Sophisticated Construction of Au Islands on Pt-Ni: an Ideal Trimetallic Nanoframes Catalyst

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1. Materials and Methods:

Chemicals.

Analytical grade benzyl alcohol, aniline, chloroauric acid, and dimethylglyoxime were obtained from Beijing Chemical Reagents, China. Pt(acac)₂, (99%) Ni(acac)₂ (99%) and 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 JEOL JEM-1200EX 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. 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 truncated octahedral PtNi₃ nanocrystals.

Our recently reported work ensured us to prepared a series of truncated octahedral PtNi_x ($1 \leq x \leq 10$) alloys with excellent shape homogeneity and monodispersity.¹ (Figure S1) In a typical synthesis of PtNi₃ octahedral nanocrystals, Pt(acac)₂, (40.0 mg), poly(vinylpyrrolidone) (PVP, MW=8000, (400.0 mg) Ni(acac)₂ (75 mg) and 0.5 mL aniline were dissolved in 25mL of benzylalcohol, followed by 10 min vigorous stirring. The resulting homogeneous green solution was transferred into a 45-mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 150 °C for a 12 h before it was cooled down to room temperature. The products were precipitated by acetone, separated via centrifugation and further purified by an ethanol-acetone mixture. After being dried in oven at 60 °C, the obtained product was re-dispersed in 10 mL ethanol for next step.

Typical procedure for the hydrogenation of nitrobenzene catalyzed by Pt-Ni alloys.

First, 51 μL nitrobenzene (0.5 mmol) in ethyl acetate (2.5 mL) and the Pt-Ni alloy (contain 0.0025 mmol Pt, 0.5 mol %) were added in a 10 mL round bottomed flask. The round flask was purged with H₂. Then, the reaction mixture was stirred at

room temperature under a H₂ 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.

Electrochemical measurement.

Electrochemical measurements were performed using a three-electrode cell at room temperature. The working electrode was a Glassy Carbon Electrode (GCE) (diameter: 5mm and area: 0.196 cm²) from Pine research Instrument. A leak-free AgCl/Ag/KCl (saturated) electrode was used as the reference and a Pt wire was used as the counter electrode. The reference electrode was placed in a separate compartment through a stopcock to prevent chloride ions from cross-contaminating the electrolyte in the working cell. The electrolyte was 0.1M perchloric acid diluted from 70% using Millipore ultrapure water.

Preparation of working electrode

The catalysts were incorporated onto active carbon (20%, Cabot, Vulcan XC-72). The sample was diluted to 0.5 mg/mL (from 0.5 to 1 mg catalysts/mL water) and sonicated for 5 mins. Then, 5 µl of the dispersion was transferred onto the GCE by a pipette. After the working electrode was dried, 5 µl Nafion dilutes (0.1 wt%) was coated on the catalyst' surface.

Electrochemically active surface area (ECSA)

Cyclic voltammetry (CV) measurements were carried out in 0.1 M HClO₄ solutions in air at a sweep rate of 50 mv/s. The electrochemical surface area (ECSA) was estimated by measuring the charges associated with Hupd adsorption/desorption (Q_H) between -0.20 and 0.2 V after double-layer correction and assuming a value of 210 µC/cm² for the adsorption of a monolayer of hydrogen on a Pt surface (q_H). Considering the loading amount of metal (m), then the specific ECSA was calculated based on the following equation:

$$\text{specific ECSA} = \frac{Q_H}{m \times q_H}$$

Electro-oxidation of methanol

Methanol oxidation was measured in 1 M methanol and 0.1 M HClO₄ with a scan rate 50 mv/s. The specific activity was checked by measuring current density (raw current divided by the ECSA).

2. Supporting Figures and Tables:

Figure S1: TEM images of a) truncated octahedral PtNi, b) truncated octahedral PtNi₂, c) truncated octahedral PtNi₆, and d) truncated octahedral PtNi₁₀.

Figure S2: Cross-sectional compositional line profiles of a truncated octahedral PtNi₃.

