

Oxidation-Induced Atom Diffusion and Surface Restructuring in Faceted Ternary Pt–Cu–Ni Nanoparticles

Xiaochen Shen,^{†,‡} Sheng Dai,^{#,‡} Shuyi Zhang,^{§,‡} Zheng Lu,[⊥] Changlin Zhang,[†] George W. Graham,^{#,§} Yu Lei,[⊥] Xiaoqing Pan,^{*,#,||} and Zhenmeng Peng^{*,†}

[†]Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, Ohio 44325, United States

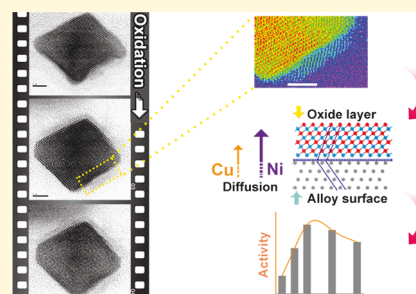
[#]Department of Materials Science and Engineering and ^{||}Department of Physics and Astronomy, University of California—Irvine, Irvine, California 92697, United States

[⊥]Department of Chemical and Materials Engineering, University of Alabama in Huntsville, Huntsville, Alabama 35899, United States

[§]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States

S Supporting Information

ABSTRACT: Ternary alloy catalysts outperform their binary counterparts in many reactions although the direct observation of structural evolution under reaction conditions to understand the structure–performance relationship significantly lacks. In situ transmission electron microscopy at atmospheric pressure provides a great opportunity to uncover dynamic structure and composition changes of ternary alloy nanoparticles. In this work, the atomic-scale elemental diffusion and surface reconstruction of ternary octahedral Pt₂CuNi alloy nanoparticles in an oxidative environment at elevated temperatures are reported. Combining them with multiple characterizations and numerical simulation, it is revealed that the oxidative condition induced the lattice atom diffusion, which leads to the NiO_x major/CuO_x minor surface oxide layers accompanied by surface restructuring and lattice rearrangement. Further analysis helped to establish the numerical model and visualize the atom distribution variation in the restructuring process. Also, the model catalytic test of the oxygen reduction reaction demonstrates that the catalytic performance of ternary Pt₂CuNi alloy nanoparticles can be tuned through oxidative treatment.



INTRODUCTION

Pt–M (M = transition metals) binary alloy nanoparticles are regarded as one of the important catalytic nanomaterials owing to their outstanding catalytic performances and thus are widely employed in catalyzing the oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), methanol and formic acid oxidation, CO preferential oxidation reaction, and so on, which are considered as promising solutions to current environmental problems and possible depletion of fossil fuels.^{1–12} Recently, the ternary Pt–M–N alloys that involve one more transition metal compared to the binary systems are found to outperform their binary counterpart in various reactions. For example, ternary Pt–Cu–Ni nanoparticles show significant enhancement of the ORR activity at the cathode of polymer electrolyte membrane fuel cells (PEMFCs) compared with the binary Pt–Ni catalyst.¹³ Ternary Pt–Rh–Ni nanocatalysts are found to better facilitate the ethanol oxidation reaction (EOR) in direct ethanol fuel cells (DEFCs) compared with the state-of-the-art catalyst.¹⁴

For the binary alloy system, people have already made progress in the study of surface elemental distribution and atomic configuration of Pt–M alloy nanoparticles for understanding and designing optimal nanocatalysts. Gan et al. revealed the preferential distribution of Ni on the Pt–Ni (111)

surface via transmission electron microscopy (TEM).¹⁵ Menning et al. predicted the segregation of 3d metals to the top {111} surfaces of Pt–M systems in the presence of oxygen by using density functional theory (DFT) calculations.^{16,17} However, when it comes to the ternary alloy system, many open questions still remain unresolved, for example, surface elemental distribution of different transition metals, segregation difference of multiple transition metals, and their restructuring behavior under reaction conditions. Unfortunately, due to the complexity, it is notable that very few studies are focusing on the surface elemental distribution and atomic arrangements of ternary Pt-based alloy nanoparticles, which are crucial to their enhanced catalytic performances compared with their binary counterparts.¹⁸ This urges the exploration of ternary Pt-based alloy system under reaction conditions to light up the pathway of ternary alloy catalyst development.

On the other hand, most of the studies rely on ex situ characterization techniques to study the evolution of surface elemental distribution, and thus, the valuable intermediate state and dynamic kinetic information is missing by only

Received: December 17, 2018

Revised: February 13, 2019

Published: February 14, 2019

comparing the initial and final states of the samples. In this regard, it is more convincing and efficient to study the catalyst dynamics with in situ techniques. For instance, Somorjai et al. reported the gas atmosphere-driven structure and composition changes of core-shell bimetallic nanoparticles using ambient-pressure X-ray photoemission spectroscopy (AP-XPS).¹⁹ Chen et al. studied the dynamic surface restructuring of a Au catalyst using optical microscopy with molecular fluorescent markers.²⁰ Toney et al. tracked the surface evolution of particles using an in situ X-ray imaging technique.²¹ Yang et al. demonstrated the structure evolution of PtNi₃ nanopolyhedra to Pt₃Ni nano-frames using in situ X-ray absorption spectroscopy (XAS) and synchrotron-based X-ray diffraction (XRD).²²

Recent development of in situ scanning transmission electron microscopy (STEM) offers an opportunity to image atomic-scale structure evolution of nanocatalysts in real time under atmospheric synthesis/reaction conditions.^{23–28} Here, we utilized this advanced technique, in combination with XRD, XAS, XPS experiments, and numerical simulation, to investigate the evolution of the surface elemental distribution and atomic configuration of ternary Pt₂CuNi alloy nanoparticles in an oxidizing environment, which is typical for the oxidation reaction conditions. Deeper insights regarding the segregation and diffusion of Ni and Cu atoms on the nanoparticle surface are obtained at atomic resolution in this work, where the NiO_x major/CuO_x minor surface oxide layers are unveiled. These interesting findings provide useful information for a better understanding of the structure–property relationship and future attempts at surface engineering of ternary Pt-based nanocatalysts.

EXPERIMENTAL SECTION

Materials and Methods. *Materials.* Platinum acetylacetonate (Pt(acac)₃, 97%), nickel acetylacetonate (Ni(acac)₃, 95%), and copper acetylacetonate (Cu(acac)₃, 99.99%) were purchased from Sigma-Aldrich. A carbon support (C, Vulcan XC-72R) was purchased from Cabot. Chloroform (CHCl₃, 99.9%) was purchased from Fisher Scientific. Hydrogen (H₂, 99.999%), carbon monoxide (CO, 99.999%), and nitrogen (N₂, 99.999%) gases were obtained from Praxair. For in situ experiments, the N₂ and O₂ gases were of 99.9995% purity.

Preparation of Octahedral Pt₂CuNi/C Nanoparticles. The octahedral Pt₂CuNi/C uniform alloy nanoparticles were prepared using a modified solid-state chemistry method as reported before.¹³ In a typical experiment for preparing the octahedral Pt₂CuNi/C (20 wt % Pt), C was thermally treated in air at 300 °C overnight for removing moisture before use. Pt(acac)₃ (40 mg or 0.1 mmol), Ni(acac)₃ (13.1 mg or 0.05 mmol), and Cu(acac)₃ (13.3 mg or 0.05 mmol) were first dissolved in chloroform (4 mL), and the solution was then added dropwise onto the pretreated C support (80 mg) under vigorous stirring. After impregnation, the mixture was immediately transferred to a furnace, which was then purged with N₂ flow for 20 min. The mixtures were reduced by heating at a ramping rate of 15 °C/min to 200 °C and maintaining at the temperature for 1 h in H₂/CO (5/120 cm³/min). The gas atmosphere was switched back to N₂, and the product was cooled down to room temperature after the reaction is complete. The samples were then collected and stored in N₂ before in situ STEM experiments.

