

Chemically Driven Phase Segregation of Alloy Nanoparticles: A Versatile Route to Dual-Plasmonic Gold@Copper Chalcogenide Heteronanostructures

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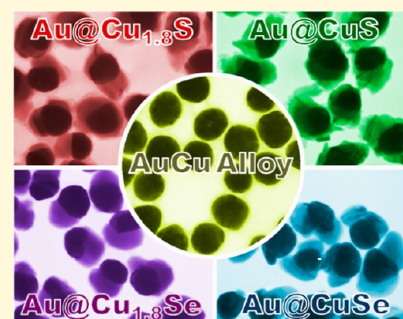


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Supporting Information

ABSTRACT: Multicomponent heteronanostructures have emerged as a class of structurally and compositionally tunable multifunctional nanomaterials whose electronic, optical, and catalytic properties can be fine-engineered for targeted applications. Heteronanostructures composed of Au and copper chalcogenide domains represent a unique hybrid material system that integrates two distinct types of plasmon resonances arising from the conduction electrons and valence holes, respectively, in a single nanoscale entity. Success in fine-tuning the optical properties of these dual-plasmonic heteronanostructures relies critically on our capabilities to precisely tailor not only the structural arrangements but also the crystalline phases of the constituent domains. Here, we report a robust and versatile colloidal synthetic approach that allows us to selectively access a series of Au@copper chalcogenide heteronanostructures with tailored intraparticle architectures, tunable domain sizes, and targeted crystalline phases through chemically triggered phase segregation of Au–Cu bimetallic alloy and intermetallic nanoparticles. Under our reaction conditions, the chalcogen precursor concentration and the reaction temperature serve as two fine-adjustable synthetic knobs that enable us to deliberately control the crystalline phases of the copper chalcogenide domains, while the relative domain dimensions in the heteronanostructures can be precisely preprogrammed by tuning the Cu/Au stoichiometries of the parental bimetallic nanoparticles. Both the Cu/Au stoichiometries and atomic ordering in the bimetallic nanoparticles are found to be key structural factors that kinetically maneuver the phase segregation process and thereby profoundly influence the structure-transforming behaviors of the nanoparticles.



INTRODUCTION

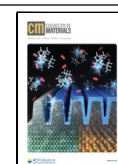
The past 2 decades have witnessed tremendous interest in multicomponent hybrid heteronanostructures with increasing architectural complexity and compositional diversity.^{1–8} Integration of structurally dissimilar and functionally divergent building blocks in a single hybrid nanoscale entity creates interface-rich, multifunctional nanomaterial systems whose collective electronic, optical, and catalytic properties can be deliberately fine-tuned to match the need for targeted applications. Au and copper chalcogenides (denoted as Cu_xE, where 1 ≤ x ≤ 2 and E = S, Se, or Te) constitute a particularly interesting combination of metal and semiconductor materials for constructing hybrid heteronanostructures with unique dual-plasmonic characteristics.^{9–18} Both Au and Cu_xE nanoparticles (NPs) exhibit intriguing plasmon-dominated optical properties that can be systematically tuned over broad spectral ranges by tailoring the particle sizes and shapes.^{19–31} The plasmonic characteristics of nanoparticulate Au and Cu_xE, however, differ substantially in several key aspects. First, the plasmon resonances supported by Au and Cu_xE NPs originate from the collective oscillations of two different types of free charge carriers, conduction electrons in Au and valence holes in Cu_xE, respectively.^{31–35} Second, in NPs with comparable dimensions, the Cu_xE plasmons are typically resonant at significantly longer

wavelengths than the Au plasmons because of intrinsically lower concentrations of free carriers in Cu_xE than in Au.^{31–35} Third, while the concentration of free electrons in Au is essentially fixed, the free hole concentrations in Cu_xE are structure- and composition-dependent, enabling us to tune the resonance frequencies of Cu_xE plasmons by varying the crystalline phases and Cu/E stoichiometric ratios.^{25–27,31,36–38} Combining Au and Cu_xE domains in a hybrid heteronanostructure allows us to fine-tune the frequencies of two types of plasmon resonances, either simultaneously or independently, over distinct spectral ranges. When functioning as plasmonic photocatalysts and photothermal transducers, Au@Cu_xE heteronanostructures may remarkably outperform their single-component Au and Cu_xE counterparts, benefiting from the synergy between the plasmonic electron and hole oscillations.^{10,11,13–17}

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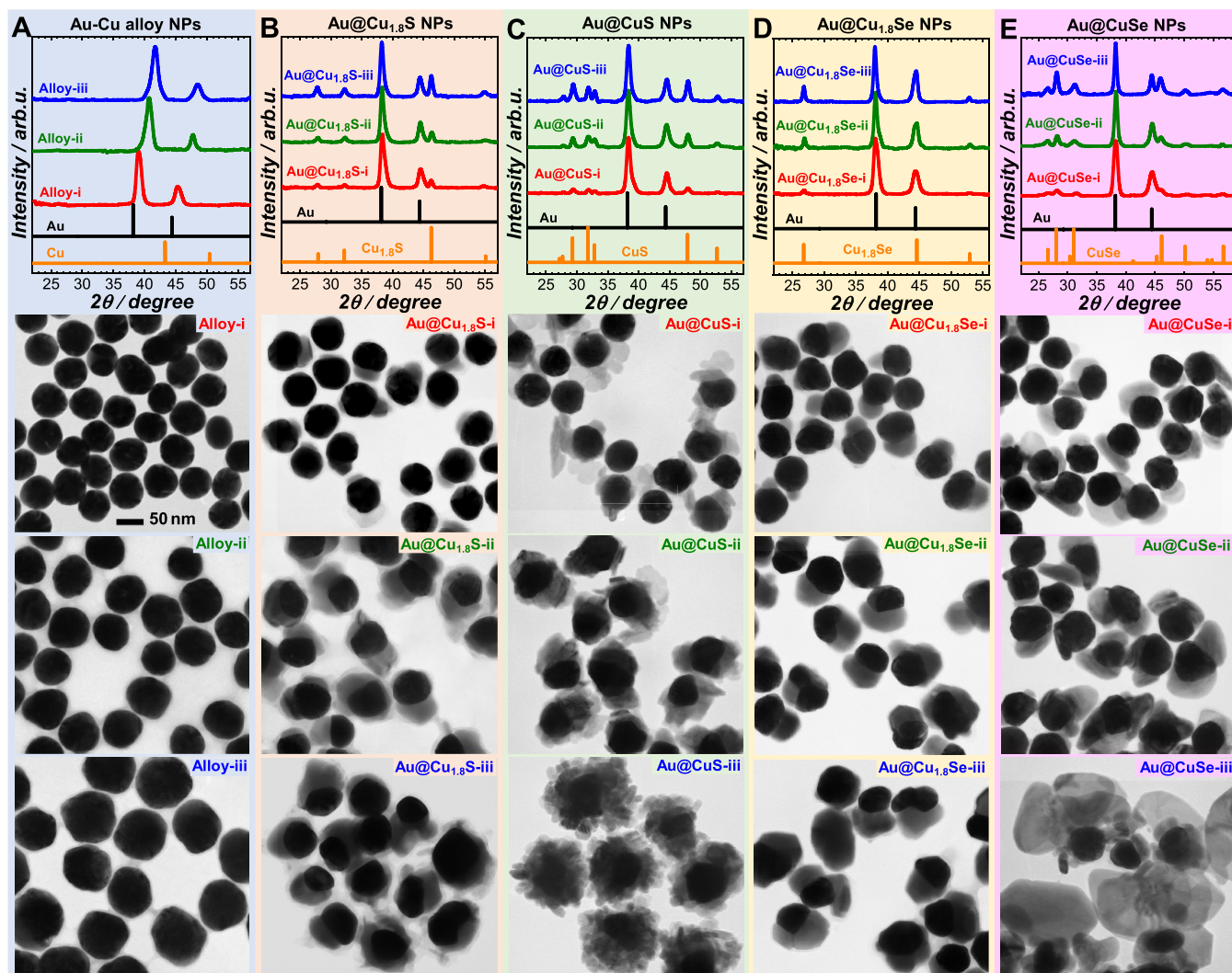


Figure 1. PXRD patterns and TEM images of (A) Au–Cu alloy NPs, (B) Au@Cu_{1.8}S, (C) Au@CuS, (D) Au@Cu_{1.8}Se, and (E) Au@CuSe heteronanostructures. The PXRD patterns are shown in the first row. The standard diffraction patterns of Au (JCPDS 04-0784), Cu (JCPDS 04-0836), Cu_{1.8}S (digenite, JCPDS 24-61), CuS (covellite, JCPDS 6-464), Cu_{1.8}Se (berzelianite, JCPDS 6-680), and CuSe (klockmannite, JCPDS 6-427) are also shown as the references for comparison. TEM images of the heteronanostructures derived from Alloy-i, Alloy-ii, and Alloy-iii NPs are shown in the second, third, and fourth rows, respectively. All TEM images share the same scale bar.

Deliberately designed colloidal syntheses mediated by seeds or templates provide us with access to a library of Au@Cu_xE heteronanostructures with architecturally distinct configurations, such as core–shell,^{9,12–15,17,39–41} yolk–shell,^{42,43} and heterodimer NPs.^{10,11,16,44,45} Due to the intrinsic structural dissimilarity and large lattice mismatches between Au and Cu_xE, it remains challenging to directly deposit Cu_xE on the surfaces of Au seeds to form well-defined heteronanostructures. Therefore, success in seed-mediated synthesis relies critically on surface-capping molecular ligands, which form an interfacial bridging layer facilitating the growth of Cu_xE on Au surfaces.^{11,12,14,15,17,39–41} Au@Cu_xE heteronanostructures can also be derived from preformed templates composed of synthetically more tractable heteronanostructures, such as Au@Ag,¹⁵ Au@Se,⁹ and Au@CdSe core–shell NPs,¹³ through multistep chemical conversions involving combination reactions and/or ion-exchange processes. An alternative synthetic approach of particular interest involves the use of Au–Cu alloy NPs as the starting materials, which undergo chemically triggered phase segregation to form colloidal Au@Cu_xE

heteronanostructures.^{44,45} Compared to the seed- and template-mediated methods, this synthetic strategy has several unique advantages: (1) the Au/Cu stoichiometries of the heteronanostructures are preprogrammed in the parental alloy NPs; (2) upon phase segregation of the alloy NPs, Au and Cu_xE domains remain adjoined without the need to judiciously engineer the surface chemistry of the NPs; (3) the alloy-to-heterostructure transformations can be accomplished through a straightforward one-pot process without involving tedious, multistep synthetic procedures. The feasibility of this phase segregation-based approach was first demonstrated by Schaak and co-workers,⁴⁴ who synthesized Au@Cu₂S heterodimers by reacting colloidal AuCu alloy NPs (Au/Cu atomic ratio = 1:1) with elemental sulfur under aerobic thermal conditions. Jiang and co-workers⁴⁵ also demonstrated that Au@Cu₂S heterodimers could be derived from AuCu alloy NPs using 1-dodecanethiol as both the sulfur source and a complexing agent. The versatility, universality, and potential of this synthetic approach, however, are far from having been fully realized, with many fundamentally intriguing aspects still

remaining open to further investigations. Au and Cu are highly miscible, forming alloys over a wide Au/Cu stoichiometric range.^{46–49} Au–Cu alloy NPs may exhibit intriguing composition-dependent transforming behaviors because the atomic mobilities are highly sensitive to the Au/Cu stoichiometries in the alloy matrices.^{48–50} In addition, Au–Cu bimetallic NPs may form atomically ordered intermetallic phases,^{48,51–53} whose dealloying and phase-segregating behaviors differ remarkably from those of their alloy counterparts.⁴⁸ Furthermore, Cu_xE compounds have numerous polymorphic crystalline phases covering a broad range of Cu/chalcogen stoichiometries.⁵⁴ How to selectively control the crystalline phases of the Cu_xE domains in the $\text{Au}@ \text{Cu}_x\text{E}$ heteronanostructures remains unexplored.

In this work, we transform atomically intermixed Au–Cu bimetallic NPs into dual-plasmonic $\text{Au}@ \text{Cu}_x\text{E}$ heteronanostructures through chalcogenization-driven phase segregation in a polyol solvent. By deliberately adjusting the chalcogen precursor concentrations and the reaction temperatures, we have been able to selectively control the crystalline phases of the Cu_xE domains in the heteronanostructures. For each targeted Cu_xE phase, we have pinpointed the optimal synthetic conditions under which the Au and Cu atoms are fully segregated in the heteronanostructures while keeping the Au and Cu_xE domains in direct contact with each other. We further demonstrate that both the Au/Cu stoichiometries and atomic ordering of the parental bimetallic NPs profoundly impact the transformation kinetics and thereby dictate the morphological evolution of the NPs during the chalcogenization-driven phase segregation.

EXPERIMENTAL SECTION

Au–Cu alloy NPs were synthesized following a previously reported protocol,⁴⁸ in which colloidal $\text{Au}@ \text{Cu}_2\text{O}$ core–shell NPs were suspended in tetraethylene glycol (TEG) and maintained at a reaction temperature of 300 °C using an oil bath for 30 min. Colloidal alloy NPs with Cu/Au atomic ratios of 3:1 and 1:1 further evolved into $\text{AuCu}_3\text{L1}_2$ and AuCuL1_0 intermetallic NPs, respectively, after they were maintained at 300 °C in TEG for 4 h. The resulting alloy and intermetallic NPs were collected through three cycles of centrifugation–redispersion and finally redispersed in ethanol for storage. The synthetic protocols for the alloy and intermetallic NPs are described in detail in the Supporting Information.

$\text{Au}@ \text{Cu}_x\text{E}$ ($x = 1.8$ or 1 ; $\text{E} = \text{S}$ or Se) heteronanostructures were synthesized by reacting the Au–Cu alloy NPs with a certain amount of chalcogen precursors in 5 mL of TEG containing 0.02 g of polyvinylpyrrolidone at an appropriate reaction temperature for 15 min. The reactant mixtures were quickly cooled in an ice bath, and the resulting $\text{Au}@ \text{Cu}_x\text{E}$ NPs were collected through three cycles of centrifugation and redispersion in ethanol and finally suspended in ethanol as colloidal NPs for storage. As discussed in greater detail later in this paper, a series of control samples were also synthesized using either the alloy or the intermetallic NPs as the parental nanostructures under various reaction conditions.

The structures, compositions, optical properties, and electrochemical behaviors of the as-synthesized NPs were characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), powder X-ray diffraction (PXRD), UV–visible–near-infrared extinction spectroscopy, and linear sweep voltammetry (LSV). More detailed description of the nanostructure characterizations is presented in the Supporting Information.

RESULTS AND DISCUSSION

Au–Cu alloy NPs were derived from $\text{Au}@ \text{Cu}_2\text{O}$ core–shell NPs through a polyol-assisted reduction–alloying process as detailed in a previously published paper.⁴⁸ We used Au NPs with an average diameter of ~ 52 nm (Figure S1 in the Supporting Information) as the cores to mediate the growth of Cu_2O shells with controlled thicknesses following a previously reported synthetic protocol.⁵⁵ Colloidal $\text{Au}@ \text{Cu}_2\text{O}$ core–shell NPs were then converted into Au–Cu alloy NPs at 300 °C in TEG, a polyol solvent with intrinsic reducing capabilities.^{48,56,57} The Au/Cu compositional stoichiometries of the alloy NPs could be finely tuned over a broad range by simply varying the Cu_2O shell thicknesses in the parental $\text{Au}@ \text{Cu}_2\text{O}$ core–shell NPs. Here, we focused on alloy NPs in three distinct Au/Cu stoichiometric regimes, specifically an Au-rich alloy at an Au/Cu ratio around 4:1 (labeled as Alloy-i), an alloy with equimolar Au and Cu (labeled as Alloy-ii), and a Cu-rich alloy at an Au/Cu ratio around 1:3 (labeled as Alloy-iii). The Au and Cu atoms were fully intermixed to form face-centered cubic (fcc) solid solutions without any phase-segregated monometallic Au or Cu domains detectable by PXRD (Figure 1A). As an increasing amount of Cu was alloyed with Au, the alloy NPs became larger in size, while their quasi-spherical morphology was well-preserved (see TEM images in Figure 1A and size distributions in Figure S2 in the Supporting Information). The Cu/Au atomic ratios quantified by EDS were in excellent agreement with those calculated based on the PXRD peak positions using the Vegard's law⁵⁸ (Figure S3 in the Supporting Information).

