Electronic Supplementary Information (ESI)

Harnessing Molecule–Solid Duality of Nanoclusters/Nanoparticles for Nanoscale Control of Size, Shape and Alloying

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1. Experimental Details

**Chemicals.** Copper(II) chloride dihydrate (CuCl\(_2\)·2H\(_2\)O 99% pure) was obtained from Lancaster; Hydrogen tetrachloroaurate (III) hydrate (HAuCl\(_4\)) was obtained from Strem, and 1–Decanethiol (96%), Potassium bromide (99%) were obtained from Sigma Aldrich; Tetra–n–octylammonium bromide (TOABr, 98%) was obtained from Alfa Aesar; Sodium borohydride (99%), hexane and other common solvents used were obtained from Aldrich. Water was purified with a Millipore Direct–Q system with a final resistance of 18.2 M Ohm.

**Synthesis.** Au nanoparticles. The synthesis of decanethiolate capped Au nanoparticles followed the modified two–phase reduction method\[^{[1,2]}\]. Cu nanoclusters. The synthesis of decanethiolate–capped Cu nanoclusters was recently described\[^{[3]}\]. Briefly, CuCl\(_2\) was dissolved in water in the presence of 4.3 M KBr. Cu\(^{2+}\) was converted to CuBr\(_4^{2–}\) which was transferred from aqueous phase to the organic phase by adding a solution of TOABr in toluene (40 mL toluene, 180 mM TOABr). After 20 minutes of vigorous stirring, the aqueous solution was removed. The toluene solution was stirred under argon purge to eliminate oxygen from the system. 0.36 mL of decanethiols was added and the solution was stirred for another 1 hr, resulting in the color change of solution from dark purple to a light green. NaBH\(_4\) solution (25 mL, 0.4 M) was added dropwise. After reaction for 2 hr under argon, the aqueous layer was removed, and the solution was stirred overnight. See Figures S1-S2.

![Figure S1](link) TEM micrographs for Au (A, 2.0 ±0.7 nm), Cu nanoparticles (B, ~0.5 nm) capped with DT monolayer, and Au nanoclusters capped by octadecanethiol (~1 nm).

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Figure S2. (A) A combined SAXS and WAXS spectrum of the nanoclusters (Inset A: two-dimensional WAXS scattering patterns (radial averaging). Inset: a scheme illustrating the interparticle distance (d) in the concentrated suspension[4]). The observed peak (q = 13.4 nm\(^{-1}\)) was used to calculate the interparticle distance (d = 2π/q, where d is the interparticle core distance) yielding an inter-core distance of 0.5 nm (Figure 1B). The average particle size was estimated to be close to or less than 0.5 nm. (B), Maldi–Tof mass spectrum for as–synthesized thiolate–capped copper nanoclusters. The spectrum in Figure S3 was collected for a sample prepared by TLC separation of the nanoclusters from a solution. The matrix used for the sample was DCTB (trans–2–[3–(4–tert–butylphenyl)–2–methyl–2–propenylidene]–malononitrile). See the following Table for peak analysis: Primary peaks identified from the Maldi–Tof spectrum, and the possible structures and masses. For this sample of nanoparticles, peaks in the region of 600 ~ 1200 (m/z) were detected. Preliminary analysis of the peak positions for the significant peaks, along with calculated masses for the associated clusters, seemed to suggest the presence of Cu\(_{5~7}\) clusters such as Cu\(_6\)(SR)\(_3\), Cu\(_5\)(SH)\(_3\)SR, Cu\(_5\)(SH)\(_2\)SR, Cu\(_7\)(SH)\(_4\)SR, and Cu\(_7\)(SH)\(_2\)(SR)\(_2\).  

