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Galvanic Replacement-Driven Transformations of Atomically Intermixed Bimetallic Colloidal Nanocrystals: Effects of Compositional Stoichiometry and Structural Ordering

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ABSTRACT:

Galvanic replacement reactions dictated by deliberately designed nanoparticulate templates have emerged as a robust and versatile approach that controllably transforms solid monometallic nanocrystals into a diverse set of architecturally more sophisticated multimetallic hollow nanostructures. The galvanic atomic exchange at the nanoparticle/liquid interfaces induces a series of intriguing structure-transforming processes that interplay over multiple time- and length-scales. Using colloidal Au-Cu alloy and intermetallic nanoparticles as structurally and compositionally fine-tunable bimetallic sacrificial templates, we show that atomically intermixed bimetallic nanocrystals undergo galvanic replacement-driven structural transformations remarkably more complicated than those of their monometallic counterparts. We interpret the versatile structure-transforming behaviors of the bimetallic nanocrystals in the context of a unified mechanistic picture that rigorously interprets the interplay of three key structure-evolutionary pathways, dealloying, Kirkendall diffusion, and Ostwald ripening. By deliberately tuning the compositional stoichiometry and atomic-level structural ordering of the Au-Cu bimetallic nanocrystals, we have been able to fine-maneuver the relative rates of dealloying and Kirkendall diffusion with respect to that of Ostwald ripening, through which an entire family of architecturally distinct complex nanostructures are created in a selective and controllable manner upon galvanic replacement reactions. The insights gained from our systematic comparative studies form a central knowledge framework that allows us to fully understand how multiple classic effects and processes interplay within the confinement by a colloidal nanocrystal to synergistically guide the structural transformations of complex nanostructures at both the atomic and the nanoparticulate levels.
1. INTRODUCTION

Galvanic replacement reactions (GRRs), which involve the atomic exchange between metallic elements with different reduction potentials, represent an intriguing redox process that entangles matter exchange with structural remodeling of metallic materials over multiple length- and time-scales.\textsuperscript{1-3} GRRs, when dictated by colloidal nanoparticulate templates, provide a simple but versatile pathway to controllably transform solid monometallic nanoparticles (NPs) into multimetallic hollow nanostructures that are typically unrealizable through other means,\textsuperscript{2-11} tremendously enhancing our capabilities to fine-tune the optical, electronic, and surface properties of metallic nanostructures for widespread applications in sensing,\textsuperscript{12-14} biomedicine,\textsuperscript{15-17} and catalysis.\textsuperscript{18-20} The remarkable level of architectural control exerted over metallic NPs through GRRs has been best manifested when using geometrically simple and synthetically tailorable Ag nanocrystals, such as nanospheres,\textsuperscript{3,14} nanocubes,\textsuperscript{2,4,21} nanoprisms,\textsuperscript{22,23} and nanowires,\textsuperscript{24} as the sacrificial templates for GRRs. A quintessential system intensively investigated over the past two decades has been Ag nanocubes, which selectively evolve into nanobox, nanocage, or nanoframe structures upon galvanic exchange of Ag with Au, Pd, or Pt under deliberately controlled synthetic conditions.\textsuperscript{4,9,16,21,25,26} Multimetallic NPs exhibiting even more complicated interior and surface architectures, such as yolk-shell nanorattles,\textsuperscript{24,27} multilayered nanomatryoshkas,\textsuperscript{2,24,28,29} ultrathin skeletal nanoframes,\textsuperscript{30,31} and popcorn-like nanostructures with multiple cavities,\textsuperscript{32} become experimentally realizable when employing multimetallic heteronanostructures\textsuperscript{29,33} or substrate-supported NPs\textsuperscript{34,35} as the sacrificial templates or by judiciously coupling GRRs with co-reduction,\textsuperscript{13,36,37} corrosion,\textsuperscript{30,31} Kirkendall diffusion,\textsuperscript{2} seeded growth,\textsuperscript{38} and regioselective surface passivation.\textsuperscript{32,39,40} While rich information can be extracted empirically from previous observations, it has long been a challenging task to build a coherent mechanistic knowledge framework that unequivocally interprets how a series of key underlying thermodynamic, kinetic, and geometric factors rigorously modulate the interplay of multiple GRR-driven structure-rearranging processes and thereby profoundly influence the NP transformations.
Atomically intermixed bimetallic nanocrystals adopting either disordered alloy configurations or ordered intermetallic structures\textsuperscript{41,42} may undergo GRR-driven structural transformations that are substantially more sophisticated and versatile than those of monometallic nanocrystals or phase-segregated bimetallic heteronanostructures. Here we demonstrate that the complex mechanisms dictating the GRR-driven transformations of alloy and intermetallic NPs can be fully elucidated within a central conceptual framework involving the interplay of three fundamentally intriguing structure-transforming pathways, namely dealloying, Kirkendall diffusion, and Ostwald ripening. Although both dealloying\textsuperscript{43-46} and Kirkendall diffusion\textsuperscript{47,48} have been intensively studied in bulk materials for decades, how they work synergistically within the confinement by a nanocrystal to guide the intricate nanoscale structural evolution upon initiation of GRRs still remains an open question. The nanocrystal transformations governed by dealloying and Kirkendall diffusion are further entangled with thermodynamically driven domain coarsening, a process known as Ostwald ripening.\textsuperscript{49-51} How to kinetically manipulate the Ostwald ripening process with respect to dealloying and Kirkendall diffusion still remains largely unexplored.

