

Nanocatalysis

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Synthesis of Core@Shell Cu-Ni@Pt-Cu Nano-Octahedra and Their Improved MOR Activity

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Abstract: Fabrication of 3d metal-based core@shell nanocatalysts with engineered Pt-surfaces provides an effective approach for improving the catalytic performance. The challenges in such preparation include shape control of the 3d metallic cores and thickness control of the Pt-based shells. Herein, we report a colloidal seed-mediated method to prepare octahedral CuNi@Pt-Cu core@shell nanocrystals using CuNi octahedral cores as the template. By precisely controlling the synthesis conditions including the deposition rate and diffusion rate of the shell-formation through tuning the capping ligand, reaction temperature, and heating rate, uniform Pt-based shells can be achieved with a thickness of <1 nm. The resultant carbon-supported CuNi@Pt-Cu core@shell nano-octahedra showed superior activity in electrochemical methanol oxidation reaction (MOR) compared with the commercial Pt/C catalysts and carbon-supported CuNi@Pt-Cu nano-polyhedron counterparts.

n comparison with a heat engine that converts thermal energy of fossil fuels to mechanical energy via the Carnot cycle, a fuel cell device can lead to exciting performance improvements for power generation by directly converting the chemical energy of a fuel into electricity. The intense interest in fuel cell technology stems from the fact that fuel cells are environmentally benign and extremely efficient (40– 70% efficiency by far).^[1] Although this energy conversion strategy has been well developed and some of the commercial fuel cell products have been already available, there are still several issues and challenges associated with the fuel cell catalysts. For proton-exchange membrane fuel cells (PEMFCs), the slow kinetics of reactions on electrodes and the high cost of Pt electrocatalysts are still the main obstacles blocking the commercialization.^[2] Nevertheless, Pt-based nanomaterials are the best electrocatalysts for promoting both the cathodic reaction (oxygen reduction reaction, ORR) and anodic reactions (oxidation of hydrogen and small molecular hydrocarbons such as methanol, ethanol, and formic acid).^[3] In this regard, there have been considerable efforts on the design and development of novel-structure catalysts to reduce the utilization of Pt and to improve the electrocatalytic performance.^[4]

Current efforts on improving the Pt-based fuel cell catalysts can be outlined in three strategies: alloying Pt with another metal such as a 3d transition element (e.g. Cu, Ni, Co, and Fe),^[5] tailoring desirable crystallographic facets on the catalyst surfaces,^[6] and structure/composition manipulation (e.g. core@shell fabrication) with an alternation of surface lattice strains.^[4b,7] For example, M@Pt-Ni core@shell nanostructures have been synthesized using a seed-mediated method, in which a non-Pt noble metal (M) acts like the seeds and Pt-based alloy as the shells.^[8] This design could not only decrease the usage of Pt significantly but also improve the electrocatalytic performance by creating the surface strain (compressive or tensile strain) effect that arises from the lattice mismatch at the interface between the core and shell through tuning the shell thickness.^[4d,9] As a further improvement in the synthesis, strategies of crystallographic plane control and core@shell scheme were combined to strengthen the surface function of well-defined Pt facets. For instance, Xia et al. have successfully coated an ultrathin Pt layer on morphology-controlled Pd nanocrystals such as Pd nanocubes,^[7c] nano-octahedra,^[7c,9b] and nano-icosahedra.^[7d] Since the Pt thin-layer is grown on the Pd(111) surface, the epitaxial strain in the Pt(111) shell can be manipulated to favorably

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alter the bonding energy between the relevant reaction species and the Pt surface sites. These shape-controlled core@shell nano-architectures demonstrated much enhanced ORR performance.^[7c,d,9b] However, the lattice parameter differences among the selected noble metals (the core and the shell) are still not large enough to result in sufficient lattice mismatch and strain effect (e.g., Pd-Pt, the lattice parameter difference $f_r < 1\%$). Consequently, synthesis of shape-controlled core@shell nanostructures with large f_r (generally, $f_r > 5\%$) still remains a challenge.^[4a,h,9c]

