Halide-Dependent Dealloying of Cu_x/Au_y Core/Shell Nanoparticles for Composition Analysis by Anodic Stripping Voltammetry

Supporting Information

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Anodic Stripping Voltammograms of Cu_1/Au_x Core/Shell Alloy Nanoparticles with Low Au Content (x = 0.001 and 0.01)

Figure S1 shows ASVs in 0.1 M $HClO_4$, 0.01 M KBr + 0.1 M $HClO_4$, and 0.01 M KCl + 0.1 M $HClO_4$ of $Cu_1/Au_{0.001}$ (Frame A) and $Cu_1/Au_{0.01}$ (Frame B) core/shell nanoparticles (NPs) attached to glass/ITO/APTES electrodes. These ASVs display a current range that enhances the smaller multiple oxidation peaks that are difficult to observe in the figures of the main paper. Depending on the electrolyte used, there are either 2 or 3 additional oxidation peaks more positive of the main Cu oxidation peak labeled as Cu^1 near -0.1 to 0.0 V. We note that it is difficult to assign these other oxidation peaks conclusively because the peak oxidation potentials depend on several factors, including metal coverage, NP size, and the atom coordination environment. The various peaks could be due to Cu oxidation for Cu atoms coordinated to Au atoms with different coordination number or due to Au oxidation of very small Au NPs or clusters that remain after Cu dealloying. Au oxidation potentials could be as low as 0.2 V, depending on the Au NP size. Some of these peaks could also be a combination of Au and Cu oxidation as observed for oxidation of Cu/Au core/shell NPs in KBr for higher Au

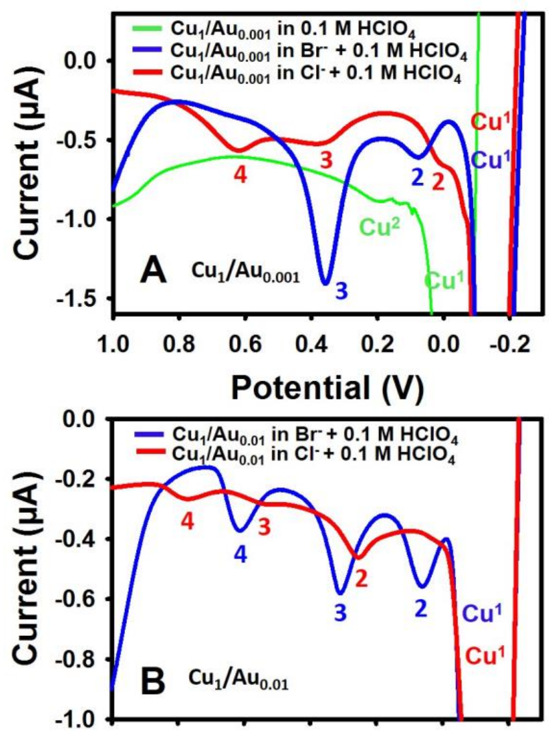

Figure S1. ASVs of (A) $Cu_1/Au_{0.001}$ and (B) $Cu_1/Au_{0.01}$ core/shell nanoparticles in 0.1 M $HClO_4$ (green), 0.01 M KBr + 0.1 M $HClO_4$ (blue), and 0.01 M KCl + 0.1 M $HClO_4$ (red) as indicated. The peaks labeled as Cu^1 or Cu^2 are known for sure and the peaks labeled with a number are uncertain.

content in the main paper. Alternatively, all of the peaks could be due to Cu oxidation, with the amount of Au being too small to detect. The ASV of $Cu_1/Au_{0.001}$ NPs in $HClO_4$ only (Figure S1A, green plot) should give the oxidation of Cu only, since Au will not oxidize without the halides. Considering that ASV, one could assume that all of the peaks higher than about 0.2 V are due to Au or some combination of Au and Cu oxidation. Considering all of the possibilities and lack of experimental data testing them, we did not want to speculate on the peak assignments, but did want to show the interesting voltammetry. We are currently conducting studies to better understand the voltammetry of these low Au content Cu/Au core/shell NPs.

