Controlled Dealloying of Alloy Nanoparticles toward Optimization of Electrocatalysis on Spongy Metallic Nanoframes

Guangfang Grace Li,† Esteban Villarreal,† Qingfeng Zhang,† Tingting Zheng,†‡ Jun-Jie Zhu,‡ and Hui Wang*†

†Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States
‡State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210093, China

Supporting Information

ABSTRACT: Atomic-level understanding of the structural transformations of multimetallic nanoparticles triggered by external stimuli is of vital importance to the enhancement of our capabilities to fine-tailor the key structural parameters and thereby to precisely tune the properties of the nanoparticles. Here, we show that, upon thermal annealing in a reducing atmosphere, Au@Cu2O core−shell nanoparticles transform into Au−Cu alloy nanoparticles with tunable compositional stoichiometries that are predetermined by the relative core and shell dimensions of their parental core−shell nanoparticle precursors. The Au−Cu alloy nanoparticles exhibit distinct dealloying behaviors that are dependent upon their Cu/Au stoichiometric ratios. For Au−Cu alloy nanoparticles with Cu atomic fractions above the parting limit, nanoporosity-evolving percolation dealloying occurs upon exposure of the alloy nanoparticles to appropriate chemical etchants, resulting in the formation of particulate spongy nanoframes with solid/void bicontinuous morphology composed of hierarchically interconnected nanoligaments. The nanoporosity evolution during percolation dealloying is synergistically guided by two intertwining structural rearrangement processes, ligament domain coarsening driven by thermodynamics and framework expansion driven by Kirkendall effects, both of which can be maneuvered by controlling the Cu leaching rates during the percolation dealloying. The dealloyed nanoframes possess large open surface areas accessible by the reactant molecules and high abundance of catalytically active undercoordinated atoms on the ligament surfaces, two unique structural features highly desirable for high-performance electrocatalysis. Using the room temperature electro-oxidation of methanol as a model reaction, we further demonstrate that, through controlled percolation dealloying of Au−Cu alloy nanoparticles, both the electrochemically active surface areas and the specific activity of the dealloyed metallic nanoframes can be systematically tuned to achieve the optimal electrocatalytic activities.

KEYWORDS: percolation dealloying, nanoporosity, electrocatalysis, nanoframes, undercoordinated surface atoms, alloy nanoparticles

INTRODUCTION

Multimetallic nanoparticles (NPs), either heteronanostructures or homogeneous alloys, may undergo intriguing postsynthesis structural transformations upon intraparticle atomic migrations triggered by thermal,† electrical,‡ or chemical stimuli,§ providing a versatile pathway to deliberately tailor the geometries and thereby fine-tune the optical, electronic, and catalytic properties of the NPs. The chemical or electrochemical dealloying of metallic alloy materials, which involves selective leaching of the less-noble components from the alloy matrices accompanied by structural remodeling of the more-noble components, represents an intriguing structural rearrangement that entangles multiple surface and bulk atomic dissolution and migration processes over the nanometer length scale.¶ A prototypical system of particular interest has been the percolation dealloying of bulk membranes of Au−Ag bimetallic alloys, which results in a unique nanoporous, solid/void bicontinuous structure consisting of a three-dimensional (3D) network of hierarchically interconnected Au-rich nanoligaments.¶–§ Strikingly distinct from the bulk Au films that are catalytically inactive, the dealloyed nanoporous Au membranes exhibit exceptionally high catalytic activities commensurate with those of the oxide-supported sub-5 nm Au NPs that have long been used for heterogeneous catalysis.¶–§ The locally curved surfaces of the nanoligaments are essentially enclosed by high densities of undercoordinated surface atoms, which serve as the active sites for catalyzing a series of interfacial chemical and electrochemical reactions.¶–§

Alloy NPs may undergo dealloying-induced structural transformations that are substantially more complicated than

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those of their macroscopic bulk counterparts displaying a planar surface to the electrolyte. Upon dealloying, an alloy NP may evolve into a variety of distinct nanostructures, such as a heterostructure with an alloy core encapsulated by a noble metal shell,10−13 a sponge-like particle with hierarchical nanoporosity,10−13 or a skeletal nanoframe (NF) covered by a noble metal skin,14−16 depending on the size, crystalline structure, compositional stoichiometry, and compositional gradient of the starting alloy NPs as well as the conditions under which the dealloying occurs. While each one of these structural transformations gives rise to drastically enhanced catalytic activities,10,13,14,17,18 the origin of the catalytic enhancements cannot be simply interpreted in the context of a single unified mechanism because multiple effects interplay and contribute synergistically to the overall catalytic activities. The specific surface area of a NP accessible for catalysis may drastically increase upon dealloying, especially when a solid alloy NP is converted into either a skeletal NF or a spongy nanoporous particle with hollow interior and open surface structures.10,13,14,18 The specific catalytic activity of the NPs, on the other hand, may also be greatly enhanced upon dealloying as a consequence of two intrinsically interconnected effects, geometric and electronic effects, both of which are intimately tied with the nature and density of the active sites on the NP surfaces.2,19−21 Unraveling the detailed structure−composition−activity correlations that underpin the intriguing catalytic behaviors of the dealloyed metallic NPs, nevertheless, remains challenging largely due to the intrinsic structural and compositional complexity and diversity of the materials systems as well as lack of a versatile approach through which both the specific surface area and specific catalytic activity of a dealloyed NP can be precisely fine-tuned.

Here, we endeavor to push the structural control of dealloyed metallic nanocatalysts to a new level of precision and versatility with the goal of paving an avenue toward the rational optimization of electrocatalysis. Dealloyed spongy nanoframes (NFs) represent a particularly interesting geometry with unique structural characteristics highly desirable for electrocatalysis. The enormous surface-to-mass and surface-to-volume ratios of the spongy NFs are highly advantageous for achieving superior mass activities, which become especially crucial when precious noble metals, such as Au, Pt, and Pd, are used as the catalysts.14,22−24 On the other hand, the locally curved surfaces of the nanoligaments are rich in catalytically active sites occupied by coordinatively unsaturated surface atoms.8,9 Using the methanol electro-oxidation as a model reaction, we demonstrate that both the catalytically active surface area and the density of active sites on the surfaces of spongy NFs can be deliberately tuned toward the optimization of electrocatalysis through controlled percolation dealloying of Au−Cu alloy NPs under mild conditions.