Based on these developments, in this work, we replaced the noble metal cores using 3d transition alloy (CuNi) nanocrystals (NCs) that are terminated with {111} facets to increase the core@shell lattice mismatch. Moreover, in this novel nano-architecture (designed as "CuNi@Pt-Cu nanooctahedra"), our structural characterization suggested a thin layer of Pt-Cu alloy as the shell, instead of the pure Pt. Such structures after a carbon loading treatment (designed as "CuNi@Pt-Cu nano-octahedra/C") would further improve the catalytic performance. As a counterpart, a similar nanoarchitecture was also comparatively synthesized without a shape control (designed as "CuNi@Pt-Cu nano-polyhedra"), carbon-loaded (designed as "CuNi@Pt-Cu nanopolyhedra/C"), and characterized.

To fabricate CuNi@Pt-Cu core@shell nanocatalysts, CuNi nano-octahedra as the seeds were prepared in the first step, followed by a Pt-based shell formation in a colloidal system. The entire preparation procedure is illustrated in Scheme 1. In a typical synthesis, CuNi octahedra were pre-synthesized by co-reducing 13.0 mg of copper(II) acetylacetonate and 13.0 mg of nickel(II) acetylacetonate using a borane morpholine solution at 230°C in a colloidal system containing oleylamine, oleic acid, and diphenyl ether.^[10] The detailed preparation is given in Supporting Information. Figure 1a shows a representative transmission electron microscopy (TEM) image of the shape-controlled CuNi octahedra. Their self-assembly further indicated the high quality in terms of size and shape.^[11] Based on the TEM image, the average size of the CuNi NCs was measured as 13.0 ± 1.0 nm, with a uniform distribution of octahedral particles. Figure 1b is a high-resolution TEM image of a selected individual CuNi NC along the [011] zone axis. It presents the CuNi crystallographic fine structure with a (111) lattice spacing of 0.21 nm. This value is consistent with the (111) lattice spacing determined from the powder XRD pattern of CuNi nanooctahedra previously.[10b,c] The HAADF-STEM image and corresponding energy dispersive X-ray (EDX) elemental mapping are presented in Figure S1A-D. Unlike the previous report,^[10a] the CuNi octahedron showed a heterogeneous



Scheme 1. Schematic illustration of the as-synthesized CuNi@Pt-Cu core@shell nano-octahedra through a seed-mediated process.



Figure 1. a) TEM image of CuNi nano-octahedra. b) High-resolution TEM of a typical CuNi nano-octahedron along the zone axis of [011]; Inset is the corresponding Fast Fourier Transform pattern of the HRTEM image.

elemental distribution according to the EDX elemental mapping. The elemental analysis indicates that the inner core is dominated by Cu whereas the outer region shows a uniform distribution of Cu and Ni, leading to a core@shell structure. This may arise from the modified synthesis condition in this work. For example, one of the modifications in the present work was to choose a lower nucleation temperature (230 vs. 240°C) in the "hot injection" process when the reducing reagent solution was introduced.^[10] The formation of a heterogeneous structure in CuNi nanooctahedra is also due to the reduction potential difference of the precursors at a low temperature. The reduction potential of Ni²⁺/Ni⁰ (-0.26 V vs. RHE) is more negative than that of Cu^{2+}/Cu^{0} (+0.34 V vs. RHE) (room temperature data). Therefore Cu²⁺ would be reduced first, generating Cubased nuclei at the initial stage. Once such seeds were yielded, the further reduced Ni and Cu atoms would epitaxially grow on the Cu-based seeds easily and result in Cu-Ni alloy as the outer component. In the bulk of NCs, the average Cu fraction was determined as \approx 52 at % based on the analysis of inductively coupled plasma-optical emission spectroscopy (ICP-OES), which is well consistent with the STEM-EDX result (\approx 51 at %) (Table S1).

