum bis(acetylacetonate) ($\text{Pt}(\text{acac})_2$), $\text{Ni}(\text{acac})_2$, $\text{Cu}(\text{acac})_2$, $\text{Rh}(\text{acac})_3$, $\text{Fe}(\text{acac})_3$, and poly (vinylpyrrolidone) (PVP, MW=8000, AR) were purchased from Alfa Aesar. All of the chemicals used in this experiment were analytical grade and used without further purification.

Characterization

The crystalline structure and phase purity were determined by Rigaku RU-200b X-ray powder diffractometer with CuK α radiation ($\lambda=1.5418\text{\AA}$). The composition of the product was measured by the inductively coupled plasma-mass spectrometry (ICP-MS) and energy dispersive spectrometer (EDS). TEM images were recorded by a Hitachi-7700 working at 100 kV. HRTEM images were recorded by a FEI Tecnai G2 F20 S-Twin high-resolution transmission electron microscope working at 200 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. X-ray photoelectron spectroscopy (XPS) experiments were performed on a ULVAC PHI Quantera microprobe. Binding energies (BE) were calibrated by setting the measured BE of C 1s to 284.8 eV. The catalytic reaction result was measured by gas chromatography (GC) (SP-6890) and ^1H NMR. The NMR spectroscopy was conducted on a JEOL JNM-ECX 400MHz instrument.

Preparation of octahedral PtNi_3 nanocrystals.

In a typical synthesis of octahedral Pt_3Ni nanocrystals, $\text{Pt}(\text{acac})_2$ (40.0 mg), PVP (MW=8000, (400.0 mg)) $\text{Ni}(\text{acac})_2$ (75 mg) and benzoic acid (250 mg) were dissolved in 25 mL of benzylalcohol and then vigorously stirred for 10 min. The obtained transparent green solution was transferred into a 40-mL Teflon-lined stainless-steel autoclave, followed by 12 h thermal treating 150 °C. After being cooled down to room temperature, the products were precipitated by acetone, separated via centrifugation and further purified by an ethanol-acetone mixture.

Preparation of concave octahedral Pt₃Ni nanocrystals.

In a typical synthetic method to prepare the concave octahedral Pt₃Ni seeds, the as-prepared PtNi₃ (8 mg, based on ICP-MS measurement) precursor was redispersed in 2 mL H₂O, followed by the addition of 20 mg dimethylglyoxime solved in 2 mL ethanol. Then, the reaction mixture was stirred overnight. Next, 10 mL acetic acid (50%) was added and the solution was kept stirred for a further 15 min at room temperature. Finally, the products were obtained via centrifugation and further washed by ethanol for three times.

Second growth of Ni using concave Pt₃Ni as seeds.

The 4 mg sample of concave Pt₃Ni alloy seeds was diluted by 5 mL benzoic alcohol to 0.8 mg/mL (containing 0.0185 mmol of Pt and 0.0064 mmol Ni base on ICP-MS measurement) and sonicated for 5 mins. Then, 13.3 mg Ni(acac)₂ (0.052 mmol) was added and further stirred for 5 min. The as-obtained turbid liquid was transferred into a 12-mL Teflon-lined stainless-steel autoclave, followed by 6 h thermal treating at 150 °C. The products were finally obtained via centrifugation and further washed by ethanol.

Second growth of M (M=Au, Rh, Cu, Ag, Fe) using concave Pt₃Ni as seeds

As a similar procedure, the growth of M (M=Au, Rh, Cu, Ag, Fe) were conducted by simply replacing the Ni(acac)₂ by other metal salts. The salts of M were HAuCl₄·4H₂O, Rh(acac)₃, Cu(acac)₂, AgNO₃, and Fe(acac)₃, respectively. Firstly, the HAuCl₄·4H₂O and AgNO₃ were dissolved in 1 mL H₂O. The Rh(acac)₃, Cu(acac)₂, and Fe(acac)₃ were dissolved in 1 mL benzyl alcohol. Then, the solution containing M (it depends from 0.017 mmol to 0.0064 mmol to 0.052 mmol) were added into a 5 mL benzyl alcohol which contained 0.05 g benzoic acid and 0.05 g PVP. The resulting turbid liquid was transferred to a 12-mL Teflon-lined stainless-steel autoclave, followed by 6 h thermal treating at 150 °C. The products of Pt₃Ni @ M core-shell structures were finally obtained through centrifugation and washing.