Colloidal Au–Cu alloy NPs were transformed into $\text{Au}@ \text{Cu}_x\text{E}$ heteronanostructures through chalcogenization-driven phase segregation in a polyol solvent, TEG in our case, at appropriate reaction temperatures below the boiling point of the solvent. We chose thioacetamide (TAA) and selenourea (SU) as the sulfur and selenium precursors, respectively, which effectively triggered the separation of Au and Cu atoms into two distinct domains in the heteronanostructures and selectively chalcogenized the Cu atoms into targeted crystalline phases of Cu_xE ranging from the Cu-deficient covellite (CuS) and klockmannite (CuSe) to the Cu-rich digenite ($\text{Cu}_{1.8}\text{S}$) and berzelianite ($\text{Cu}_{1.8}\text{Se}$), all of which were plasmonically active. Figure 1B–E show the PXRD patterns and TEM images of a series of $\text{Au}@ \text{Cu}_x\text{E}$ heteronanostructures synthesized under optimized reaction conditions, which were labeled as $\text{Au}@ \text{Cu}_x\text{E-N}$. Here, $x = 1.8$ (digenite and berzelianite) or 1 (covellite and klockmannite), $\text{E} = \text{S}$ or Se , and $\text{N} = \text{i, ii, or iii}$ (the Roman number, N, in the label of a heteronanostructure sample followed the label of its parental alloy NPs). The detailed reaction conditions under which these heteronanostructure samples were synthesized are listed in Table 1. The Au domains appeared darker than the Cu_xE domains in the TEM images, exhibiting clearly defined Au/ Cu_xE interfaces in each particle. The Au and Cu atoms were fully separated into segregated but still adjoined domains without any residual alloys detectable by PXRD. We quantified the compositional stoichiometries of Au, Cu, and E using EDS (Figures S4–S6 in the Supporting Information) and further mapped out the spatial distributions of the Au, Cu, and E elements through correlated SEM–EDS measurements (Figures S7 and S8 in the Supporting Information). The Au/Cu atomic ratios remained essentially unchanged after the alloy NPs were converted into the $\text{Au}-\text{Cu}_x\text{E}$ heteronanostructures, and the Cu/E stoichio-

Table 1. Detailed Experimental Parameters for the Synthesis of Various Au@Cu_xE Heteronanostructure Samples

Sample label	Parental alloy NPs	Chalcogen precursor	Chalcogen precursor concentration	Reaction temperature
Au@Cu _{1.8} S-i	Alloy-i	TAA	20 mM	280 °C
Au@Cu _{1.8} S-ii	Alloy-ii		10 mM	
Au@Cu _{1.8} S-iii	Alloy-iii		6.0 mM	
Au@CuS-i	Alloy-i	TAA	45 mM	220 °C
Au@CuS-ii	Alloy-ii		36 mM	
Au@CuS-iii	Alloy-iii		30 mM	
Au@Cu _{1.8} Se-i	Alloy-i	SU	0.70 mM	240 °C
Au@Cu _{1.8} Se-ii	Alloy-ii		0.60 mM	
Au@Cu _{1.8} Se-iii	Alloy-iii		0.30 mM	
Au@CuSe-i	Alloy-i	SU	1.4 mM	200 °C
Au@CuSe-ii	Alloy-ii		1.2 mM	
Au@CuSe-iii	Alloy-iii		0.90 mM	

metric ratios quantified by EDS were fully consistent with the expected values of the crystalline phases of Cu_xE assigned based on the PXRD results (Figure S9 in the Supporting Information).

Several interesting trends were clearly observed when comparing the detailed particle morphologies (Figure 1B–E) and the optimal synthetic conditions for various targeted Cu_xE phases (Table 1). First, the relative domain sizes of Cu_xE versus Au in the heteronanostructures were directly correlated to the Cu/Au stoichiometries of the alloy NPs. Both the Au@Cu_{1.8}S and Au@Cu_{1.8}Se heteronanostructures exhibited pea-

nut-shaped heterodimer configurations (Figure 1B,D). As the Cu/Au atomic ratios in the parental alloy NPs increased, the Cu_{1.8}E domains became larger in size, while the sizes of the Au domains remained essentially unchanged. The CuS and CuSe domains in the heteronanostructures, however, exhibited a distinct plate-like morphology, as shown by both TEM (Figure 1C,E) and SEM images (Figure S10 in the Supporting Information). As the parental alloy NPs became more Cu-rich, increasing numbers of CuS nanoplates emerged on the surfaces of Au, eventually forming a multicrystalline spiky shell encapsulating each Au core (Figures 1C and S11A in the Supporting Information). In contrast, the CuSe domains in the Au@CuSe heteronanostructures preferentially underwent a two-dimensional (2D) lateral growth process to form larger nanosheets as the Cu percentage in the parental alloy NPs increased (Figures 1E and S11B in the Supporting Information). Unlike the Cu-rich digenite and berzelianite with fcc structures, the Cu-deficient covellite and klockmannite exhibited interesting lamellar structures in their crystalline lattices^{59–62} (Figure S12 in the Supporting Information). Such intrinsic structural anisotropy served as the primary driving force for the formation of the quasi-2D Cu_xE morphologies in the Au@CuS and Au@CuSe heteronanostructures. Second, the chalcogenization-driven phase segregation involved the diffusion of Au and Cu atoms across the alloy matrices. For each specific Cu_xE phase, higher chalcogen precursor concentrations were needed to kinetically boost the phase segregation when the alloy NPs became more Au-rich (Table 1) because the atomic mobility was inversely correlated with the Au/Cu stoichiometry of the alloy NPs. After reacting with 5.0 mM TAA in TEG at 280 °C for 15 min, the Au and Cu

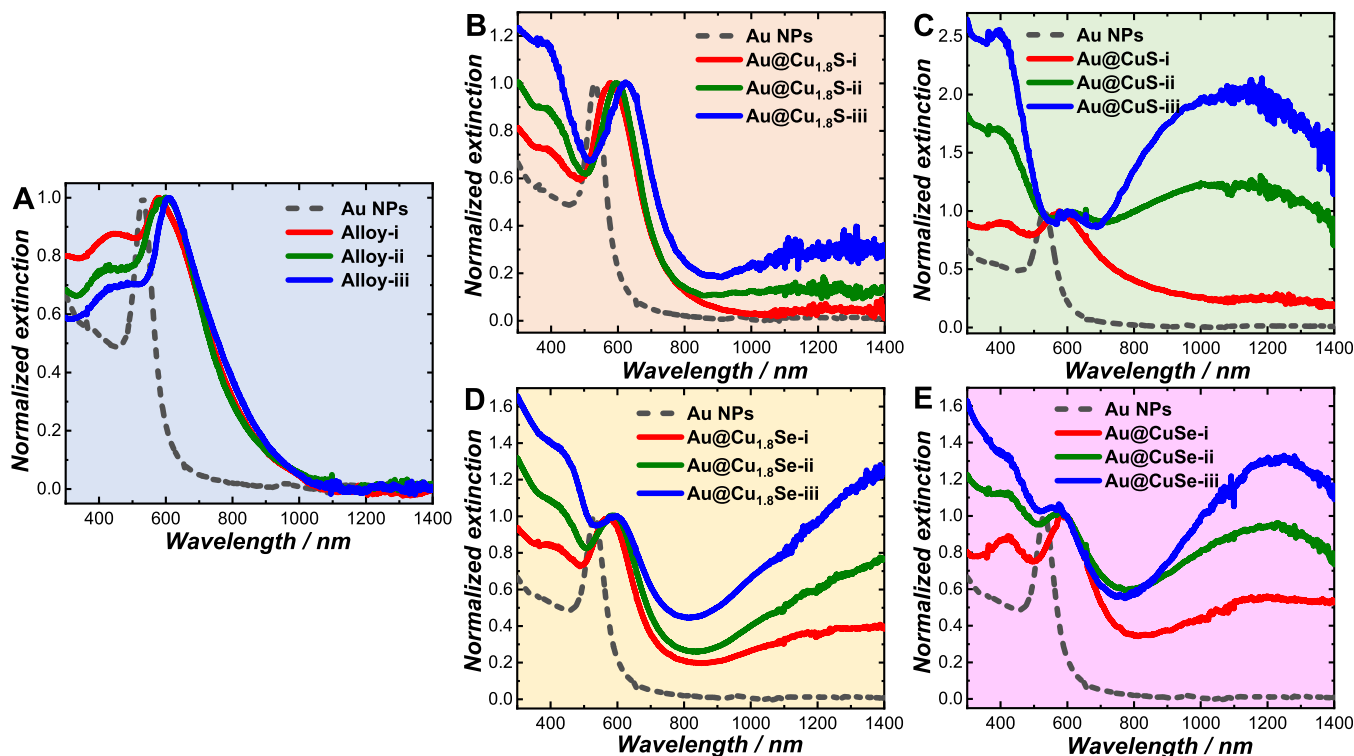


Figure 2. Optical extinction spectra of (A) Au–Cu alloy NPs, (B) Au@Cu_{1.8}S, (C) Au@CuS, (D) Au@Cu_{1.8}Se, and (E) Au@CuSe heteronanostructures. The extinction spectra were collected from colloidal NPs suspended in ethanol at room temperature. The extinctions at the Au plasmon resonance wavelengths in the visible region were normalized to 1 for all spectra. The extinction spectrum of Au NPs (52.3 ± 5.6 nm in diameter) is shown as the grey dashed curve in each panel.

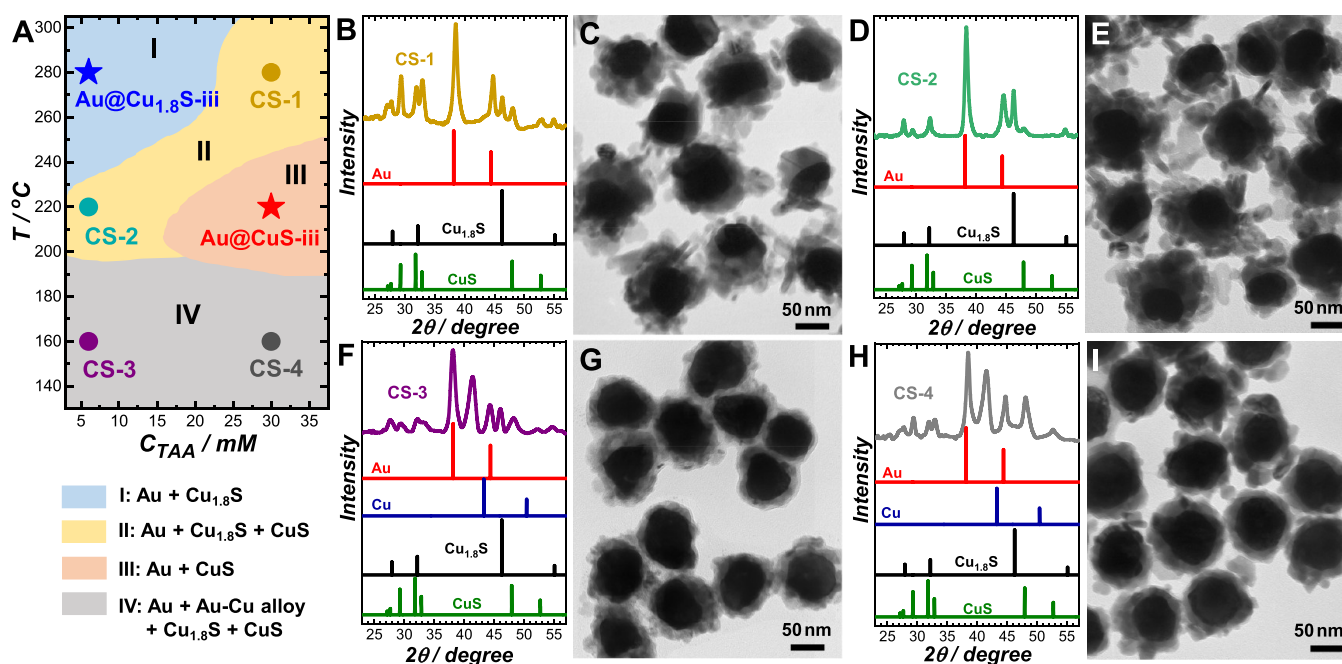


Figure 3. (A) Reaction temperatures and TAA concentrations at which various heteronanostructures were synthesized. In this set of experiments, Alloy-iii NPs served as the parental NPs for the sulfidation-induced phase segregation. The reaction temperatures and TAA concentrations utilized in the standard synthetic protocols for Au@Cu_{1.8}S-iii and Au@CuS-iii NPs are labeled with the blue and red stars, respectively. The reaction temperatures and TAA concentrations at which various control samples (denoted as CS-1, CS-2, CS-3, and CS-4) were synthesized are labeled as closed circles. The temperature and concentration ranges for producing heteronanostructures composed of different phases are highlighted schematically using different colors (see details in the legend labels underneath the plots). PXR patterns of (B) CS-1, (D) CS-2, (F) CS-3, and (H) CS-4. The standard PXR patterns of Au, Cu, Cu_{1.8}S, and CuS are also shown as the references for comparison. TEM images of (C) CS-1, (E) CS-2, (G) CS-3, and (I) CS-4.

atoms in the Cu-rich Alloy-iii NPs were fully segregated, whereas the Au-rich Alloy-i NPs remained essentially unreactive and partial phase segregation was observed in Alloy-ii NPs (Figure S13 in the Supporting Information). We also used LSV to measure the electrochemical critical potentials for the percolation dealloying of the alloy NPs,^{48–50,63} which positively shifted due to decreased atomic mobilities in the alloy matrices when the alloy NPs became more Au-rich (Figure S14 in the Supporting Information). In our synthetic protocols, we optimized both the reaction temperatures and the chalcogen precursor concentrations for each pair of parental alloy NPs and targeted Cu_xE phases such that the NP transformations occurred rapidly to form fully segregated Au and Cu_xE domains typically within a few minutes (Figures S15 and S16 in the Supporting Information). Alloy NPs with an even higher Cu/Au atomic ratio of ~7 (denoted as Alloy-iv) exhibited even higher atomic mobilities than Alloy-iii NPs (Figure S17 in the Supporting Information). In this case, the particle morphologies became non-uniform and the Cu_xE domains started to fall apart from the Au domains after the chalcogenization-driven phase segregation (Figure S18 in the Supporting Information). To keep the Au and Cu_xE domains adjoined, the nucleation of Cu_xE needed to be spatially confined at the NP/solution interfaces, which could be accomplished when the diffusion of Cu atoms across the alloy matrices was slower than the chalcogenization reactions. However, if Cu diffusion became even faster than chalcogenization, some Cu atoms were leached out from the alloy NPs, allowing the nucleation of Cu_xE to occur in the solution phase as well. As a consequence, self-nucleated Cu_xE nanocrystals emerged in the final products. Third, it required

higher reaction temperatures to fully chalcogenize Cu into the Cu_{1.8}E phases than for the CuE phases within a fixed reaction time of 15 min (Table 1). TEG was a polyol solvent whose reducing capability increased with the reaction temperature.^{48,56,57} Therefore, when the NPs were suspended in TEG, a more strongly reducing reaction environment was created at higher temperatures, which selectively favored the formation of the Cu-rich Cu_{1.8}E phases compared to the Cu-deficient CuE phases.