Followed by the successful synthesis of the CuNi nanooctahedra as the core components, CuNi@Pt-Cu core@shell nanocatalysts were prepared in tandem as illustrated in Scheme 1. The Pt-based shell growth was carried out by introducing PtCl4 into the CuNi colloidal system at 60°C and was stirred for ≈ 30 min to generate a uniform mixture under Argon (Ar) gas protection (for the details see the Supporting Information). Since the temperature and the Pt reducing rate are the key factors in this process,^[9c] precise control of the deposition rate and diffusion rate is crucial to the successful formation of the core@shell CuNi@Pt-Cu nano-octahedra. Figure 2a is a TEM image of the as-prepared CuNi@Pt-Cu core@shell nano-octahedra with an average size of $13.3 \pm$ 1.2 nm. The octahedral core@shell nanostructure was also imaged using HAADF-STEM (Figure 2b,c) and EDX elemental mapping (Figure S1E-I), respectively. EDX elemental mapping reveals a core@shell octahedral structure, indicating that Pt atoms are mainly located on the surface while the interior consists of Cu-Ni alloy. The Cu- and Ni-EDX elemental mapping (Figure S1E,F) shows that Cu is still the



Figure 2. a) TEM image of CuNi@Pt-Cu core@shell nano-octahedra. b) HAADF-STEM image of a typical CuNi@Pt-Cu core@shell nanooctahedron. c) Crystal structure model of the HAADF-STEM image.

most abundant element in the core center. This is well consistent with the observation of the CuNi octahedron (Figure S1B-D). Such a result indicates that the Pt deposition process mainly occurred on the surface of the CuNi octahedral template whereas the CuNi core kept the same. Based on these characterizations, no hollow or porous structure was observed, either. It is, therefore, believed that the Pt-based shell would protect the CuNi core from etching in the later evolution stage once it forms. The EDX elemental mapping further exhibits the presence of Cu signal from the surface region, implying that the shell component contains both Pt and Cu elements, instead of a sole Pt constituent. Since the reduction potential of Ni²⁺/Ni⁰ is much lower than those of Cu^{2+}/Cu^{0} , $PtCl_{4}/Pt^{2+}$, and Pt^{2+}/Pt^{0} , [12] the reduction of Pt ions into metallic Pt was most likely achieved through a galvanic replacement with Ni atoms on the CuNi surface, producing the CuNi@Pt-Cu core@shell nanostructure. The ICP-OES composition analysis indicated that the Cu/Ni molar ratio increased from ≈ 1.1 (52:48) to ≈ 2.0 (60:30) after the Pt deposition (Table S1). Assuming that the content of Cu in the core was unchanged and no additional Cu atoms were deposited on the shell during the shell formation process, the analysis shows a significant decrease of the Ni molar fraction in the Cu-Ni-based core@shell structure after the shell formation. This further supports the occurrence of the Pt⁴⁺-Ni⁰ galvanic replacement reaction during the shell growth, leading to alloying between the deposited Pt and the residual Cu on the core surface.

Based on Table S1, the core@shell bulk composition is Cu₆₀Ni₃₀Pt₁₀. The elemental mapping (Figure S1E–I) further reveals that the thickness of the Pt-Cu shell is less than 1 nm. To further identify the near-surface composition, these samples were also characterized using X-ray photoelectron spectroscopy (XPS), a surface/near-surface sensitive technique^[4i,7a,13] (Figures S2–S3). XPS suggested a composition of Cu44Ni15Pt41 on the surface/near-surface of CuNi@Pt-Cu nano-octahedra/C. Compared with the ICP-based (as well EDX-based) bulk composition Cu₆₀Ni₃₀Pt₁₀ (or as $Cu_{59}Ni_{31}Pt_{11}$) presented in Table S1 (note that the average molar ratio between Cu and Ni in the core is roughly 1:1), XPS reveals extra Cu on the shell together with Pt, supporting the binary component in the shell structure. By carefully examining the elemental fraction of CuNi@Pt-Cu nanopolyhedra/C determined by XPS (Cu₃₂Ni₂₀Pt₄₈) and ICP (Cu₅₈Ni₃₀Pt₁₂), one can identify the similar Pt-Cu component in their shell structure. Compared to Cu in the shell, the higher Pt contents suggested by XPS possibly indicate that Pt atoms expose on the shell-surfaces in both samples.