Typical procedure for the Suzuki-Miyaura reaction cross coupling reaction

In a typical procedure, the catalysts (Pt₃Ni or Pt₃Ni @ Au, both contain 0.005 mmol Pt, 0.5 atom%) and 1.2 mmol of arylboronic acid (purchased from Alfa Aesar) and 3 equiv. (3 mmol) of K₃PO₄ were added to an solution (3 ml) of H₂O / ethanol (v/v = 3 : 2) with magnetic stirring. Then, 1 mmol 4-bromoanisole (99%, Alfa Aesar) was dropped into the reaction vial. The temperature of reaction was kept at 30°C until the reaction

stopped. When GC monitoring indicates the complete consumption of the substrate, (see GC detailed conditions at Table S4) the catalyst was separated from the mixture by centrifugation and the liquid phase was concentrated under reduced pressure. The product was purified by column chromatography (silica gel/hexane) and subsequently characterized by ^1H NMR.

Typical procedure for hydrogenation of nitrobenzene using the formic acid as hydrogen source

First, 51 μL nitrobenzene (0.5 mmol), 3 equiv. formic acid (1.5 mmol) and the catalysts (contain 0.0025 mmol Pt, 0.5 atom%) were solved in 2.5 mL ethyl acetate and then transferred in a 25 mL vial. The round flask was purged with N_2 . Then, the reaction mixture was stirred at 70 $^\circ\text{C}$ under a N_2 balloon. When GC monitoring indicates the complete consumption of the substrate, (see GC detailed conditions at Table S4) the catalyst was separated from the mixture by centrifugation and the liquid phase was concentrated under reduced pressure. The product was purified by column chromatography and subsequently characterized by ^1H NMR.

Typical procedure of gas-phase selective oxidation of benzoic alcohol

The gas-phase selective oxidation of alcohols on these catalysts with molecular oxygen was carried out on a fixed-bed quartz tube reactor (inner diameter, 16 mm) under atmospheric pressure. The catalysts were loaded on active carbon (containing 2% Pt) packed layer-up-layer into the tube reactor. Alcohols were fed continuously using a high-performance liquid pump (weight hourly space velocity (WHSV) was 20 h^{-1}), in parallel with an O_2 (oxidant) and N_2 (diluted gas) feed using the calibrated mass flow controllers, into the reactor heated to the desired reaction temperature. The effluent was cooled using an ice-salt bath ($-15\text{ }^\circ\text{C}$) to liquefy the condensable vapors for analyzing by an SP-6890 gas chromatography-flame ionization detector (GC-FID). The gas-phase products such as H_2 , CO_x and $\text{C}_1\text{-C}_3$ hydrocarbons were analyzed by an SP-6890 GC with a thermal conductivity detector (TCD).

Calculation Details

Spin-polarized density functional theory (DFT) with a GGA-PW91 functional¹, as implemented in the Vienna ab initio simulation package (VASP)², was used for all the total energy and electronic structure calculations. The projector augmented wave method^{3,4} and the ultrasoft pseudopotentials⁵ were adopted to describe the electron-ion interaction and the ionic cores, respectively. A cutoff energy of 270 eV was utilized. Atomic step of concave Pt_3Ni nanocrystals was modeled by the (221) surface that it is of {111} structure. 3 layers of atoms was employed in all slab-calculations. In line with the experimental observation⁶, the Pt-segregated surface of concave Pt_3Ni NCs was built from the corresponding slab by exchanging

Ni atoms from the first layer with Pt atoms in the second layer. The top two layers were allowed to relax, while the bottom layer was fixed at their bulk-truncated structure during structural optimizations. The vacuum region between two slabs was 10 Å. Monkhorst-Pack **k**-point meshes of 3 x 3 x 1 and 19 x 19 x 1 were employed for total energy and electronic structure calculations, respectively. Structural optimizations were deemed sufficiently converged when the forces on all relaxed ions were less than 0.02 eV/Å. The binding energy E_b was obtained from the following expression: $E_b = E_{\text{NCs+M}} - E_{\text{NCs}} - E_M$, where $E_{\text{NCs+M}}$, E_{NCs} , E_M were the total energies of the M-deposited Pt₃Ni, the concave Pt₃Ni and the metal atom M, respectively.