Using colloidal Au-Cu alloy and intermetallic NPs as sacrificial templates for GRRs, we demonstrate that the compositional stoichiometry and structural ordering serve as two key factors that rigorously maneuver the relative rates of the three key structure-transforming processes, enabling atomically intermixed Au-Cu bimetallic nanocrystals to selectively transform into an entire family of architecturally distinct complex nanostructures through straightforward GRRs under mild reaction conditions.

2. RESULTS AND DISCUSSION

2.1. Syntheses of Au-Cu Alloy and Intermetallic NPs.

Precise structural and compositional control over the Au-Cu bimetallic NPs was achieved through colloidal syntheses deliberately designed using the bulk phase diagram\textsuperscript{52} as a guiding principle. As shown in Figure 1A, Au and Cu atoms are thermodynamically miscible over the entire stoichiometric range,
forming face centered cubic (fcc) alloy structures spanning a broad temperature range up to the melting points of the alloys. Two atomically ordered intermetallic phases with specific Au/Cu stoichiometric ratios of 1:3 and 1:1 are thermodynamically favored at temperatures below ~ 400 °C. Despite a decrease in entropy, the enthalpy-driven transitions of disordered alloys to intermetallic compounds become spontaneous at low temperatures because the formation of Au-Cu intermetallic bonds is energetically more favorable than that of Au-Au and Cu-Cu bonds. Cluster expansion calculations also predicted AuCu₃ and AuCu as two thermodynamically stable intermetallic phases for the Au-Cu binary system (Figure 1B), further confirming the prediction by the experimental phase diagram. The AuCu₃ intermetallic compound (denoted as AuCu₃-I) adopts the fcc structure (Figure 1C), while the atoms in the AuCu intermetallic compound (denoted as AuCu-I) are organized into a face-centered tetragonal (fct) structure (Figure 1D).

As schematically illustrated in Figure 1E, colloidal Au@Cu₂O core-shell NPs underwent a stepwise chemical reduction, intraparticle alloying, and structural ordering process to evolve into Au-Cu alloy and intermetallic NPs upon thermal treatment at 300 °C in tetraethylene glycol (TEG), a liquid polyol serving as both the solvent and the reducing agent. The Au/Cu stoichiometric ratios of the alloy NPs were essentially predetermined by the relative core and shell dimensions of their parental Au@Cu₂O core-shell NPs, which could be fine-tuned over a broad range using a seed-mediated growth method we previously developed. At Au/Cu stoichiometric ratios of 1:3 and 1:1, NPs of disordered alloys represented the metastable structures that were kinetically trapped immediately after the Au and Cu atoms were fully intermixed. The AuCu₃ and AuCu alloy NPs, denoted as AuCu₃-A and AuCu-A NPs respectively, further underwent a structural ordering process to form intermetallic NPs when maintained at 300 °C in TEG over longer reaction times. The transformations of core-shell NPs into alloy and intermetallic NPs were visualized through transmission electron microscopy (TEM) imaging (Figures 1F and 1I) and further confirmed by correlated scanning electron microscopy (SEM) imaging and energy-dispersive spectroscopy (EDS)-based elemental mapping (Figure S1 in the Supporting Information).
Figure 1. Au-Cu alloy and intermetallic NPs. (A) Experimental phase diagram of bulk Au-Cu bimetallic materials. (B) Formation energies of Au-Cu bimetallic structures with varying compositional stoichiometries calculated by cluster expansion calculations. The green ×s are the results of density functional theory (DFT) calculations. The red +s come from cluster analysis of the DFT results. The blue +s identify the predicted thermodynamically stable structures. Unit cell structures of (C) AuCu3 and (D) AuCu intermetallic compounds, denoted as AuCu3-I and AuCu-I, respectively. The red and yellow spheres represent Cu and Au atoms, respectively. (E) Scheme illustrating the transformations of Au@Cu2O core-shell NPs into Au-Cu alloy and intermetallic NPs. (F) TEM images of Au@Cu2O core-shell NPs (average core diameter of 107 nm and shell thickness of 50 nm), AuCu3-A NPs, and AuCu3-I NPs. (G) PXRD patterns of AuCu3-A and AuCu3-I NPs. The standard diffraction patterns for bulk Au (JCPDS 04-0784), Cu (JCPDS 04-0836), and AuCu3-I (JCPDS 35-1537) are also included. The spectra are offset for clarity. (H) Size distributions of Au@Cu2O core-shell, AuCu3-A, and AuCu3-I NPs. (I) TEM images of AuCu3-A NPs, and AuCu-I NPs. (J) PXRD patterns of AuCu-A and AuCu-I NPs. The standard diffraction patterns for bulk Au, Cu, and AuCu-I (JCPDS 25-1220) are also shown. (K) Size distributions of Au@Cu2O core-shell, AuCu-A, and AuCu-I NPs.
As revealed by powder X-ray diffraction (PXRD), the as-synthesized AuCu₃-A and AuCu-A NPs exhibited fcc homogenous alloy structures comprising fully intermixed Au and Cu atoms (Figures 1G and 1J), absent of any detectable phase-segregated monometallic Au or Cu domains or copper oxide phases. Using the Bragg’s law, we calculated the lattice parameters of the solid solutions based on the PXRD patterns, which allowed us to further calculate the Au/Cu stoichiometries of various alloy NP samples using the Vegard’s law. The Au/Cu atomic ratios calculated from the PXRD results agreed with those quantified by inductively coupled plasma mass spectrometry (ICP-MS) and EDS (Table S1 in Supporting Information). Upon atomic ordering of the alloy NPs, the primary PXRD peaks (labeled with #) were shifted accompanied by the emergence of characteristic superlattice peaks (labeled with *), signifying the formation of AuCu₃ and AuCu intermetallic phases (Figures 1G and 1J). The AuCu₃-I and AuCu-I NPs exhibited PXRD features in excellent agreement with those of the standard patterns and previously reported intermetallic NP samples. While both the quasi-spherical morphology and Au/Cu stoichiometric ratios were well-preserved, the NP sizes decreased significantly after the Au@Cu₂O core-shell NPs transformed into alloy NPs (Figures 1H and 1K) as a consequence of loss of oxygen atoms and intermix of Au and Cu atoms. When the alloy NPs were further converted into intermetallic NPs, less significant but nonnegligible size shrinkage was also observed possibly due to the disappearance of lattice vacancies upon atomic ordering.