Figure 1. Nanoparticle structural evolution during nanoscale alloying and dealloying. (A) Schemes illustrating the transformation of Au@Cu2O core−shell NPs into Au−Cu alloy NPs upon alloying and the transformation of Au−Cu alloy NPs into spongy NFs upon dealloying. (B) SEM image of Au@Cu2O core−shell NPs (average core diameter: 104 nm; average shell thickness: 51 nm). The inset shows a TEM image of one Au@Cu2O core−shell NP. (C) SEM image of Au0.19Cu0.81 alloy NPs. The inset shows a TEM image of one alloy NP. (D) SEM and (E) TEM images of spongy Au0.72Cu0.28 alloy NFs obtained through dealloying of the Au0.19Cu0.81 alloy NPs in 0.5 M HNO3 for 3 h. (F) HAADF-STEM image (left panel) and EDS elemental distribution of Au (upper right panel) and Cu (lower right panel) of an individual Au0.72Cu0.28 alloy NP particle. The compositions of the alloy NPs and dealloyed NFs were quantified by EDS.

RESULTS AND DISCUSSION

Our synthetic approach to the electrocatalytically active spongy NFs involves two key steps (Figure 1A). We started from Au@Cu2O core−shell NPs, which underwent chemical reduction followed by intraparticle alloying to evolve into Au−Cu alloy NPs upon thermal annealing in a reducing atmosphere, such as H2. The Au−Cu alloy NPs further transformed into spongy NPs through percolation dealloying when exposed to a
chemical etchant, such as nitric acid (HNO₃). We used a combination of scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), and powder X-ray diffraction (PXRD) to systematically track the structural and compositional changes of the NPs during the nanoscale alloying and dealloying processes. The Au–Cu₂O hybrid NPs exhibited a well-defined core–shell heterostructure clearly resolvable by electron microscopies (Figure 1B) and EDS elemental analysis (Figure S1). After the core–shell NPs were thermally annealed in a flow of H₂ (50 sccm) under 100 Torr at 450 °C for 15 min, the contrast between the core and the shell in the electron microscopy images completely disappeared (Figure 1C), indicating the formation of Au–Cu bimetallic alloy NPs. The EDS elemental mapping results (Figure S2) further verified that the Au and Cu atoms were homogeneously intermixed in the alloy NPs. During the percolation dealloying, the alloy NPs further evolved into compositionally Au-rich spongy NPs as Cu was selectively dissolved from the alloy matrix. Figure 1D–F showed the SEM, TEM, and high-angle annular dark-field scanning electron microscopy (HAADF-STEM) images, respectively, of the spongy NPs obtained through dealloying of Au₀.₁₉Cu₀.₈₁ alloy NPs in 0.₅ M HNO₃ for 3 h at room temperature. Each particle exhibited a bicontinuous nanoporous structure composed of nanocurved ligaments that were 5 to 25 nm thick. The diameters of the pores were in the range from 10 to 40 nm. While the Cu/Au atomic ratio significantly decreased after percolation dealloying, the ligaments of the dealloyed NPs were still composed of Au–Cu alloys rather than segregated monometallic domains (see STEM-EDS mapping results in Figure 1F and PXRD results in Figure S3).

The core and shell dimensions of the starting Au@Cu₂O core–shell NPs could be fine-controlled over a broad size range using a seed-mediated growth method we recently developed, ₂₆ which enabled the fine-tuning of the alloy NP compositions. While the overall particle sizes shrank significantly upon alloying, both the quasi-spherical morphology and the Cu/Au stoichiometric ratios of the NPs were well-preserved (Figure S4). Therefore, the Cu/Au stoichiometric ratios of the alloy NPs were essentially determined by the relative core and shell dimensions of the Au@Cu₂O core–shell NP precursors and could be systematically tuned over a broad range approximately from 0.₃ to 4. Figure S5A showed the PXRD patterns of Au–Cu alloy NPs with various Cu/Au atomic ratios together with those of monometallic Au NPs and Cu NPs (Figure S6). The as-fabricated Au–Cu alloy NPs were essentially composed of random alloys, ₂₁ rather than ordered Au–Cu intermetallics with specific Cu/Au stoichiometries, such as Au₃Cu, Au₅Cu, or Au₇Cu₅. ₂₇,₂₈ The lattice parameters of the face-centered cubic (fcc) Au–Cu alloy NPs were calculated using Bragg’s law

\[
d_{hkl} = \frac{\lambda}{2\sin(\theta_{hkl})}
\]

where \(\lambda\) is the wavelength of the incident X-ray (\(\lambda = 1.5406 \, Å\) for Cu Kα), \(d_{hkl}\) is the lattice spacing of the crystalline plane with Miller index of \{hkl\}, and \(\theta_{hkl}\) is the angle of incidence on the \{hkl\} plane. We calculated the Cu/Au stoichiometric ratios of various Au–Cu alloy NPs based on the position of the (111) diffraction peak, assuming that the lattice parameters of a solid solution agree with a linear relationship between the two end points of alloying elements, an empirical rule known as Vegard’s law. ₂₉ Although some bimetallic alloys may deviate significantly from Vegard’s law, Au–Cu binary random alloys only exhibit slight deviations from Vegard’s law. ₃₀ The Cu/Au atomic ratios calculated from the PXRD results were in very good agreement with those quantified by inductively coupled plasma mass spectrometry (ICP-MS) and EDS (Figure S5B). Colloidal Au@Cu₂O core–shell NPs exhibited strong dipolar plasmon resonances that progressively red-shifted as the thickness of the Cu₂O shell increased. ₂₆,₃₁,₃₂ (Figure S7A). The transformation of core–shell NPs into alloy NPs introduced drastic modifications to the resonance frequencies and spectral line-shapes of the NP plasmons (Figure S7B). As the Cu/Au stoichiometric ratio and the particle size increased, the plasmon resonance of the alloy NPs red-shifted, accompanied by significant peak broadening due to the plasmon damping caused by alloying of Au with Cu. ₃₃–₃₅ The key extinction spectral features observed experimentally were well reproduced by the Mie scattering theory calculations (Figure S7C,D).