The as-synthesized colloidal Au@Cu_xE heteronanostructures exhibited well-resolved dual-plasmonic spectral features in the visible and near-infrared regions. Figure 2 shows the optical extinction spectra collected from colloidal alloy NPs and Au@Cu_xE heteronanostructures suspended in ethanol in the wavelength range from 300 nm up to 1400 nm (limited by the strong absorption of ethanol at wavelengths longer than ~1450 nm). The optical extinctions at the Au plasmon resonance wavelengths were normalized to 1 for all the measured colloidal samples to highlight the spectral shifts of the Au plasmons and compare the relative intensities of the plasmon resonance peaks of the metallic versus Cu_xE domains in the heteronanostructures. Au NPs exhibited a well-defined extinction peak centered at 530 nm, which was a spectral feature associated with the dipolar Au plasmons. The extinction peaks of the colloidal alloy NPs progressively red-shifted by several tens of nanometers in wavelength, accompanied by significant broadening of the peak widths, as the alloy NPs became larger in size and more Cu-rich in composition (Figure 2A). When the alloy NPs were converted into Au@Cu_xE heteronanostructures, a broad plasmon resonance band emerged in the near-infrared region (Figure

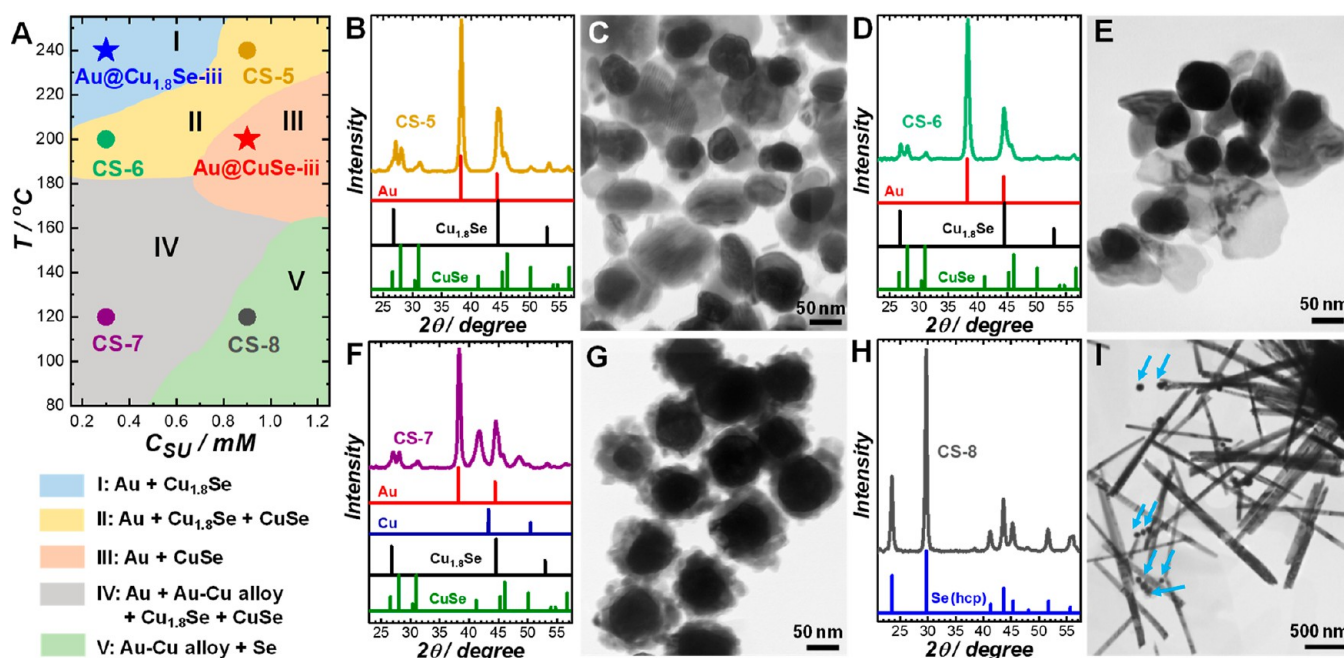


Figure 4. (A) Reaction temperatures and SU concentrations at which various heteronanostructures were synthesized. In this set of experiments, Alloy-iii NPs served as the parent NPs for the selenidation-induced phase segregation. The reaction temperatures and SU concentrations utilized in the standard synthetic protocols for Au@Cu_{1.8}Se-iii and Au@CuSe-iii NPs are labeled with the blue and red stars, respectively. The reaction temperatures and SU concentrations at which various control samples (denoted as CS-5, CS-6, CS-7, and CS-8) were synthesized are labeled as closed circles. The temperature and concentration ranges for producing heteronanostructures composed of different phases are highlighted schematically using different colors (see details in the legend labels underneath the plots). PXRD patterns of (B) CS-5, (D) CS-6, (F) CS-7, and (H) CS-8. The standard PXRD patterns of Au, Cu, Cu_{1.8}Se, CuSe, and hcp phase Se (JCPDS 06-362) are also shown as the references for comparison. TEM images of (C) CS-5, (E) CS-6, (G) CS-7, and (I) CS-8.

2B–2E), which was the spectral signature of the Cu_xE plasmons.^{25–31} Meanwhile, the plasmon resonance peak of Au remained in the visible region but was red-shifted relative to the plasmon peak of colloidal Au NPs because the refractive indices of Cu_xE were significantly higher than those of ethanol. As the Cu_xE domains became larger in size, the extinction peak of the Cu_xE plasmon resonances became increasingly more pronounced. In the family of Cu_xE binary compounds, the most Cu-rich phases, Cu₂S and Cu₂Se, were plasmonically inactive due to the lack of free holes in their valence bands.^{25,26,64} Free holes could be created by introducing Cu vacancies in the crystalline lattices of Cu₂S and Cu₂Se, which led to the formation of Cu_{1.8}S and Cu_{1.8}Se, both of which became plasmonically active.^{25,26} At this level of Cu vacancy doping, the concentrations of free holes in the materials were more than 1 order of magnitude lower than the concentrations of the free electrons in Au.^{25,26} Therefore, both Cu_{1.8}S and Cu_{1.8}Se plasmons were resonant at much longer wavelengths (beyond 1400 nm) than the Au plasmons, exhibiting weak extinction intensities and very broad spectral line shapes spanning much of the near-infrared region (Figure 2B,D). In comparison to their Cu-rich counterparts, the Cu-deficient CuS and CuSe exhibited stronger plasmon resonance peaks that were resonant at shorter wavelengths in the near-infrared (Figure 2C,E) because CuS and CuSe had much higher free hole concentrations than Cu_{1.8}S and Cu_{1.8}Se.^{64–66} In the short-wavelength range below ~530 nm, strong light extinction due to the interband transitions in both Cu_xE and Au was clearly observed. The spectral overlap between the Au plasmons and the interband transitions of Cu_xE in the wavelength range of ~540–700 nm caused additional damping of Au plasmons, as

reflected by the broadening and weakening of the Au plasmon peaks of the Au@Cu_xE heteronanostructures. The rich spectral features shown in Figure 2 clearly revealed that the relative domain sizes of Cu_xE versus Au and the crystalline phase of the Cu_xE domains, both of which were synthetically tailorable structural parameters, rigorously determined the detailed extinction spectral features of the dual-plasmonic Au@Cu_xE heteronanostructures.

Under our reaction conditions, the reaction temperature and chalcogen precursor concentration were identified as two key synthetic knobs that allowed us to not only kinetically maneuver the phase segregation process but also selectively control the crystalline phases of the Cu_xE domains in the heteronanostructures. Figure 3A highlights the reaction temperatures (*T*) and TAA concentrations (*C*_{TAA}) at which Alloy-iii NPs were selectively transformed into a series of heteronanostructures with representative combinations of materials phases within a fixed reaction time of 15 min. The optimal synthetic conditions for Au@Cu_{1.8}S-iii (*T* = 280 °C, *C*_{TAA} = 6.0 mM) and Au@CuS-iii (*T* = 220 °C, *C*_{TAA} = 30 mM) were highlighted with a blue star and a red star, respectively, in Figure 3A. To fully unravel the intercorrelations among *T*, *C*_{TAA}, and the detailed structures of the NPs, a series of control samples were synthesized at several combinations of *T* and *C*_{TAA} that deviated significantly from those of the optimal synthetic conditions for Au@Cu_{1.8}S-iii and Au@CuS-iii heteronanostructures. In the control sample synthesized at *T* of 280 °C and *C*_{TAA} of 30 mM (labeled as CS-1), the Au and Cu atoms were fully segregated with no residual alloy domains detectable by PXRD (Figure 3B). However, the Cu_xE domains were composed of mixed Cu_{1.8}S and CuS phases. In each CS-1

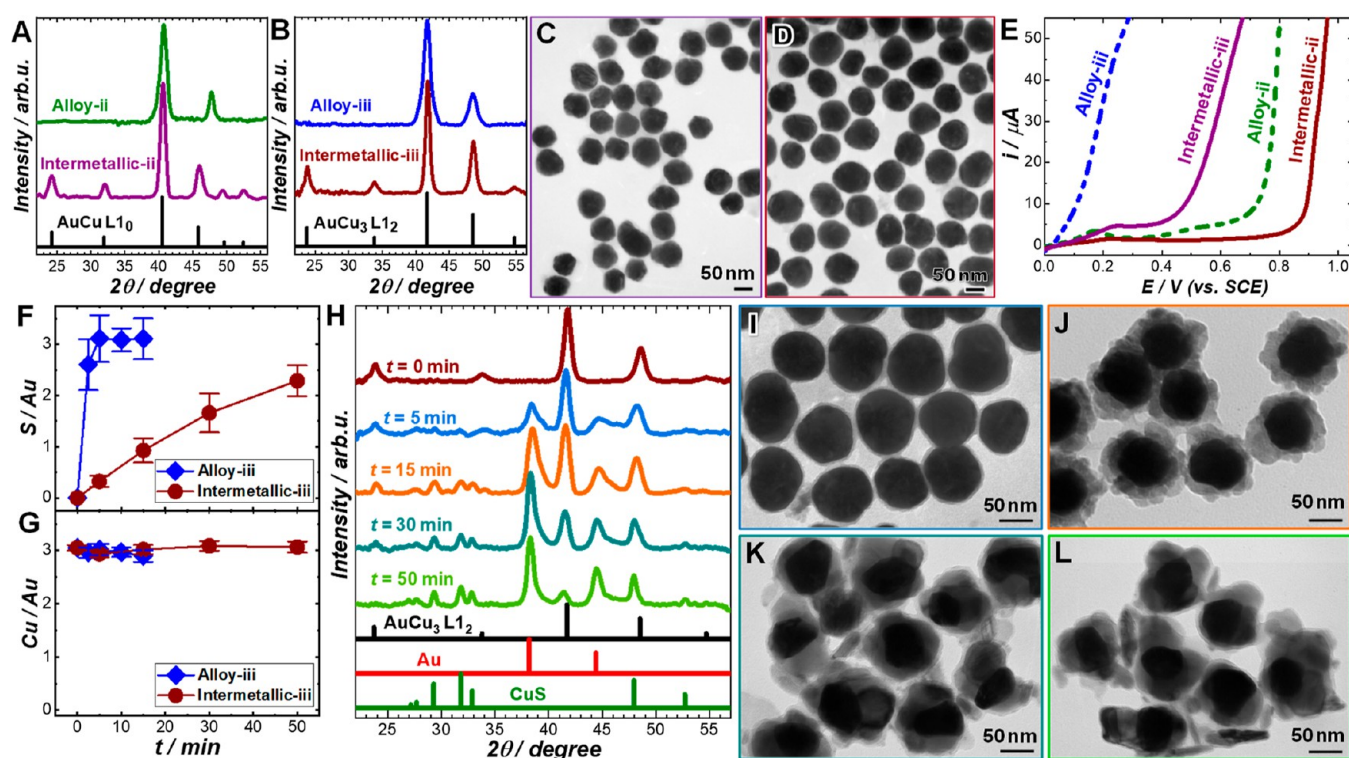


Figure 5. PXRD patterns of (A) Intermetallic-ii and (B) Intermetallic-iii NPs. The PXRD patterns of Alloy-ii and Alloy-iii NPs and the standard patterns of AuCu L1₀ (JCPDS 25-1220) and AuCu₃ L1₂ (JCPDS 25-1220) intermetallic phases are also shown for comparison. TEM images of (C) Intermetallic-ii and (D) Intermetallic-iii NPs. (E) LSV curves of Alloy-ii, Intermetallic-ii, Alloy-iii, and Intermetallic-iii NPs loaded on GCEs in a 0.5 M H₂SO₄ electrolyte at a potential sweep rate of 50 mV s⁻¹. Temporal evolution of (F) S/Au and (G) Cu/Au atomic ratios (quantified by EDS) during the sulfidation of Alloy-iii and Intermetallic-iii NPs at a reaction temperature of 220 °C and an initial TAA concentration of 30 mM. (H) PXRD patterns of the heteronanostructures kinetically trapped at various reaction times during the sulfidation of Intermetallic-iii NPs. (I) TEM images of the heteronanostructures obtained at reaction times of (I) 5, (J) 15, (K) 30, and (L) 50 min during the sulfidation of Intermetallic-iii NPs.

NP, the Au domain was encapsulated inside a polycrystalline Cu_xE shell with a highly spiky surface morphology (Figure 3C). At *T* of 220 °C and *C*_{TAA} of 6.0 mM, the as-synthesized heteronanostructures (labeled as CS-2) also exhibited a similar core-shell morphology with Au and Cu fully segregated, and the polycrystalline, spiky Cu_xE shells consisted of both Cu_{1.8}S and CuS phases (Figure 3D,E). These results showed that the reactions were kinetically fast enough to achieve complete phase segregation of Au and Cu within 15 min when keeping *T* above ~220 °C. In this high-*T* regime, higher *C*_{TAA} favored the formation of the Cu-deficient CuS phase due to the Cu/Au stoichiometric requirement, whereas elevation of *T* favored the formation of the Cu-deficient Cu_{1.8}S phase because of stronger reducing capability of TEG at higher *T*. At lower temperatures, the sulfidation-driven phase segregation became kinetically slower, resulting in partial segregation of Au and Cu within 15 min. The two control samples synthesized at *T* of 160 °C, labeled as CS-3 (*C*_{TAA} of 6.0 mM) and CS-4 (*C*_{TAA} of 30 mM), respectively, were both core-shell NPs comprising multiple phase-segregated but interconnected crystalline domains, including monometallic Au, the Au-Cu alloy, Cu_{1.8}S, and CuS (Figure 3F-I). At even lower temperatures below 100 °C, the sulfidation reactions became kinetically even slower, and the Alloy-iii NPs remained essentially unreacted with almost no phase segregation observed within 15 min. Based on all the observations mentioned above, we were able to sketch a phase diagram (Figure 3A), in which *T*-*C*_{TAA} regimes for synthesizing heteronanostructures composed of several targeted materials

phases were highlighted using different colors. Although it required massive experimental data to quantitatively define the boundaries between different phases, this sketched phase diagram presented a simplified, qualitative picture that fully captured the essence of the *T*- and *C*_{TAA}-dependent transforming behaviors of Au-Cu alloy NPs during the sulfidation-driven phase segregation.