<table>
<thead>
<tr>
<th>Peak Position (Primary Peak)</th>
<th>Possible Structure</th>
<th>Calculated Mass</th>
</tr>
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<tbody>
<tr>
<td>655.11</td>
<td>Cu(_6)(SH)(_3)SR</td>
<td>653.77</td>
</tr>
<tr>
<td>750.99</td>
<td>Cu(_5)(SH)(_3)SR</td>
<td>750.38</td>
</tr>
<tr>
<td>857.01</td>
<td>Cu(_5)(SH)(_2)(SR)(_2)</td>
<td>857.58</td>
</tr>
<tr>
<td>1013.77</td>
<td>Cu(_7)(SH)(_2)SR</td>
<td>1011.02</td>
</tr>
<tr>
<td>1185.01</td>
<td>Cu(_7)(SH)(_2)(SR)(_2)</td>
<td>1184.35</td>
</tr>
</tbody>
</table>

AuCu alloy nanoparticles. The synthesis of AuCu nanoparticles was following the modified two–phase reduction method[1,2]. Briefly, CuCl\(_2\) and HAuCl\(_4\) were dissolved in water in controlled ratio. With the presence of 4.3 M KBr, Cu\(^{2+}\) is converted to CuBr\(_2\) which was transferred from aqueous phase to the organic phase by adding a solution of TOABr in toluene (40 mL toluene, 180 mM TOABr). After 20 minutes of vigorous stirring, the aqueous solution was removed. The toluene solution was stirred under argon purge to eliminate all oxygen from the system. 0.36 mL decanethiol was added and the solution was stirred for another 1 hr. NaBH\(_4\) solution (25mL, 0.4 M) was added dropwise. The solution was stirred for 4 hr.

Thermal processing. The solutions of the as–synthesized Au nanoparticles and Cu nanoclusters were mixed in a controlled ratio[5,6]. The mixed solution was then concentrated by a factor of ~15 in a glass reactor, and was kept in an oven under controlled temperature (150–170 °C) and reaction time. 156 °C was identified as an optimal temperature for forming nanocubes by examining a series of temperatures ranging from 150 to 172 °C. At a lower temperature (e.g., 150 °C), various shapes (spheres, triangles, cubes, hexagons, etc) were observed. At a higher temperature (e.g., 172 °C), the particles were largely aggregated. The final products were subjected to cleaning cycles via suspension in ethanol and acetone, and centrifugation at least four times to ensure a complete removal of solvent and any possible byproducts. The thermal processing of AuCu alloy nanoparticles was carried our similarly.
**Figure S3.** TEM micrographs of Au_{66}Cu_{34} alloy nanocubes formed from a binary solution of Cu nanoclusters and Au nanoparticles (Cu:Au molar ratio ~8, T=156 °C, t_i=3 hr).

**Instrumentation and measurements.** The nanoparticles were characterized using Small Angle X–Ray Spectroscopy (SAXS) and Wide Angle X–Ray Spectroscopy (WAXS), Transmission Electron Microscopy (TEM), and X–Ray Photoelectron Spectroscopy (XPS) to characterize the nanoparticles. SAXS and WAXS patterns of copper nanoparticle suspensions were recorded at room temperature with CuKα radiation from a 1.2 kW rotating anode X–ray generator (007 HF, Rigaku Denki Co. Ltd, Japan), and both two–dimensional multi–wire detector and image plate were used for low and high scattering angle respectively. The sample–detector distance of 1.5 m (SAXS) and 34.8mm (WAXS) allowed a “q range” from 0.006 to 0.12 Å–1 and 0.1 to 4 Å–1 \([q = 4\pi/\lambda \sin(\theta/2), \text{where } \lambda \text{ is x–ray wavelength and } \theta \text{ is scattering angle}]. \) The scattering intensity after subtraction of the empty cell and background was circularly averaged.

Maldi–Tof mass spectra were collected with an Etтан instrument from GE Healthcare operated in reflection mode with the accelerating voltage held constant at 20 kV. The calibration standards used were proteins of molecular weight 1046.54 and 2464.91. The matrix used for the sample was DCTB (trans–2–[3–(4–tert–butylphenyl)–2–methyl–2–propenylidene]–malononitrile), while that used for calibrants was sinapinic acid.