The Au–Cu alloy NPs exhibited interesting composition-dependent chemical dealloying behaviors (Figure S8). Upon exposure to 0.₅ M HNO₃ at room temperature, Cu-rich alloy NPs with a Cu atomic percentage (at %) above ~70% underwent nanoporosity-evolving percolation dealloying, during which the Cu/Au atomic ratios progressively decreased accompanied by ligament thickening and pore volume expansion until complete leaching of Cu within a few hours. In striking contrast, Au-rich alloy NPs (Cu at % < ~65%) exhibited unnoticeable morphological and compositional changes even over a few days under identical dealloying conditions. Such composition-dependent dealloying behaviors of Au–Cu alloy NPs can be interpreted in the context of the percolation limit and critical potential for the plasmon dealloying. ₃₁

For a macroscopic AₓBₘ binary alloy (A and B represent the more-noble and the less-noble elements, respectively, and \(p\) is atomic fraction of B), percolation dealloying occurs only when the \(p\) is higher than a threshold value known as the percolation limit. In Ag–Au alloys, this percolation limit was measured to be ~55% at Ag. ⁴ The critical potential, \(E_c\), which is the electrochemical parameter signifying the onset of percolation dealloying, is related to the molar volume of A, \(\Omega_A\), the B/electrolyte interfacial free energy, \(γ_{B/electrolyte}\), and the equilibrium potential, \(E_{eq}\), above which the surface dealloying at the topmost atomic layer occurs. The relationship between \(E_c\) and \(E_{eq}\) is given by

\[
E_c(p) = E_{eq}(p) + \frac{4γ_{B/electrolyte}Ω_A}{npξ^2}
\]

where \(n\) is the number of electrons transferred upon oxidation of 1 atom of B, \(P\) is the Faraday constant, and \(ξ\) represents the local radius of the surface where a cylindrical pit is created at the initial stage of nanoporosity evolution. \(ξ\) is related to both \(p\) and the nearest-neighbor spacing, \(a\), as shown by

\[
ξ = \frac{1}{1 - p} \times a
\]

For macroscopic bimetallic alloys, both the \(E_c\) and \(E_{eq}\) are functions of the alloy composition and the \(E_c\) values are more positive than \(E_{eq}\) when the solid-state mass transport is slower than the imposed rate of dealloying. At a potential above the \(E_c\) nanoporosity-evolving percolation dealloying occurs, while below \(E_c\) only superficial dealloying can occur, forming a
The composition-dependent electrochemical dealloying behaviors of the Au–Cu alloy NPs were further investigated by linear sweep voltammetry (LSV) measurements in 1.0 M KNO₃ electrolyte (pH = 7) at a sweep rate of 5.0 mV s⁻¹ by linear sweep voltammetry (LSV) measurements in 1.0 M KOH electrolyte, possibly due to the surface passivation by the surface passivating atomic layer of the more-noble component which inhibits the nanoporosity formation.²³,³⁸ For a spherical AₓBᵧ alloy NP of radius r, the critical potential becomes dependent not only on the composition but also on the size of the NP. Accordingly, the Eᵣ(p, r) of the alloy NP is given by⁴¹

\[ Eᵣ(p, r) = E₀ - [γ_{Alloy}(Ωₐ) + f_{Alloy}(Ωₐ - Ωₐ)] \times \left( \frac{2}{nF_r} \right) \]

where γ_{Alloy} and f_{Alloy} represent the free energy and the stress at the alloy/electrolyte interface, respectively. Ωₐ is the partial molar volume of A in the alloy, and Ωₐ is the average molar volume of the alloy. When r is greater than ~5 nm, eqs 2 and 4 generate virtually the same results because the maximum values of γ_{Alloy} and f_{Alloy} are ~2 and ~6 J m⁻², respectively.⁴⁹ Therefore, alloy NPs beyond ~10 nm in size typically undergo dealloying-induced structural transformations analogous to those of their bulk counterparts with the same compositions. It was shown that Au–Ag alloy NPs larger than 10 nm evolved into spongy nanoporous structures whereas their sub-10 nm counterparts transformed into core–shell NPs under identical dealloying conditions. Since the particle sizes under the current investigations were far beyond 10 nm, the Au–Cu alloy NPs evolved into spongy NFs when the Cu content was higher than the parting limit, which was determined to be ~70 at % of Au. Dealloying of the Au₀.₃₁Cu₀.₆₉ alloy NPs resulted in a mixture of solid alloy NPs and spongy NFs owing to the intrinsic particle-to-particle compositional variations within the sample (Figure S8C).