We also studied the selenidation-driven transformations of Alloy-iii NPs at various *T*s and SU concentrations (*C*_{SU}) within a fixed reaction time of 15 min. The phase diagrams for the selenidation and sulfidation of Alloy-iii NPs shared a set of similar features. In Figure 4A, the optimal synthetic conditions for Au@Cu_{1.8}Se-iii (*T* = 240 °C, *C*_{SU} = 0.3 mM) and Au@CuSe-iii (*T* = 200 °C, *C*_{TAA} = 0.9 mM) were marked with a blue star and a red star, respectively. The control sample synthesized at *T* of 240 °C and *C*_{SU} of 0.9 mM (labeled as CS-5) was composed of Au, Cu_{1.8}Se, and CuSe domains (Figure 4B). CS-5 exhibited irregular NP shapes, and some of the Cu_{1.8}Se or CuSe domains were detached from the Au NPs (Figure 4C), suggesting that in this high-*T* and high-*C*_{SU} regime, the phase segregation might occur even faster than the selenidation of Cu, causing self-nucleation of Cu_xE to occur in the solution phase. At *T* of 200 °C and *C*_{SU} of 0.3 mM, Au and Cu were fully segregated to form heteronanostructures (labeled as CS-6) composed of Au, Cu_{1.8}Se, and CuSe domains (Figure 4D,E). Increasing *C*_{SU} preferentially promoted the formation of the Cu-deficient CuSe phase, whereas the Cu-rich Cu_{1.8}Se phase became the favored product

at higher T , which was fully consistent with the general trend observed on the sulfidation-driven transformations of the NPs. Incomplete phase segregation of Au and Cu was observed in the low- T and low- C_{SU} regime due to slow reaction kinetics. The control samples synthesized at T of 120 °C and C_{SU} of 0.3 mM (labeled as CS-7) exhibited a core-shell morphology comprising four segregated phases, including monometallic Au, the Au–Cu alloy, $\text{Cu}_{1.8}\text{Se}$, and CuSe (Figure 4F,G). Interestingly, the control sample synthesized at T of 120 °C and C_{SU} of 0.9 mM was composed of a mixture of Au–Cu alloy NPs (labeled with blue arrows in the TEM image) and Se nanowhiskers in the hexagonal close-packed (hcp) phase (Figure 4H,I). In this case, SU was decomposed to form elemental Se, while Au–Cu alloy NPs remained unreacted. Apparently, elemental Se was incapable of inducing the selenidation-driven phase segregation of the alloy NPs in TEG at T of 120 °C. The formation of Se could be considered as a low-temperature side reaction at high C_{SU} , which competed with the selenidation of the alloy NPs by SU. Therefore, the synthesis of $\text{Au@Cu}_x\text{Se}$ heteronanostructures with targeted Cu_xSe phases should be conducted at temperatures significantly higher than 120 °C.

The kinetics of atomic diffusion in atomically intermixed Au–Cu bimetallic NPs was profoundly influenced not only by the Cu/Au stoichiometries but also by the ordering of the Au and Cu atoms. As shown by the phase diagram of the Au–Cu binary system (Figure S19 in the Supporting Information), at Cu/Au stoichiometric ratios of 1:1 and 3:1, atomically ordered intermetallic phases are thermodynamically more stable than the atomically disordered alloys at temperatures below 400 °C. We converted the colloidal Alloy-ii and Alloy-iii NPs suspended in TEG into intermetallic NPs through a thermodynamically driven atomic ordering process at 300 °C for 4 h. The intermetallic NPs derived from Alloy-ii and Alloy-iii NPs were labeled as Intermetallic-ii and Intermetallic-iii, respectively. The PXRD patterns of Intermetallic-ii and Intermetallic-iii NPs were in excellent agreement with the standard diffraction patterns of the AuCu L1_0 and $\text{AuCu}_3 \text{L1}_2$ intermetallic compounds (Figure 5A,B), respectively. The quasi-spherical particle morphology (Figure 5C,D) and the Cu/Au stoichiometries (Figure S20 in the Supporting Information) were both well preserved during the alloy-to-intermetallic conversion, while the particle sizes decreased slightly by less than 4% (Figure S21 in the Supporting Information) upon the formation of the intermetallic phases. At the same Cu/Au stoichiometric ratios, the atomic diffusion rates in the intermetallic NPs were significantly lower than those in the alloy NPs,⁴⁸ as evidenced by the positive shifts of the critical potentials for percolation dealloying (Figure 5E). Such a difference in intraparticle atomic diffusivities led to remarkably different transforming behaviors of alloy and intermetallic NPs during the chalcogenization-driven phase segregation.

We compared the structure-transforming kinetics of Alloy-iii and Intermetallic-iii NPs in greater detail during sulfidation-driven phase segregation at T of 220 °C and C_{TAA} of 30 mM. In this set of experiments, we quenched the sulfidation reactions at specific reaction times by rapidly cooling down the samples in an ice batch and then characterized the kinetically trapped intermediate structures using EDS, PXRD, and TEM. During the reactions, the S/Au atomic ratios kept increasing over time until approaching a value of 3 (Figure 5F), while the Cu/Au atomic ratios remained very close to 3 (Figure 5G).

According to the temporally evolving profiles of S/Au atomic ratios (Figure 5F), the sulfidation of Intermetallic-iii NPs was remarkably slower than that of Alloy-iii NPs. Although the Au and Cu in Alloy-iii NPs became fully segregated after ~ 2 min, it took more than 50 min to achieve complete phase segregation in Intermetallic-iii NPs under identical sulfidation reaction conditions. The PXRD results clearly showed that the sulfidation-driven phase segregation led to the emergence and growth of both monometallic Au and CuS domains as the intermetallic $\text{AuCu}_3 \text{L1}_2$ domains were gradually consumed (Figure 5H). As shown by the TEM images (Figure S1–J), a uniform thin shell of CuS was produced on the intermetallic NP surfaces at the early stage of the reaction, which became thicker and spikier as the sulfidation-driven phase segregation further proceeded. Meanwhile, the metallic domains in the heteronanostructures, which appeared darker than the CuS domains in the TEM images, became smaller in size as the Cu atoms in the intermetallic $\text{AuCu}_3 \text{L1}_2$ domains diffused into the growing CuS domains (Figure S22 in the Supporting Information). We further systematically compared the structures and morphologies of the heteronanostructures derived from sulfidation- and selenidation-driven phase segregation of alloy and intermetallic NPs at Cu/Au stoichiometries of both 1:1 and 3:1 under a series of reaction conditions after a fixed reaction time of 15 min (Figures S23–S30 in the Supporting Information). In all these cases, the phase segregation of the intermetallic NPs occurred more slowly than that of their alloy counterparts. Only partial phase segregation of the intermetallic NPs was achieved after 15 min, whereas the Au and Cu in the alloy NPs were fully segregated. The crystalline phases of the Cu_xE domains in the heteronanostructures, however, were primarily determined by the reaction temperature and the chalcogen precursor concentrations, almost independent of the Cu/Au stoichiometries and the atomic ordering in the parental bimetallic NPs.

CONCLUSIONS

This work reports a versatile synthetic pathway based on chemically driven phase segregation, through which colloidal bimetallic NPs composed of intermixed Au and Cu atoms, including both alloy and intermetallic NPs, are controllably transformed into a series of architecturally distinct Au@Cu_xE heteronanostructures with tunable domain sizes and specifically targeted Cu_xE phases. The as-synthesized colloidal Au@Cu_xE heteronanostructures exhibit unique dual-plasmonic characteristics that can be deliberately tuned by tailoring the geometric arrangements, dimensions, and crystalline phases of the constituent domains. Our synthetic approach allows us to precisely preprogram the relative domain sizes of Cu_xE versus Au in the heteronanostructures by tuning the stoichiometric ratios of Cu/Au in the parental alloy NPs. The crystalline phases of the Cu_xE domains in the heteronanostructures can be selectively controlled by judiciously adjusting the chalcogen precursor concentrations and the reaction temperatures. The morphological evolution of the NPs is intimately tied to the kinetics of the chalcogenization-driven phase segregation, which is profoundly influenced by both the Au/Cu stoichiometries and atomic ordering of the parental bimetallic NPs. This work sheds light on the versatile transforming behaviors of alloy and intermetallic NPs during chemically triggered phase segregation processes, providing important guiding principles for developing new synthetic approaches that enable us to derive complex heteronanostructures with

targeted intraparticle architectures, compositions, crystalline phases, and functionalities from parental nanostructures that are structurally simpler and synthetically more tractable.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.1c04451>.

Additional experimental details, TEM images, SEM images, EDS results, PXRD patterns, size distributions, optical extinction spectra, and electrochemical results (PDF)

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Author Contributions

M.S. synthesized and characterized the nanostructures. Z.W. conducted the electrochemical measurements. M.S. and H.W. analyzed the data. H.W. designed the project, supervised the research, acquired funding support, and wrote the paper with contribution from all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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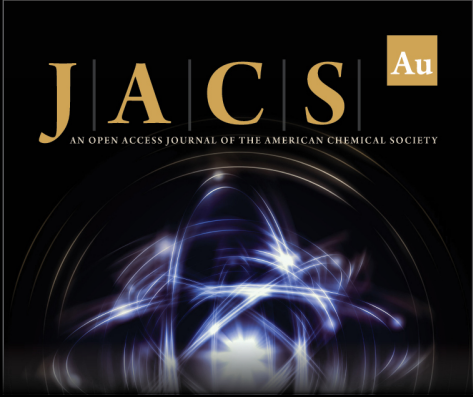
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Supporting Information for

Chemically Driven Phase Segregation of Alloy
Nanoparticles: A Versatile Route to Dual-Plasmonic
Gold@Copper Chalcogenide Heteronanostructures

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1. Additional Experimental Details

1.1. Chemicals and Materials

Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), chloroauric acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), polyvinylpyrrolidone (average molecular weight of 58,000), selenourea ($\text{CH}_4\text{N}_2\text{Se}$), tetraethylene glycol (TEG), and thioacetamide ($\text{C}_2\text{H}_5\text{NS}$) were purchased from Alfa Aesar. Trizma base (TB), hydrazine solution ($\text{N}_2\text{H}_4 \cdot 3\text{H}_2\text{O}$, 35 wt%), and Nafion perfluorinated resin solution (5 wt%) were purchased from Sigma-Aldrich. Trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), sodium hydroxide (NaOH), and ethanol (200 proof) were purchased from Fisher Scientific. All reagents were used as received without further purification. Ultrapure Milli-Q water ($18.2 \text{ M}\Omega \cdot \text{cm}$) was used for all experiments.

1.2. Synthesis of Au Nanoparticles (NPs)

Colloidal Au NPs ($52.3 \pm 5.6 \text{ nm}$ in diameter) were synthesized using a previously developed, seed-mediated growth method.^{S1} Briefly, colloidal Au seeds with an average diameter of $\sim 17 \text{ nm}$ were first synthesized by reducing chloroauric acid with trisodium citrate in an aqueous solution. 1.5 mL of 1 wt % trisodium citrate aqueous solution was added into 48 mL of boiling water under magnetic stir. Then 0.5 mL of 25 mM chloroauric acid was injected into the solution. The reactant mixture was refluxed at boiling temperature for 30 minutes. The resulting 17 nm Au NPs were used as the seeds to mediate the overgrowth of Au NPs upon reduction of chloroauric acid with trizma base (TB). Typically, 2 mL of 0.1 M of TB was added into 45 mL of boiling water under magnetic stir. After 10 minutes of stirring, 1 mL of 25 mM of chloroauric acid and 2 mL of the Au seed colloids were added. The reactant mixture was maintained at the boiling temperature for 30 minutes. The resulting Au NPs were stored as synthesized for future use.

1.3. Synthesis of Au-Cu Alloy and Intermetallic NPs

Au-Cu alloy NPs were synthesized following a previously published protocol.^{S2, S3} First, Au@Cu₂O core-shell NPs were synthesized by growing a Cu₂O nanoshell surrounding each Au NP core.^{S4} Typically, 2 mL of the as-synthesized Au NPs and various amounts of $\text{Cu}(\text{NO}_3)_2$ were added into 30 mL of 2 wt % polyvinylpyrrolidone (PVP) aqueous solution. Then 0.067 mL of 5.0 M NaOH and 0.030 mL of $\text{N}_2\text{H}_4 \cdot 3\text{H}_2\text{O}$ were added under magnetic stirring at 300 rpm. After keeping the reactant mixtures under magnetic stir in an ice bath for 15 minutes, the as-synthesized Au@Cu₂O core@shell NPs were centrifuged and redispersed in 10 mL of TEG containing 0.1 g of PVP. The colloidal Au@Cu₂O core@shell NPs in TEG transformed into Au-Cu alloy NPs at 300 °C after 30 minutes. The Cu/Au stoichiometries and particle sizes of the Au-Cu alloy NPs were determined by the relative core and shell dimensions of the parental Au@Cu₂O core-shell NPs, which could be synthetically tuned by adjusting the relatively amount of $\text{Cu}(\text{NO}_3)_2$ with respect to that of the Au NPs. The resulting Au-Cu alloy NPs were collected through three centrifugation-redispersion cycles and finally redispersed in ethanol for storage. When dispersed in TEG and maintained at 300 °C for 4 hours, the alloy NPs with Cu/Au ratios of 3:1 and 1:1 further underwent intraparticulate atomic ordering processes to evolve into AuCu₃ L1₂ and AuCu L1₀

intermetallic phases, respectively. The resulting intermetallic NPs were collected through three centrifugation-redispersion cycles and finally redispersed in ethanol for storage.

1.4. Structural Characterizations of NPs

The transmission electron microscopy (TEM) images were obtained using a Hitachi H-7800 transmission electron microscope, operated at an accelerating voltage of 120 kV. Samples for TEM measurements were dispersed in ethanol and drop-dried on 300 mesh carbon-coated Cu grids (Electron Microscopy Science Inc.). The scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) measurements were conducted using a Zeiss Gemini500 thermal field emission scanning electron microscope. An EDS unit attached to the microscope was used to quantify the Au, Cu, S, and Se stoichiometries in the samples. Atomic ratios were quantified based on the relative area of the Au $M\alpha$, Cu $L\alpha$, S $K\alpha$ and Se $K\alpha$ peaks in the EDS spectra. Samples for SEM and EDS measurements were dispersed in ethanol and drop-dried on silicon wafers (University Wafers). Powder X-ray diffraction (PXRD) patterns were collected on a SAXSLab Ganesha at the South Carolina Collaborative (Cu $K\alpha$ = 1.5405 Å). Optical extinction spectra were collected from colloidal NPs dispersed in ethanol using a Cary 5000 UV/vis/NIR spectrophotometer.

1.5. Electrochemical measurements

Linear sweep voltammetry (LSV) measurements were conducted using a CHI 660E Electrochemical Workstation (CH Instruments, Austin, Texas) with a three-electrode system composed of a Pt wire as the auxiliary, a saturated calomel electrode (SCE) as the reference, and a glassy carbon electrode (GCE, 3 mm diameter) loaded with NPs as the working electrode. The GCEs were polished with 0.3 μm alumina slurry, followed by washing with water and ethanol before use. 5 μL of colloidal ink containing 2 μg of Au-Cu alloy or intermetallic NPs were drop-casted and air-dried on each pretreated GCE at room temperature. Then 2 μL of Nafion solution (0.2 wt %) was drop-dried on the electrode surface to hold the NPs. LSV curves of various NPs were measured at room temperature in 0.5 mM H_2SO_4 electrolyte at a potential sweep rate of 50 mV s^{-1} .