Furthermore, the (111) diffraction peaks of *fcc* Pt-Cu shell and *fcc* Cu-abundant CuNi core can be readily distinguished in the X-ray diffraction (XRD) patterns of core@shell CuNi@Pt-Cu nano-octahedra/C as presented in Figure S4. Compared with the standard ICDD card^[14] and previous work (Table S2),^[15] we identified a right-shift at the (111) peak of the Pt-Cu shell (41.35°). This indicates a compressive lattice strain from the shell induced by the CuNi core that has a smaller lattice parameter. This effect was also reported in many core–shell systems previously, such as Au@FePt₃, AgPd@Pt, Ni@FePt, and FePt@Pt NCs.^[4b,5d,16] In addition, the asymmetric shape of the diffraction peak (Figure S4) further supports the presence of the lattice strain.

It is worth pointing out that several reaction conditions are crucial to the success of this shape-controlled core@shell synthesis. First, optimizing the reaction temperature is essential to tune the equilibrium between the Pt deposition rate and diffusion rate during the shell formation stage. Coinciding with the previous reports,^[7c,d,9a,b] we identified that 180 °C is a promising temperature, at which reduced Pt atoms successfully deposited on truncated corners or edges of the CuNi nano-octahedra and subsequently transferred to their {111} facets.^[6c,9b] Second, the ramp rate of heating plays a significant role in this shell formation process. We determined that a slow ramp rate of heating (e.g. $1-2^{\circ}$ Cmin⁻¹) favors the well-defined shell growth on the octahedral CuNi NCs. In contrast, a fast ramp rate of heating (e.g. $> 6 \,^{\circ} C \,^{min^{-1}}$) could result in branched structures in the products (refer to Figure S5). Third, as reported earlier,^[10c] chloride ions (Cl⁻) as a kind of capping agents prefer their adsorption on the CuNi {100} facets (such as the truncated vertices), leading to a successful "coating" of Pt atoms on the uncapped CuNi {111} facets. We have alternately re-conducted this shell growth synthesis in the absence of Cl⁻ by replacing PtCl₄ precursor with Pt(acac)₂. As a result, "core-satellite"-like nanostructures were received as shown in Figure S6. Last, we noticed that this shell formation process is sensitive to oxygen. Once the surfaces of CuNi NCs were oxidized, it would be impossible for Pt atoms to deposit on the CuNi cores and yield the core@shell nano-architecture. Figure S7 represents an unfavorable example. With oxidized shells on the CuNi NCs, Pt atoms would not continuously deposit and grow on the oxide surface according to the HAADF-STEM EDX elemental mapping analysis. It is worth pointing out that the developed CuNi@Pt-Cu nano-octahedra (Figure 2) are more truncated compared with the CuNi octahedral cores. The possible reason is that the Cu or Ni atoms located at the vertices/edges possess higher surface energy. Compared with the atoms on {111} facets, they are more active to be oxidized and dissolved into the reaction system. This "etching"-based development reported previously^[17] further validates the aforementioned hypothesis, that is, the Pt deposition started from the corners or edges.