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The nanoporosity evolution during percolation dealloying is essentially a multiscale structural rearrangement governed by two intertwining and competing processes, ligament domain coarsening and framework expansion. The percolation dealloying was initiated upon the dissolution of a Cu atom at the alloy surface, leaving behind a terrace vacancy coordinated with undercoordinated Cu atoms that were more susceptible to further dissolution. As the entire terrace was stripped, the coordinatively unsaturated Au atoms leaving behind the dealloying frontiers underwent fast surface migration to agglomerate into Au-rich local islands. Therefore, the surface of the alloy upon initiation of dealloying was comprised of Au-rich domains that locally passivated the surface and patches of undealloyed material directly exposed to electrolyte. As the percolation dealloying further proceeded, the interfacial dissolution of Cu atoms and coarsening of the Au-rich domains continued, gradually evolving into bicontinuous spongy structures. Meanwhile, the outward migration of Cu atoms was faster than the inward migration of Au atoms in the alloy matrix, providing an additional contribution to the expansion of the pores during the nanoporosity evolution. This effect, known as the Kirkendall effect, has been harnessed to fabricate hollow NPs with fine-tailored interior structures. For an alloy NP, the ligaments domain coarsening resulted in the thickening of the ligaments and shrinkage of the overall particle size, whereas the framework expansion driven by the Kirkendall effect led to increased overall particle size and pore volumes. The relative rates of the ligament domain coarsening and framework expansion could be maneuvered by tuning the rates of Cu leaching during the percolation dealloying.

We systematically studied the kinetics and thermodynamics of the Cu leaching from Au₀.₁₉Cu₀.₈₁ alloy NPs during percolation dealloying in the presence of three different chemical etchants, HNO₃, Fe(NO₃)₃, and ammonia, in an aqueous environment under ambient conditions (Figure S11). Both HNO₃ and Fe(NO₃)₃ are oxidative etchants that directly oxidize metallic Cu and selectively dissolve the Cu from the alloy NPs, thereby giving rise to relatively fast Cu leaching upon percolation dealloying. The leaching of Cu from the alloy NPs exposed to ammonia, however, is essentially a consequence of oxidation of Cu by the oxygen dissolved in the aqueous solution followed by the formation of water-soluble Cu(NH₃)₂⁺ and Cu(NH₃)₄⁺ complexes. Therefore, the rate of Cu leaching upon dealloying in ammonia appeared much slower than those in HNO₃ and Fe(NO₃)₃. The Cu/Au atomic ratios progressively decreased as the percolation dealloying proceeded until reaching a thermodynamic equilibrium point. Because of their different standard redox potentials, HNO₃, Fe(NO₃)₃, and O₂/ammonia resulted in different equilibrium Cu/Au stoichiometries. While complete Cu leaching (less than 3 at % residual Cu) was achieved after dealloying within 1 h in 2.0 M HNO₃, Fe(NO₃)₃, and O₂/ammonia only resulted in partial leaching of Cu when reaching the thermodynamic equilibria. These partially dealloyed NPs obtained in Fe(NO₃)₃ or O₂/ammonia underwent further Cu leaching upon exposure to HNO₃ (Figure S12).

Although the Cu leaching from the Au₀.₁₉Cu₀.₈₁ alloy NPs under the nonequilibrium conditions was a continuous process, further dealloying of the partially dealloyed NPs could be effectively inhibited by separating the particles from the etchants through centrifugation and redispersion in water.
This allowed us to kinetically trap partially dealloyed NFs with fine-controlled pore volumes, ligament thicknesses, and Cu/Au stoichiometries. As shown in Figure 2, the degree of Cu leaching and the structural features of the dealloyed NFs could be systematically tuned by changing the etchants or the concentration of each etchant at fixed dealloying times. When fixing the dealloying time at 1 h, increasing the HNO$_3$ concentration resulted in more Cu leaching, larger average pore sizes, thicker ligaments, and smaller overall sizes of the dealloyed NFs. In HNO$_3$, the leaching of Cu from the alloy NPs was faster than the atomic diffusion of Cu in the alloy matrix. Therefore, the nanoporosity evolution was dominated by the ligament domain coarsening rather than framework expansion, leading to significant thickening of the ligaments and shrinkage of the overall size of the dealloyed NFs as an increasing amount of Cu was dissolved. A similar volume shrinkage of macroscopic Ag–Au alloy bulk materials by up to 30 vol % was previously observed during fast electrochemical dealloying as a consequence of the lattice defect formation and local plastic deformation both associated with ligament coarsening.$^{18}$ When the percolation dealloying occurred in ammonia, however, the overall particle sizes were observed to increase with the ammonia concentration when the dealloying time was fixed at 2 h. In ammonia, as Cu leaching became slower than the atomic diffusion of Cu, the Kirkendall effects started to dominate the nanoporosity evolution, which resulted in the expansion of the particle frameworks. In Fe(NO$_3$)$_3$, the rates of Cu leaching and atomic diffusion of Cu were comparable, and thus, the overall size of the dealloyed NFs remained almost unchanged regardless of the concentration of Fe(NO$_3$)$_3$ and the amount of Cu leached during the percolation dealloying.

We used high-resolution HAADF-STEM to fine-resolve the surface and bulk structures of the dealloyed NFs at the atomic level. As shown in Figure 3A, a representative particle in the dealloyed Au$_{0.19}$Cu$_{0.81}$ NF sample (obtained through dealloying of Au$_{0.19}$Cu$_{0.81}$ alloy NPs in 2.0 M HNO$_3$ for 1 h) exhibited a bicontinuous architecture consisting of hierarchically inter-
connected nanoligaments whose compositions were dominated by Au. Panels A-a and A-b show the high-resolution HAADF-STEM images of two regions in Panel A labeled as a and b, respectively. The insets in panels A-a and A-b are the FFT patterns of the regions labeled as i, ii, and iii, respectively. In the high-resolution HAADF-STEM images, the crystalline domains were projected along the [011̅] zone axis. The corresponding fast Fourier transform (FFT) patterns further confirmed the orientation of the crystalline domains in the ligaments. The lattice fringes corresponding to the face center cubic phase of Au were well resolved in the high-resolution HAADF-STEM images. No segregated monometallic Cu domains were observed either in the bulk or on the surfaces of the ligaments, suggesting that the residual Cu was randomly intermixed with Au. When the atomic fraction of the residual Cu was below 3%, the Cu signals in EDS became indistinguishable from the noise, making it difficult to characterize the spatial distribution of Cu elements in the ligaments through EDS elemental mapping. However, the residual Cu was clearly resolvable by X-ray photoelectron spectroscopy (XPS), which is a sensitive surface analysis technique. While the binding energies of the Au 4f peaks slightly up-shifted by ~0.05 eV in comparison to those of the bulk Au, the Cu 2p XPS peaks exhibited more pronounced down-shifts by ~0.5 eV with respect to those of the bulk Cu due to the alloying of Cu with Au.