2. Additional Figures

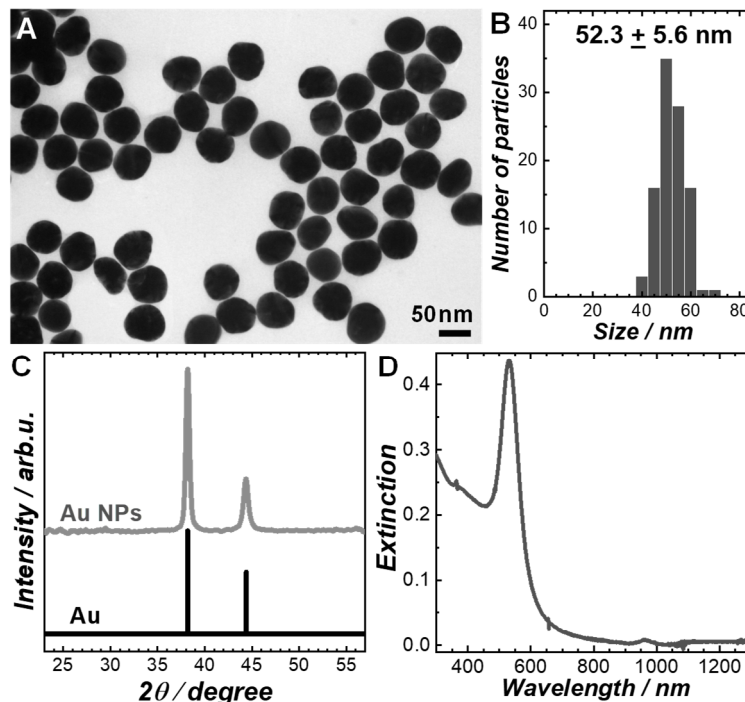


Figure S1. (A) TEM image, (B) size distribution, (C) PXRD pattern, and (D) optical extinction spectrum of Au NPs. The histogram shown in panel B was obtained from 100 particles in the TEM images. In panel C, the standard diffraction pattern of Au (JCPDS 04-0784) was also shown as the reference. The extinction spectrum in panel D was collected from colloidal Au nanoparticles suspended in ethanol.

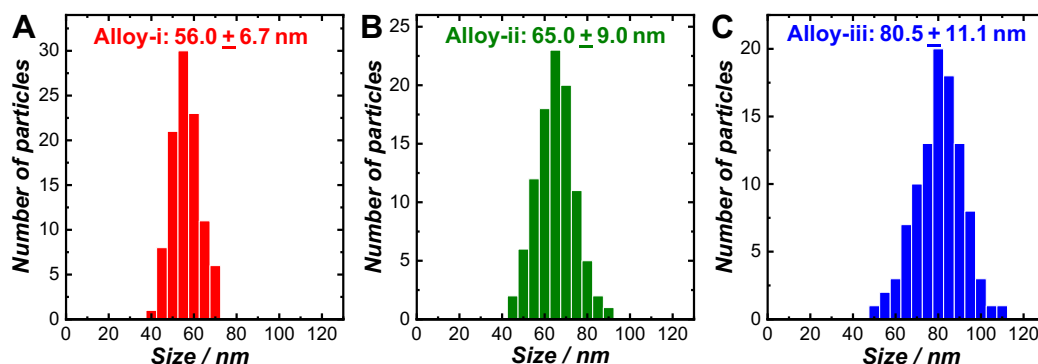


Figure S2. Size distributions of (A) Alloy-i, (B) Alloy-ii, and (C) Alloy-iii NPs. The histograms were obtained from 100 particles in the TEM images of each sample. The average diameters and standard deviations of the NPs were shown in each panel.

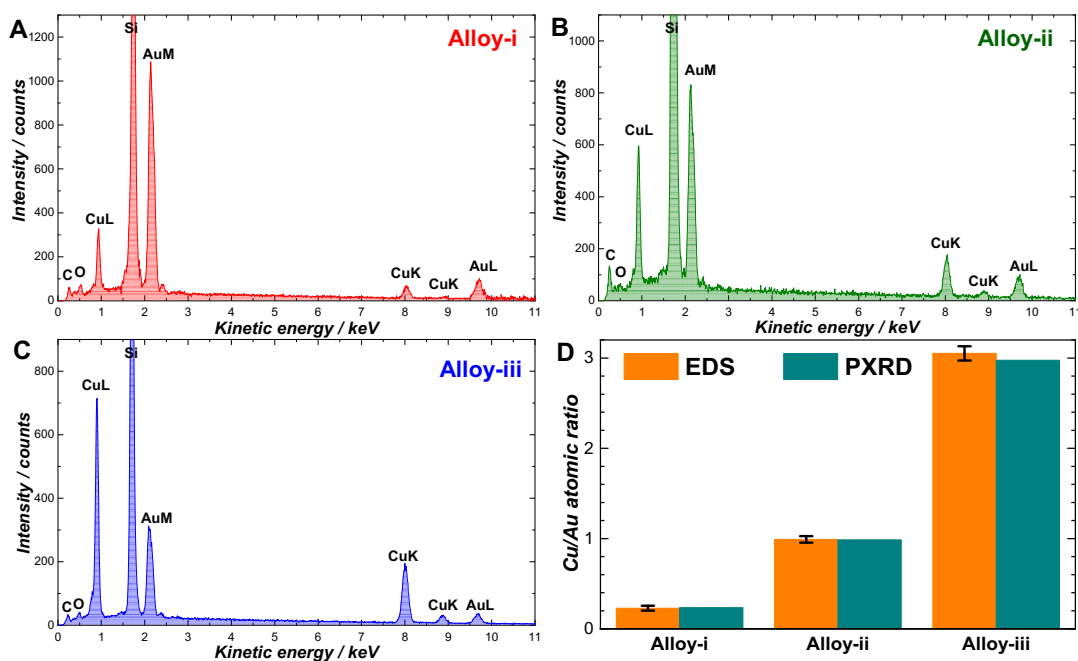


Figure S3. Energy dispersive spectra (EDS) of (A) Alloy-i, (B) Alloy-ii, and (C) Alloy-iii NPs. (D) Cu/Au atomic ratios quantified by EDS and PXRD of Alloy-i, Alloy-ii, and Alloy-iii NPs. When analyzing the EDS results, the Cu/Au atomic ratios were quantified based on the intensities of Cu L and Au M lines. The Si signals were from the Si substrates. The error bars represented the standard deviations of the results collected from 3 different regions of each specimen. The Cu/Au atomic ratios were also calculated according to the peak position of the (111) diffraction in the PXRD patterns using the Vegard's law.

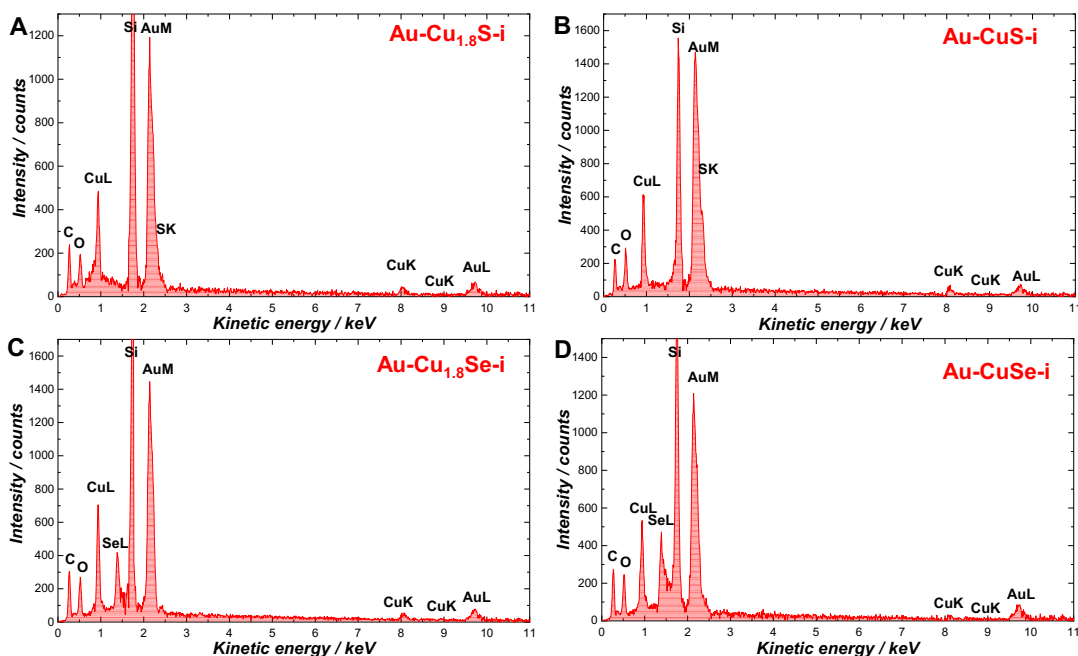


Figure S4. EDS of (A) Au@Cu_{1.8}S-i, (B) Au@CuS-i, (C) Au@Cu_{1.8}Se-i, and (D) Au@CuSe-i NPs.

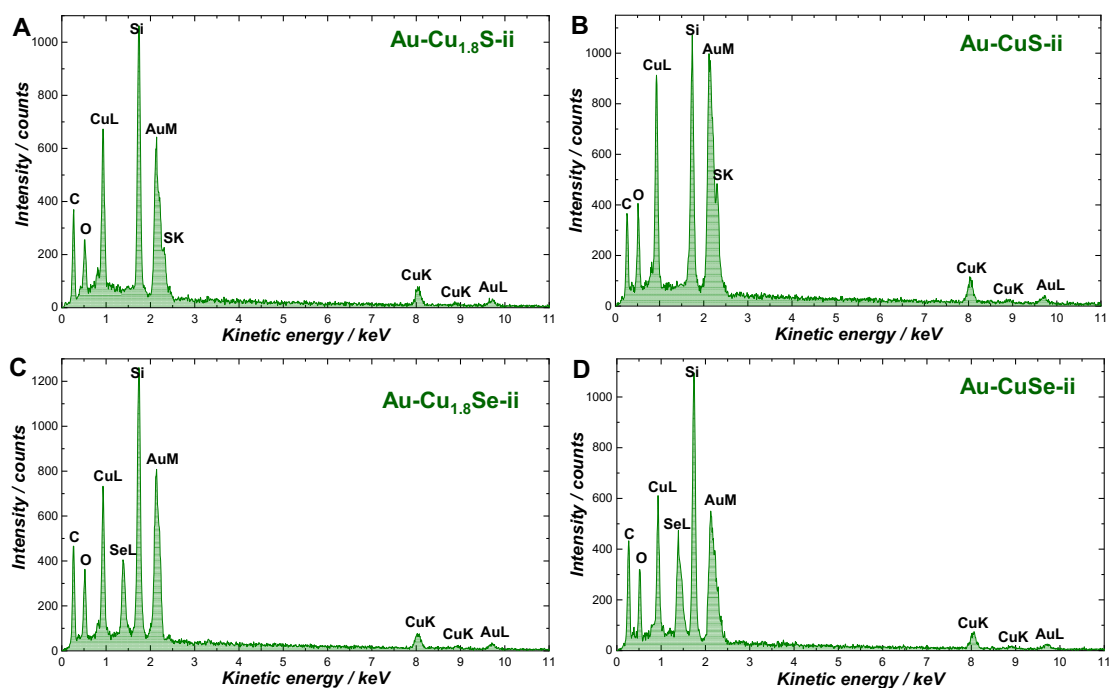


Figure S5. EDS of (A) Au@Cu_{1.8}S-ii, (B) Au@CuS-ii, (C) Au@Cu_{1.8}Se-ii, and (D) Au@CuSe-ii NPs.

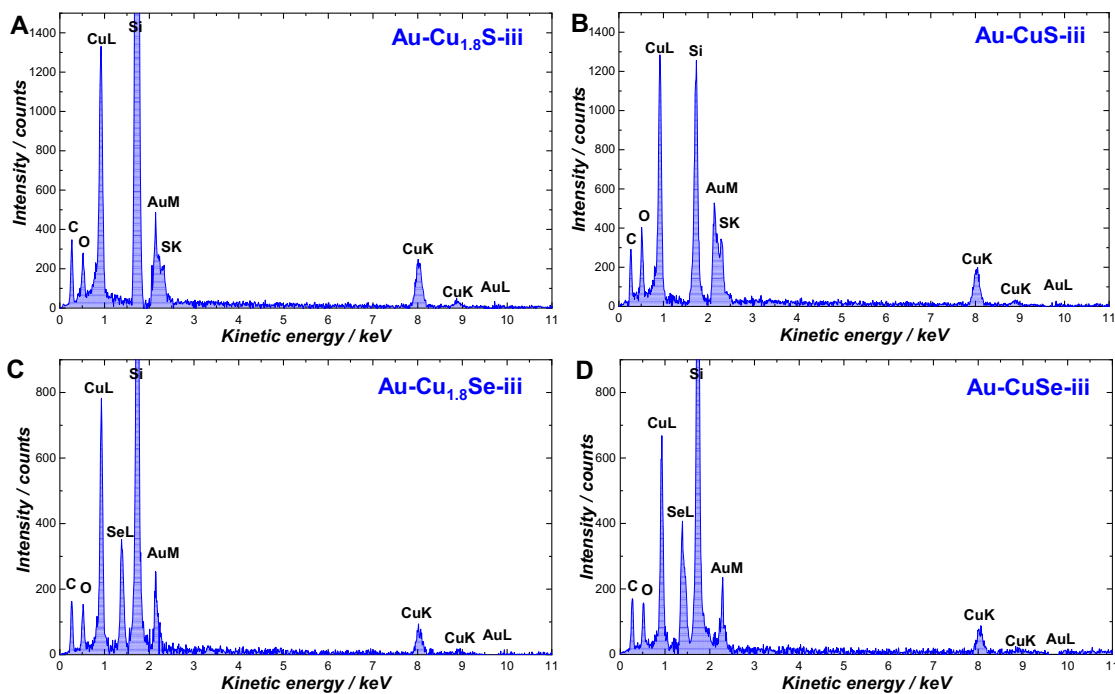


Figure S6. EDS of (A) Au@Cu_{1.8}S-iii, (B) Au@CuS-iii, (C) Au@Cu_{1.8}Se-iii, and (D) Au@CuSe-iii NPs.

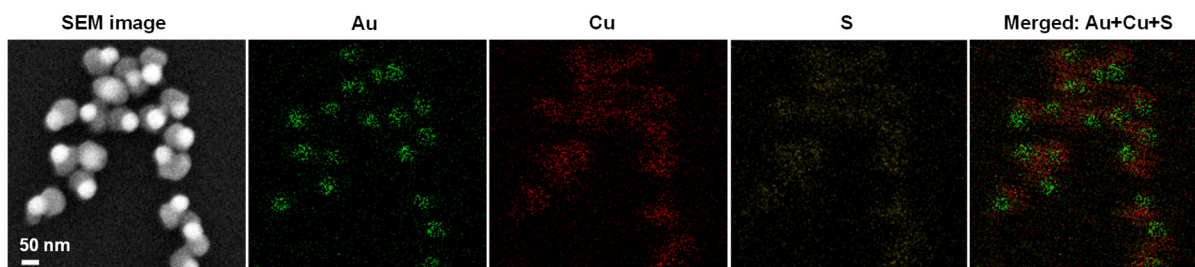


Figure S7. SEM image and EDS-elemental maps (Au, Cu, S, merged Au+Cu+S) of Au@Cu_{1.8}S-ii NPs.

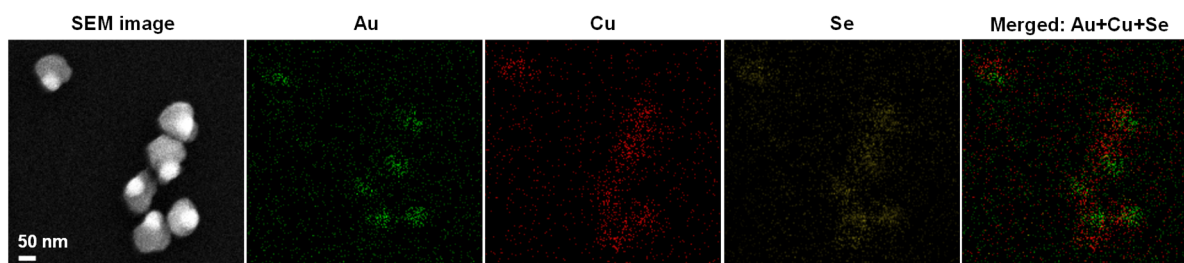


Figure S8. SEM image and EDS-elemental maps (Au, Cu, Se, merged Au+Cu+Se) of Au@Cu_{1.8}Se-ii NPs.