In Situ Gas-Phase STEM. The in situ gas-phase scanning transmission electron microscopy (STEM) study was performed on a JEOL 3100-R05 microscope with double spherical aberration (Cs) correctors and equipped with a Protochips Atmosphere system.²⁵ In a typical procedure, the as-prepared sample was dispersed in anhydrous methanol and then deposited directly onto a thermal E-chip, which is equipped with a thin ceramic heating membrane controlled by the

Protochips Atmosphere system. A second E-chip window was then placed on top of the thermal chip in the holder, creating a thin gas cavity sealed from the high vacuum of the TEM column. The sample was situated between two SiN membranes, each with 30–50 nm thickness, with a 5 μm gap in between as shown in Figure S1. The operation accelerating voltage was 300 kV with a small probe current of 20 pA to minimize the beam effect (details in the Supporting Information),²⁹ and the heating temperature for the gas cell was 300 °C (the reported temperatures are based on Protochips calibration) with 150 Torr high purity O₂ and 610 Torr high purity Ar at a total pressure of 1 atm (760 Torr). The electron energy loss spectroscopy (EELS) line scan of different reacted samples was acquired with Gatan #965 Quantum Imaging filter (GIF).

XAS Experiments. X-ray absorption spectroscopy (XAS) measurements, including extended X-ray absorption fine-structure spectroscopy (EXAFS), and X-ray absorption near-edge structure spectroscopy (XANES), were conducted at the Cu K (8979 eV), Ni K (8333 eV), and Pt L₃ (11564 eV) edges at the beamline 10-BM of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source (APS) at Argonne National Laboratory. Cu, Ni, and Pt foil spectra were acquired simultaneously with each measurement for energy calibration. The XAS spectra were recorded in transmission mode. The samples were pressed into a cylindrical holder, which can hold six samples simultaneously. The loading of the sample was optimized to achieve a step height of 1 (an empirical number represents the ratio of incident X-ray energy over transmitted X-ray energy for optimal signal-to-noise ratio at the beamline).

Electrochemistry Test. The oxygen reduction reaction activities of the oxidation-treated samples were evaluated through a typical three-electrode configuration as reported previously. In brief, 1 mg_{cat}/mL ink was firstly prepared by ultrasonically dispersing the catalyst in mixed solvent ($V_{\text{water}}/V_{\text{isopropanol}}/V_{5\% \text{ Nafion}} = 6:4:0.04$), and 10 μL of the ink was drop-coated onto a polished rotating disk electrode (RDE) ($\Phi = 5$ mm) and dried (catalyst loading is $\sim 51.0 \mu\text{g cm}^{-2}$). The thin film RDE was mounted onto a rotation controller (AFMSRCE, Pine Instrument Co.) as the working electrode. A platinum wire is used as the counter electrode, and the reference electrode is a HydroFlex reference electrode (ET070, Edaq Inc.). The electrochemical data was recorded through a CHI 760D electrochemical workstation (CH Instruments, Inc.). The electrochemically active surface area (ECSA) was measured in Ar-purged 0.1 M HClO₄ solution. Briefly, CV data were collected in the potential range of 0.04–1.0 V at a scan rate of 50 mV/s. The ECSA value was obtained by integrating the hydrogen adsorption signals at ~ 0.04 to 0.40 V with the equation $\text{ECSA}(\text{cm}^2_{\text{Pt}}) = (\int_{E_{\text{low}}}^{E_{\text{high}}} IdE)/\nu Q$, where I is the current (A), E is the potential (V), E_{low} and E_{high} are the integration potential range (V), ν is the scan rate (V/s), and Q is the charge density transferred accounting for hydrogen adsorption on Pt ($210 \mu\text{C}/\text{cm}^2_{\text{Pt}}$). The ORR activity test was performed in O₂-saturated 0.1 M HClO₄ solution in the potential range of 0.2–1.0 V with a linear sweep voltammetry (LSV) technique at a scan rate of 10 mV/s and RDE rotation speed of 1600 rpm. The specific activity is calculated at 0.9 V (vs RHE) and normalized to ECSA.

Characterizations. X-ray diffraction (XRD) was performed after the samples were treated in the proposed condition, and data were collected on a Bruker AXS Dimension D8 X-Ray diffractometer operating at 40 kV and 35 mA (Cu K α , $\lambda = 0.154184$ nm). The energy-dispersive X-ray spectroscopy (EDS) line scan/mapping was recorded using an FEI Tecnai G2 F20 microscope operating at 200 kV. The numerical modeling and visualization were accomplished by the R programming language using the open source packages plot3D and Rgraphics with function image2D and persp3D.^{30,31}

RESULTS AND DISCUSSION

Ternary octahedral Pt₂CuNi alloy nanoparticles were synthesized via a modified solid-state chemistry method (more details are provided in the Supporting Information) and characterized via aberration-corrected STEM (AC-STEM).^{13,29} Images in the first column of Figure 1A,B exhibit representative bright-

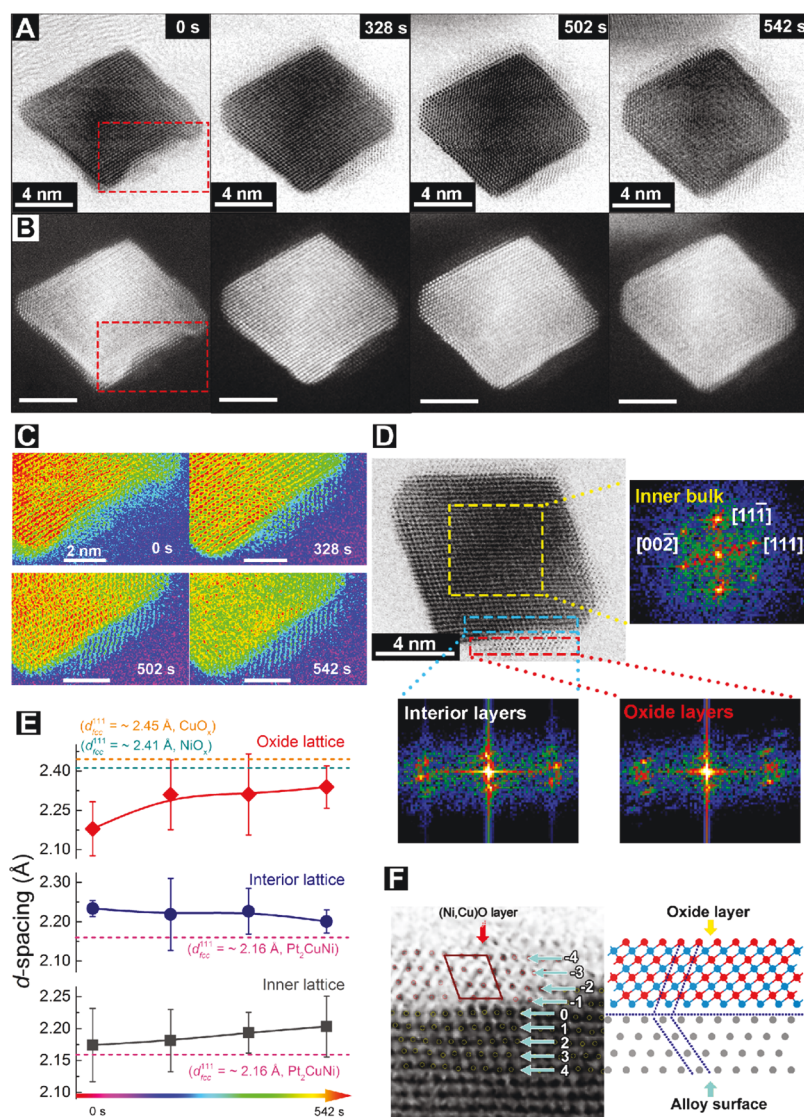


Figure 1. (A) Sequential in situ bright-field and (B) corresponding HAADF images of the Pt₂CuNi octahedral nanoparticle exposed to the oxidative condition. (C) False-color BF-STEM images of one representative {111} facet showing oxidative evolution. (D) Three regions for FFT analysis (inner bulk, interior layers, and oxide layers) with the resultant FFT patterns, and (E) corresponding time-dependent *d* spacing profile. (F) Atomic view of fully relaxed metal oxide layers on the alloy surface and the schematic interface model (red: O; blue: Ni/Cu; gray: Pt/Ni/Cu).