Figure 3. Atomic-level surface structures and electrocatalytic activity of fully dealloyed spongy NFs. (A) HAADF-STEM image of an individual Au0.97Cu0.03 NF particle. High-resolution HAADF-STEM images showing the atomic-level structures of regions a and b are shown in panel A-a and panel A-b, respectively. The insets in panels A-a and A-b are the FFT patterns of the regions labeled as i, ii, and iii, respectively. In the high-resolution HAADF-STEM images, the crystalline domains were projected along the [011̅] zone axis. SEM images of (B) a Au SRNP with solid interior core and (C) a Au QSNP. (D) CV curves of Au0.97Cu0.03 NFs, Au SRNPs, and Au QSNPs in 0.5 M H2SO4 at a potential sweep rate of 5.0 mV s−1. The electrochemical signals from SRNPs and QSNPs were multiplied by a factor of 5 for clearer comparison. (E) CV curves of Au0.97Cu0.03 NFs, Au SRNPs, and Au QSNPs in 1.0 M methanol and 0.5 M KOH at a potential sweep rate of 10 mV s−1. The CV curve of Au0.97Cu0.03 NFs in the absence of methanol is shown as the dashed curve. (F) Mass activities (MAs), electrocatalytically active surface areas (ECSAs), and specific activities (SAs) of Au0.97Cu0.03 NFs, Au SRNPs, and Au QSNPs in 1.0 M methanol and 0.5 M KOH at a potential sweep rate of 10 mV s−1.

The surfaces of the ligaments were enclosed by a mixture of both high-index and low-index local facets (Figure 3A). The locally flat surface regions of a monocristalline domain were typically covered by low-index {111} facets, whereas in the locally curved regions, the surfaces were terminated with high-index facets with high densities of undercoordinated surface atoms at the atomic steps, kinks, and terrace edges. Coordinatively unsaturated surface atoms were also present at the boundaries between two twinned crystalline domains. The high abundance of undercoordinated surface atoms is a unique feature of the dealloyed NFs.
Figure 4. Electrocatalytic performance of dealloyed NFs for MOR. (A) CV curves of MOR on Au$_{0.19}$Cu$_{0.81}$ alloy NPs and various dealloyed NFs in 1.0 M methanol and 0.5 M KOH at a potential sweep rate of 10 mV s$^{-1}$. The NF samples labeled as NF-i, NF-ii, NF-iii, and NF-iv correspond to the samples obtained through dealloying of Au$_{0.19}$Cu$_{0.81}$ alloy NPs in 0.2, 0.5, 1.0, and 2.0 M Fe(NO$_3$)$_3$ for 2 h, respectively. The sample labeled as NF-v was obtained through dealloying of Au$_{0.19}$Cu$_{0.81}$ alloy NPs in 2.0 M HNO$_3$ for 1 h. HAADF-STEM images of one representative particle for each NF sample are also shown as the insets. All the HAADF-STEM images share the same scale bar. (B) Cu atomic percentages (quantified by EDS and ICP-MS), MAs, ECSAs, and SAs of Au–Cu alloy NPs and various dealloyed NFs. (C) CA curves collected on Au$_{0.19}$Cu$_{0.81}$ alloy NPs and various dealloyed NFs for MOR at 0.1 V (vs SCE) and 0.3 V (vs SCE). All CA measurements were carried out in solutions containing 0.5 M KOH and 1.0 M methanol deoxygenated with N$_2$. The error bars of the particle compositions and the CA results represent the standard deviations obtained from 3 samples. The error bars of the MAs and ECSAs represent the standard deviations obtained from 5 samples.

The feature of NPs with highly curved surfaces, such as the catalytically active sub-5 Au NPs$^{30}$ and Au surface-roughened nanoparticles (SRNPs). We synthesized Au SRNPs with overall particle diameters of 120 ± 7.2 nm using a seed-mediated nanocrystal growth method previously developed by our group.$^{51}$ The Au SRNPs exhibited nanoscale surface roughness (Figure 3B) with high densities of undercoordinated atoms at the locally curved surface sites (see more detailed structural characterizations in a previously published paper from our group$^{52}$). The Au SRNPs exhibited much smaller specific surface areas than the dealloyed NF particles because of their solid interiors. In contrast to the Au SRNPs and dealloyed NFs, the surfaces multifaceted Au quasi-spherical nanoparticles (QSNPs, diameter of 104 ± 6.5 nm) were essentially dominated by low-index facets bound with close-packed surface atoms (Figure 3C) with only a small fraction of undercoordinated surface atoms present at the particle corners, edges, crystalline boundaries, and surface defects. We used cyclic voltammetry (CV) as an electrochemical tool to further characterize the atomic-level surface structures and specific surface areas of the dealloyed NFs, Au SRNPs, and Au QSNPs. CV-based electrochemical oxide stripping is a method commonly used to study the surface structures of bulk Au$^{1,2,4}$ and more recently Au NPs$^{35,56}$ as well. Figure 3D showed the CV curves of various samples obtained in 0.5 M H$_2$SO$_4$ at a sweep rate of 5.0 mV s$^{-1}$. During the potential positive scans of the CV measurements, both the dealloyed Au$_{0.97}$Cu$_{0.03}$ NPs and Au SRNPs exhibited oxidation peaks in the range of 0.95–1.25 V vs saturated calomel electrode (SCE), whereas Au QSNPs exhibited an oxidation peak in higher potential range above 1.40 V (vs SCE). The negative shift of oxidation peaks observed on the dealloyed NFs and SRNPs suggested that the surfaces of the NFs and SRNPs were easier to get oxidized to form an oxide surface layer due to the presence of highly abundant undercoordinated surface atoms while the close-packed surface atoms on Au QSNPs were more resistant against oxidation. During the negative potential scans, the sharp reduction peak centered around 0.9 V (vs SCE) signified the electrochemical stripping of the surface oxide layers formed in the previous positive potential scan. Although the onset potentials of the surface atom oxidation were sensitively dependent on the surface atomic coordination numbers, the electrochemical stripping of the gold oxide surface layers occurred in essentially the same potential range from ~0.98 to ~0.85 V (vs SCE), which was in line with previous observations on Au bulk films$^{53,54}$ and NPs.$^{55,58}$ Assuming the specific charge associated with gold oxide stripping to be 450 μC cm$^{-2}$, the mass-specific electrochemically active surface area (ECSA) of the dealloyed NFs was estimated to be ~20 m$^2$ g$^{-1}$, approximately 1 order of magnitude higher than that of SRNPs and 2 orders of magnitude higher than that of the QSNPs, respectively, despite the fact that the dealloyed NFs, SRNPs, and QSNPs all had similar overall particle sizes.