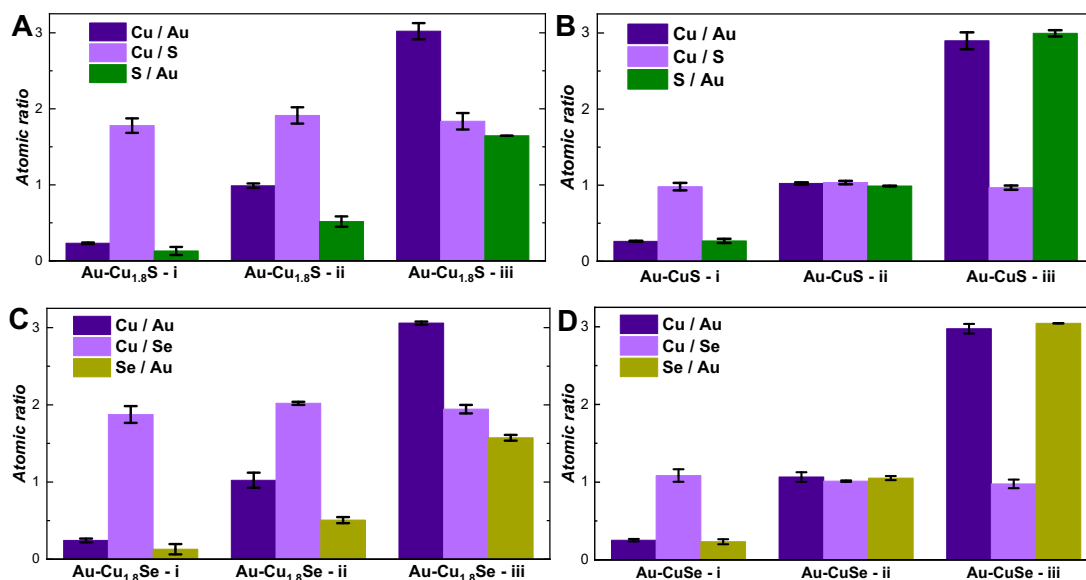


Figure S9. Atomic ratios of Cu/Au, Cu/E, and E/Au (quantified by EDS, E = S or Se) of (A) Au@Cu_{1.8}S, (B) Au@CuS, (C) Au@Cu_{1.8}Se, and (D) Au@CuSe heterostructured NPs.

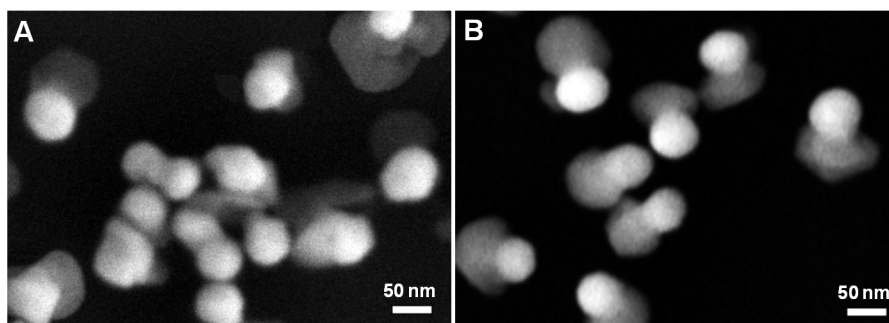


Figure S10. SEM images of (A) Au@CuS-i and (B) Au@CuSe-i NPs.

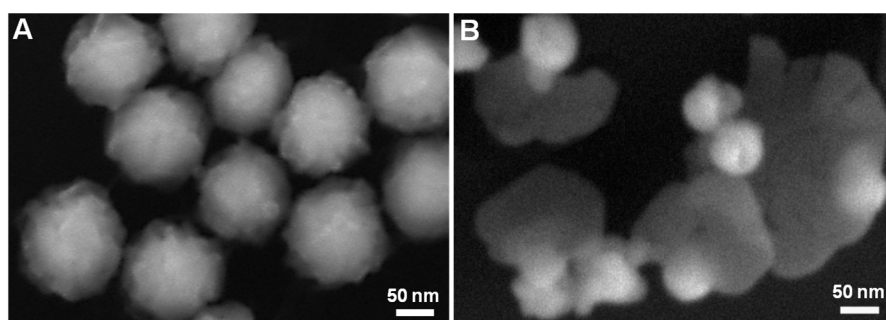


Figure S11. SEM images of (A) Au@CuS-iii and (B) Au@CuSe-iii NPs.

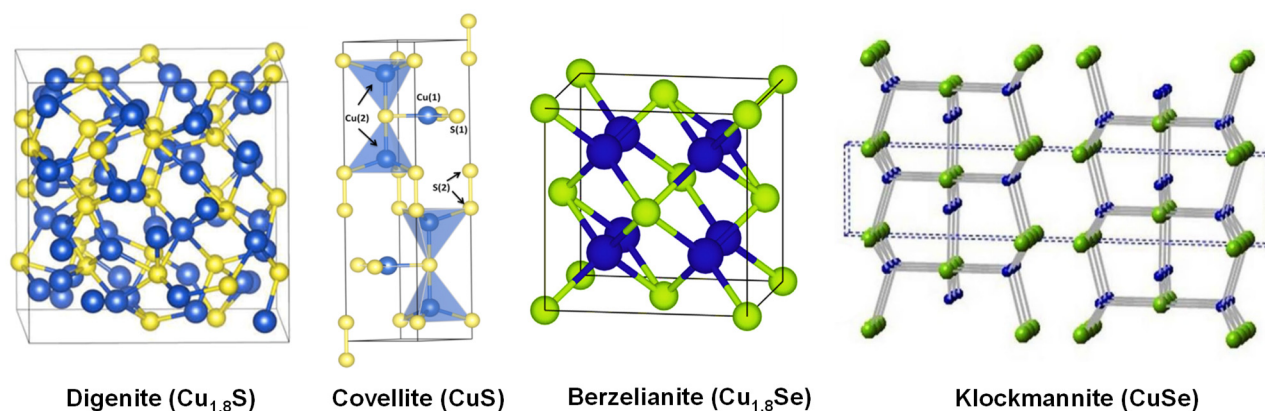


Figure S12. Structures of the unit cells of digenite (Cu_{1.8}S), covellite (CuS), berzelianite (Cu_{1.8}Se), and klockmannite (CuSe). The blue, yellow, and green spheres represent Cu, S, and Se atoms, respectively. The unit cell structure of Cu_{1.8}S was reprinted with permission from ref. S5. Copyright 2012 American Institute of Physics. The unit cell structure of CuS was reprinted with permission from ref. S6. Copyright 2014 American Chemical Society. The unit cell structure of Cu_{1.8}Se was reprinted with permission from ref. S7. Copyright 2015 Elsevier. The unit cell structure of CuSe was reprinted with permission from ref. S8. Copyright 2014 Nature Publishing Groups.

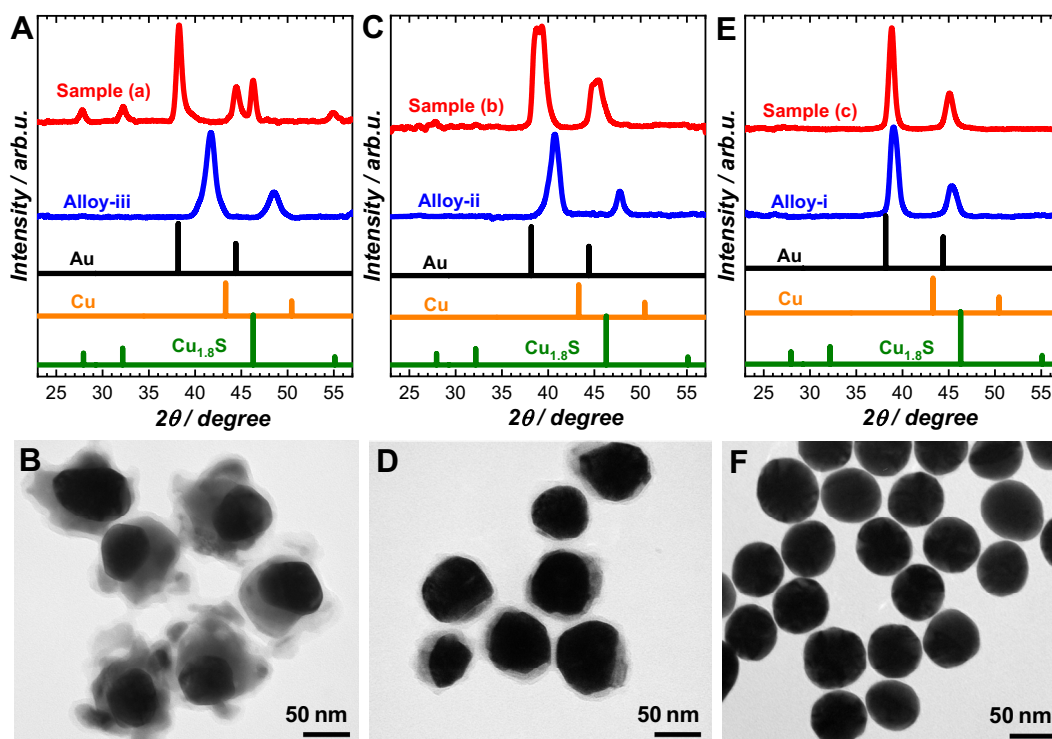


Figure S13. (A) PXR D pattern and (B) TEM image of Sample (a). (C) PXR D pattern and (D) TEM image of Sample (b). (E) PXR D pattern and (F) TEM image of Sample (c). Samples (a), (b), and (c) were synthesized by reacting Alloy-iii, Alloy-ii, and Alloy-i NPs, respectively, with 5.0 mM thioacetamide in TEG at 280 °C for 15 min. In panels A, C, and E, the standard patterns of Au, Cu (JCPDS 04-0836), and $\text{Cu}_{1.8}\text{S}$ (digenite, JCPDS 24-61), as well as the PXR D patterns of the parental alloy NPs are also shown for comparison.

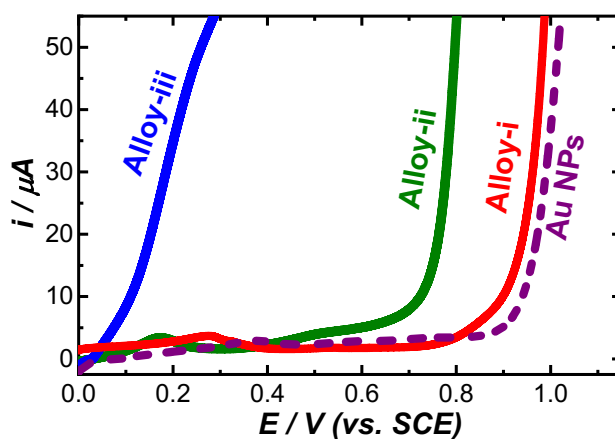


Figure S14. Linear sweep voltammetry (LSV) curves of Au, Alloy-i, Alloy-ii, and Alloy-iii NPs on glassy carbon electrodes in a 0.5 M H_2SO_4 electrolyte at a potential sweep rate of 50 mV s^{-1} .

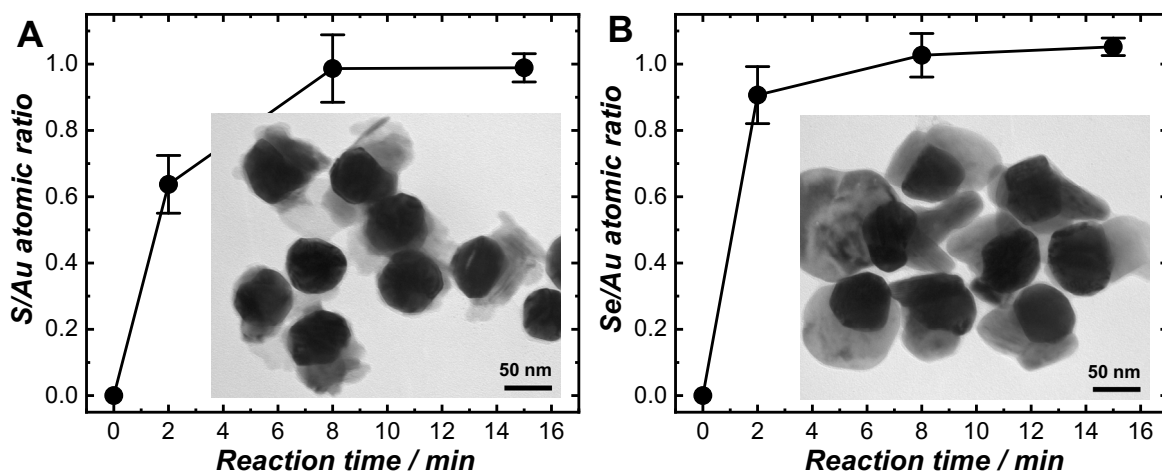


Figure S15. (A) Temporal evolution of S/Au atomic ratios (quantified by EDS) during the reactions between Alloy-ii NPs and 36 mM thioacetamide in TEG at 220 °C. (B) Temporal evolution of Se/Au atomic ratios (quantified by EDS) during the reactions between Alloy-ii NPs and 1.2 mM selenourea in TEG at 200 °C. The insets show the TEM images of the Au@CuS and Au@CuSe products kinetically trapped at a reaction time of 2 min.

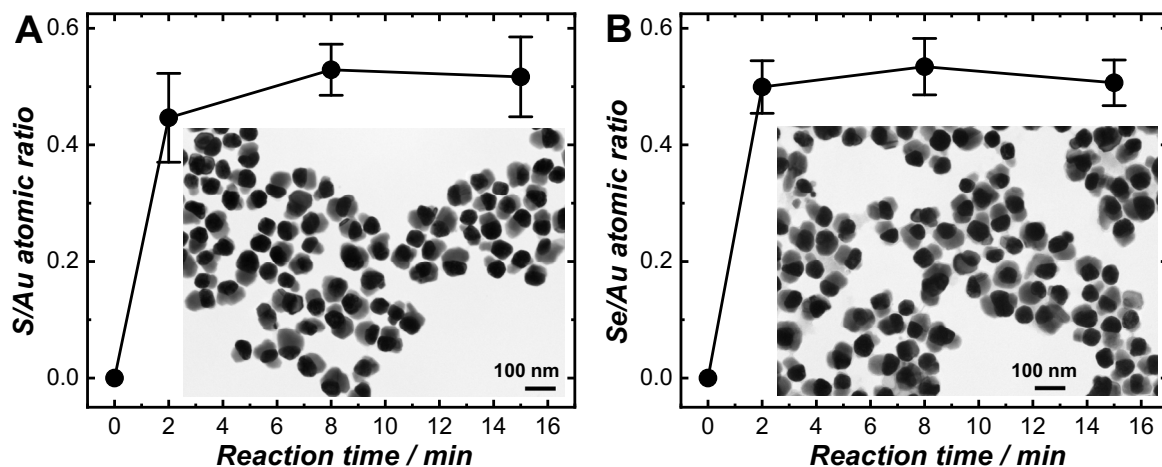


Figure S16. (A) Temporal evolution of S/Au atomic ratios (quantified by EDS) during the reactions between Alloy-ii NPs and 10 mM thioacetamide in TEG at 280 °C. (B) Temporal evolution of Se/Au atomic ratios (quantified by EDS) during the reactions between Alloy-ii NPs and 0.60 mM selenourea in TEG at 240 °C. The insets show the TEM images of the Au@Cu_{1.8}S and Au@Cu_{1.8}Se products kinetically trapped at a reaction time of 2 min.