Acid digestates of samples were analyzed using Inductively-coupled plasma optical emission spectroscopy (ICP-OES), which was performed using a Perkin Elmer 2000 DV ICP-OES utilizing a cross flow nebulizer with the following parameters: plasma 18.0 L Ar\textsubscript{g}/min; auxiliary 0.3 L Ar\textsubscript{g}/min; nebulizer 0.73 L Ar\textsubscript{g}/min; power 1500 W; peristaltic pump rate 1.40 mL/min. Reported values <1.0 mg/L were analyzed using a Meinhard nebulizer coupled to a cyclonic spray chamber to increase analyte sensitivity at the following parameters: 18.0 L Ar\textsubscript{g}/min; auxiliary 0.3 L Ar\textsubscript{g}/min; nebulizer 0.63 L Ar\textsubscript{g}/min; power 1500 W; peristaltic pump rate 1.00 mL/min. Elemental concentrations were determined by measuring one or more emission lines (nm) to check for interferences. The nanoparticle samples were dissolved in concentrated aqua regia, and then diluted to concentrations in the range of 1 to 50 ppm for analysis. Multi-point calibration curves were made from dissolved standards with concentrations from 0 to 50 ppm in the same acid matrix as the unknowns. Laboratory check standards were analyzed every 6 or 12 samples, with instrument re-calibration if check standards were not within ±5% of the initial concentration. Instrument reproducibility (n=10) determined using 1 mg/L elemental solutions resulted in <±2% error for all elements. The metal composition was expressed as atomic percentage of the element in the nanoparticles.

High resolution TEM was carried out using a JEOL JEM 2010F with an acceleration voltage of 200kV and a routine point–to–point resolution of 0.194nm. TEM analysis was performed on an FEI Tecnai T12 Spirit Twin TEM/SEM electron microscope (120 kV). The nanoparticle samples were suspended in hexane solution and were drop cast onto a carbon–coated copper grid followed by solvent evaporation in air at room temperature.

XPS measurements were collected using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. This system uses a focused monochromatic Al Kα x–ray (1486.7 eV) source and a spherical section analyzer. The instrument has a 16 element multichannel detector. The x–ray beam used was a 100 W, 100 mm diameter that was rastered over a 1.3 mm by 0.2 mm rectangle on the sample. The x–ray
beam is incident normal to the sample and the photoelectron detector was at 45° off–normal. Wide scan data was collected using a pass energy of 117.4 eV. For the Ag3d5/2 line, these conditions produce FWHM of better than 1.6 eV. High energy resolution photoemission spectra were collected using a pass energy of 46.95. For the Ag3d5/2 line, these conditions produced FWHM of better than 0.77 eV. The binding energy (BE) scale is calibrated using the Cu2p3/2 feature at 932.62 ± 0.05 eV and Au4f at 83.96 ± 0.05 eV for known standards. The sample experienced variable degrees of charging. The vacuum chamber pressure during analysis was < 1.3x10^{-6} Pa. Samples were dropped onto a molybdenum substrate and were allowed to dry. The C1s peak was used as an internal standard (284.9 eV) for the calibration of the binding energy.

XRD data was collected on a Philips X’Pert diffractometer using Cu Kα radiation (λ = 1.5418 Å). The measurements were done in reflection geometry and the diffraction (Bragg) angles 2θ were scanned at a step of 0.025°. Each data point was measured for at least 20 seconds and several scans were taken of the sample.