In the following tables, the stripping peaks correspond to the following potentials in the corresponding electrolyte solutions for the three peaks that were assignable:

<u>0.01 M KBr + 0.1 M $HClO_4$:</u>

Au^1 = 0.6-0.8 V, Cu^1 = -0.2-0.0 V, Cu^2 = 0.2-0.3 V

<u>0.01 M KCl + 0.1 M $HClO_4$:</u>

Au^1 = 0.8-1.0 V, Cu^1 = -0.2-0.0 V, Cu^2 = 0.2-0.3 V

Table S1. Integrated charge under the stripping peaks of Au and Cu in 0.01 M KBr plus 0.1 M $HClO_4$ electrolyte to calculate the Au to Cu ratio of Cu_1/Au_2 core/shell alloy nanoparticles.

Au^1	Cu^2	Au/Cu	Average Au/Cu	Theoretical Au/Cu
3.54 x 10^{-4} C	1.27 x 10^{-5} C	27.87		
2.18 x 10^{-4} C	9.07 x 10^{-6} C	24.03	26 ± 2	3.0
1.09 x 10^{-3} C	3.90 x 10^{-5} C	27.95		
1.23 x 10^{-4} C	4.84 x 10^{-6} C	25.41		

Table S2. Integrated charge under the stripping peaks of Au and Cu in 0.01 M KCl plus 0.1 M $HClO_4$ electrolyte to calculate the Au to Cu ratio of Cu_1/Au_2 core/shell alloy nanoparticles.

Au^1	Cu^2	Au/Cu	Average Au/Cu	Theoretical Au/Cu
1.78 x 10^{-4} C	1.42 x 10^{-5} C	12.62		
9.83 x 10^{-5} C	5.71 x 10^{-6} C	17.21	14 ± 2	3.0
1.26 x 10^{-4} C	1.01 x 10^{-5} C	12.47		
8.20 x 10^{-5} C	5.34 x 10^{-6} C	15.36		

Table S3. Integrated charge under the stripping peaks of Au and Cu in 0.01 M KBr plus 0.1 M $HClO_4$ electrolyte to calculate the Au to Cu ratio of Cu_1/Au_1 core/shell alloy nanoparticles.

Au^1	Cu^2	Au/Cu	Average Au/Cu	Theoretical Au/Cu
5.99 x 10^{-4} C	1.40 x 10^{-4} C	4.28		
6.43 x 10^{-4} C	1.60 x 10^{-4} C	4.02	4.0 ± 0.2	1.5
8.40 x 10^{-4} C	2.14 x 10^{-4} C	3.93		
4.31 x 10^{-4} C	1.12 x 10^{-4} C	3.85		

Table S4. Integrated charge under the stripping peaks of Au and Cu in 0.01 M KCl plus 0.1 M $HClO_4$ electrolyte to calculate the Au to Cu ratio of Cu_1/Au_1 core/shell alloy nanoparticles.

Au[1]	Cu[2]	Au/Cu	Average Au/Cu	Theoretical Au/Cu
1.54×10^{-4} C	9.30×10^{-5} C	1.66		
1.68×10^{-4} C	1.25×10^{-4} C	1.34	1.6 ± 0.2	1.5
2.38×10^{-4} C	1.47×10^{-4} C	1.62		
1.87×10^{-4} C	1.17×10^{-4} C	1.60		

Table S5. Integrated charge under the stripping peaks of Au and Cu in 0.01 M KBr plus 0.1 M $HClO_4$ electrolyte to calculate the Au to Cu ratio of $Cu_1/Au_{0.5}$ core/shell alloy nanoparticles.