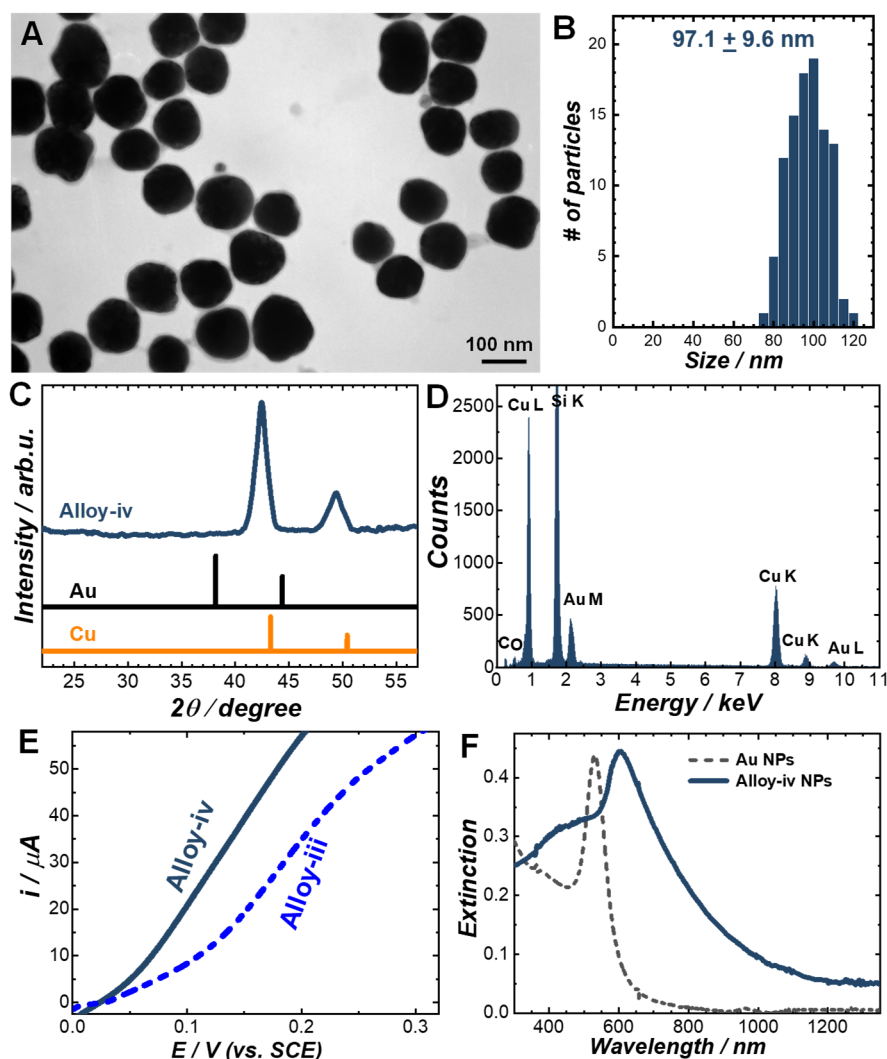


Figure S17. (A) TEM image and (B) size distribution of Alloy-iv NPs. The histogram shown in panel B was obtained from 100 nanoparticles in the TEM images. (C) PXRD pattern of Alloy-iv NPs. The standard diffraction patterns of Au and Cu are also shown as the reference. (D) EDS of Alloy-iv NPs. The Si signals were from the Si substrates. The Cu/Au atomic ratio was quantified to be 6.92 ± 0.29 based on the intensities of Cu L and Au M lines. The Cu/Au atomic ratio quantified by EDS was in good agreement with the value calculated from the PXRD pattern using the Vegard's law (7.12). (E) LSV curves of Alloy-iv (solid curve) and Alloy-iii (dash curve) NPs on glassy carbon electrodes in a 0.5 M H_2SO_4 electrolyte at a potential sweep rate of 50 mV s^{-1} . (F) Optical extinction spectrum of Alloy-iv NPs (solid curve). The extinction spectra were collected from colloidal NPs suspended in ethanol at room temperature. The extinction spectrum of Au NPs (52.3 ± 5.6 nm in diameter) is shown as the dash curve for comparison.

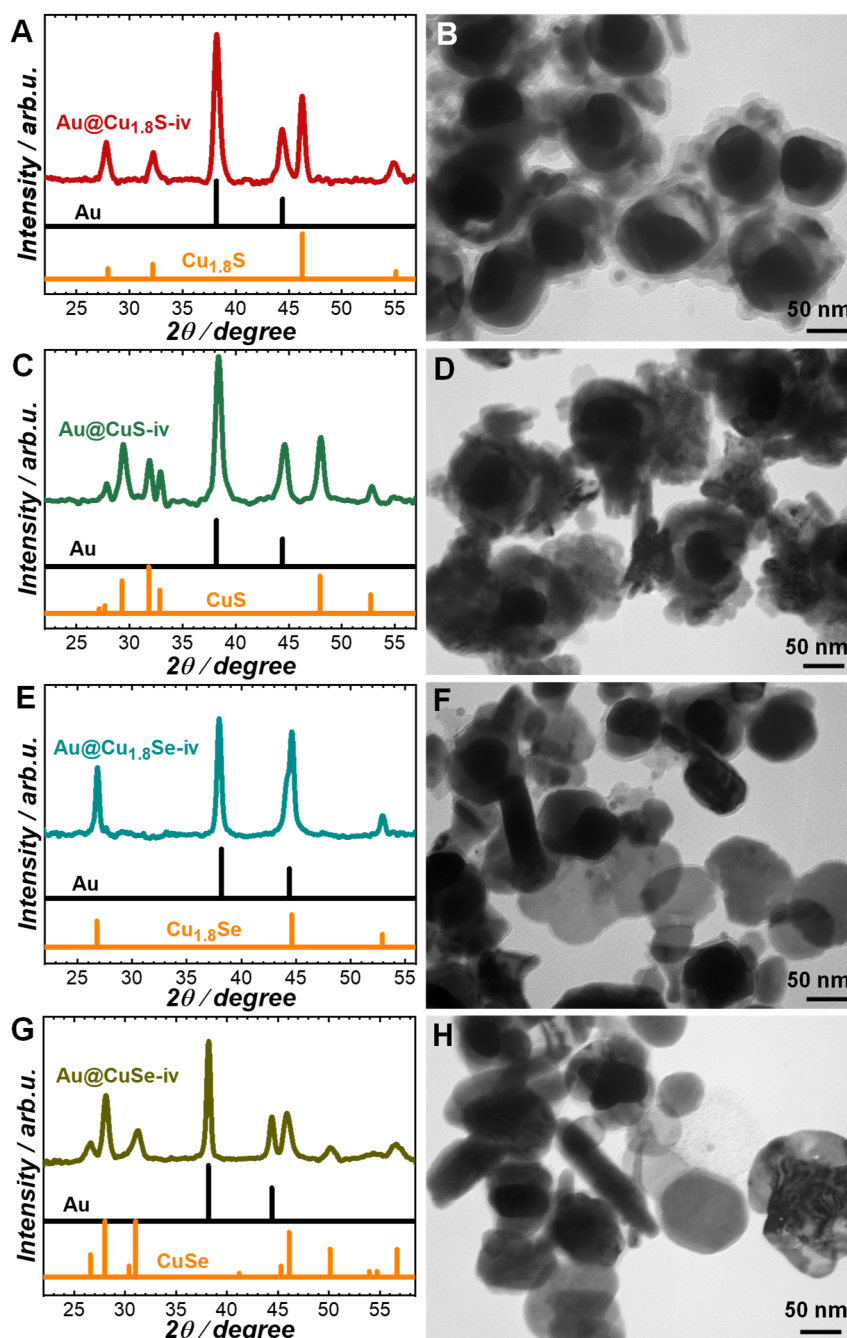


Figure S18. (A) PXRD pattern and (B) TEM image of Au@Cu_{1.8}S-iv NPs, which were synthesized by reacting Alloy-iv NPs with 4.0 mM thioacetamide in TEG at 280 °C for 15 min. (C) PXRD pattern and (D) TEM image of Au@CuS-iv NPs, which were synthesized by reacting Alloy-iv NPs with 25 mM thioacetamide in TEG at 220 °C for 15 min. (E) PXRD pattern and (F) TEM image of Au@Cu_{1.8}Se-iv NPs, which were synthesized by reacting Alloy-iv NPs with 0.20 mM selenourea in TEG at 240 °C for 15 min. (G) PXRD pattern and (H) TEM image of Au@CuSe-iv NPs, which were synthesized by reacting Alloy-iv NPs with 0.80 mM selenourea in TEG at 200 °C for 15 min. The standard diffraction patterns of Au, Cu_{1.8}S, CuS (covellite, JCPDS 6-464), Cu_{1.8}Se (berzelianite, JCPDS 6-680), and CuSe (klockmannite, JCPDS 6-427) are shown as the references for comparison in panels A, C, E, and G.

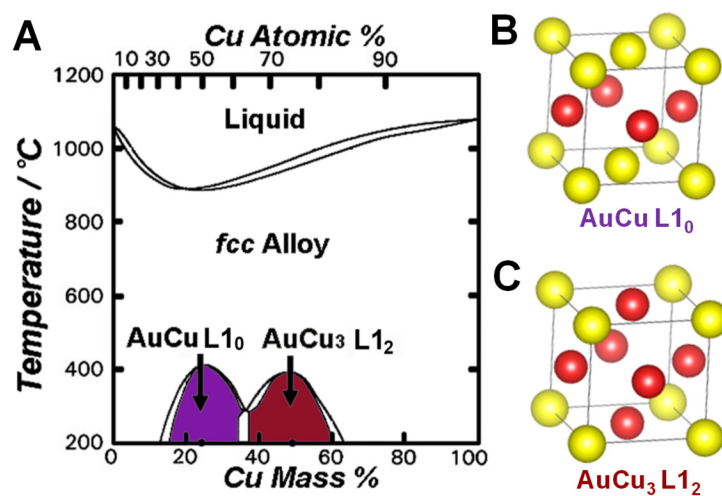


Figure S19. (A) Phase diagram of bulk Au–Cu bimetallic materials. Unit cell structures of (B) AuCu L1₀ and (D) AuCu₃ L1₂ intermetallic compounds. The yellow and red spheres represent Au and Cu atoms, respectively. Reprinted with permission from ref. S2. Copyright 2018 American Chemical Society.

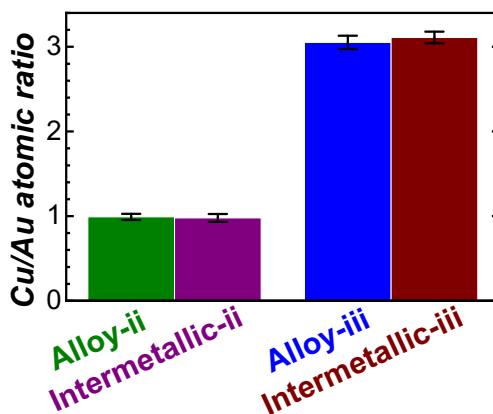


Figure S20. Cu/Au atomic ratios (quantified by EDS) of Alloy-ii, Intermetallic-ii, Alloy-iii, and Intermetallic-iii NPs.

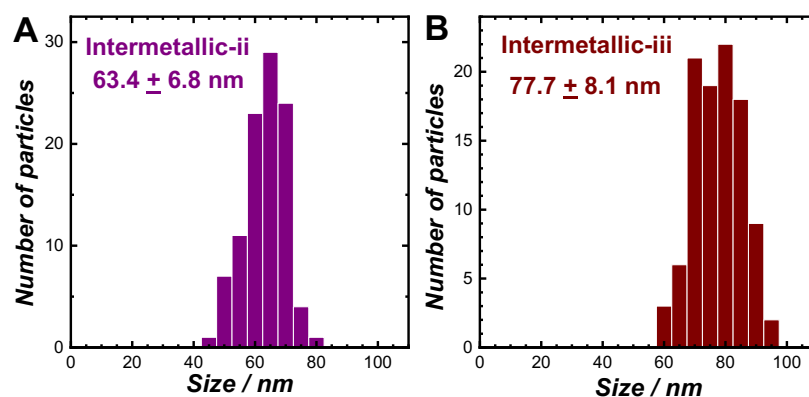


Figure S21. Size distributions of (A) Intermetallic-ii and (B) Intermetallic-iii NPs. The histograms were obtained from 100 NPs in the TEM images of each sample. The average diameters and standard deviations of the NPs were shown in each panel.

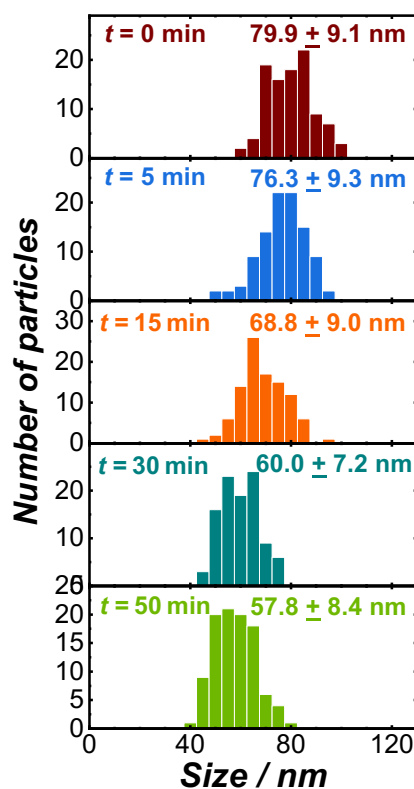


Figure S22. Temporal evolution of size distributions of the metallic domains in the heteronanostructures when reacting Intermetallic-iii NPs with 30 mM thioacetamide in TEG at 220 °C. The histograms were obtained from 100 NPs in the TEM images of each sample. The average diameters and standard deviations of the NPs were shown in each panel.

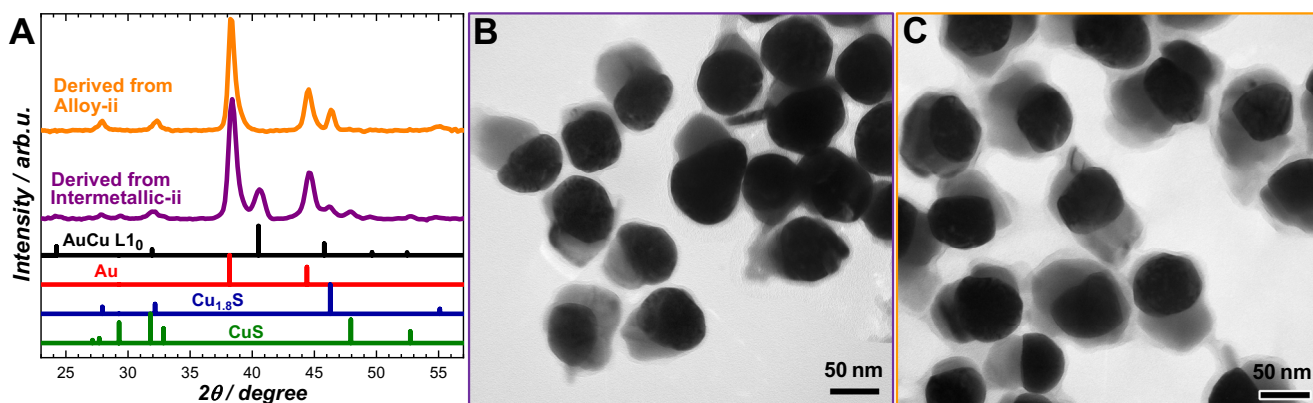


Figure S23. (A) PXRD patterns and TEM images of the heteronanostructures derived from (B) Intermetallic-ii and (C) Alloy-ii NPs after reacting with 10 mM thioacetamide in TEG at 280 °C for 15 min. The standard PXRD patterns of Au, Cu_{1.8}S, CuS, and intermetallic AuCu L1₀ (JCPDS 25-1220) are also shown in panel A for reference. The TEM image in panel C is the same as the one in Figure 1B.