To evaluate the electrocatalytic performance of these nanocatalysts, we carried out a methanol oxidation reaction (MOR) over the nanocatalysts after a carbon loading treat-

ment (CuNi@Pt-Cu octahedra/C). The detailed procedure is described in the Supporting Information. For comparison, CuNi@Pt-Cu nano-polyhedra/C and a commercial Pt/C (20 wt % Pt) sample were co-evaluated as well (see Supporting Information, Figures S8 and S9). Cyclic voltammograms (CVs) of those catalysts were recorded using N₂-saturated 0.1 M HClO₄ solution at a scan rate of 50 mV s⁻¹ (Figure S10) and their CO-stripping tests were conducted in N2-saturated 0.1 M HClO₄ solution between -0.2 and 0.9 V (vs. Ag/AgCl) at a sweep rate of 50 mV s^{-1} . The electrochemical surface areas (ECSAs) were integrated using the region between 0.4 and 0.8 V (vs. Ag/AgCl), depicted in Figure S11 and Table S3. As illustrated in Figure S11, the onset potential of CO electrooxidation peaks on CuNi@Pt-Cu nano-octahedra/C is over 30 mV more negative than that on the commercial Pt/C and $\approx 5 \text{ mV}$ negative than that on the CuNi@Pt-Cu nano-polyhedra/C, indicating a weaker CO adsorption affinity on the active sites of CuNi@Pt-Cu nano-octahedron surfaces and higher electrochemical oxidation activity. Moreover, Table S3 summarizes the $Q_{CO}/2Q_{H}$ ratios, where CuNi@Pt-Cu nanooctahedra/C (1.13) and CuNi@Pt-Cu nano-polyhedra/C (1.29) are higher than that of the commercial Pt/C (1.03), implying the presence of the non-Pt element (Cu, in this work) on the outer surfaces of the core@shell catalysts. This result is consistent with the EDX elemental mapping analysis discussed above.

The catalytic activity of the CuNi@Pt-Cu nano-octahedra/ C, as well as the counterparts towards MOR, was subsequently investigated. CV profiles of CuNi@Pt-Cu nanooctahedra/C in N2-saturated solution containing 0.1 M $HClO_4 + 1$ M methanol are shown in Figure 3a and b. For comparison, results from CuNi@Pt-Cu nano-polyhedra/C and commercial Pt/C samples are also included. Figure 3 a is based on the specific activities that were calculated using the ECSA determined from the CO-stripping experiments, whereas Figure 3b is based on the mass activities that were calculated from the loaded Pt mass on the electrodes. The electrode potentials are reported versus an Ag/AgCl electrode. The CVs show that the highest MOR current density was determined from CuNi@Pt-Cu nano-octahedra/C. For example, the maximum peak value of MOR current density on CuNi@Pt-Cu octahedra/C is 7.49 mA cm⁻² (or 0.99 A mg_{Pt}⁻¹),



Figure 3. a,b) CV curves by normalizing with (a) specific area and (b) Pt loading mass of the three nano-catalysts (CuNi@Pt-Cu nano-octahedra/ C, CuNi@Pt-Cu nano-polyhedra/C, and commercial Pt/C) in N₂-saturated 0.1 M HClO₄ + 1 M methanol solution at a sweep rate of 50 mVs⁻¹. c) Chronoamperometry (CA) curves of the three nano-catalysts at 0.75 V vs. Ag/AgCl measured in N₂-saturated 0.1 M HClO₄ + 1 M methanol solution. d) Specific activities and mass activities of the three nano-catalysts at 0.75 V vs. Ag/AgCl.