field (BF) and high-angle annular dark-field (HAADF) STEM images of as-prepared Pt₂CuNi nanoparticles at the initial state (denoted as $t = 0$ s) under 150 Torr of O₂ (to mimic the oxygen partial pressure of air) at 300 °C, which clearly exhibits an octahedral shape with well-resolved {111} lattice fringes. It also reveals the existence of terraces and steps on the edge, as well as some tiny surface oxidation evidenced by the slightly blurred facet, which could be ascribed to the short-time exposure to air during STEM sample preparation. Notably, the electron dose was reduced to minimize the possible beam effect according to our previous work.²⁹ After 328 s of exposure to the oxidative condition, distinct oxide layers (low-contrast layers on the surface) can be observed forming on the octahedra surface, which are identified as mostly NiO_x using XPS and XAS techniques in the following characterizations. With an increase of the oxygen annealing time, the oxide layers become even thicker on those planes, and the sharp corners and surface concaves gradually disappear, indicating severe surface restructuring.

A closer look into one typical facet's oxidation trajectory is shown in Figure 1C, with the false-color BF-STEM images for a better illustration of the process and the cyan dots on the surface being ascribed to the growing oxides (i.e., Ni/Cu oxides) as can be seen from the intensity difference in the *Z* contrast images.³² These false-color images clearly show the surface oxide layers gradually grow into an epitaxial structure on the {111} facet of the nanoparticle indicated by the ordered lattice fringes of oxide layers ($t = 502$ – 542 s). To better investigate the changes in the crystal structure, we selected three regions on the octahedral nanoparticle shown in Figure 1D and created fast Fourier transform (FFT) patterns for crystal structure analysis and lattice measurement. The FFT pattern of the inner bulk region shows a typical sixfold diffraction points, which indicates a good fcc crystal structure. When it comes to the interior metal surface and oxide layers, the FFT patterns still show the sixfold fcc structural characteristics.

Based on the FFT patterns of the octahedral nanoparticle along with the oxidation treatment, we measured the real-time

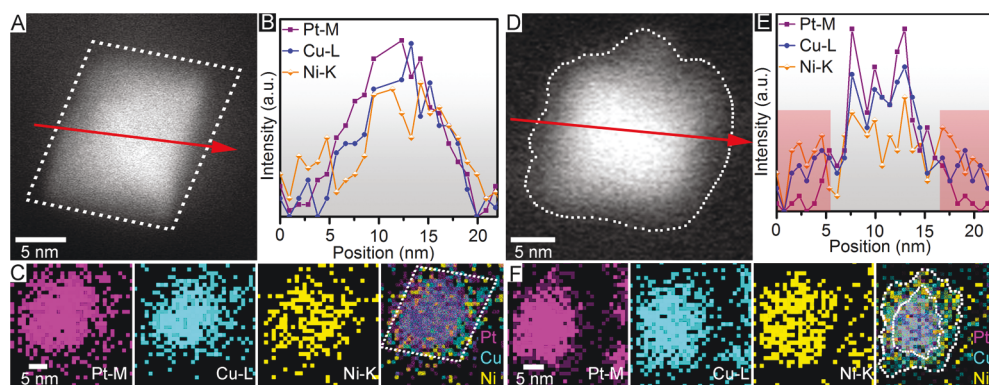


Figure 2. (A, D) HAADF-STEM images with (B, E) corresponding EDS elemental line scans and (C, F) maps of individual as-prepared and oxidation-treated Pt₂CuNi nanoparticles, respectively.

changes in the d spacing of the three regions, and the plots are shown in Figure 1E. Initially, the inner bulk lattice shows a matched (111) facet d spacing value (~ 2.17 Å) compared with that of the theoretical Pt₂CuNi uniform alloy (~ 2.16 Å) (Figure S2). Also, the d spacing of interior layers (i.e., interface lattice) is measured to be ~ 2.23 Å, which is closer to the value of Pt (111) planes (~ 2.27 Å) and suggests that the interface lacks Cu/Ni atoms compared with the bulk Pt₂CuNi.³³ Meanwhile, the d spacing of the thin oxide layer induced by the TEM sample preparation process is measured to be ~ 2.18 Å and shows large deviation compared with that of the (111) planes of cubic NiO_x/CuO_x, which implies a strong compressive strain caused likely by large lattice mismatch between the oxides and Pt₂CuNi.³³ This also indicates that the Ni/Cu in the initial oxide layer comes from the initial nanoparticle surface that caused the interface to be Pt-enriched because the Pt₂CuNi octahedra possess a uniform elemental distribution based on our previous results.¹³ Along with the oxidation treatment, the d spacing of the inner bulk lattice slightly increased indicating the loss of Ni/Cu atoms. In other words, these atoms in the bulk are diffusing out during this process. Meanwhile, for the interior layers, the d spacing shows a slight decrease with respect to the treatment time, and the final value at 542 s is ~ 2.20 Å, which is still higher than the theoretical Pt₂CuNi value. This decrease could be associated with the outward diffusion of Ni/Cu, causing the lattice fringe shrinking; however, the value is still higher than the theoretical one, which confirms that the outward-diffused Ni/Cu atoms continue migrating to the oxide layers and only a few stay at the interface, which keeps the interface still Pt-enriched.³⁴ On the other hand, for the oxide layers, the d spacing of oxides gradually expands to ~ 2.34 Å exhibiting a relaxation process. However, this value is still below the d spacing of the theoretical value of (111) planes of either cubic NiO_x (~ 2.41 Å) or CuO_x (~ 2.45 Å), indicating that there are significant strains in the oxide layers (for example, -2.9% for NiO_x and -4.5% for CuO_x) and that the oxides may majorly be NiO_x for its smaller d spacing.³³

For the relatively relaxed grown oxide layers as shown in Figure 1F, an epitaxial grown structure can clearly be observed between the oxide layers and alloy interior layers. Considering the large lattice difference between the Pt₂CuNi alloy and Ni / Cu oxides, the epitaxial growth explains the observed large lattice strain in the oxide layers. These reveal the aforementioned atomic rearrangement and provide a vivid

visualization of the near-surface atomic restructuring under heating and oxidative conditions.