We quantitatively compared the electrocatalytic activities of the dealloyed NFs, SRNPs, and QSNPs using the room-temperature electrocatalytic methanol oxidation reaction (MOR) in an alkaline aqueous environment as a model reaction. As shown in Figure 3E, while the Au QSNPs exhibited poor electrocatalytic activity toward MOR, both the dealloyed Au$_{0.97}$Cu$_{0.03}$ NPs and Au SRNPs were much more active. The
onset oxidation potential and peak potential for MOR were around 0.1 V (vs SCE) and 0.3 V (vs SCE), respectively. By normalizing the oxidation peak current against the mass of Au on each electrode, a mass activity (MA) of ~12 μA μg⁻¹ was obtained at 0.3 V on the dealloyed Au₁₀₀₀Au₀₉₀ NFs at a sweep rate of 10.0 mV s⁻¹, which was about 1 order of magnitude higher than that of the SRNPs. For Au, Pt, and Pd NPs, the undercoordinated surface atoms have been identified to be the electrocatalytically active sites for MOR and other alcohol oxidation reactions.²⁶,⁶⁶ Therefore, the superior electrocatalytic activity toward MOR observed on the dealloyed Au₀₉₀₀Au₀₃ NFs originated from both their large specific ECSA and high density of surface active sites. By normalizing the MAs against ECSAs, the specific activities (SAs) of the NPs were obtained, which were directly related to the active site density on the NP surfaces. In Figure 3F, we compared the MAs, ECSAs, and SAs of the dealloyed Au₀₉₀₀Au₀₃ NFs with those of the Au SRNPs and QSNPs. Interestingly, the Au SRNPs exhibited a SA only slightly lower than that of dealloyed NFs, indicating comparable densities of surface active sites, i.e., undercoordinated surface atoms, on the dealloyed NFs and Au SRNPs. However, the dealloyed NFs exhibited much higher MA than Au SRNPs because of their significantly larger ECSA. For a low-index faceting Au QSNP, the undercoordinated surface atoms are located at the particle corners and edges and thus only account for a vanishingly small fraction of the surface atoms when the particle size becomes larger than 10 nm.²⁶ Therefore, the Au QSNPs exhibited diminished electrocatalytic activity for MOR due to their limited SA and ECSA.

The controlled percolation dealloying of Au–Cu alloy NPs allowed us to systematically tune both the ECSAs and the SAs of the dealloyed NFs to achieve the optimal MAs for MOR. In Figure 4A, we compared the MAs, ECSAs, and SAs of 5 dealloyed NF samples with different degrees of Cu leaching. The NF samples labeled as NF-i, NF-ii, NF-iii, and NF-iv corresponded to the samples obtained through dealloying of Au₀₁₉₉Cu₀₈₁ alloy NPs in 0.2, 0.5, 1.0, and 2.0 M Fe(NO₃)₃ for 2 h, respectively. The sample labeled as NF-v was obtained through dealloying of Au₀₁₉₉Cu₀₈₁ alloy NPs in 2.0 M HNO₃ for 1 h. The HAADF-STEM images highlighting the key structural features of individual NF particles representing each sample were also shown as the insets of Figure 4A. From NF-i to NF-v, the Cu/Au stoichiometric ratios decreased (Figure 4B, top panel) while both the average ligament thicknesses and pore sizes increased. All the NF samples exhibited much higher MAs than the solid alloy NPs, and NF-ii exhibited the highest MA among the NF samples. Dealloyed spongy NFs exhibited drastically higher activities than the solid Au–Cu alloy NPs with similar Cu/Au stoichiometric ratios (Figure S15), strongly indicating that the enhanced MAs of the dealloyed NFs were primarily determined by the NF surface areas and the densities of surface active sites rather than the Cu/Au stoichiometric ratios.