2. Figures:

Figure S1: HRTEM image with spherical aberration correction showed exposed surface of an individual concave Pt₃Ni seed contained rich steps and defects.

octahedral Pt_3Ni alloy $\xrightarrow{\text{seed growth}}$ octahedral PtNi_3 alloy

Figure S2: TEM images showing the seed growth from a) octahedral Pt_3Ni alloy seeds (11.8 ± 1.0 nm) to b) octahedral PtNi_3 alloy (14.2 ± 1.9 nm).

Figure S3: TEM images of a) $\text{Pt}_3\text{Ni} @ \text{Au}_{0.5}$, b) $\text{Pt}_3\text{Ni} @ \text{Au}_2$, and c) $\text{Pt}_3\text{Ni} @ \text{Au}_8$.

Figure S4: XRD patterns showing the phase evolution process of Au grow on the surface of concave Pt_3Ni and finally form $\text{Pt}_3\text{Ni} @ \text{Au}$ core-shell structures.

Figure S5: TEM image of NPs obtained by seeds growth of Au with an excess quantity of chloroauric acid. (molar ratio of Pt : Au is 1:6)

Figure S6: a) TEM image, b) HRTEM image, and c) EDX patterns of Pt-Ni-Au NPs synthesized by one pot co-reduction. (molar ratio of precursors: Pt : Ni : Au = 3 : 1 : 3) d₁) HAADF-STEM image, and corresponding elemental maps of d₂) Pt (L), d₃) Ni (K), d₄) Au (L).

Figure S7: TEM image of NPs obtained by seeds growth of Fe, using concave Pt₃Ni as seeds. (molar ratio of Pt : Fe is 1:3)

Figure S8: TEM images of a) Pt₃Ni @ Ag_{0.5}, d) Pt₃Ni @ Ag₂, and Pt₃Ni @ Ag₈. d) HRTEM images of Pt₃Ni @ Ag₈. e) EDS line profiles of an individual Pt₃Ni @ Ag₈ nanoparticle. f₁) HAADF-STEM image, and corresponding elemental maps of f₂) Pt (L), f₃) Ni (K), f₄) Ag (L).

Figure S9: TEM images of a) $\text{Pt}_3\text{Ni} @ \text{Cu}_{0.5}$, d) $\text{Pt}_3\text{Ni} @ \text{Cu}_2$, and $\text{Pt}_3\text{Ni} @ \text{Cu}_8$. d) HRTEM images of $\text{Pt}_3\text{Ni} @ \text{Cu}_8$. e) EDS line profiles of an individual $\text{Pt}_3\text{Ni} @ \text{Cu}_8$ nanoparticle. f_1) HAADF-STEM image, and corresponding elemental maps of f_2) Pt (L), f_3) Ni (K), f_4) Cu (K).

Figure S10: TEM images of a) Pt₃Ni @ Rh_{0.5}, d) Pt₃Ni @ Rh₂, and Pt₃Ni @ Rh₈. d) HRTEM images of Pt₃Ni @ Rh₈. e) EDS line profiles of an individual Pt₃Ni @ Rh₈ nanoparticle. f₁) HAADF-STEM image, and corresponding elemental maps of f₂) Pt (L), f₃) Ni (K), f₄) Rh (L).

Figure S11: XRD patterns for a) $\text{Pt}_3\text{Ni} @ \text{Ag}_8$, c) $\text{Pt}_3\text{Ni} @ \text{Cu}_8$, and e) $\text{Pt}_3\text{Ni} @ \text{Rh}_8$ core-shell structures. EDX patterns for b) $\text{Pt}_3\text{Ni} @ \text{Ag}_8$, d) $\text{Pt}_3\text{Ni} @ \text{Cu}_8$, and f) $\text{Pt}_3\text{Ni} @ \text{Rh}_8$ core-shell structures.