We also recorded the Pt₂CuNi nanoparticles in 150 Torr O₂ with the temperature up to 500 °C as shown in Figure S3. At above 400 °C, some octahedral particles located close to each other start to sinter while some isolated ones may still relatively maintain their morphology. When the temperature goes even higher, all the nanoparticles seem to lose their octahedral shape and transform into a sphere-like morphology. These results suggest that the high temperature induced faster atom diffusion leading to severe surface restructuring along with the particle agglomeration and coalescence. Similar phenomena have been reported with other metallic systems in previous studies.^{35,36}

To investigate the spatial distribution of Pt, Cu, and Ni elements, the Pt₂CuNi nanoparticles are characterized using energy-dispersive X-ray spectroscopy (EDS) mapping before and after the oxidation exposure at 300 °C. Figure 2A shows one typical as-prepared Pt₂CuNi nanoparticle with an octahedral shape, and the edge-to-edge elemental line scan (Figure 2B) shows slight Ni enrichment at the edges, indicating the occurrence of slight oxidation during STEM sample preparation, which agrees with the result in Figure 1. The intensity distribution of the Ni–K signal in the bulk area is similar to that of the Pt–M, suggesting that the Ni distribution is uniform in the Pt₂CuNi nanoparticles as well as the distribution of Cu elements. The elemental maps of Ni, Cu, and Pt in Figure 2C also manifest the uniform element distribution throughout the entire nanoparticle, which could also be visualized from an overlay of the three element maps. After exposure to the oxidative atmosphere, the shape of the Pt₂CuNi nanoparticle is damaged as mentioned above due to the oxidation-induced surface change. The elemental line scan in Figure 2E shows significant Ni/Cu-enriched edges, indicating the formation of oxide layers. Also, interestingly, the Ni content is higher than the Cu content at the oxidized edges, which implies that the oxide layers possess more NiO_x than CuO_x. Figure 2F also confirms clear Ni / Cu oxide layers existing on the particle surface, which agrees with the outward diffusion of Ni/Cu elements. The findings are also consistent with the EELS results (Figures S4 and S5).

To gain further insight into the atomic restructuring in the Pt₂CuNi, X-ray absorption spectroscopy (XAS) measurements were conducted to study the local environments, including average interatomic distances and coordination numbers before and after oxygen exposure. The obtained spectra are compared with those of reference metal foils, as shown in

Figure 3A–C. Compared with Pt foil, the Pt L₃-edge X-ray absorption near-edge structure (XANES) spectra of both as-

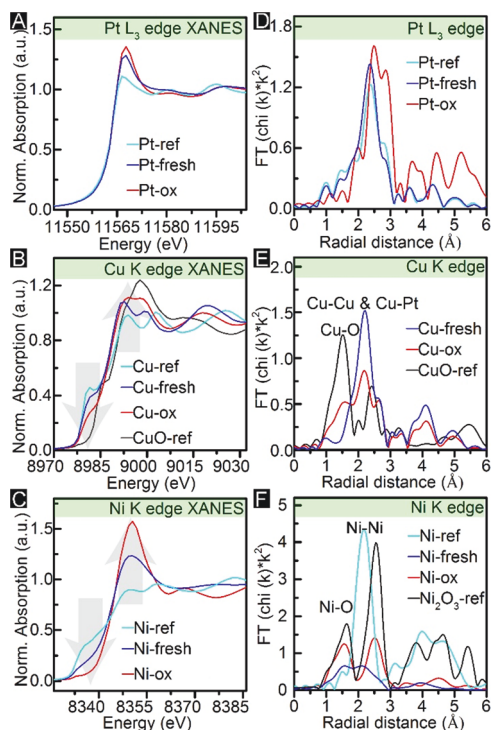


Figure 3. Normalized XANES spectra at the (A) Pt L₃ edge, (B) Cu K edge, and (C) Ni K edge for as-prepared and oxidation-treated Pt₂CuNi. Pt foil, Cu foil, and Ni foil are used as reference standards. Magnitude of Fourier transformed k^2 -weighted EXAFS spectra at the (D) Pt L₃ edge, (E) Cu K edge, and (F) Ni K edge.

prepared and restructured Pt₂CuNi samples in Figure 3A show no obvious shift, suggesting that Pt mainly remained in the metallic state. An increase in the white line intensity of the Pt L₃ edge is observed after the reaction, indicating a decrease in the Pt 5d orbital filling due to less hybridization (i.e., an increase in Pt d band vacancy) and decreased alloying degree.^{37,38}

XANES spectra of the Cu K edge of the Pt₂CuNi are also collected and compared with those of Cu foil and the CuO reference in Figure 3B and Figure S6, which show that Cu is only partially oxidized with coexistence with metallic Cu.³⁹ Interestingly, an obvious shape deformation is detected on the XANES spectra of the Ni K edge. Compared with the counterpart spectra of Ni foil and the fresh Pt₂CuNi, the Ni K-edge spectra of the oxidized Pt₂CuNi in Figure 3C and Figure S7 show a dramatic decrease in the pre-edge region between 8330 and 8344 eV, accompanied by a pronounced increase at 8551 eV. This strongly suggests that the electronic states of Ni have been dramatically changed due to the reduced filling of Ni 3d states and an increase in the symmetry of restructured lattice.⁴⁰

To achieve quantitative structural information from much more local electron scattering, Fourier transformed extended X-ray absorption fine structure (EXAFS) data is shown and analyzed in Figure 3D–F. The Pt L₃-edge EXAFS radial distance plot of the Pt₂CuNi alloy in Figure 3D presents a different distribution compared with that of Pt foil, which indicates the alloy formation. Figure 3E shows that Cu is mainly in the metallic state for the fresh sample and is only partially oxidized after exposure to oxygen. The same trend can be observed from the Ni K-edge radial distance plots in Figure 3F. However, it can be noticed that the Ni–O band is more pronounced in the oxidized sample compared with the Cu K edge, which implies that a higher ratio of Ni is oxidized than Cu after oxidation treatment, and is consistent with the results in Figure 1 that the oxide layers consist of NiO_x in major amount. The high quality of EXAFS fitting is confirmed by the well-matched experimental and fitted results (Figure S8–S19). The bond lengths, coordination numbers (CN), and neighbor bond configurations surrounding the resonance scattering are also obtained from the EXAFS fitting and summarized in Table S1.

The XPS survey scans are recorded on both fresh and oxidized samples in Figure 4A. The surface composition of the fresh Pt₂CuNi is determined to be 25% Pt 4f, 14% Cu 2p, 29% Ni 2p, and 32% O 1s. XPS quantitative results show that the ratio of Pt/Cu/Ni on the surface is 2/1.1/2.3. The surface ratio shows a higher Cu and Ni content, whereas a much higher content of surface Ni can be observed. The 32% O

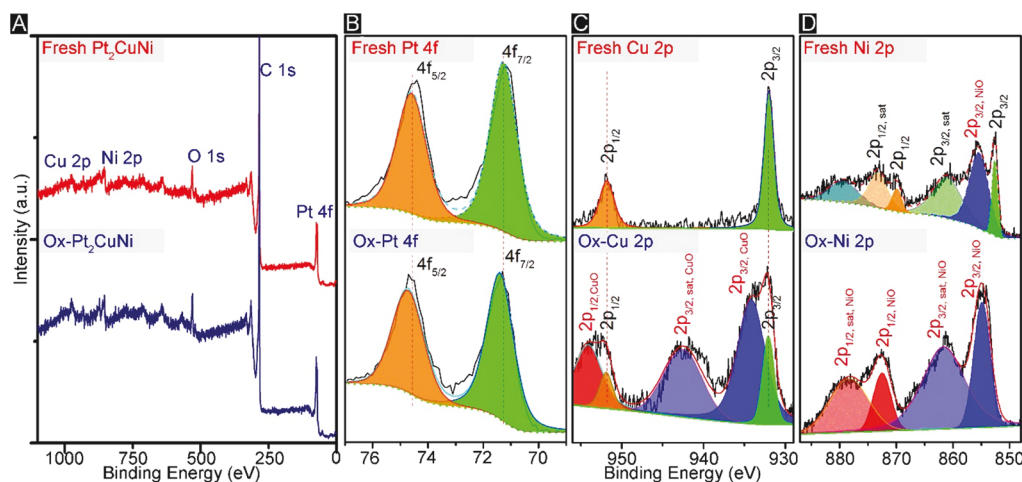


Figure 4. X-ray photoelectron spectra of (A) Pt₂CuNi and high-resolution spectra of (B) Pt 4f, (C) Cu 2p, and (D) Ni 2p for the as-prepared and oxygen-induced surface restructured samples. The red dotted line represents the peak positions of metallic Pt and Ni in fresh samples.

could be primarily from the surface oxides formed during the XPS sample preparation similar to the STEM experiments, as well as the oxygen-containing groups on the surface of carbon support. After being exposed to air at 300 °C for 1 h, the surface composition of Pt₂CuNi is changed to 11% Pt 4f, 8% Cu 2p, 32% Ni 2p, and 49% O 1s. The surface contents of Ni, Cu, and O elements have significant changes, which is consistent with the oxygen-induced surface oxidation and restructuring. Additionally, the Pt/Cu/Ni ratio becomes 2/1.5/5.8, which clearly confirms the outward diffusion of Ni and Cu atoms. Also, the much higher Ni content confirms the major NiO_x composition in the surface oxides, which matches with the above results.