The structural evolution of Au, Cu, and a physical mixture of Au and Cu nanoparticles subjected to heat treatment in the 25–225°C temperature range was examined in–situ, and in real–time with synchrotron–based x–ray diffraction. The experiment was performed at the National Synchrotron Light Source, Brookhaven National Laboratory, on beamline X20C using an x–ray energy of 6.9 keV (1.69Å wavelength). A linear position sensitive detector was employed to simultaneously record the entire XRD pattern around the face–centered cubic (111) and (200) peaks with two–second resolution time. The integrated intensity of the XRD peaks in the measured 2θ range of 42–56° is proportional to the volume of the crystalline (fcc) phase therefore providing information about the nanoparticle re–crystallization process.

2. Additional Theoretical and Experimental Data

![Figure S4. Theoretical melting curves for Au, Cu, Ag, and Pt particles as a function of particle radius (r) (The parameters used in the calculation are shown in Table S1. The theoretical melting curves calculated for different metal particles as a function of particle sizes (r–radius) are derived the thermodynamic model[7].)](image-url)

\[ \frac{T_p - T_{\infty}}{T_{\infty}} = -\frac{4}{\rho L 2 r} \left[ \gamma_s - \gamma_l \left( \frac{\rho_s}{\rho_l} \right)^{2/3} \right] \]

where \( T_p \) and \( T_{\infty} \) are melting temperatures of the particle and the bulk solid, respectively, \( r \) is the radius of the particle, \( \rho_s \) and \( \rho_l \) are the density of the solid and the liquid, \( \gamma_s \) and \( \gamma_l \) are the surface energy of the solid and the liquid, and \( L \) is the heat of fusion. The parameters used are listed in Table S1.
Table S1. Physical parameters used in the calculation of melting curves

<table>
<thead>
<tr>
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<th>ρ_s (kg/m³)</th>
<th>ρ_L (kg/m³)</th>
<th>T_∞ (K)</th>
<th>L (J/kg)</th>
<th>γ_s (J/m²)</th>
<th>γ_L (J/m²)</th>
</tr>
</thead>
</table>

Note: a) calculated based on the bimetallic composition and the data from the monometallic compositions; b) calculated based on an average between the monometallic data.

Figure S5. XPS spectra for a sample of Au₆₆Cu₃₄ nanoparticles obtained by thermal evolution (T=156 °C, tₜ = 3 hr). (A) O 1s region; (B) C 1s region; (C) Cu 2p region; (D) Au 4f region; (E) S 2p region; (F) Cu LMM region. (Au: Cu atomic ratio found by XPS: 48:52). Discussion: XPS analysis of the AuCu alloy nanoparticles (S.I. Figure S10) showed doublet peaks characteristic of Cu (2p) (932.5 eV for Cu (2p₃/2) and 952.5 eV for Cu (2p₁/2)), consistent with the literature values [11, 12]. In the S (2p) region, the doublet peak is detected at 163.5 eV and 162.3 eV for 2p₃/2 and 2p₁/2 respectively. The binding energy values for Cu (2p₁/2) and Au (4f) were found to be in good agreement with those reported [13]. In the Cu LMM region, the main peak position (569.1 eV) indicates that copper is in Cu (0) state for the alloy nanocubes. The higher–energy shoulder indicates the presence of Cu²⁺ peak from Cu₂S. The S 2p and Au 4f peaks are consistent with the presence of thiolate–capping molecules and Au in the nanoparticles. The nanoalloy character was also supported by the surface plasmon resonance band at ~560 nm (S.I. Figure S11), characteristic of AuCu alloys with sizes larger than 3 nm [14].
Figure S6. UV-visible spectra for a sample of AuCu nanoparticles (a) and a sample after thermal processing of a binary solution of Cu and Au nanoparticles (b).

Figure S7. HRTEM micrograph and FFT patterns for a sample of Au$_{51}$Cu$_{49}$ nanoparticles obtained by thermal evolution (T=156°C, th=3 hr).