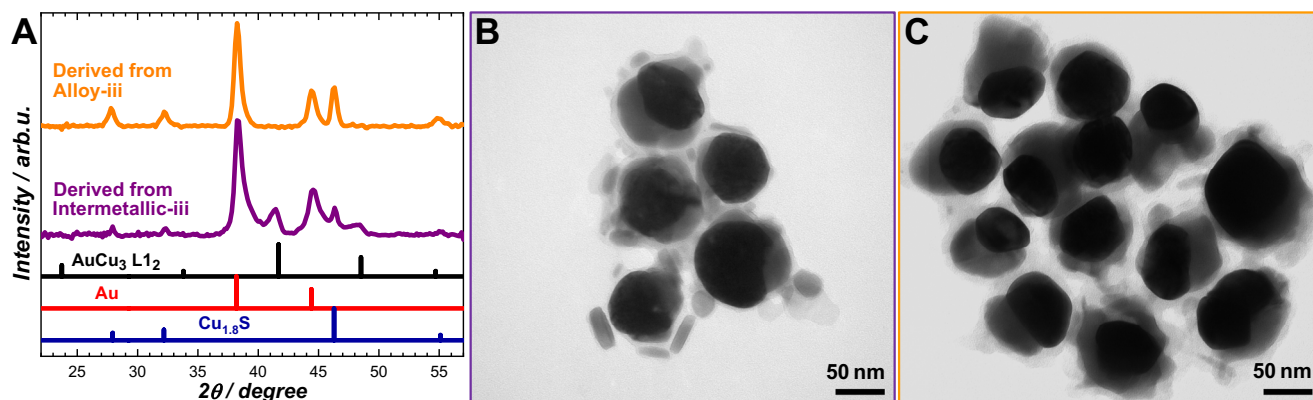


Figure S24. (A) PXRD patterns and TEM images of the heteronanostructures derived from (B) Intermetallic-iii and (C) Alloy-iii NPs after reacting with 6.0 mM thioacetamide in TEG at 280 °C for 15 min. The standard PXRD patterns of Au, Cu_{1.8}S, and intermetallic AuCu₃ L1₂ (JCPDS 35-1537) are also shown in panel A for reference. The TEM image in panel C is the same as the one in Figure 1B.

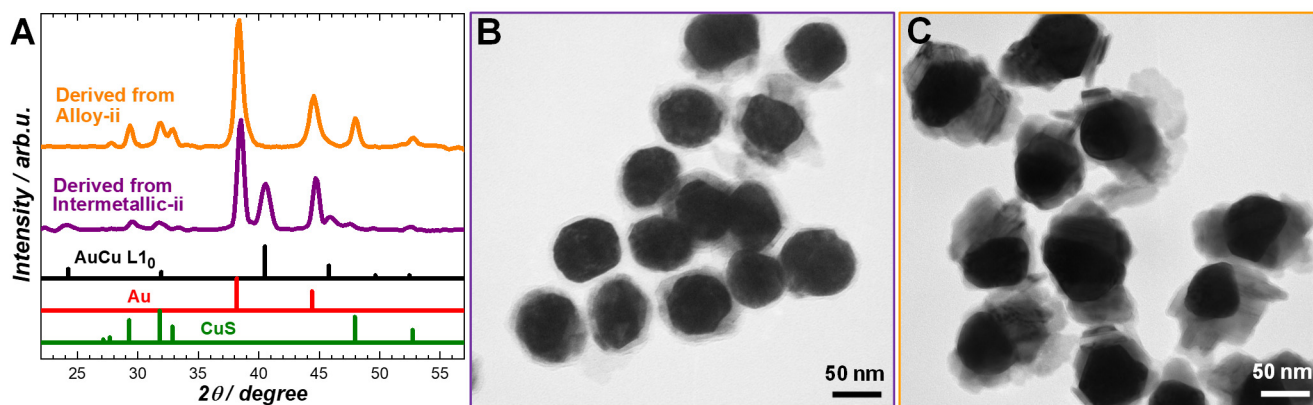


Figure S25. (A) PXRD patterns and TEM images of the heteronanostructures derived from (B) Intermetallic-ii and (C) Alloy-ii NPs after reacting with 36 mM thioacetamide in TEG at 220 °C for 15 min. The standard PXRD patterns of Au, CuS, and intermetallic AuCu L₁₀ are also shown in panel A for reference. The TEM image in panel C is the same as the one in Figure 1C.

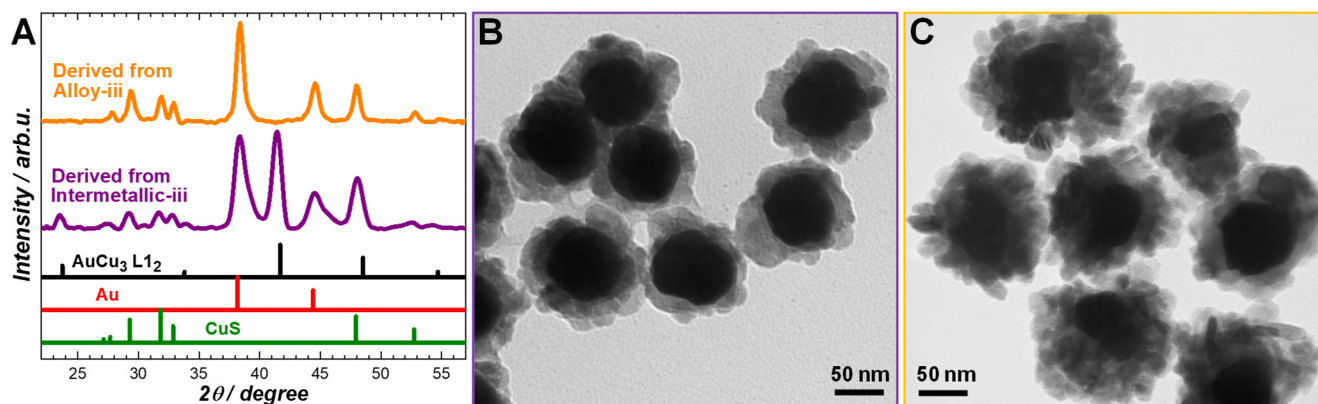


Figure S26. (A) PXRD patterns and TEM images of the heteronanostructures derived from (B) Intermetallic-iii and (C) Alloy-iii NPs after reacting with 30 mM thioacetamide in TEG at 220 °C for 15 min. The standard PXRD patterns of Au, CuS, and intermetallic AuCu₃ L₁₂ are also shown in panel A for reference. The TEM image in panel B is the same as the one in Figure 5J. The TEM image in panel C is the same as the one in Figure 1C.

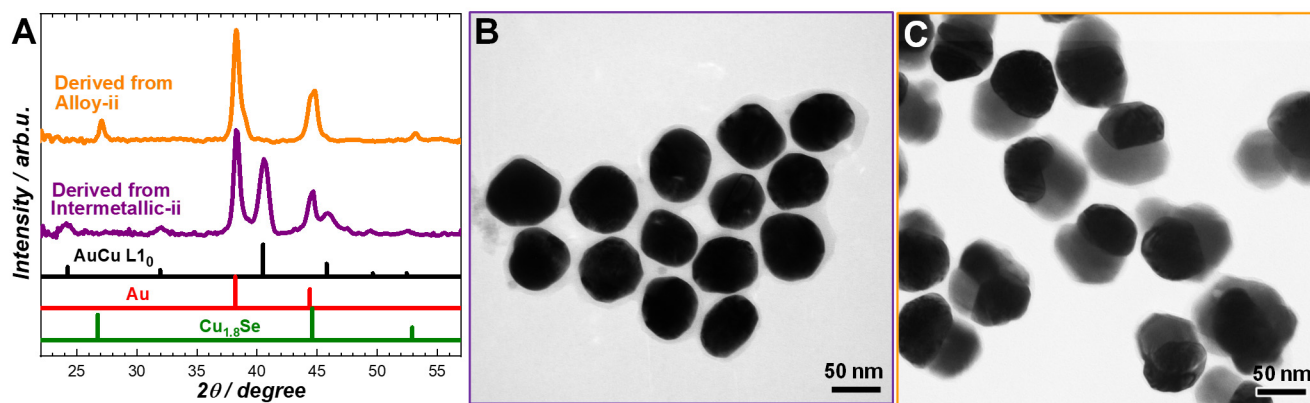


Figure S27. (A) PXRD patterns and TEM images of the heteronanostructures derived from (B) Intermetallic-ii and (C) Alloy-ii NPs after reacting with 0.6 mM selenourea in TEG at 240 °C for 15 min. The standard PXRD patterns of Au, Cu_{1.8}Se, and intermetallic AuCu L₁₀ are also shown in panel A for reference. The TEM image in panel C is the same as the one in Figure 1D.

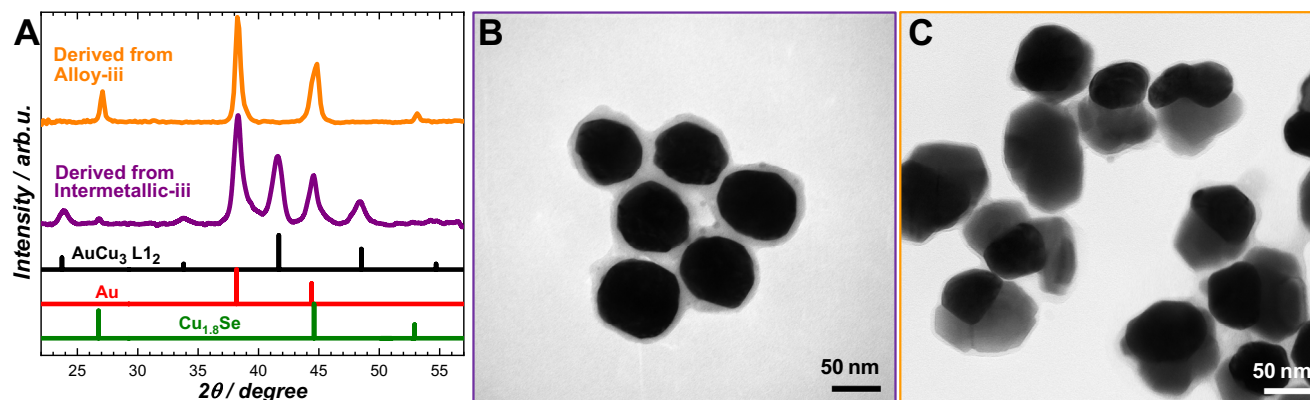


Figure S28. (A) PXRD patterns and TEM images of the heteronanostructures derived from (B) Intermetallic-iii and (C) Alloy-iii NPs after reacting with 0.3 mM selenourea in TEG at 240 °C for 15 min. The standard PXRD patterns of Au, Cu_{1.8}Se, and intermetallic AuCu₃ L₁₂ are also shown in panel A for reference. The TEM image in panel C is the same as the one in Figure 1D.

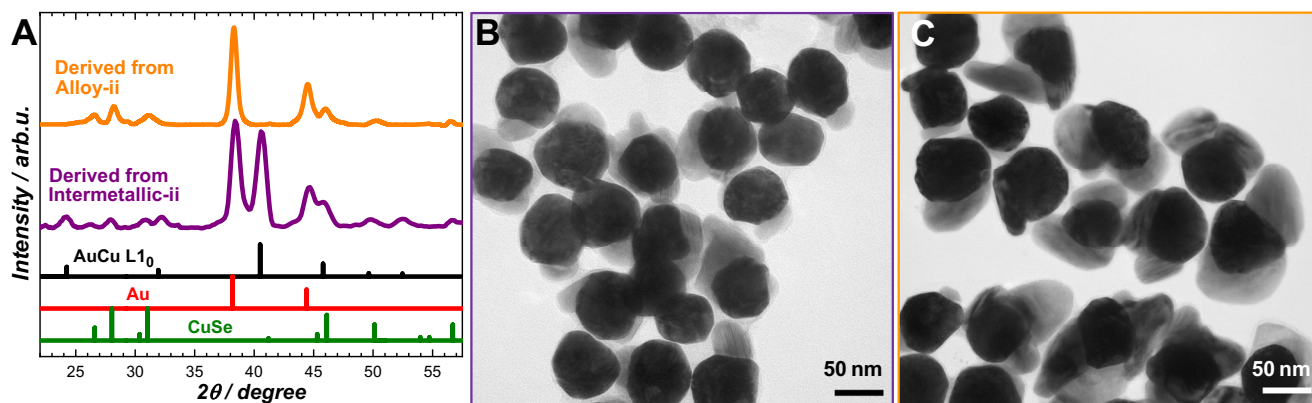


Figure S29. (A) PXRD patterns and TEM images of the heteronanostructures derived from (B) Intermetallic-ii and (C) Alloy-ii NPs after reacting with 1.2 mM selenourea in TEG at 200 °C for 15 min. The standard PXRD patterns of Au, CuSe, and intermetallic AuCu L₁₀ are also shown in panel A for reference. The TEM image in panel C is the same as the one in Figure 1E.

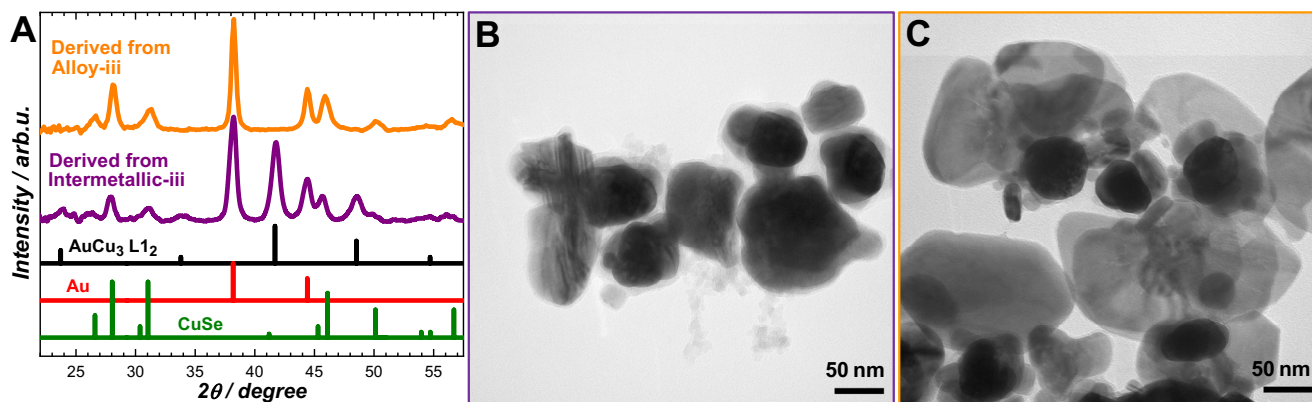


Figure S30. (A) PXRD patterns and TEM images of the heteronanostructures derived from (B) Intermetallic-iii and (C) Alloy-iii NPs after reacting with 0.90 mM selenourea in TEG at 200 °C for 15 min. The standard PXRD patterns of Au, CuSe, and intermetallic AuCu₃ L₁₂ are also shown in panel A for reference. The TEM image in panel C is the same as the one in Figure 1E.

3. References for Supporting Information

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