Au[1]	Cu[2]	Au/Cu	Average Au/Cu	Theoretical Au/Cu
3.18×10^{-4} C	1.41×10^{-4} C	2.25		
2.09×10^{-4} C	1.21×10^{-4} C	1.73	2.0 ± 0.3	0.75
2.81×10^{-4} C	1.52×10^{-4} C	1.85		
3.52×10^{-4} C	1.63×10^{-4} C	2.15		

Table S6. Integrated charge under the stripping peaks of Au and Cu in 0.01 M KCl plus 0.1 M $HClO_4$ electrolyte to calculate the Au to Cu ratio of $Cu_1/Au_{0.5}$ core/shell alloy nanoparticles.

Au[1]	Cu[2]	Au/Cu	Average Au/Cu	Theoretical Au/Cu
1.93×10^{-4} C	2.19×10^{-4} C	0.88		
2.85×10^{-4} C	4.05×10^{-4} C	0.70	0.80 ± 0.08	0.75
1.74×10^{-4} C	2.21×10^{-4} C	0.77		
1.22×10^{-4} C	1.42×10^{-4} C	0.85		

Table S7. Integrated charge under the stripping peaks of Au and Cu in 0.01 M KBr plus 0.1 M $HClO_4$ electrolyte to calculate the Au to Cu ratio of $Cu_1/Au_{0.3}$ core/shell alloy nanoparticles.

Au[1]	Cu[1]	Cu[2]	Au/Cu	Average Au/Cu	Theoretical Au/Cu
1.69×10^{-4} C	1.15×10^{-4} C	6.50×10^{-5} C	0.94		
6.21×10^{-5} C	2.10×10^{-5} C	1.90×10^{-5} C	1.55	1.2 ± 0.3	0.45
1.25×10^{-4} C	6.01×10^{-5} C	5.13×10^{-5} C	1.12		
2.44×10^{-4} C	5.33×10^{-5} C	1.30×10^{-4} C	1.33		

Table S8. Integrated charge under the stripping peaks of Au and Cu in 0.01 M KCl plus 0.1 M $HClO_4$ electrolyte to calculate the Au to Cu ratio of $Cu_1/Au_{0.3}$ core/shell alloy nanoparticles.

Au[1]	Cu[1]	Cu[2]	Au/Cu	Average Au/Cu	Theoretical Au/Cu
1.53×10^{-4} C	1.57×10^{-4} C	1.24×10^{-4} C	0.54		
6.62×10^{-5} C	5.20×10^{-5} C	6.65×10^{-5} C	0.56	0.50 ± 0.06	0.45
6.76×10^{-5} C	8.60×10^{-5} C	6.68×10^{-5} C	0.44		
1.55×10^{-4} C	1.22×10^{-4} C	2.04×10^{-4} C	0.48		

Table S9. Integrated charge under the stripping peaks of Au and Cu in 0.01 M KBr plus 0.1 M $HClO_4$ electrolyte to calculate the Au to Cu ratio of $Cu_1/Au_{0.2}$ core/shell alloy nanoparticles.

Au^1	Cu^1	Cu^2	Au/Cu	Average Au/Cu	Theoretical Au/Cu
4.03×10^{-5} C	3.38×10^{-5} C	1.90×10^{-5} C	0.76		
1.30×10^{-4} C	1.26×10^{-4} C	3.44×10^{-5} C	0.81	0.80 ± 0.03	0.30
1.37×10^{-4} C	1.39×10^{-4} C	3.65×10^{-5} C	0.78		
1.34×10^{-4} C	1.28×10^{-4} C	3.30×10^{-5} C	0.83		

Table S10. Integrated charge under the stripping peaks of Au and Cu in 0.01 M KCl plus 0.1 M $HClO_4$ electrolyte to calculate the Au to Cu ratio of $Cu_1/Au_{0.2}$ core/shell alloy nanoparticles.