Figure S3: TEM images of a) corroded PtNi, b) corroded PtNi₂, c) corroded PtNi₆, and d) corroded PtNi₁₀. (Insets are the magnified TEM images. The scale bars are 10 nm)

As shown in Figure S3, a gradual increase in the ratio of Ni to Pt (from 1 : 1 to 2 : 1, 3 : 1, 6 : 1, and 10 : 1) resulted in a significant increase in the hollowness of the final obtained nanoframes. The terminated stable phase was confirmed to be Pt₃Ni according to the data obtained from powder X-ray diffraction (XRD) (Figure S4) measurements, which were further supported by energy dispersive spectroscopy (EDS) and ICP-MS (Figure S5 and Table S1 of SI).

Figure S4: XRD patterns of as-prepared Pt-Ni alloys and Au on Pt-Ni nanoparticles.

We also performed XRD and EDS measurements to monitor the internal crystalline and compositional evolution of Au on the Pt-Ni structures. The XRD data show two distinct sets of diffraction peaks that correspond to each of the crystalline phases in the hybrid Au-Pt-Ni systems. The patterns exhibited by the Au and Pt-Ni alloys could be indexed to the {111}, {200}, and {220} diffractions of a face-centered-cubic (fcc) structure. The alloy phases of Au-Pt and Au-Ni could be ruled out based on the XRD data. After chemical etching, all of the peaks indexed to Pt-Ni alloys shifted slightly to a lower 2θ value compared to those of uncorroded Pt-Ni alloys, which could be attributed to the increase in lattice spacing resulting from the etching of most of the Ni from the Ni-rich precursors. As the volume of the H₂AuCl₄ solution increased, the peaks belonging to Au islands become significantly more intense. This unique Au islands decorated trimetallic nanoframe structure can be also confirmed by the site-specific EDS analysis, demonstrating the quantity of Au at corner area is apparently higher than that at edge area. (Figure S11)

Figure S5: EDS patterns of Pt-Ni and Au on Pt-Ni nanoparticles.

Figure S6: a) TEM image, b) magnified TEM image, and c) HRTEM images of 20%Au on Pt₃Ni. d) EDS elemental mapping images of 20% Au on Pt₃Ni.

Figure S7: a) TEM image, b) HRTEM image, and c) HAADF-STEM images of 50%Au on Pt₃Ni. d) EDS elemental mapping images of 50% Au on Pt₃Ni.

It is noteworthy that the amount of Au deposited could also be controlled by simply varying the volume of the HAuCl₄ solution. As shown in Figure S6 and S7, Au clusters could grow on the external corners or edges of the nanoframes but could not diffuse into the Pt₃Ni cores.

Figure S8: a) TEM image, b) HRTEM image, and c) HAADF-STEM images of 10% Pd on Pt₃Ni. d) EDS elemental mapping images of 10% Pd on Pt₃Ni.

Figure S9: a) TEM image, b) HRTEM image, and c) HAADF-STEM images of 10% Cu on Pt₃Ni. d) EDS elemental mapping images of 10% Cu on Pt₃Ni.

By simply replacing HAuCl₄ with Na₂PdCl₄ or Cu(NO₃)₂, it was possible to extend this method to construct Pd or Cu islands on Pt₃Ni hybrid nanoframes (Figure S8 and S9). Indeed, considering the reactivity of copper, which is affected by electronegativity, is really close to nickel, the temperature of replacement reaction has to be elevated from room temperature to 100°C. Though the galvanic kinetic significantly being affected by electronegativity, the deposition of Cu islands didn't vary the nanoframe morphology obtained. We can ascribe this phenomenon to the molar ratio of Cu deposited on the Pt-Ni alloy is relative small respect to the Ni that being etched.

Figure S10: HRTEM image (equipped with a spherical aberration (Cs) corrector) of 10%Au on Pt₃Ni.

It has been reported that metals with small lattice spacings (such as Cu or Ni) can diffuse from Au or Pt surfaces to form an alloy phase.^{2,3} Because Au possesses a larger crystal lattice, the diffusion of Au into the Pt-Ni crystal lattice could not take place after nucleation. Naturally, Au nuclei tended to deposit on the surface of Pt-Ni cores, forming unique Au islands on the Pt₃Ni frames structures. Spherical-aberration-corrected HRTEM imaging further confirmed that the lattice fringes at the corner (marked by red circles) could be indexed to Au {111} facets (Figure S10). Moreover, the distance between the lattice fringes at the edges suggested that the crystalline phase was dominated by Pt₃Ni.