Figure S12: TEM image of octahedral PVP-capped Au NCs for the measurement of XPS. The octahedrons were synthesized as follows: PVP (MW=8000, 50 mg) and $\text{H}_2\text{C}_2\text{O}_4$ (0.5 mmol, 50 mg) were dissolved into 5 mL formamide and heated to 120 °C. Then $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ aqueous solution (0.2 mL, 0.1 g/mL) was injected into the above solution and maintained at 120 °C for 30 min. After the reaction, acetone was added and the dispersion was centrifuged at 14500 rpm for 10 min. The final product could be dispersed in water or Ethanol.

Figure S13: a) High-resolution scans of the Ni 2p XPS data for the initial concave octahedral Pt_3Ni and $\text{Pt}_3\text{Ni} @ \text{Au}$ core-shell NCs. b) High-resolution scans of the Au 4f XPS data for the as-prepared octahedral PVP-capped Au NCs and octahedral $\text{Pt}_3\text{Ni} @ \text{Au}$ core-shell NCs.

Tables:

Table S1. Binding energies of M (M=Au, Ag, Cu, Rh, Ni, Fe) on the {111} Pt₃Ni step (in eV/atom). The atomic radius (in Å) and crystal structure of M are shown together.

entry	Metal	E _b ,ST	E _b ,SE	Atomic radius	Crystal structure
1	Au	-2.35	-3.11	1.79	fcc
2	Ag	-2.09	-2.68	1.75	fcc
3	Cu	-2.79	-3.55	1.57	fcc
4	Rh	-3.81	-4.99	1.83	fcc
5	Fe	-3.79	-4.76	1.72	bcc
6	Ni	-3.71	-4.61	1.62	fcc
7	Pt	-	-	1.83	fcc

Table S2: Surface composition and BE [a] peaks of as-prepared octahedral trimetallic Pt₃Ni @ Au nanostructures. [b]

entry	catalysts	4f _{7/2} peak of Pt	2p _{3/2} peak of Ni	4f _{7/2} peak of Au	Analyzed atomic ratios (Pt : Ni : Au)
1	Concave Pt ₃ Ni	71.6	852.9		0.76 : 0.24 : 0
2	Pt ₃ Ni@Au _{0.5}	71.3	852.6	84.5	0.62 : 0.21 : 0.17
3	Pt ₃ Ni@Au ₂	71.2	852.5	84.4	0.37 : 0.8 : 0.55
4	Pt ₃ Ni@Au ₈	71.1	852.3	84.3	0.25 : 0.05 : 0.70
5	Au NCs [c]			84.0	

[a] BE = binding energy

[b] Determined by XPS measurements.

[c] The TEM image of Au NCs is shown in Figure S11.

Table S3: Composition of as-prepared octahedral trimetallic Pt₃Ni @ M (M= Au, Ag, Cu, Rh) nanostructures.

entry	catalysts	Analyzed molar ratios (Pt : Ni : M) by EDS	Analyzed molar ratios (Pt : Ni : M) by ICP-MS	Average Particles size (vertex to vertex, nm)
1	Octahedral PtNi ₃	0.33 : 0.67 : 0	0.24 : 0.76 : 0	12.4 ± 1.1
2	Concave Pt ₃ Ni	0.69 : 0.31 : 0	0.72 : 0.28 : 0	11.8 ± 1.0
3	Pt ₃ Ni @ Au _{0.5}	0.58 : 0.22 : 0.20	0.64 : 0.25 : 0.11	11.9 ± 1.2
4	Pt ₃ Ni @ Au ₂	0.45 : 0.12 : 0.43	0.38 : 0.17 : 0.45	12.2 ± 1.8
5	Pt ₃ Ni @ Au ₈	0.21 : 0.09 : 0.70	0.28 : 0.14 : 0.058	13.3 ± 2.0
6	Pt ₃ Ni @ Ag _{0.5}	0.61 : 0.19 : 0.20	0.57 : 0.22 : 0.21	11.8 ± 1.1
7	Pt ₃ Ni @ Ag ₂	0.49 : 0.16 : 0.35	0.50 : 0.12 : 0.38	12.0 ± 1.3
8	Pt ₃ Ni @ Ag ₈	0.11 : 0.06 : 0.83	0.16 : 0.05 : 0.79	12.6 ± 1.5
9	Pt ₃ Ni @ Cu _{0.5}	0.58 : 0.22 : 0.20	0.64 : 0.25 : 0.11	11.8 ± 1.1
10	Pt ₃ Ni @ Cu ₂	0.53 : 0.13 : 0.34	0.40 : 0.17 : 0.43	12.2 ± 1.2
11	Pt ₃ Ni @ Cu ₈	0.20 : 0.12 : 0.68	0.18 : 0.12 : 0.70	12.5 ± 1.5
12	Pt ₃ Ni @ Rh _{0.5}	0.48 : 0.22 : 0.30	0.58 : 0.29 : 0.13	11.8 ± 1.0
13	Pt ₃ Ni @ Rh ₂	0.55 : 0.10 : 0.35	0.48 : 0.12 : 0.40	12.4 ± 1.3
14	Pt ₃ Ni @ Rh ₈	0.26 : 0.09 : 0.65	0.25 : 0.10 : 0.65	12.5 ± 1.5