High-resolution XPS of the fresh Pt₂CuNi shows that the spectra of Pt 4f_{5/2} (74.4 eV) and Pt 4f_{7/2} peaks (71.1 eV) are positioned at lower binding energy than those of reference peaks (Pt 4f_{5/2} (74.5 eV) and Pt 4f_{7/2} peaks (71.2 eV)), attributed to the electron donation from Cu and Ni, suggesting the alloy formation of Pt₂CuNi (Figure 4B).^{41,42} After the surface oxidation, slight shifts to higher energy positions are observed for both the Pt 4f peaks, indicating a decreased interaction with Ni/Cu due to losing them in Pt's surrounding. The absence of a Pt–O peak confirms that Pt maintains a metallic status throughout the experiments. The Cu 2p band spectra in Figure 4C clearly show that the Cu element in the fresh Pt₂CuNi sample is in its metallic state. Compared to the reference peak positions of Cu 2p (952.5 eV for Cu 2p_{1/2} and 932.6 eV for Cu 2p_{3/2}), both Cu 2p_{1/2} (952.6 eV) and Cu 2p_{3/2} (932.7 eV) peaks shift to positions with higher binding energy, which confirms the electron donation in the Pt₂CuNi alloy. After exposure to oxygen, the Cu 2p_{1/2,CuO} (953.7 eV), Cu 2p_{3/2,CuO} (933.9 eV), and Cu 2p_{3/2,CuO} satellite peaks (943.0 eV) appear, suggesting the oxidation of Cu on the surface.⁴³ Also, some of the Cu atoms maintain their metallic state, evidenced by the existence of Cu 2p_{1/2} (952.6 eV) and Cu 2p_{3/2} (932.7 eV). However, it is found that the Ni element is more susceptible to oxidation. The Ni 2p_{3/2,NiO} and Ni 2p_{1/2,NiO} can even be detected in the fresh samples shown in Figure 4D, accompanied by metallic Ni 2p_{3/2} and Ni 2p_{1/2} peaks.⁴⁴ Furthermore, the oxidation Ni 2p_{NiO} peaks become much bigger and even overlay the metallic Ni 2p peaks that we did not deconvolute after oxidation at 300 °C for 1 h, indicating a large amount of oxidized Ni. Thus, these XPS measurements reveal that the atomic restructuring on the surface of Pt₂CuNi is dominated by the surficial oxidation of Ni/Cu, where Ni is more crucial. This generates Ni-rich surface oxide layers accompanied by minor oxidized Cu atoms. The oxygen-induced surface restructuring can be related to the much higher binding energies of Ni–O and Cu–O than that of Pt–O and the tendency to reduce surface energy anisotropy of the nanoparticle.

Sequential XRD patterns are also recorded at difference temperatures and time intervals to study the oxygen-induced surface restructuring of the Pt₂CuNi nanoparticles. As shown in Figure 5A, an obvious elemental redistribution can be inferred from the temperature sequences of XRD patterns. For the as-prepared sample, the characteristic diffraction peak located at 41.7° corresponds to the fcc (111) planes of the Pt₂CuNi alloy nanoparticles, in good agreement with the theoretical value for a uniform Pt₂CuNi alloy and suggesting the uniform distribution of all three elements.³⁴ As the temperature increases from room temperature, the (111) peak shifts to a lower diffraction angle, indicating a decreased

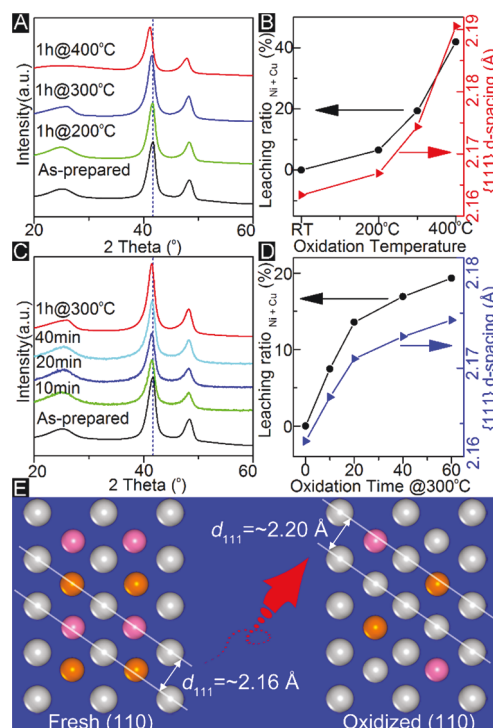


Figure 5. (A, B) Temperature and (C, D) time sequences of powder X-ray diffraction patterns and corresponding Ni + Cu leaching ratio and *d* spacing of the (111) planes of Pt₂CuNi nanoparticles. (E) Schematic illustration of the lattice change of the Pt₂CuNi (111) planes when exposed to oxidative conditions (view from the (110) plane, gray: Pt; pink: Ni; orange: Cu).

alloying degree of the Pt₂CuNi nanoparticles resulting from the outward diffusion of Ni and Cu. The leaching ratio of Ni and Cu elements is calculated using Vegard's law, and the corresponding *d* spacing of the (111) planes is evaluated using Bragg's law (Figure 5B).⁴⁵ Both the leaching ratio and the *d* spacing of the (111) planes are observed to strongly depend on the temperature with a positive correlation. When the Pt₂CuNi is exposed to air for 1 h at 400 °C, the total leaching ratio of Ni and Cu approaches 42% with a *d* spacing of the (111) planes of 2.19 Å. The value is significantly larger than that of fresh Pt₂CuNi (2.16 Å), revealing a higher oxidation temperature favoring a faster atom diffusion and oxidation, which is consistent with the observed results from Figure S3.

The rate of surface restructuring of Pt₂CuNi upon exposure to air is also studied by recording the XRD patterns in time sequences (Figure 5C). Compared to the fresh sample, the (111) diffraction peak of the restructuring sample gradually shifts to a lower diffraction position, indicating a continuous decrease in the Ni and Cu content in the crystalline domains. Noticeably, the variation rate of the *d* spacing in Figure 5D (i.e., the slope) is decreasing, indicating a decreasing diffusion rate with respect to oxidation time. This can be ascribed to the element concentration gradient, which reduces along with Ni/Cu diffusion, and the reduced concentration gradient would lead to a slower diffusion rate in return. The lattice relaxation process is illustrated in Figure 5E, in which the Ni and Cu atoms gradually diffuse toward the surface and get oxidized, leaving a Pt-rich bulk structure with expanded lattice spacing. These XRD results further depict the temperature and concentration gradient-controlled diffusion of Ni/Cu and are

in good agreement with other characterizations (i.e., in situ STEM imaging, XAS, and XPS measurements).