The structural and compositional tunability of the Au-Cu binary NP system provided unique opportunities for us to pinpoint the effects of compositional stoichiometry and structural ordering on the GRR-driven transformations of atomically intermixed bimetallic nanocrystals. In this work, we conducted the GRRs at room temperature in an aqueous environment using colloidal Au-Cu alloy or intermetallic NPs as the sacrificial templates and HAuCl₄ as the Au precursor in the absence of any additional surface capping ligands. Under our GRR conditions, Cu was oxidized into Cu(II) rather than Cu(I) ionic species.
(Figure S2 in Supporting Information) while HAuCl₄ was reduced to metallic Au, exhibiting a net reaction outcome of every three Cu atoms substituted by two Au atoms.

### 2.2. Dealloying, Kirkendall Diffusion, and Ostwald Ripening.

The galvanic exchange between Cu and Au involves selective etching of Cu from the Au-Cu alloy or intermetallic matrices, a process known as dealloying. Bimetallic alloys exhibit interesting composition-dependent dealloying behaviors. For example, a macroscopic Au-Ag alloy membrane may selectively undergo either nanoporosity-evolving percolation dealloying or surface atomic dealloying at the membrane/electrolyte interfaces, depending on the atomic fraction of Ag and detailed dealloying conditions. The electrochemical parameter signifying the onset potential of percolation dealloying is termed as critical potential, $E_c$. The $E_c$ of a spherical binary alloy NP with a radius of $r$ and a compositional formula of $A_{1-p}B_p$ (A and B represent the nonleachable noble and the leachable less-noble elements, respectively, and $p$ is atomic fraction of B) is a function of both $p$ and $r$, as expressed as follows:

$$E_c(p, r) = E_c(p) - \left[ \gamma_{Alloy}(\Omega_A) + f_{Alloy}(\hat{\Omega}_A < \Omega >) \right] \times \left( \frac{2}{nFr} \right)$$  \hspace{1cm} (1),

where $\gamma_{Alloy}$ and $f_{Alloy}$ are the free energy and the stress at the alloy/electrolyte interface, respectively. $\hat{\Omega}_A$ is the partial molar volume of A in the alloy. $<\Omega>$ represents the average molar volume of the alloy. $n$ is the number of electrons every B atom loses upon oxidation. $F$ is the Faraday constant. $E_c$ is the critical potential of the bulk alloy, which is a function of $p$ and related to the molar volume of A, $\Omega_A$, the interfacial free energy of B exposed to the electrolyte, $\gamma_{B/elec}$, the local radius of the surface where a cylindrical pit is created upon dealloying, $\zeta$, and the equilibrium potential, $E_{eq}$, above which the surface dealloying at the top-most atomic layer occurs, as shown by the following equation

$$E_c(p) = E_{eq}(p) + \frac{4\gamma_{B/elec} \Omega_A}{nF\zeta}$$  \hspace{1cm} (2).
Because the maximum possible values of $\gamma_{\text{Alloy}}$ and $f_{\text{Alloy}}$ are $\sim 2$ and $\sim 6 \text{ J m}^{-2}$, respectively, $E_c$ becomes virtually equivalent to $\overline{E}_c$ when an alloy NP becomes larger than 10 nm ($r > 5 \text{ nm}$). Under certain dealloying conditions, almost all binary alloys have been observed to display a characteristic threshold $p$ value known as the parting limit, above which percolation dealloying occurs. The parting limits of Au-Ag and Au-Cu alloys were measured to be $\sim 55$ atomic % of Ag\textsuperscript{64} and $\sim 70$ atomic % of Cu\textsuperscript{65,66} respectively, in acidic electrolytes at room temperature. The origin of the characteristic parting limits of alloys can be fully interpreted in the context of the composition-dependent $E_c$ as discussed above.