Au^1	Cu^1	Cu^2	Au/Cu	Average Au/Cu	Theoretical Au/Cu
5.72×10^{-5} C	9.09×10^{-5} C	8.36×10^{-5} C	0.33		
5.69×10^{-5} C	1.36×10^{-4} C	7.58×10^{-5} C	0.27	0.32 ± 0.03	0.30
8.46×10^{-5} C	1.53×10^{-4} C	9.80×10^{-5} C	0.34		
7.98×10^{-5} C	1.43×10^{-4} C	9.20×10^{-5} C	0.33		

Table S11. Integrated charge under the stripping peaks of Au and Cu in 0.01 M KBr plus 0.1 M $HClO_4$ electrolyte to calculate the Au to Cu ratio of $Cu_1/Au_{0.1}$ core/shell alloy nanoparticles.

Au^1	Cu^1	Cu^2	Au/Cu	Average Au/Cu	Theoretical Au/Cu
2.14×10^{-5} C	4.14×10^{-5} C	7.76×10^{-6} C	0.44		
2.66×10^{-5} C	4.66×10^{-5} C	8.55×10^{-6} C	0.48	0.43 ± 0.04	0.15
7.67×10^{-5} C	1.60×10^{-4} C	3.16×10^{-5} C	0.40		
6.66×10^{-5} C	1.38×10^{-4} C	3.21×10^{-5} C	0.39		

Table S12. Integrated charge under the stripping peaks of Au and Cu in 0.01 M KCl plus 0.1 M $HClO_4$ electrolyte to calculate the Au to Cu ratio of $Cu_1/Au_{0.1}$ core/shell alloy nanoparticles.

Au^1	Cu^1	Cu^2	Au/Cu	Average Au/Cu	Theoretical Au/Cu
1.35×10^{-5} C	7.28×10^{-5} C	1.67×10^{-5} C	0.15		
2.10×10^{-5} C	1.06×10^{-4} C	2.52×10^{-5} C	0.16	0.15 ± 0.01	0.15
2.51×10^{-5} C	1.46×10^{-4} C	3.15×10^{-5} C	0.14		
5.16×10^{-5} C	3.02×10^{-4} C	6.28×10^{-5} C	0.14		

Table S13. Integrated charge under the stripping peaks of Au and Cu to calculate the Au to Cu ratio of Cu_1/Au_1 core/shell alloy nanoparticles by first stripping in 0.01 M KBr plus 0.1 M $HClO_4$ solution from -0.2 to 0.4 V and then stripping the same electrode in 0.01 M KCl plus 0.1 M $HClO_4$ solution from -0.2 to 1.6 V.

Au^1	Cu^2 (from Br^-)	Cu^2 (from Cl^-)	Au/Cu	Average Au/Cu	Theoretical Au/Cu
8.83×10^{-4} C	1.96×10^{-4} C	1.38×10^{-6} C	4.47		
7.68×10^{-4} C	2.05×10^{-4} C	1.29×10^{-6} C	3.71	3.9 ± 0.4	1.5
7.21×10^{-4} C	1.91×10^{-4} C	2.99×10^{-6} C	3.71		
6.06×10^{-4} C	1.61×10^{-4} C	5.38×10^{-7} C	3.75		

Table S14. Integrated charge under the stripping peaks of Au and Cu to calculate the Au to Cu ratio of $Cu_1/Au_{0.5}$ core/shell alloy nanoparticles by first stripping in 0.01 M KBr plus 0.1 M $HClO_4$ solution from -0.2 to 0.4 V and then stripping the same electrode in 0.01 M KCl plus 0.1 M $HClO_4$ solution from -0.2 to 1.6 V.

Au	Cu^2 (from Br^-)	Cu^2 (from Cl^-)	Au/Cu	Average Au/Cu	Theoretical Au/Cu
2.33×10^{-4} C	1.17×10^{-4} C	2.44×10^{-6} C	1.95		
2.07×10^{-4} C	1.11×10^{-4} C	4.33×10^{-6} C	1.81	2.0 ± 0.2	0.75
2.62×10^{-4} C	1.27×10^{-4} C	8.19×10^{-7} C	2.02		
2.69×10^{-4} C	1.21×10^{-4} C	2.66×10^{-6} C	2.17		

Sample calculation for determining the amount of Cu under the Au peak from ASV.