To achieve a deeper understanding of the atom diffusion that leads to Pt₂CuNi surface oxidation and restructuring, unsteady-state atomic diffusion of Ni and Cu is semi-quantitatively simulated with a numerical model using Fick's second law based on the data obtained from aforementioned measurements. Because the Ni and Cu distribute uniformly in the Pt₂CuNi nanoparticles before their exposure to oxygen, an assumption of isotropic diffusion would be reasonable and simplify Fick's second law to a one-dimensional model shown as follows⁴⁶

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial C}{\partial x} \right] \quad (1)$$

where C describes the normalized spatiotemporal concentration of Ni and Cu, which is a function of exposure time t (h) and distance x (nm) from the center of the particle. D is the nonconstant diffusion coefficient that depends on the real-time concentration of Ni and Cu because the diffusion is not a steady-state process evidenced by the time-dependent XRD patterns. The general form of solution to this unsteady-state partial differential equation can be described as⁴⁷

$$C(x, t) = k_1 + k_2 \int_0^\lambda \frac{d\lambda}{D} \exp \left\{ \int_0^\lambda \left[-\frac{\lambda}{2D} d\lambda \right] \right\} \quad (2)$$

where

$$\lambda = \frac{x}{\sqrt{t}} \quad (3)$$

and k_1 and k_2 are the integration constants.

Based on the time-dependent XRD data acquired at 300 °C, the effective diffusion coefficient over a determined time interval could be generated from the Gaussian fitting function and cross-validated by the measured data, which can be shown as

$$D = b_0 + b_1 \exp(-b_3 t) \quad (4)$$

where b_0 , b_1 , and b_2 are constants generated from the regression and t is the evolution time over 300 °C. To get simulated results from eq 2, boundary conditions can be set based on the elemental distributions. $C_1(0,0) = 1$ refers to the initial concentration in the center of the particle, $C_2(5, 0.091) = 0$ refers to the state where the surface oxidation was observed at 328 s (0.091 h) by in situ STEM, and $C_3(0,10000) = 0$ refers to the final state where the Ni and Cu in the lattice have completely diffused out (imagined extreme condition). The numerical elemental distribution mapping generated from the simulation is illustrated in Figure 6. As shown in Figure 6A, the Ni and Cu concentrations on the particle surface dramatically decrease, which is consistent with the rapid surface oxidation of Ni and Cu. Also, it can be noticed that during the oxidation process, the concentration gradient is not uniform as the core part shows a higher gradient with more condensed contour plots, which is reasonable because this is a concentration gradient-controlled diffusion where there are more Ni and Cu residual in the core region. The spatiotemporal element mapping and corresponding concentration gradient could also be visualized using the 3D coordinates, in which higher steepness of the plane means a more rapid decrease in the concentrations. These generated numerical results are in good

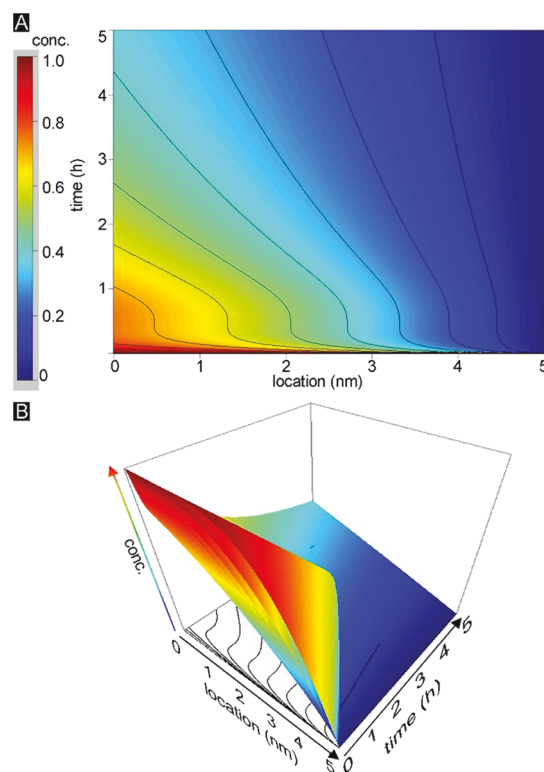


Figure 6. Spatiotemporal visualization of unsteady-state atomic diffusion of elements Ni and Cu in Pt₂CuNi under oxidative conditions. (A) Contour map and (B) 3D surface plot of residual concentration of Ni and Cu as a function of location and reaction time.

agreement with both the in situ and ex situ measurements and visually validate the proposed diffusion model.

Furthermore, this oxidative condition not only mimics the real oxidation reaction environment to help understand the surface restructuring and segregation phenomena that affect the structure–performance relationship^{48,49} but is also utilized for the post-treatment of nanocatalysts for the alteration of their catalytic performances.^{50–52} For example, Zhao et al. employed the oxygen annealing to introduce the surface Ni segregation in Pt–Ni alloy nanoparticles, achieving the highest mass activity for the hydrogen evolution reaction.⁵³ In this regard, it is worth mentioning that the catalytic performances of ternary Pt₂CuNi alloy nanoparticles can be tuned through the surface segregation of transition metals. We here show an example demonstrating the tunable ORR activity of the Pt₂CuNi nanoparticles with different segregation extents through the air annealing treatment. As a result, Figure 7 illustrates the specific ORR activity of Pt₂CuNi nanoparticles oxidized for 0, 10, 20, 40, and 60 min. It is clear that the ORR activity was enhanced in all oxidized Pt₂CuNi nanoparticles. Particularly, a "volcano shape" is found in Figure 7 with respect to the oxidation time, indicating that the optimized surface/composition can be achieved at 20 min oxidation treatment. Thus, understanding of the oxidation-induced composition/structure dynamic changes in alloy catalyst nanoparticles will benefit the design of transition-metal alloy catalysts.

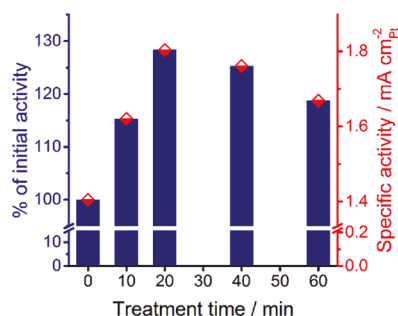


Figure 7. Tuned ORR activity of Pt₂CuNi nanoparticles oxidized at 300 °C for 0, 10, 20, 40, and 60 min.

CONCLUSIONS

In conclusion, by employing various advanced characterization techniques, particularly the in situ atmospheric STEM, the real-time surface elemental distribution and reconstruction trajectories of ternary octahedral Pt₂CuNi alloy nanoparticles are observed in an oxidative environment at atomic resolution. The results reveal that Ni atoms in the alloy are more susceptible to oxidation than Cu, and both of them diffuse to the surface to be oxidized under an oxidative atmosphere. The majority of surface oxide layers are found to consist of NiO_x. In addition, it is also demonstrated that surface segregation helps to tune the ORR activity of the Pt₂CuNi nanoparticles. The capability of direct imaging of the dynamic surface change in response to real synthesis/reaction conditions at the atomic level broadens the avenue for exploring potential structure–property relationships of ternary alloy catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.chemmater.8b05199](https://doi.org/10.1021/acs.chemmater.8b05199).

Additional TEM images, EELS results, and XAS data (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: xiaoqin@uci.edu (X.P.).

*E-mail: zpeng@uakron.edu (Z.P.).

ORCID

Sheng Dai: 0000-0001-5787-0179

Changlin Zhang: 0000-0002-1207-4264

Yu Lei: 0000-0002-4161-5568

Xiaoqing Pan: 0000-0002-0965-8568

Zhenmeng Peng: 0000-0003-1230-6800

Author Contributions

[‡]X.S., S.D., and S.Z. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (CHE-1665265 (Z.P.) and DMR-1506535 (X.P.)) and UC Irvine's Office of Research (X.P.). Additional support was provided by the Irvine Materials Research Institute (IMRI). The HRTEM data were obtained at the (cryo)TEM facility at the Liquid Crystal Institute, Kent State University, supported

by the Ohio Research Scholars Program Research Cluster on Surfaces in Advanced Materials. The authors thank Dr. Min Gao for technical support with the TEM experiments.