We semiquantitatively assessed the ECSAs of various NF samples based on the electrochemical oxide stripping results. For the Au–Cu alloy NFs, Cu leaching occurred during the electrochemical oxide stripping experiments at relatively slow potential sweep rates (e.g., 5 mV s⁻¹), which prevented us from obtaining meaningful ECSA results. Therefore, to accurately measure the ECSAs of the Cu-containing alloy NFs, the CV measurements were carried out at much faster potential sweep rates to effectively suppress the kinetically slow Cu leaching process. As demonstrated on Au₀₉₀₀Cu₀₃ NFs (no further Cu leaching during CV scans), the ECSA values measured at various potential sweep rates in the range from 5 to 500 mV s⁻¹ were highly consistent (Figure S16), though the multipeaked features in the potential range of 1.0–1.3 V (vs SCE) signifying the electrochemical oxidation of the undercoordinated surface atoms became less well-resolved as the potential sweep rate increased. At sufficiently fast potential sweep rates (e.g., 500 mV s⁻¹), the Cu leaching from Au₀₃₀₀Cu₀₇₀ alloy NFs was effectively suppressed while the ECSA remained almost unchanged during multiple cycles of CV scans (Figure S17). In Figure 4B, we further compared the ECSAs and SAs of various NF samples and the solid alloy NPs. Upon the percolation dealloying, the ECSA first increased and then decreased as an increasing amount of Cu was dissolved and NF-ii exhibited the largest ECSA among the NF samples. The SA of the dealloyed NFs, on the other hand, reached its maximum value upon initiation of nanoporosity formation and kept decreasing as the Cu leaching further proceeded during the nanoporosity evolution. At the initiation stage of percolation dealloying, the surface pitting upon Cu atomic dissolution created highly abundant undercoordinated surface atoms that contributed to the high SA of the NPs. As more Cu was dissolved from the alloy matrix, the ligament domain coarsening drove the migration of the undercoordinated surface atoms to form thermodynamically more stable local facets. As a consequence, the active sites became less abundant, resulting in decreased SA. Therefore, the optimization of the MAs on the spongy NFs requires deliberate tuning of both the ECSA and SA of the NFs, which could be achieved through the controlled percolation dealloying of Au–Cu alloy NPs as demonstrated in this work.

Among the various dealloyed NF samples, NF-ii exhibited the highest MA and ECSA while NF-i exhibited the highest SA (Figure 4B). It was recently reported that nanoporous Au shells⁶⁵ and Au bowls⁶² overgrown on sacrificial AgCl templates exhibited MAs approximately 1.4 and 2.3 times higher than that of the macroscopic dealloyed nanoporous Au foams,⁹ respectively, for the electrocatalytic MOR in alkaline electrolytes. NF-ii was about 3 times better than the nanoporous Au bowls and 5 times better than the nanoporous Au shells, respectively, in terms of the MAs normalized to Au mass. The ECSA of NF-ii was about 2.5 times higher than the largest ECSAs achievable on the nanoporous Au shells and bowls.⁶⁵,⁶² The SAs of the dealloyed spongy NFs, macroscopic nanoporous Au foams, and the nanoporous Au shells and bowls, however, were all comparable to each other possibly due to similar densities of the undercoordinated atoms on their highly curved surfaces.

To assess the electrocatalytic durability of the spongy NFs, chronoamperometry (CA) measurements were carried out at both the onset oxidation potential (0.1 V, vs SCE) and the oxidation peak potential (0.3 V, vs SCE). As shown in Figure 4C, the oxidation currents underwent a fast decay in the first few seconds followed by a much slower decay over minutes until reaching a steady-state plateau. The fast decay of the oxidation currents arose from the development of the electrochemical double-layer after a potential was applied on the samples until reaching the equilibrium after a few seconds. The slower current decay was found to be associated with the surface structural remodeling of the NFs during electrocatalytic reactions, which resulted in the activity deterioration to certain extent. Although the nanoporous morphology of the Au₀₃₀₀Cu₀₇₀ NFs (NF-ii) was well-preserved with a limited amount of Cu further leaching before the steady-state current
was reached, thickening of the ligaments and expansion of pore sizes were clearly observed (Figure S18) as a consequence of surface atomic migrations. Such surface structural remodeling during electrocatalytic reactions, which was previously also observed on dealloyed macroscopic Au membranes, resulted in a decrease of both the ECSAs and densities of active sites on the NF surfaces (Figure S19). The spongy NFs obtained through electrochemical dealloying exhibited significantly lower electrocatalytic activities than their chemically dealloyed counterparts (Figure S20), further indicating that the undercoordinated surface atoms located at the catalytic active sites could migrate to form thermodynamically more stable but catalytically less active surface structures when a potential bias was applied to the NFs.

**CONCLUSIONS**

The percolation dealloying of Au–Cu alloy NPs is a multiscale structural remodeling process involving nanoscale atomic dissolution and migration that led to the formation of spongy NFs with unique structural characteristics highly desired for electrocatalysis. The solid-void bicontinuous NFs consisting of hierarchically interconnected nanoligaments are found to be a unique structure generated from percolation dealloying of Au–Cu alloy NPs with Cu at % above the parting limit. The nanoporosity evolution during percolation dealloying is synergistically guided by two intertwining and competing structural rearrangement processes, ligament domain coarsening driven by thermodynamics and framework expansion driven by Kirkendall effects, both of which can be maneuvered by controlling the Cu leaching rates during the percolation dealloying. The controlled percolation dealloying of Au–Cu alloy NPs provides a unique way to systematically tune both the catalytically active surface areas and the surface densities of active sites of the dealloyed NFs such that the optimal electrocatalytic activity can be achieved. The undercoordinated surface atoms, which serve as the catalytically active sites, undergo nanoscale surface migrations over a time scale of minutes during electrocatalytic MOR until reaching the steady-state catalytic currents, resulting in structural remodeling of the NFs that causes partial deterioration of the catalytic activities. Development of new approaches to further stabilize the surface active sites on the dealloyed NFs through either incorporation of structure-stabilizing residual components or deliberate introduction of compositional gradients to the nanoligaments is currently underway with the ultimate goal of retaining the superior mass-specific electrocatalytic activities of the spongy NFs over extended time periods for direct methanol fuel cell (DMFC) applications.