Table S4: Turnover frequencies (TOFs [h^{-1}]) of the hydrogenation of nitrobenzene catalyzed by various catalysts. [a]

<div style="display: flex; align-items: center; justify-content: center;"> <div style="border: 1px solid black; padding: 5px; margin-right: 10px;"> </div> <div style="text-align: center; margin-right: 10px;"> <p>3 equiv. HCOOH</p> <p>1 atm N₂, 70°C, 2h, Catalyst</p> </div> <div style="border: 1px solid black; padding: 5px; margin-left: 10px;"> </div> </div>				
entry	catalyst	Conversion [%]	Yield[%] [b]	TOFs [h^{-1}] [c]
1	Octahedral PtNi ₃	5	5	9
2	Concave Pt ₃ Ni	9	8	12
3	Pt ₃ Ni @ Au _{0.5}	>99	97	124
4	Pt ₃ Ni @ Au ₂	24	23	86
5	Pt ₃ Ni @ Au ₈	4	4	6
6	Pt ₃ Ni @ Ag _{0.5}	16	15	18
7	Pt ₃ Ni @ Cu _{0.5}	69	67	74
8	Pt ₃ Ni @ Rh _{0.5}	5	5	8

[a] Conditions: substrate (0.5 mmol), 0.5 mol% catalyst (base on Pt) with respect to the substrate and tetrahydrofuran solvent (2.5 mL) were stirred under nitrogen balloon/ 70°C conditions.

[b] The yields of products were determined by GC using n-tridecane as an internal standard. The conditions about the measurement of GC are as follows: GC chromatography was performed on SP-6890 with a FID detector equipped with a capillary column (SE-54, 30 m × 0.50 μm × 0.53 mm). Parameters were as follows: initial oven temperature, 60 °C, 3 min; ramp, 15 °C/min; final temperature, 300 °C; final time, 5 min; injector temperature, 300 °C; detector temperature, 300 °C; injection volume, 1 μL .

[c] TOFs [h^{-1}] = converted number of molecules of substrate in 30 min / (number of Pt in catalysts × 0.5 h)

Table S5: Turnover frequencies (TOFs [h^{-1}]) of the hydrogenation of nitroarenes catalyzed by various catalysts. [a]

catalyst	Temp.(°C)	Conversion(%)	Selectivity (%) [b]
Pt ₃ Ni @ Ag _{0.5}	210	92.1	96.2
	230	96.2	96.1
	250	98.4	96.0
Pt ₃ Ni @ Ag ₂	210	85.9	91.2
	230	93.4	91.4
	250	97.1	91.0
Pt ₃ Ni @ Ag ₈	210	63.3	96.5
	230	74.1	96.5
	250	92.4	96.5
Pt ₃ Ni @ Rh _{0.5}	230	43.7	84.8
	250	30.9	62.0
	280	30.2	73.9
Pt ₃ Ni @ Au _{0.5}	230	12.3	95.1
	250	12.1	95.6
	280	13.4	96.1
Pt ₃ Ni @ Cu _{0.5}	230	90.7	95.0
	250	91.6	91.3
	280	85.9	90.2

[a] All catalysts samples were pre-activated underwent selective oxidation of benzyl alcohol at 280 °C for 1h, using O₂ / benzyl alcohol = 0.6 (mol / mol) and WHSV = 20 h⁻¹ and then evaluated at the specified temperature.

[b] The main by-products were the benzoic acid.

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