Au atomic%	10% Au on Pt ₃ Ni catalyst	20% Au on Pt ₃ Ni catalyst	50% Au on Pt ₃ Ni catalyst
a	5.2 ± 4.9%	12.8 ± 7.1%	20.5 ± 9.1%
b	50.7 ± 5.3%	73.2 ± 6.8%	91.2 ± 8.6%

Figure S11: Site-specific EDX analysis results for the samples of three representative stages.

Figure S12: Ni 2p_{3/2} XPS spectra of Pt₃Ni frame and 10%Au on Pt₃Ni.

Figure S13: Cyclic voltammograms of as-prepared truncated octahedral Pt₃Ni alloys Pt₃Ni nanoframe and 10%Au on Pt₃Ni nanoframe.

Figure S14: TEM image of as-prepared Au nanoparticles and the Au XPS spectra of 10% Au on Pt₃Ni and Au nanoparticles.

Figure S15: HRTEM images of Pt₃Ni nanoframes from different orientations.

Figure S16: The exact concentration profiles in different samples.

Tables:

Table S1: Composition of as-prepared truncated octahedral Pt-Ni alloys and hybrid Au on Pt-Ni nanoframes.

entry	catalysts	Analyzed molar ratios (Pt : Ni : Au) by EDS	Analyzed molar ratios (Pt : Ni : Au) by ICP-MS	Average Particles size (opposite faces, nm)
1	Truncated octahedral PtNi ₃	0.28 : 0.72 : 0	0.25 : 0.75 : 0	12.7 ± 1.3
2	Truncated Pt ₃ Ni nanoframe	0.69 : 0.31 : 0	0.72 : 0.28 : 0	12.5 ± 1.5
3	10%Au on PtNi ₃	0.28 : 0.72 : 0.030	0.27 : 0.73 : 0.013	12.8 ± 1.6
4	10%Au on PtNi	0.57 : 0.43 : 0.052	0.54 : 0.46 : 0.053	12.6 ± 1.8
5	10%Au on Pt ₃ Ni	0.73 : 0.27 : 0.070	0.75 : 0.25 : 0.072	12.3 ± 1.6
6	20%Au on Pt ₃ Ni	0.76 : 0.24 : 0.11	0.74 : 0.26 : 0.13	13.3 ± 2.0
7	50%Au on Pt ₃ Ni	0.78 : 0.22 : 0.39	0.76 : 0.24 : 0.38	13.6 ± 2.3

Table S2: Turnover frequencies (TOFs [h⁻¹]) of the hydrogenation of nitroarenes catalyzed by various catalysts.[a]

entry	catalyst	TOF[b]	Selectivity / %		
			AD	NA	AA
1	truncated octahedral PtNi ₃	33	56	44	ND
2	truncated Pt ₃ Ni nanoframe	156	47	53	ND
3	10%Au on PtNi ₃	75	85	15	ND
4	10%Au on PtNi	131	91	9	ND
5	10%Au on Pt ₃ Ni	208	>99	ND	ND
6	20%Au on Pt ₃ Ni	186	>99	ND	ND
7	50%Au on Pt ₃ Ni	58	>99	ND	ND
8	Au octahedron[c]	86	>99	ND	ND

[a] Conditions: substrate (0.5 mmol), 0.5 mol% catalyst (base on Pt) with respect to the

substrate and Ethyl acetate solvent (2.5 mL) were stirred under hydrogenation balloon/room temperature conditions.

[b] All the substrates could be completely transformed if the reaction last for a sufficient time with nearly 100% selectivity. 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 $\times$ 0.50 μ m $\times$ 0.53 mm). Parameters were as follows: initial oven temperature, 60 $^{\circ}$ C, 3 min; ramp, 15 $^{\circ}$ C/min; final temperature, 300 $^{\circ}$ C; final time, 5 min; injector temperature, 300 $^{\circ}$ C; detector temperature, 300 $^{\circ}$ C; injection volume, 1 μ L.

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

[c] The synthesis of Au octahedron⁴ follow the reference 2.