Below is the calculation of the amount of Au and Cu in the alloys, including the amount of Cu that dealloyed separately from Au compared to the Cu that oxidized with the Au. This is for Cu_1/Au_x core/shell nanoparticles oxidized (stripped) in 0.01 M KBr plus 0.1 M $HClO_4$ electrolyte and is based on the integrated peak charge in Coulombs for the Au and Cu oxidation peaks and the known ratio of Au and Cu used in the synthesis.

Cu_1/Au_x is the ratio used during the synthesis.

x = the amount of Au relative to the amount of Cu.

$Q_{Cu(sep)}$ = the integrated charge of Cu from the well-separated Cu peaks that appeared negative of Au oxidation. (Peaks Cu^1+Cu^2)

Q_{Au+Cu} = the integrated charge due to Au and Cu oxidation that occurred at the Au oxidation potential. (Peak Au^1)

$Q_{Cu(withAu)}$ = the integrated charge due to Cu that oxidized along with Au at the Au oxidation potential. (Part of Au^1 that is due to Cu oxidation)

$$Au/Cu = x$$

$$[(Q_{Au+Cu} - Q_{Cu(withAu)})/3]/[(Q_{Cu(sep)} + Q_{Cu(withAu)})/2)] = x$$

$$(2Q_{Au+Cu} - 2Q_{Cu(withAu)})/(3Q_{Cu(sep)} + 3Q_{Cu(withAu)}) = x$$

$$2Q_{Au+Cu} - 2Q_{Cu(withAu)} = 3xQ_{Cu(sep)} + 3xQ_{Cu(withAu)}$$

$$(3x+2)Q_{Cu(withAu)} = 2Q_{Au+Cu} - 3xQ_{Cu(sep)}$$

$$Q_{Cu(withAu)} = (2Q_{Au+Cu} - 3xQ_{Cu(sep)})/(3x+2)$$

This gives the charge of Cu underneath the Au^1 peak in terms of the known synthesis ratio x and known values from the ASVs (Cu^1, Cu^2, and Au^1). The remaining amount of charge under the Au^1 peak is due to Au oxidation. The following equation allows one to convert the Q to moles of Cu and moles of Au as follows:

Q/nF, where n = number of electrons in the oxidation and F is Faraday's constant.

Example with Values: Cu_1/Au_1 core/shell. This shows how we calculated the values in Table 2 of main paper.

Q under the Au oxidation peak = Q_{Au+Cu} = 6.43 x 10^{-4} Coulombs

Sum of the Q from all Cu oxidation peaks = $Q_{Cu(sep)}$ = 1.60 x 10^{-4} Coulombs

x = 1

$Q_{Cu(withAu)} = (2Q_{Au+Cu} - 3xQ_{Cu(sep)})/(3x+2)$

$Q_{Cu(withAu)} = (2(6.43 \times 10^{-4}) - 3(1.60 \times 10^{-4}))/(5)$

$= (1.286 \times 10^{-3} - 4.80 \times 10^{-4})/5$

$= 1.61 \times 10^{-4}$ Coulombs

Total Mole Au = (6.43 x 10^{-4} Coulombs – 1.61 x 10^{-4} Coulombs)/(3*96500) = 1.66 x 10^{-9} mole Au

Total Mole Cu = (1.61 x 10^{-4} Coulombs + 1.60 x 10^{-4} Coulombs)/(2*96500) = 1.66 x 10^{-9} mole Cu

Mole Cu under Au = 1.61 x 10^{-4} Coulombs/(2*96500) = 8.34 x 10^{-10} mole Cu

Au/Cu ratio under Au = 1.66 x 10^{-9} mole/8.34 x 10^{-10} mole = 1.99

% of Cu retained by Au = (8.34 x 10^{-10} mole/1.66 x 10^{-9} mole)*100% = 50.2%

Calculation of NP Composition and Size Before and After Cu Dealloying and Rearrangement

$Cu_1/Au_{0.5}$ core/shell alloy NP

The Cu core radius was determined to be 2.23 nm based on the average 3.5 nm core/shell radius of the Cu_1/Au_2 alloy NP determined by TEM.