REFERENCES

- (1) Chen, T.; Rodionov, V. O. Controllable Catalysis with Nanoparticles: Bimetallic Alloy Systems and Surface Adsorbates. *ACS Catal.* **2016**, *6*, 4025–4033.
- (2) Hermans, S.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Sankar, G.; Gleeson, D. Solvent-Free, Low-Temperature, Selective Hydrogenation of Polyenes using a Bimetallic Nanoparticle Ru–Sn Catalyst. *Angew. Chem. Int. Ed.* **2001**, *40*, 1211–1215.
- (3) Yu, W.; Porosoff, M. D.; Chen, J. G. Review of Pt-based bimetallic catalysis: from model surfaces to supported catalysts. *Chem. Rev.* **2012**, *112*, 5780–5817.
- (4) Matsubu, J. C.; Zhang, S.; DeRita, L.; Marinkovic, N. S.; Chen, J. G.; Graham, G. W.; Pan, X.; Christopher, P. Adsorbate-mediated strong metal–support interactions in oxide-supported Rh catalysts. *Nat. Chem.* **2017**, *9*, 120–127.
- (5) Stamenkovic, V. R.; Mun, B. S.; Arenz, M.; Mayrhofer, K. J. J.; Lucas, C. A.; Wang, G.; Ross, P. N.; Markovic, N. M. Trends in electrocatalysis on extended and nanoscale Pt-bimetallic alloy surfaces. *Nat. Mater.* **2007**, *6*, 241–247.
- (6) Kitchin, J. R.; Nørskov, J. K.; Barteau, M. A.; Chen, J. G. Role of strain and ligand effects in the modification of the electronic and chemical properties of bimetallic surfaces. *Phys. Rev. Lett.* **2004**, *93*, 156801.
- (7) Liao, H.; Fisher, A.; Xu, Z. J. Surface Segregation in Bimetallic Nanoparticles: A Critical Issue in Electrocatalyst Engineering. *Small* **2015**, *11*, 3221–3246.
- (8) Peng, L.; Ringe, E.; Van Duyne, R. P.; Marks, L. D. Segregation in bimetallic nanoparticles. *Phys. Chem. Chem. Phys.* **2015**, *17*, 27940–27951.
- (9) Zhang, C.; Hwang, S. Y.; Peng, Z. Size-dependent oxygen reduction property of octahedral Pt–Ni nanoparticle electrocatalysts. *J. Mater. Chem. A* **2014**, *2*, 19778–19787.
- (10) Zhang, C.; Hwang, S. Y.; Trout, A.; Peng, Z. Solid-State Chemistry-Enabled Scalable Production of Octahedral Pt–Ni Alloy Electrocatalyst for Oxygen Reduction Reaction. *J. Am. Chem. Soc.* **2014**, *136*, 7805–7808.
- (11) Hwang, S. Y.; Zhang, C.; Yurchekfrod, E.; Peng, Z. Property of Pt–Ag Alloy Nanoparticle Catalysts in Carbon Monoxide Oxidation. *J. Phys. Chem. Lett.* **2014**, *118*, 28739–28745.
- (12) Hwang, S. Y.; Yurchekfrod, E.; Zhang, C.; Peng, Z. Low-Temperature Preferential Oxidation of Carbon Monoxide on Pt₃Ni Alloy Nanoparticle Catalyst with Engineered Surface. *ChemCatChem* **2016**, *8*, 97–101.
- (13) Zhang, C.; Sandorf, W.; Peng, Z. Octahedral Pt₂CuNi Uniform Alloy Nanoparticle Catalyst with High Activity and Promising Stability for Oxygen Reduction Reaction. *ACS Catal.* **2015**, *5*, 2296–2300.
- (14) Erini, N.; Rudi, S.; Beermann, V.; Krause, P.; Yang, R.; Huang, Y.; Strasser, P. Exceptional Activity of a Pt–Rh–Ni Ternary Nanostructured Catalyst for the Electrochemical Oxidation of Ethanol. *ChemElectroChem* **2015**, *2*, 903–908.
- (15) Gan, L.; Cui, C.; Heggen, M.; Dionigi, F.; Rudi, S.; Strasser, P. Element-specific anisotropic growth of shaped platinum alloy nanocrystals. *Science* **2014**, *346*, 1502–1506.
- (16) Menning, C. A.; Hwu, H. H.; Chen, J. G. Experimental and Theoretical Investigation of the Stability of Pt–3d–Pt(111) Bimetallic Surfaces under Oxygen Environment. *J. Phys. Chem. B* **2006**, *110*, 15471–15477.
- (17) Menning, C. A.; Chen, J. G. Thermodynamics and kinetics of oxygen-induced segregation of 3d metals in Pt–3d–Pt(111) and Pt–3d–Pt(100) bimetallic structures. *J. Chem. Phys.* **2008**, *128*, 164703.
- (18) Wang, C.; Li, D.; Chi, M.; Pearson, J.; Rankin, R. B.; Greeley, J.; Duan, Z.; Wang, G.; van der Vliet, D.; More, K. L.; Markovic, N. M.

Stamenkovic, V. R. Rational Development of Ternary Alloy Electrocatalysts. *J. Phys. Chem. Lett.* **2012**, *3*, 1668–1673.

(19) Beaumont, S. K.; Alayoglu, S.; Pushkarev, V. V.; Liu, Z.; Kruse, N.; Somorjai, G. A. Exploring surface science and restructuring in reactive atmospheres of colloidal prepared bimetallic CuNi and CuCo nanoparticles on SiO₂ in situ using ambient pressure X-ray photoelectron spectroscopy. *Faraday Discuss.* **2013**, *162*, 31–44.

(20) Xu, W.; Kong, J. S.; Yeh, Y.-T. E.; Chen, P. Single-molecule nanocatalysis reveals heterogeneous reaction pathways and catalytic dynamics. *Nat. Mater.* **2008**, *7*, 992–996.

(21) Weker, J. N.; Huang, X.; Toney, M. F. In situ X-ray-based imaging of nano materials. *Curr. Opin. Chem. Eng.* **2016**, *12*, 14–21.

(22) Becknell, N.; Kang, Y.; Chen, C.; Resasco, J.; Kornienko, N.; Guo, J.; Markovic, N. M.; Somorjai, G. A.; Stamenkovic, V. R.; Yang, P. Atomic Structure of Pt₃Ni Nanoframe Electrocatalysts by in Situ X-ray Absorption Spectroscopy. *J. Am. Chem. Soc.* **2015**, *137*, 15817–15824.

(23) Zhang, S.; Chen, C.; Cargnello, M.; Fornasiero, P.; Gorte, R. J.; Graham, G. W.; Pan, X. Dynamic structural evolution of supported palladium-ceria core-shell catalysts revealed by in situ electron microscopy. *Nat. Commun.* **2015**, *6*, 7778.

(24) Zhang, S.; Cargnello, M.; Cai, W.; Murray, C. B.; Graham, G. W.; Pan, X. Revealing particle growth mechanisms by combining high-surface-area catalysts made with monodisperse particles and electron microscopy conducted at atmospheric pressure. *J. Catal.* **2016**, *337*, 240–247.

(25) Zhang, S.; Plessow, P. N.; Willis, J. J.; Dai, S.; Xu, M.; Graham, G. W.; Cargnello, M.; Abild-Pedersen, F.; Pan, X. Dynamical Observation and Detailed Description of Catalysts under Strong Metal-Support Interaction. *Nano Lett.* **2016**, *16*, 4528–4534.