3. Supplementary Discussions of DFT Calculations:

Methodology and calculation model

All calculations were performed using the density functional theory in the generalized gradient approximation (GGA) with the Perdew and Wang functional⁵ for the exchange-correlation effects, as implemented in the Vienna ab-initio simulation package.⁶ The electron-ion interaction was described by the projector augmented wave method,^{7,8} and the cutoff energy for plane-wave basis set was 400 eV. The 4 x 4 x 1 Monkhorst-Pack k-point mesh was applied to sample the Brillouin zone. In the slab models, the (100), (110) and (111) surfaces were modeled with four, six and three layers, respectively, and the extended [110] edges with five layers. In the pyramid model, the corner of hybrid Au-Pt-Ni nanoframes was modeled with six layers, containing three Au layers and three Pt₃Ni layers (see the inset of Figure 4a). The vacuum spacing between the calculation units along the direction perpendicular to the unit was at least 12 Å. Except the bottom layer, all atoms were fully relaxed until the force on each ion was less than 30 meV/Å. Bader charge analysis was used to calculate the charge transfer.⁹

With the thermodynamic standpoint, the dissolution energy of metal atoms in solution could be approximated to the surface cohesive energy by the addition of a constant,¹⁰ which mainly contains the ionization potentials, vaporization entropy, and solvation energy. Here, we revisited the approximation from a new perspective at the nanoscale, and suggested that in nanoparticles, the local atomic cohesive energy (E_{coh}) instead of surface one was defined as the energy needed to remove a metal atom (M) from the site (i.e., surface, edge and corner),

$$E_{\text{coh}} = E_{N-1} + E_M - E_N, \quad (1)$$

where E_{N-1} and E_N were the cohesive energies of systems with the number of N-1 and N atoms, respectively, and E_M was the energy of M removed. Despite ignoring the difference in the constant term, the eqn (1) gave that all E_{coh} of Ni are smaller than those of Pt in the PtNi₃ nanoparticles (Figure 2), consistent with the present etching experiment: the Ni atoms rather than the Pt atoms were preferentially dissolved in solution. We could therefore believe that the approximation was reliable and valid for elucidating the etching profile evolution of PtNi₃ nanoparticles, which were also supported by the recently reported etching experiments of Pt_xNi_{1-x} octahedral.¹¹

Proposed chemical etching process and mechanism

The chemical etching of truncated PtNi₃ polyhedra starts from the exposed {100} and {111} surfaces, as evident in our experiments. In what follows, by using density functional theory calculations on local atomic cohesive energy, crystal structure analysis of surfaces, and susceptibility of metal to chemical condition, we investigated the etching processes and mechanisms of (111) and (100) surfaces and the growth of [110] edge of PtNi₃, as schematically illustrated in Figure 2, for the better understanding of morphological and compositional evolution of truncated PtNi₃ polyhedra in solution.

(111) surface etching: The close-packed (111) surfaces of PtNi₃ have only one structural characteristic (Figure 2a1): the Pt atom separated by 6 coordinated Ni atoms, ensuring the Ni/Pt ratio of 3:1. At the early stage, the Ni atoms are dissolved readily due to smaller E_{coh} than the Pt atoms, thereby leaving isolated Pt atoms on the surface (Figure 2a2). The low number of and the large distance between Pt atoms (~5.30 Å) result in only cluster-like Pt segregation by surface migration. Also, recent experimental evidence showed that the Pt preferentially segregate at the frames in Pt-Ni octahedral.¹² Consequently, the exposed subsurface Ni atoms are open to dimethylglyoxime solution, allowing quick and easy removal of Ni²⁺ by dimethylglyoxime (Figure 2a3). In a word, the etching of {111} surfaces in PtNi₃ polyhedra proceeds in a layer-by-layer fashion, only leaving Pt-rich sinking atomic steps and terraces.¹¹