Using 0.128 nm radius for Cu, we obtain 0.00878 nm^3 for the volume of a Cu atom based on volume of a sphere, $(4/3)\pi r^3$.

Using 0.144 nm radius for Au, we obtain 0.01250 nm^3 for the volume of an Au atom based on volume of a sphere, $(4/3)\pi r^3$.

A 2.23 nm radius NP with 70% packing efficiency leads to 3700 Cu atoms in the Cu core.

A total radius of 3.50 nm (2.23 nm core + 1.27 nm shell) leads to 7400 Au atoms, giving a Cu_1/Au_2 ratio and composition of Cu_{3700}/Au_{7400}.

For $Cu_1/Au_{0.5}$, the initial composition is Cu_{3700}/Au_{1850} based on the Cu_1/Au_2 composition.

We determined that 41% of the Cu is retained for the $Cu_1/Au_{0.5}$ NP after initial Cu oxidation, which is equal to:

3700 x 0.41 = 1518 Cu atoms left after initial oxidation

That gives a composition of Cu_{1518}/Au_{1850} after initial Cu oxidation up to 0.42 V.

The core volume would be as follows, assuming 70% packing efficiency:

$V_{1518\text{ Cu core}} = (V_{\text{Cu atom}} \times 1518)/0.7 = (0.00878\text{ nm}^3 \times 1518)/0.7 = 19.04\text{ nm}^3$

We can then solve for radius in terms of volume as follows:

r (1518 Cu atoms) = $(3V/4\pi)^{1/3} = [(3 \times 19.04)/4\pi]^{1/3}$ = 1.66 nm Cu core radius after initial ox.

To get the shell thickness we have to determine the volume of the Au from the number of atoms. This would be:

$V_{1850\text{ Au atoms}} = (V_{\text{Au atom}} \times 1850)/0.7 = (0.01250\text{ nm}^3 \times 1850)/0.7 = 33.05\text{ nm}^3$

The total volume of the NP is then:

$V_T = V_{1850\text{ Au atoms}} + V_{1518\text{ Cu core}} = 33.05\text{ nm}^3 + 19.04\text{ nm}^3 = 52.09\text{ nm}^3$

The radius of the rearranged NP is then:

$r = (3V/4\pi)^{1/3} = [(3 \times 52.09)/4\pi]^{1/3}$ = 2.32 nm Cu/Au core/shell NP radius

1.66 nm radius Cu_{1518} core and 0.66 nm thick Au_{1850} shell = 2.32 nm radius core/shell NP

0.66 nm/0.288 nm = 2.3 atomic Au layers

The original $Cu_1/Au_{0.5}$ core/shell NP was:

2.23 nm radius Cu_{3700} core

$V_{Cu3700} = (4/3)\pi r^3 = (4/3)\pi(2.23\text{ nm})^3 = 46.45\text{ nm}^3$

$V_T = V_{1850\text{ Au atoms}} + V_{3700\text{ Cu core}} = 33.05\text{ nm}^3 + 46.45\text{ nm}^3 = 79.50\text{ nm}^3$

$r = (3V/4\pi)^{1/3} = [(3 \times 79.50)/4\pi]^{1/3}$ = 2.67 nm Cu_{3700}/Au_{1850} core/shell NP radius

2.23 nm Cu_{3700} core plus 0.44 nm thick Au_{1850} shell = 2.67 nm Cu_{3700}/Au_{1850} core/shell NP

0.44 nm/0.288 nm = 1.5 atomic Au layers.

The NP goes from a 2.67 nm radius (5.4 nm diameter) Cu_{3700}/Au_{1850} NP to a 2.32 nm radius (4.6 nm diameter) Cu_{1518}/Au_{1850} NP after 41% Cu oxidation and Au rearrangement.