(26) Shen, X.; Zhang, C.; Zhang, S.; Dai, S.; Zhang, G.; Ge, M.; Pan, Y.; Sharkey, S. M.; Graham, G. W.; Hunt, A.; Waluyo, I.; Miller, J. T.; Pan, X.; Peng, Z. Deconvolution of octahedral Pt₃Ni nanoparticle growth pathway from in situ characterizations. *Nat. Commun.* **2018**, *9*, 4485.

(27) Liang, W.-I.; Zhang, X.; Zan, Y.; Pan, M.; Czarnik, C.; Bustillo, K.; Xu, J.; Chu, Y.-H.; Zheng, H. In Situ Study of Fe₃Pt–Fe₂O₃ Core–Shell Nanoparticle Formation. *J. Am. Chem. Soc.* **2015**, *137*, 14850–14853.

(28) Pan, Y.-T.; Wu, J.; Yin, X.; Yang, H. In situ ETEM study of composition redistribution in Pt–Ni octahedral catalysts for electrochemical reduction of oxygen. *AIChE J.* **2016**, *62*, 399–407.

(29) Shen, X.; Dai, S.; Zhang, C.; Zhang, S.; Sharkey, S. M.; Graham, G. W.; Pan, X.; Peng, Z. In Situ Atomic-Scale Observation of the Two-Dimensional Co(OH)₂ Transition at Atmospheric Pressure. *Chem. Mater.* **2017**, *29*, 4572–4579.

(30) Soetaert, K. plot3D: Plotting Multi-Dimensional Data. <https://cran.r-project.org/web/packages/plot3D/index.html>

(31) Murrell, P. *RGraphics: Data and Functions from the Book R Graphics, Second Edition.*, CRC Press, 2012, <https://cran.r-project.org/web/packages/RGraphics/index.html>

(32) Crewe, A. V.; Wall, J.; Langmore, J. Visibility of Single Atoms. *Science* **1970**, *168*, 1338.

(33) Swanson, H. E.; Tatge, E.; Fuyat, R. K. *Standard X-ray diffraction powder patterns*. U. S. Dept. of Commerce, National Bureau of Standards: Washington D.C., 1953.

(34) Denton, A. R.; Ashcroft, N. W. Vegard's law. *Phys. Rev. A* **1991**, *43*, 3161.

(35) Maillard, F.; Schreier, S.; Hanzlik, M.; Savinova, E. R.; Weinkauff, S.; Stimming, U. Influence of particle agglomeration on the catalytic activity of carbon-supported Pt nanoparticles in CO monolayer oxidation. *Phys. Chem. Chem. Phys.* **2005**, *7*, 385–393.

(36) Nanda, K. K.; Maisels, A.; Kruis, F. E.; Fissan, H.; Stappert, S. Higher surface energy of free nanoparticles. *Phys. Rev. Lett.* **2003**, *91*, 106102.

(37) Lei, Y.; Jelic, J.; Nitsche, L. C.; Meyer, R.; Miller, J. Effect of particle size and adsorbates on the L₃, L₂ and L₁ X-ray absorption near edge structure of supported Pt nanoparticles. *Top. Catal.* **2011**, *54*, 334–348.

(38) Pearson, D. H.; Ahn, C. C.; Fultz, B. White lines and d-electron occupancies for the 3d and 4d transition metals. *Phys. Rev. B* **1993**, *47*, 8471.

(39) Verma, A. A.; Bates, S. A.; Anggara, T.; Paolucci, C.; Parekh, A. A.; Kamasamudram, K.; Yezerets, A.; Miller, J. T.; Delgass, W. N.; Schneider, W. F.; Ribeiro, F. H. NO oxidation: a probe reaction on Cu-SSZ-13. *J. Catal.* **2014**, *312*, 179–190.

(40) Gu, Z.; Dong, J.; Allan, C. B.; Choudhury, S. B.; Franco, R.; Moura, J. J. G.; Moura, I.; LeGall, J.; Przybyla, A. E.; Roseboom, W.; Albracht, S. P. J.; Axley, M. J.; Scott, R. A.; Maroney, M. J. Structure of the Ni sites in hydrogenases by X-ray absorption spectroscopy. Species variation and the effects of redox poise. *J. Am. Chem. Soc.* **1996**, *118*, 11155–11165.

(41) Shukla, A. K.; Neergat, M.; Bera, P.; Jayaram, V.; Hegde, M. S. An XPS study on binary and ternary alloys of transition metals with platinized carbon and its bearing upon oxygen electroreduction in direct methanol fuel cells. *J. Electroanal. Chem.* **2001**, *504*, 111–119.

(42) Schneider, W.-D.; Laubschat, C. Actinide—noble-metal systems: An x-ray-photoelectron-spectroscopy study of thorium-platinum, uranium-platinum, and uranium-gold intermetallics. *Phys. Rev. B* **1981**, *23*, 997.

(43) Ghodselahi, T.; Vesaghi, M. A.; Shafiekhani, A.; Baghizadeh, A.; Lameii, M. XPS study of the Cu@Cu₂O core-shell nanoparticles. *Appl. Surf. Sci.* **2008**, *255*, 2730–2734.

(44) Grosvenor, A. P.; Biesinger, M. C.; Smart, R. S. C.; McIntyre, N. S. New interpretations of XPS spectra of nickel metal and oxides. *Surf. Sci.* **2006**, *600*, 1771–1779.

(45) Pendry, J. B. Low-energy electron diffraction. In *Interaction of Atoms and Molecules with Solid Surfaces*, Springer: 1990; pp 201–211.

(46) Smith, W. F.; Hashemi, J. *Foundations of materials science and engineering*. McGraw-Hill: 2011.

(47) Mehrer, H. *Diffusion in solids: fundamentals, methods, materials, diffusion-controlled processes*. Springer Science & Business Media: 2007; Vol. 155.

(48) Tao, F.; Grass, M. E.; Zhang, Y.; Butcher, D. R.; Renzas, J. R.; Liu, Z.; Chung, J. Y.; Mun, B. S.; Salmeron, M.; Somorjai, G. A. Reaction-driven restructuring of Rh-Pd and Pt-Pd core-shell nanoparticles. *Science* **2008**, *322*, 932–934.

(49) Xin, H. L.; Alayoglu, S.; Tao, R.; Genc, A.; Wang, C.-M.; Kovarik, L.; Stach, E. A.; Wang, L.-W.; Salmeron, M.; Somorjai, G. A.; Zheng, H. Revealing the atomic restructuring of Pt–Co nanoparticles. *Nano Lett.* **2014**, *14*, 3203–3207.

(50) Gao, W.; Zhang, Z.; Li, J.; Ma, Y.; Qu, Y. Surface engineering on CeO₂ nanorods by chemical redox etching and their enhanced catalytic activity for CO oxidation. *Nanoscale* **2015**, *7*, 11686–11691.

(51) Xu, Y.; Chun, D. H.; Jang, J. H.; Demura, M.; Wee, D. M.; Hirano, T. Catalytic Activity of Oxidation-Reduction Pre-Treated Ni₃Al for Methane Steam Reforming. *Adv. Mater. Res.* **2010**, *89–91*, 645–650.

(52) Matsui, T.; Okanishi, T.; Fujiwara, K.; Tsutsui, K.; Kikuchi, R.; Takeguchi, T.; Eguchi, K. Effect of reduction–oxidation treatment on the catalytic activity over tin oxide supported platinum catalysts. *Sci. Technol. Adv. Mater.* **2006**, *7*, 524–530.

(53) Zhao, Z.; Liu, H.; Gao, W.; Xue, W.; Liu, Z.; Huang, J.; Pan, X.; Huang, Y. Surface-Engineered PtNi–O Nanostructure with Record-High Performance for Electrocatalytic Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2018**, *140*, 9046–9050.