When an Au-Cu alloy NP undergoes galvanic exchange with HAuCl\textsubscript{4}, its structural transformations become remarkably more complicated than those induced by dealloying alone. The deposition of Au on the surfaces of an alloy NP creates interfacial compositional gradient, which triggers the interdiffusion of Au and Cu atoms across the interface between the alloy and monometallic Au domains. The nonequivalent diffusion rates of Cu and Au atoms causes the alloy/Au interface to migrate toward one direction while forming cavities at the materials boundaries, a classic effect of atomic interdiffusion known as the Kirkendall effect.\textsuperscript{47,67} The velocity at which the boundary interface travels can be described by the Darken’s equation\textsuperscript{68}

$$v = (D_A - D_B) \frac{dN_A}{dx} \quad (3),$$

where $D_A$ and $D_B$ are the diffusion coefficients of component A and B, respectively. $dN_A/dx$ represents the compositional gradient of A across the boundary. Previously observed GRR-induced hollowing of metallic NPs can all be interpreted in the context of the Kirkendall effect.\textsuperscript{2,3,6,11,14,32,36,38}

During the nanoscale GRRs, the dealloying and Kirkendall diffusion are inevitably entangled with thermodynamically driven domain coarsening processes known as Ostwald ripening, a phenomenon first observed by Wilhelm Ostwald back in 1896.\textsuperscript{49} During a typical Ostwald ripening process, smaller nanocrystals are dissolved and re-deposited onto larger nanocrystals, resulting in the growth of larger NPs at the expense of smaller ones.\textsuperscript{69,70} The growth rate of the larger NPs is related to the interfacial energy,
σ, the molar volume, \( V_m \), the solubility, \( C_\infty \), and the diffusion coefficient, \( D \), of the particle material, as shown in the following equation \(^{69}\)

\[
\frac{dr}{dt} = \frac{2\sigma V_m^2 C_\infty}{RT(1/D + 1/k_d r)} \left( \frac{1}{r_b} - \frac{1}{r} \right)
\]  

(4),

where \( r \) is the radius of the NP, \( t \) is time, \( R \) is the ideal gas constant, and \( T \) is the absolute temperature. \( k_d \) is the rate constant of surface deposition reaction obeying simple first-order kinetics. \( r_b \) is defined as the critical radius, which separates the smaller particles (\( r < r_b \)) shrinking in size from the larger growing particles (\( r > r_b \)). For a given material/solvent system, the values of \( \sigma, V_m, D, k_d, \) and \( r_b \) are all essentially fixed. However, the kinetics of particle coarsening can be further maneuvered through modulation of \( C_\infty \) by coupling Ostwald ripening with deliberately designed redox reactions.\(^{70}\) Intraparticle Ostwold ripening may also occur among multiple crystalline domains within the same NPs. When an Au-Cu alloy or intermetallic NP is exposed to HAuCl\(_4\) for GRRs, the intraparticle Ostwald ripening can be triggered due to increased \( C_\infty \) of Au by a reversible disproportionation reaction shown below\(^{71}\)

\[
2\text{Au} + \text{AuCl}_4^- \rightleftharpoons 3\text{Au}^+ + 4\text{Cl}^-
\]  

(5).

By varying the amount of HAuCl\(_4\) in the reaction mixtures, the rates of Ostwald ripening can be further maneuvered relative to those of dealloying and Kirkendall diffusion, greatly influencing the NP transformations upon GRRs. As shown in this work, colloidal Au-Cu alloy and intermetallic NPs with tunable compositional stoichiometries serve as a unique materials system that enables us to gain mechanistic insights on how the compositional stoichiometry and structural ordering of colloidal bimetallic NPs modulate the interplay of dealloying, Kirkendall diffusion, and Ostwald ripening. We systematically investigated GRR-driven transformations of Au-Cu alloy and intermetallic NPs in two strikingly distinct compositional regimes divided by the parting limit for percolation dealloying (~70 atomic % of Cu). To eliminate additional complications associated with the NP size effects, we focused
on Au-Cu bimetallic NPs significantly larger than 10 nm, which exhibited composition-dependent dealloying behaviors analogous to those of their bulk counterparts.