Figure S8. TEM micrographs comparing AuCu nanoparticles obtained under different conditions: (a) th =1.5 hr (size ~3.5 nm & <2nm); (b) th =4.5 hr (size ~ 5.5 nm); (c) th =6 hr, (size ~4.5 nm) (a–c: Au$_{34}$Cu$_{66}$); (d) th =3 hr (size ~6 nm, Au$_{66}$Cu$_{34}$); (e) th =3 hr (size ~3.8nm, Au$_{66}$Cu$_{34}$); and (f) th =45 min (Au$_{21}$Cu$_{79}$). Feeding Cu:Au molar ratio: 8.5 (a, b, c, e), 4.0 (d), and 12.8 (f). (a–f: T=156°C).
**Figure S9.** XRD (A) and synchrotron XRD (x-ray energy: 6.9 keV) (B) patterns: (A) (a) Au$_{66}$Cu$_{34}$ nanocubes (i.e., sample in Figure 1); (b) Au$_{34}$Cu$_{66}$ nanoparticles (i.e., sample in Figure S8a). (B) (a) the initial Au$_{66}$Cu$_{34}$ nanocubes/Si; (b) after in situ heating at 260 °C for 10 min.

**Figure S10.** In–situ real–time synchrotron XRD for the evolution of a binary solution of Au nanoclusters (<1 nm) and Cu nanoclusters with a Cu:Au molar ratio of 8.5. (A–B) a map showing evolution of (111) and (200) during uniform ramping from 25 to 225 °C, a snapshot of XRD pattern at 215 °C, and XRD temperature evolution. Discussion: The detailed structural evolution was further probed for a binary system consisting of Cu and Au nanoclusters (<1nm) by real–time synchrotron XRD. Since both particles were small (<1 nm), we were able to capture the relative changes of (111) and (200) peaks in the structural evolution. During uniform temperature ramping from 25 to 225 °C, both crystallographic directions show a transient peak around 160 °C which we associate with the formation and dissolution of Cu$_2$S nanodisks.

**Figure S11.** TEM micrographs for samples from binary solutions of Cu + Pt and Cu + Ag nanoparticle systems. (A) a sample from heating a binary solution of Cu nanoclusters and Pt nanoparticles (T=220 °C, t$_h$ =1.5 hr); (B) Pt
nanoparticles; (C) a sample from heating a binary solution of Cu nanoclusters and Ag nanoparticles (T=145 °C, t_h =1.5 hr); (D) Ag nanoparticles. (All particles are capped with decanethiolate monolayers). 

**Figure S12:** TEM micrographs for samples from binary solutions of Au + Cu²⁺ absent with reducing agent and Au + Cu²⁺ present with reducing agent systems. (A) a sample from heating a binary solution of Cu precursors and Au nanoparticles absent with reducing agent (T=156 °C, t_h =3 hr) (Au:Cu=79:21) (size: 8.9±0.8 nm); (B) a sample from heating a binary solution of Cu precursors and Au nanoparticles present with reducing agent (T=156 °C, t_h =3 hr) (Au:Cu=66:34) (size: 9.4 ± 1.2 nm (length of rods); 2.6 ± 0.3 nm (width of rods); 5.8 ± 0.5 nm (sphere)).

**Discussion:** While larger–sized (9 nm) Au nanoparticles were obtained in the former case, and a mixture of larger–sized (9 nm) Au nanoparticles and Cu₂S nanorods/disks (2.6 nm width and 5.8 nm length) were detected in the latter case, there is no indication of the formation of the 3–4 nm sized alloy nanocubes, demonstrating the requirement of the nanoparticle/nanocluster precursors for the alloy nanocubes. This observation was also substantiated by XRD characterization of samples from binary solutions of Au + Cu²⁺ absent with reducing agent and Au + Cu²⁺ present with reducing agent systems. The XRD pattern resemble for the former resembles that for 8-9 nm sized Au nanoparticles. The XRD pattern resemble for the latter resembles those with a mixture of 5-6 nm sized Au nanoparticles. None of them detected patterns resembling the alloy nanocubes.

**References:**