**EXPERIMENTAL DETAILS**

**Chemicals and Materials.** Cu(NO$_3$)$_2$, Fe(NO$_3$)$_3$, and polyvinylpyrrolidone (PVP) were purchased from J.T. Baker. Methanol, NaOH, KNO$_3$, and KOH were purchased from ACS Chemicals and Materials. Au QSNPs (diameter of 104 ± 6.5 nm) were synthesized through seed-mediated NP growth following a protocol we recently published.51,52

**Synthesis of Au@Cu$_2$O Core–Shell NPs.** Au QSNPs (diameter of 104 ± 6.5 nm) were used as the core materials for the fabrication of Au@Cu$_2$O core–shell NPs following a previously published protocol.46 A varying amount (0.3–3 mL) of 0.1 M Cu(NO$_3$)$_2$ solution was added into 300 mL of 2 wt % PVP aqueous solution containing colloidal Au QSNPs. The reaction mixtures were transferred into an ice bath, and then, 0.67 mL of 5 M NaOH and 0.3 mL of N$_2$H$_4$·3H$_2$O solution were added under magnetic stirring. After 10 min, the NPs were centrifuged (2000 rpm, 10 min), then washed with water, and finally dispersed in ethanol. The thickness of the Cu$_2$O shells could be systematically tuned by adjusting the molar ratios between Au QSNPs and Cu(NO$_3$)$_2$. More details of the core–shell NP synthesis can be found in a paper previously published by our group.46

**Synthesis of Au–Cu Alloy NPs.** Au–Cu alloy NPs were prepared through thermal annealing of the Au@Cu$_2$O core–shell NPs at 450 °C in a flow of H$_2$ flow (50 sccm) under 100 Torr for 15 min in a tube furnace. The annealed samples were collected after cooling down to room temperature and were dispersed in 10 mL of water. It was recently revealed by thermal gravimetric analysis that PVP in various nanocomposites underwent rapid thermal degradation at temperatures above ~420 °C.63–65 Therefore, thermal annealing up to 450 °C enabled us not only to obtain fully alloyed NPs but also to effectively remove the residual PVP possibly present on the NP surfaces (the synthesis of Au@Cu$_2$O core–shell NPs involved the use of PVP).

**Synthesis of Spongy NFs.** Spongy NFs were fabricated through chemical dealloying upon the introduction of 1 mL of a chemical etchant, such as HNO$_3$, Fe(NO$_3$)$_3$, or NH$_4$OH, into 200 μL of colloidal Au–Cu alloy NPs at room temperature. After certain dealloying times, the dealloyed NPs were separated from the etchants by centrifuging the NP particles and redispersing them in water.

**Electrochemical Measurements.** Electrochemical measurements, including CV, LSV, and CA, were carried out using a CHI 660E workstation (CH Instruments, Austin, Texas) at room temperature. We used a standard three-electrode system, which was composed of a glassy carbon electrode (GCE) serving as the working electrode, a saturated calomel electrode (SCE) serving as the reference, and a Pt wire serving as the auxiliary. The GCE (3 mm diameter, CH Instruments, Austin, Texas) was first polished with 0.3 mm alumina slurry and then thoroughly washed with water and ethanol before use. Dry powders of spongy NPs, Au–Cu alloy NPs, Au QSNPs, or Au SRNPs with certain total masses were first dispersed in ethanol to form colloidal suspensions (2.0 mg of Au in 1.0 mL of water), and then, 2 μL of the colloidal ink was drop-casted on each pretreated GCE at room temperature. Finally, 2 μL of Na$_2$O solution (0.2 wt %) was drop-dried to hold the NPs on the electrode surfaces. The Au mass of the NPs loaded on each GCE was kept at 4.0 μg for comparison of the MAs and ECSAs of various samples. In a typical electrochemical test, CV scans were performed in a 0.5 M KOH solution with or without 1.0 M CH$_3$OH degassed with N$_2$ at a sweep rate of 10 mV s$^{-1}$. CV measurements for oxide stripping were conducted in N$_2$-purged 0.5 M H$_2$SO$_4$ solution at various potential sweep rates in range of 5–500 mV s$^{-1}$. The polarization trace was normalized against the Au mass of the NPs loaded on each GCE.

**Structural and Compositional Characterizations.** TEM imaging of the NP samples drop-dried on 400 mesh carbon-coated Cu grids was performed using a Hitachi H-8000 transmission electron microscope operated at an accelerating voltage of 200 kV. SEM imaging and EDS measurements were performed on NP samples supported on silicon wafers using a Zeiss Ultraplus thermal field emission scanning electron microscope. HAADF-STEM imaging and EDS mapping of NFs drop-dried on Mo grids with ultrathin carbon support film were carried out using a JEOL 2100F 200 kV FESEM/STEM microscope equipped with a CEOS CS corrector on the illumination system. The optical extinction spectra of colloidal NP samples were measured using a Beckman coulter Du 640 spectrophotometer. PXRD patterns were recorded on Bruker axs D8 Discover (Cu Kα = 1.5406 Å). XPS measurements were carried out on...
freshly prepared and vacuum-dried samples using a Krato AXIS Ultra DLD XPS system equipped with a monochromatic Al Kα source. A Finnigan ELEMENT XR double focusing magnetic sector field inductively coupled plasma-mass spectrometer (SF-ICP-MS) was used for the analysis of Cu (65, MR), Au (197, MR), and internal standard Rh (103 MR). A 0.2 mL min⁻¹ Micromist U-series nebulizer (GE, Australia), quartz torch, and injector (Thermo Fisher Scientific, USA) were used for sample introduction. Sample gas flow was at 1.08 mL min⁻¹. The forwarding power was 1250 W. The samples for ICP-MS measurements were prepared by adding 1 mL of nitric acid and 3 mL of hydrochloric acid into Te-flasks, which were digested using hot block at 180 °C for 4 h. The digestates were brought to 50 mL water. A 3-point calibration curve was used for Cu and Au. The calibration range was from 50 to 600 ppb. The R² values for the initial calibration curves were greater than 0.995.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b07309.

Additional figures including TEM images, SEM images, EDS elemental analysis, PXRD patterns, ICP-MS results, optical extinction spectra, XPS results, Mie scattering theory calculations, and results of electrochemical measurements as noted in the text (PDF)

### AUTHOR INFORMATION

**Corresponding Author**

*E-mail: wang344@mailbox.sc.edu. Phone: 1-803-777-2203. Fax: 1-803-777-9521.*

**Notes**

The authors declare no competing financial interest.

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