2.3. GRR-Driven Transformations of AuCu₃ Alloy and Intermetallic NPs.

AuCu₃-A and AuCu₃-I NPs, both of which possessed Cu content above the parting limit, underwent nanoporosity-evolving percolation dealloying when exposed to 1 M nitric acid at room temperature, resulting in the formation of bicontinuous, sponge-like NPs composed of interconnected Au-rich nanoligaments (Figures S3A and S3B in Supporting Information). Upon galvanic exchange with HAuCl₄, AuCu₃-A and AuCu₃-I NPs underwent structural transformations strikingly distinct from those induced by dealloying alone. To ensure complete galvanic exchange between Cu and Au, we exposed the AuCu₃-A and AuCu₃-I NPs to excessive HAuCl₄ for 48 h. We tracked the temporal evolution of the NP structures and compositions during the GRRs using PXRD (Figures 2A and 2B), EDS (Figure 2C), optical extinction spectroscopy (Figure 2D), SEM (Panels a in Figures 2E-2H), and TEM (Panels b in Figures 2E-2H). While the AuCu₃-A NPs also evolved into bicontinuous spongy NPs upon GRRs (Figure 2E), the GRRs proceeded drastically more rapidly than the percolation dealloying essentially due to GRR-triggered interdiffusion of Au and Cu atoms in the alloy NPs. More than 90 % of the Cu in the AuCu₃-A NPs was rapidly replaced by Au within 1 minute upon initiation of GRRs (Figures 2A-2C), whereas the leaching of Cu during the percolation dealloying in HNO₃ electrolyte occurred over much a longer period (Figure S3C in Supporting Information). In addition, the Kirkendall atomic interdiffusion further boosted the cavity formation and volume expansion of the NPs.⁶⁷ Although the percolation dealloying caused significantly shrinkage of the overall particle sizes (Figures S3A and S3B in Supporting Information), the spongy NPs formed through GRRs of AuCu₃-A NPs exhibited ~ 90 % increase in the total particle volume in comparison to their parental alloy NPs (Figure 2E). In contrast to AuCu₃-A NPs, AuCu₃-I NPs evolved into fragmented, irregularly-shaped ligaments (Figure 2G) during GRRs instead of forming bicontinuous
spongy structures as a consequence of suppressed Kirkendall interdiffusion of Au and Cu atoms. This can be interpreted by the fact that atomically ordered intermetallic structures exhibit higher energy barriers for the atomic interdiffusion than those in disordered alloys with the same compositional stoichiometries.\textsuperscript{72,73}

The selective leaching of Cu from AuCu\textsubscript{3}-I NPs was also observed to be significantly slower than that from AuCu\textsubscript{3}-A NPs during percolation dealloying, resulting in the formation of thicker ligaments and smaller overall particle sizes in comparison to the fully dealloyed AuCu\textsubscript{3}-A NPs (Figure S3 in Supporting Information).

Although the majority of Cu atoms in the AuCu\textsubscript{3}-A and AuCu\textsubscript{3}-I NPs were galvanically replaced by Au atoms within 1 minute, the NPs continued to undergo domain coarsening processes and evolved into thermodynamically more stable structures driven by Ostwald ripening. During Ostwald ripening, the bicontinuous spongy NPs underwent a ligament coarsening processes (Figure S4 in Supporting Information) and eventually transformed into nanocups as the ligaments coalesced into a continuous shell, leaving one side of the shell open (Figure 2F). The fragmented Au ligaments formed upon GRR of AuCu\textsubscript{3}-I NPs also underwent domain coarsening to form larger particles with faceted surfaces (Figure 2H and Figure S4 in Supporting Information). Interestingly, when the bicontinuous spongy NPs were separated from the reaction mixtures through centrifugation and redispersion in water immediately after the GRRs went to completion, the Ostwald ripening became kinetically sluggish because of limited solubility of Au in pure water and thus, the bicontinuous spongy morphology was well-preserved even after 48 hours (Figure S5 in Supporting Information). The structural evolution during Ostwald ripening could also be tracked based on the temporal evolution of optical extinction spectral features (Figure 2D). The spongy NPs exhibited a characteristic broad plasmon resonance band spanning much of the visible and near infrared regions,\textsuperscript{74,75} which progressively blue shifted as the ligaments underwent the coarsening process. The Ostwald ripening of the fragmented ligaments also led to blue-shift of the plasmon resonance bands, though the spectral shift was much less significant in comparison to that of the bicontinuous spongy NPs.
Figure 2. Transformations of AuCu3-A and AuCu3-I NPs upon exposure to excessive HAuCl4. PXRD patterns of NPs obtained after mixing 1 mL colloidal (A) AuCu3-A and (B) AuCu3-I NPs with 150 µL of 10 mM HAuCl4 at room temperature for 1 min and 48 h. The standard diffraction patterns for bulk Au, Cu, and AuCu3-I are also included. Temporal evolutions of (C) Cu atomic % and (D) optical extinction spectra of the NPs after mixing AuCu3-A and AuCu3-I NPs with 150 µL of 10 mM HAuCl4. SEM (X-a, X = E, F, G, H) and TEM (X-b) images of NPs obtained after exposing AuCu3-A or AuCu3-I NPs to HAuCl4 for various reaction times: (E) AuCu3-A, 1 min; (F) AuCu3-A, 48 h; (G) AuCu3-I, 1 min; (H) AuCu3-I, 48 h. All the SEM images share the same scale bar in Panel E-a, and all the TEM images share the same scale in Panel E-b.