(100) surface etching: PtNi₃ contains two kinds of {100} planes with different compositions: one is PtNi and the other full Ni (Figure 2b1). Since the Pt atoms with large radius always concentrate on the surface,¹³ we can expect that the etching starts at the Pt-Ni (100) surface, followed by the subsurface Ni (100). The confirmed sequence will be of importance for the understanding of the unique etching of truncated alloy polyhedra. With the order of E_{coh} (Figure 2b), we can see that the Ni of Pt-Ni (100) surface are preferentially dissolved (Figure 2b1). Successively, an interesting phenomenon not observed in the (111) etching is present. That is, the surface Pt atoms that are the second-nearest neighbors each other aggregate together by migration,^{14,15} and consequently such the large-scale segregation may form a “porous Pt-shell” (Figure 2b1 and inset), which is inert to dimethylglyoxime solution. This phenomenon owes to two unique features in structure and composition of PtNi₃ {100} planes: one is small Pt-Pt spacing (3.75Å) and the other high content of surface Pt (50%). It is apparent that the inert Pt-shell will close the contact between subsurface Ni and dimethylglyoxime. A direct consequence is that following the etching reaction order proposed in Ref. 8, the dissolution is controlled by outward diffusion of Ni²⁺ of subsurface (100), half of which are exposed, through the porous Pt-shell (Figure 2b2). With progressing time, under the Pt-shell there are many vacant regions which are created by the removal of Ni atoms (Figure 2b3), and they will be further condensed to form a single hole, consistent with the HRTEM observations in Figure 1c. The etching process exhibits a mechanism analogous to the Kirkendall effect,¹⁶ where the Ni-diffusion rather than the Pt-diffusion is dominated. Following the etching mechanism, the hollow structure is formed in the truncated PtNi₃ polyhedra as

the Ni-rich core, mentioned as the cross-sectional compositional line profiles in Figure S2, is completely consumed.

Formation of frame along [110] direction: Relative to {100} and {111} surfaces, the Ni atoms at the [110] edges are more easily removed due to poorly coordinated atoms (7) or

smaller E_{coh} (Figure 2c1). Consequently, the narrow (110) facets composed of Pt-rich terraces/steps form earlier than the {100} and {111} etching (Figure 2c2). From the point of view of bonding, the terraces/steps with numerous low coordinated atoms certainly will prepare numerous active sites to accept excess Pt atoms. More precisely, during the etching, without the constraint of coordinated Ni, the remaining Pt atoms from the {100} and {111} faces would occupy readily the Ni-vacancies of narrow (110) facets by surface migration, which is also supported by recent experimental evidence,¹¹ always maintaining the fcc structure. With progressing time, the Pt aggregation along the [110] edges would turn into the Pt deposition on the narrow (110) facets, and eventually the Pt-covered Pt-Ni (Pt-Ni@Pt) frames form (Figure 2c3), consistent with the HRTEM observations in Figure 1c.

Owing to different structure-dependent etching priorities on and mechanisms of exposed surfaces, the truncated octahedral PtNi₃ NPs would be carved from open {100} surfaces by a mechanism analogous to the Kirkendall Effect that develops a hole inside NPs, followed by the emptying of {111} surfaces by a layer-by-layer peel-off fashion that opens the NPs, concomitant with the deposition of Pt atoms on the Ni-poor edges in situ, and eventually transform into the Pt₃Ni nanoframes. These are consistent with the experimental observations, as shown in Figure 1. We can generalize the findings or discussion to the etching-dominated fabrication of other colloidal bimetallic NPs as well. This mechanism can be also applicable to explain Chen's work.¹⁷ We generalize the findings or discussion to the etching-dominated fabrication of other alloy NPs as well. The fundamental requirements needed contain: 1) composition of NPs: higher content of etching components relative to etching-free ones, such as PtCu₃; 2) structure of NPs: polyhedra with active surfaces following a composition-different stacking, ensuring etching priority and void formation, such as {110},¹⁷ {100}-{111} and {110}-{111} combinations of face-centered-cubic (fcc) structure, or {110}-{100} combination of body-centred cubic (bcc) structure; and 3) a selective etching solution, allowing the self-assembly of insensitive components concomitant with the etching of sensitive components. Following the proposed requirements in structure and composition of NPs and chemical solution based on the above experiences (see Supplementary Information for details), we believed the chemical etching would provide a general route to the synthesis of a large number of alloy NPs with hollow nanoframes or open nanoframes.

4. References and Notes

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