whereas those for the CuNi@Pt-Cu nano-polyhedra/C and commercial Pt/C sample are 5.57 mA cm⁻² (or 0.66 A mg_{Pt}⁻¹) and 1.30 mA cm^{-2} (or $0.23 \text{ Amg}_{Pt}^{-1}$), respectively. This indicates that MOR specific activity of core@shell CuNi@Pt-Cu nano-octahedra/C is \approx 1.34- and \approx 5.76-fold higher than those of CuNi@Pt-Cu nano-polyhedra/C and the commercial Pt/C (or \approx 1.50- and \approx 4.30-fold higher in mass activity), respectively. A recent report^[18] of hollow PtCu nano-octahedra supports that the {111}-terminated facets of octahedral Pt-Cu shell should add an advantage towards MOR in addition to lattice strain effect. It is consequently believed that the lattice strain and shape effect mainly contribute to the MOR activity enhancement in CuNi@Pt-Cu nano-octahedra/C. As a counterpart, the CuNi@Pt-Cu nano-polyhedra/C lacks {111} shape effect and therefore exhibits lower MOR activity than CuNi@Pt-Cu nano-octahedra/C (Table S4) although the strain effect may still exist as confirmed in Table S2 and Figure S8. The higher methanol oxidation current density on CuNi@Pt-Cu nano-octahedra/C was further confirmed by the chronoamperometric measurements performed at 0.75 V (vs. Ag/AgCl) as shown in Figure 3c. CuNi@Pt-Cu nano-octahedra/C exhibit the highest current density while on the contrary CuNi@Pt-Cu nano-polyhedra/C and the commercial Pt/C are either relatively decayed rapidly or remain low value. Therefore, the developed core@shell CuNi@Pt-Cu nano-octahedra/ C facilitate the synergistic enhancement in MOR activity by increasing the superior CO tolerance, which can also be supported by the lower onset potential of CO-stripping peaks (Figure S11). Figure 3d summarizes the MOR peak values of the three typical catalysts presented in Figure 3a and b, demonstrating that the CuNi@Pt-Cu nano-octahedra/C outperform the counterparts in terms of the MOR performance. After the CA durability test, the CV profiles of CuNi@Pt-Cu nano-octahedra/C and CuNi@Pt-Cu nano-polyhedra/C in N2saturated HClO₄ solution were further recorded and are presented in Figure S12. In CuNi@Pt-Cu nano-octahedra/C, the negligible change in the H_{UPD} area before and after the CA durability test exhibits the high catalytic stability and demonstrates that the compressive strain could downshift the d-band center, weaken all the poisoning species binding strength, and facilitate the MOR activity.^[19] Although the compressive strain also exists in the CuNi@Pt-Cu nanopolyhedra/C, their H_{UPD} area decreased after the CA durability test, indicating that some of the Pt sites were poisoned by the poisoning species. This further revealed that the poisoning species have weakened the binding strength on (111) facets rather than other facets, which is one of the main reasons why the CuNi@Pt-Cu nano-octahedra/C show better MOR performance than CuNi@Pt-Cu nano-polyhedra/C.

In conclusion, by taking advantage of the CuNi nanooctahedron preparation achieved previously, we have successfully demonstrated the preparation of octahedral CuNi@Pt-Cu core@shell nanocatalysts. The shell formation could be facilitated by a precise selection and tuning of the experimental conditions, including the temperature (≈ 180 °C), heating rate (≈ 2 °Cmin⁻¹), the Pt precursor/ capping ligand (PtCl₄), and other parameters. The thickness of the Pt-based shell could be controlled to less than 1 nm. The obtained CuNi@Pt-Cu core@shell nano-octahedra possess numerous structural features, such as {111} shape effect and strain effect, and exhibit superior catalytic activity towards MOR electrochemically. In the first report disseminated in this journal twelve years ago,^[5] we ever demonstrated that PtCu nanocubes terminated with {100} facets showed outstanding MOR electrocatalytic activity (current density of peak value: $\approx 4.7 \text{ mA cm}^{-2}$). Our current results indicate that the {111}-profiled Pt-Cu facets originated from these core@shell nano-architectures can further promote the MOR activity (current density of peak value: $\approx 7.5 \text{ mA cm}^{-2}$) while the use of the Pt component is greatly reduced. This work paves the way for integrating the three strategies of Ptbased electrocatalyst improvement, that is, alloying with a 3d metal, crystal shape control, and core@shell structure (with lattice strain), into one design. Since most of the electrochemical reactions are catalyst facet- and surface composition-dependent, we envisage that the CuNi@Pt-Cu nanocatalysts yielded from this approach could potentially possess high activity towards other small molecule oxidation reactions such as formic acid oxidation.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: core@shell · CuNi@Pt-Cu · MOR activity · nanocatalysts · nano-octahedra

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