While the kinetics of Ostwald ripening-driven structural evolution could be clearly resolved, it remained challenging to directly track the detailed structural evolution of AuCu3-A and AuCu3-I NPs during the kinetically much faster GRRs. Alternatively, we titrated the AuCu3-A and AuCu3-I NPs with insufficient amounts of HAuCl4 to trap the intermediate structures at various stages of GRRs. We set the reaction time at 30 minutes, which was sufficiently long for the establishment of the equilibria upon adequate consumption of HAuCl4 available for the GRRs. The GRRs of AuCu3-A NPs with HAuCl4 was
initiated upon the dissolution of Cu and deposition of Au nanocrystallites at the alloy/liquid interfaces, which subsequently induced Kirkendall interdiffusion of Au and Cu atoms in the alloy matrices, forming cavities at the alloy/Au interfaces. The growth of the Au nanocrystallites and the expansion of the cavities led to the formation of a yolk-shell structure composed of a Au-Cu alloy core encapsulated by a polycrystalline Au shell (Figure 3A). As the GRRs further proceeded, the cavities continued to expand accompanied by Au domain coarsening (Figure 3B) until the Au domains merged into bicontinuous nanoligaments when a sufficient amount of Cu was galvanically exchanged with Au (Figure 3C). The formation of cavities inside the NPs upon Kirkendall diffusion gave rise to significantly increased overall particle sizes (Figure S6 in Supporting Information).

The structural evolution of AuCu$_3$-I NPs during GRRs, nevertheless, appeared drastically different from that of AuCu$_3$-A NPs because the ordering of the atomic configurations effectively suppressed the Kirkendall diffusion process. As a consequence, monometallic Au was deposited on the outer surfaces of the intermetallic NPs without forming cavities during the GRRs (Figures 3D-3F). As an increasing amount of Cu was exchanged with Au, the surface-deposited Au domains increased in size and the intermetallic cores were progressively consumed, eventually evolving into fragmented Au ligaments with irregular shapes. When titrating the NPs with insufficient amounts of HAuCl$_4$, the Ostwald ripening process became extremely slow because of depletion of HAuCl$_4$ in the solution upon completion of GRRs, allowing us to well-preserve the as-formed intermediate nanostructures over extended time periods even without separating the NPs from the reaction mixtures (Figure S7 in Supporting Information).
Figure 3. GRR-driven transformations of AuCu$_3$-A and AuCu$_3$-I NPs. (X-a, X = A, B, C) SEM and (X-b) TEM images of NPs obtained by titrating 1 mL colloidal AuCu$_3$-A NPs with (A) 10 µL, (B) 30 µL and (C) 100 µL of 10 mM HAuCl$_4$. (Y-a, X = D, E, F) SEM and (Y-b) TEM images of NPs obtained by titrating 1 mL colloidal AuCu$_3$-I NPs with (D) 10 µL, (E) 30 µL, and (F) 100 µL. All the SEM images share the same scale bar in Panel A-a, and all the TEM images share the same scale in Panel A-b. The reaction time was 30 min. PXRD patterns of NPs obtained by titrating (G) AuCu$_3$-A NPs and (H) AuCu$_3$-I NPs with various volumes of 10 mM HAuCl$_4$. The standard diffraction patterns for bulk Au, Cu, and AuCu$_3$-I are also included. The spectra were offset for clarity. (I) LSV curves of Cu, AuCu$_3$-A, and AuCu$_3$-I NPs supported on glassy carbon electrodes in 0.5 M H$_2$SO$_4$ electrolyte in the potential sweep range from 0 V to 0.7 V (vs. SCE) at a sweep rate of 50 mV s$^{-1}$. (J) Cu atomic % of NPs obtained by titrating 1 mL colloidal AuCu$_3$-A and AuCu$_3$-I NPs with various volumes of 10 mM HAuCl$_4$.

We also used PXRD to study the evolution of the crystalline structures of NPs during GRRs. A striking difference between the AuCu$_3$-A and AuCu$_3$-I NPs was that the atomic fractions of Cu in the alloy domains of the NPs progressively decreased (Figure 3G), whereas the Au/Cu atomic ratios and the ordered atomic
configurations of the intermetallic domains were both well-preserved (Figure 3H) as the GRRs proceeded, further verifying that the formation of atomically ordered intermetallic structures effectively suppressed the Kirkendall diffusion, restricting the atomic exchange and migration exclusively at the evolving NP/liquid interfaces. We further used the linear-sweep-voltammetry (LSV) to measure the onset potentials for the percolation dissolution of Cu from the AuCu$_3$-A and AuCu$_3$-I NPs (Figure 3I). Alloying of Cu with Au at the Au/Cu ratio of 1:3 positively shifted the onset potential by about 0.1 V, and the atomic ordering of the alloy NPs further positively shifted the onset potential by about 0.2 V, proving that the Cu atoms in the AuCu$_3$-I NPs were significantly less mobile and thus more resistive against migration and leaching than those in the AuCu$_3$-A NPs. Although AuCu$_3$-A and AuCu$_3$-I NPs underwent distinct structure-transforming processes during GRRs, they exhibited similar fractions of Cu exchanged with Au when titrated with the same amount of HAuCl$_4$ (Figure 3J), suggesting that the ordering of the atomic configurations of the NPs slowed down the atomic interdiffusion process without significantly shifting the equilibria of the GRRs.

### 2.4. GRR-Driven Transformations of AuCu Alloy and Intermetallic NPs.

In the case of Cu-rich AuCu$_3$-A and AuCu$_3$-I NPs, the GRRs and Ostwald ripening were kinetically distinguishable because they took place over two drastically different time-scales. According to the Darken’s equation, decreasing the Cu/Au stoichiometric ratio of the NPs should decelerate the GRRs with respect to Ostwald ripening. For AuCu-A and AuCu-I NPs, both GRRs and Ostwald ripening were observed to occur concurrently over the same time-scale. Because their Cu atomic fractions were below the parting limit for percolation dealloying, both AuCu-A and AuCu-I NPs underwent a surface dealloying process upon exposure to 1 M HNO$_3$, forming a surface passivating Au atomic layer that inhibited further leaching of Cu from the NPs (Figure S8 in Supporting Information). Interestingly, when exposing the AuCu-A NPs to excessive HAuCl$_4$, the GRR-induced Kirkendall diffusion effectively triggered the
migration of Cu atoms from the NP interior to the NP/liquid interfaces, allowing the dealloying to proceed continuously until all Cu were galvanically replaced by Au. Upon initiation of GRRs, the AuCu-A NPs first underwent a hollowing and volume expansion process to transform into a yolk-shell structure (Figure 4A). The GRRs of AuCu-A NPs with HAuCl₄ resulted in cavity volumes significantly smaller than those in the bicontinuous spongy NPs derived from AuCu₃-A NPs, because the rate of Kirkendall atomic diffusion in the AuCu-A NPs was slower than that in AuCu₃-A NPs. In addition, the GRR-induced structural transformations of AuCu-A NPs was entangled with the Ostwald ripening-driven domain coarsening, resulting in the formation of continuous Au-rich shells instead of the bicontinuous nanoligaments. As the GRRs further proceeded, the alloy domains became fully dealloyed while the Au-rich shells became significantly thicker, resulting in the formation of nanocups, each of which was composed of a cavity enclosed by a semi-open Au-rich shell (Figure 4B). The nanocups further evolved into thermodynamically more stable solid quasi-spherical NPs after 48 hours (Figure 4C) essentially driven by continuous Ostwald ripening. Ostwald ripening-driven surface remodeling of the quasi-spherical NPs eventually led to the formation of thermodynamically more favored {111} and {100} crystallographic facets when the NPs were aged in the reaction mixtures for a few days (Figure S9 in Supporting Information).
Figure 4. GRR-driven transformations of AuCu-A and AuCu-I NPs. (X-a, X = A, B, C) SEM and (X-b) TEM images of NPs obtained after mixing 1 mL colloidal AuCu-A NPs with 150 µL of 10 mM HAuCl₄ for (A) 30 min, (B) 9 h, and (C) 48 h. (Y-a, X = D, E, F) SEM and (Y-b) TEM images of NPs obtained by mixing 1 mL colloidal AuCu-I NPs with 150 µL of 10 mM HAuCl₄ for (D) 30 min, (E) 9 h, and (F) 48 h. All the SEM images share the same scale bar in Panel A-a, and all the TEM images share the same scale in Panel A-b. PXRD patterns of NPs obtained after mixing (G) AuCu-A and (H) AuCu-I NPs with HAuCl₄ for various reaction times. The standard diffraction patterns for bulk Au, Cu, and AuCu-I are also included. Temporal evolutions of (I) Cu atomic % and (J) particle size of the NPs after mixing AuCu-A and AuCu-I NPs with 150 µL of 10 mM HAuCl₄. (K) LSV curves of AuCu-A and AuCu-I NPs in 0.5 M H₂SO₄ electrolyte at a sweep rate of 50 mV s⁻¹.

In striking contrast to the AuCu-A NPs, AuCu-I NPs evolved into heterostructured quasi-spherical core-shell NPs, each of which was composed of a AuCu intermetallic core surrounded by a monometallic Au shell (Figure 4D). The absence of observable hollowing process during the GRRs of AuCu-I NPs with HAuCl₄ suggested that the Kirkendall atomic interdiffusion was suppressed due to the formation of the intermetallic phases. As the reaction time further increased, the surfaces of the quasi-spherical core-shell
NPs became increasingly faceted due to Ostwald ripening (Figures 4E, 4F, and Figure S9 in Supporting Information). Such Ostwald ripening-driven faceting of NPs became unobservable when the AuCu-A and AuCu-I NPs were exposed to insufficient amounts of HAuCl₄ for GRRs because of the elimination of Ostwald ripening upon depletion of HAuCl₄ (Figure S10 in Supporting Information). The spatial distributions of Au and Cu atoms in the quasi-spherical Au-rich, yolk-shell, and core-shell NPs obtained at various stages of GRRs were mapped by correlated SEM/EDS (Figure S11 in Supporting Information). The structural and compositional evolutions of the AuCu-A and AuCu-I NPs were further tracked using \textit{ex situ} PXRD (Figures 4G and 4H) and EDS elemental analysis (Figure 4I), both of which clearly showed that the leaching of Cu from AuCu-I NPs was significantly slower than that from AuCu-A NPs, further verifying that structural ordering slowed down the rate of Au and Cu atomic interdiffusion. The sizes of the AuCu-A NPs first increased at the early stage of GRRs due to the Kirkendall effects and then progressively decreased as the Ostwald ripening started to dominate the structure-transforming process, whereas the particle sizes remained almost unchanged throughout the entire process when AuCu-I NPs were exposed to HAuCl₄ for GRRs (Figure 4J). At the Au/Cu atomic ratio of 1:1, the transition of alloy NPs into intermetallic NPs raised the energy barriers for Cu-Au atomic interdiffusion and thereby positively shifted the onset potential for the percolation dissolution of Cu (Figure 4K), which was in line with the trend observed in the AuCu₃-A and AuCu₃-I NPs. We further investigated the GRR-driven structural transformations of Au-rich alloy NPs with an Au/Cu atomic ratio of 3:1 (Figure S12 in Supporting Information). For the Au-rich Au₃Cu alloy NPs, both Cu leaching and Kirkendall diffusion became kinetically even slower than those in the AuCu-A NPs. Therefore, the Au₃Cu alloy NPs transformed into alloy core-Au shell NPs through a GRR-driven structural evolution process similar to that of the AuCu-I NPs (Figure S13 in Supporting Information). Neither cavity formation nor particle size expansion was observed on the Au₃Cu alloy NPs throughout the entire GRR process.
3. CONCLUSION

This work exemplifies how classic effects and paradigms, when applied to colloidal NP systems, can be revisited from a different perspective and interlinked within a coherent conceptual network to generate new insights into the complex mechanisms underpinning the intriguing atomic exchange, matter relocation, and structural remodeling processes both at the atomic and nanoparticulate levels. Using the atomically intermixed Au-Cu bimetallic NPs as a model materials system, we have demonstrated that the versatile structural evolutions of multimetallic NPs driven by GRRs are synergistically dictated by three intertwining structure-transforming processes, dealloying, Kirkendall diffusion, and Ostwald ripening. Through systematic comparative studies, we have identified the compositional stoichiometries and the atomic-level structural ordering of the bimetallic NPs as two key factors that kinetically maneuver the dealloying and Kirkendall diffusion processes during GRRs, while the rate of the Ostwald ripening-driven domain coarsening can be further modulated by coupling the GRRs with reversible disproportionation reactions. Dealloying, Kirkendall diffusion, and Ostwald ripening are all broadly involved in the growth, deformation, and restructuring of a large library of structurally sophisticated multimetallic NPs. For example, detailed, dynamic structural information obtained from recent single-particle spectroscopic measurements and in situ liquid-cell electron microscopy imaging implies that the Kirkendall diffusion-driven cavity expansion inside an Ag NP under non-equilibrium GRR conditions interplays with the Ostwald ripening of localized crystalline domains. It has also been recently observed that Au-Cu alloy nanorods undergo an unconventional asymmetric hollowing process upon GRRs when local compositional gradient exists in the nanorods, which can be well-interpreted in the context of the composition-dependent dealloying and Kirkendall diffusion. When exposed to excessive HAuCl₄ for GRRs, an Au-Cu alloy nanorod transforms into a dumbbell-shaped NP that eventually splits into thermodynamically more stable nanospheroids as a consequence of Ostwald ripening, which is essentially triggered by the reversible disproportionation reactions of Au. The insights gained from this
work may serve as a bridge transcending our current knowledge gaps and blind zones toward thorough understanding of nanoscale structural transformations when revisiting the ample examples already existing in the literature. This work also provides generic design principles guiding the rational development of new synthetic approaches to multimetallic colloidal nanostructures with further enhanced architectural complexity, compositional diversity, and property tunability.

4. METHODS

Au@Cu₂O core-shell NPs with tunable core and shell dimensions were synthesized following our previously developed protocol⁵³ (see details in Supporting Information). Au-Cu alloy and intermetallic NPs were synthesized using a polyol-assisted growth method. Typically, 1.0 mL of Au@Cu₂O core-shell NPs with an Au/Cu atomic ratio of 1:3 were added into 20.0 mL TEG containing 0.1 g polyvinylpyrrolidone (PVP). AuCu₃ alloy and intermetallic NPs were synthesized by keeping the reaction mixtures at 300 °C for 1 hour and 10 hours, respectively. AuCu alloy and intermetallic NPs were synthesized by keeping Au@Cu₂O core-shell NPs with an Au/Cu atomic ratio of 1:1 suspended in TEG at 300 °C for 20 minutes and 4 hours, respectively. The as-synthesized alloy NPs were quickly cooled by placing the samples in an ice bath, whereas the intermetallic NPs were cooled down to room temperature naturally under ambient air. The resulting NPs were washed with ethanol 5 times, and finally redispersed in 1.0 mL of water. In a typical GRR, 100 µL of an aqueous suspension of Au-Cu alloy or intermetallic NPs were added into 1.0 mL deionized water in a small glass vial. Varying amount (10 ~ 150 µL) of 10 mM HAuCl₄ was subsequently added under magnetic stir at room temperature. The resulting NPs were separated from the reaction mixtures by centrifugation after certain reaction times, washed with ethanol 3 times, and finally redispersed in water. The NPs were characterized by TEM, SEM, PXRD, EDS, ICP-MS, LSV, and optical extinction spectroscopy (see details in Supporting Information). The details of cluster expansion calculations were also shown in Supporting Information.
ASSOCIATED CONTENT

Supporting Information. Additional experimental details, cluster expansion calculations, a table listing the Cu atomic % of various NP samples, and additional figures including SEM images, TEM images, EDS elemental analysis, PXRD patterns, optical extinction spectra, and LSV results as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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TOC Graphic: