Unravelling the nucleation mechanism of bimetallic nanoparticles with composition-tunable core-shell arrangement

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Supplementary Information

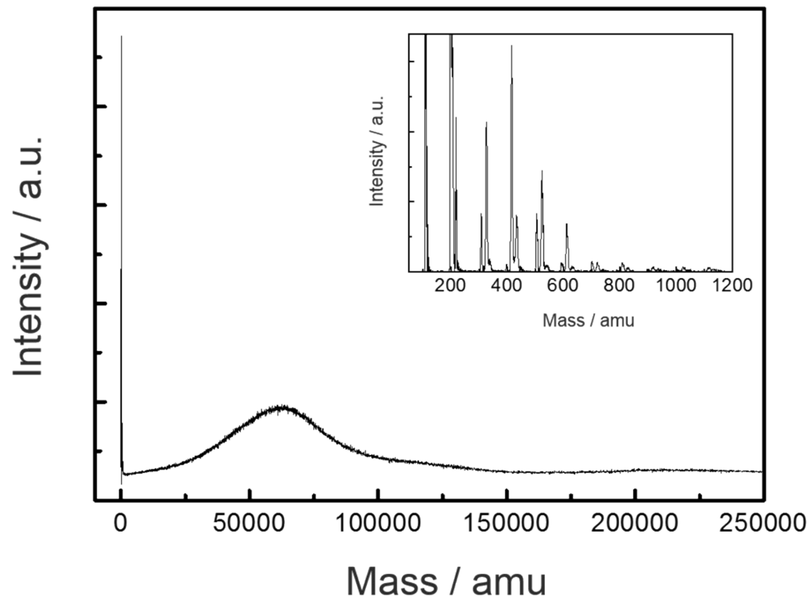

Figure S1. Full RToF mass spectrum of Au_xAg_{1-x} clusters taken from Au-Ag alloy target 35 at% Au and 65 at% Ag from few atoms region to the main production region.

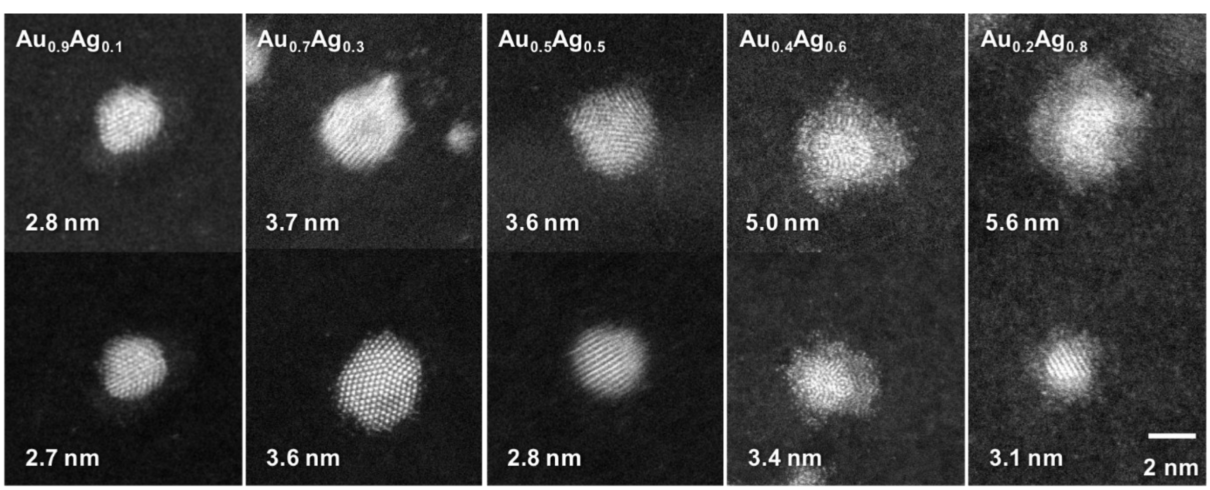

Figure S2. STEM images of Au_xAg_{1-x} BNPs with larger (upper row) and smaller (lower row) sizes

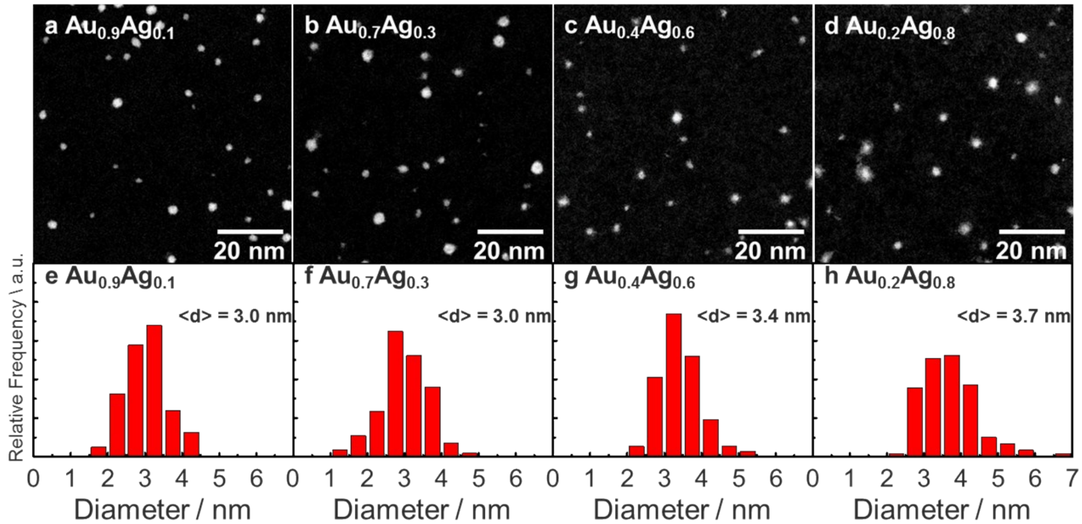

Figure S3. STEM images and histograms of diameter distributions of Au_xAg_{x-1} BNPs: (a, e) $Au_{0.9}Ag_{0.1}$; (b, f) $Au_{0.7}Ag_{0.3}$; (c, g) $Au_{0.3}Ag_{0.7}$; (d, h) $Au_{0.2}Ag_{0.8}$.

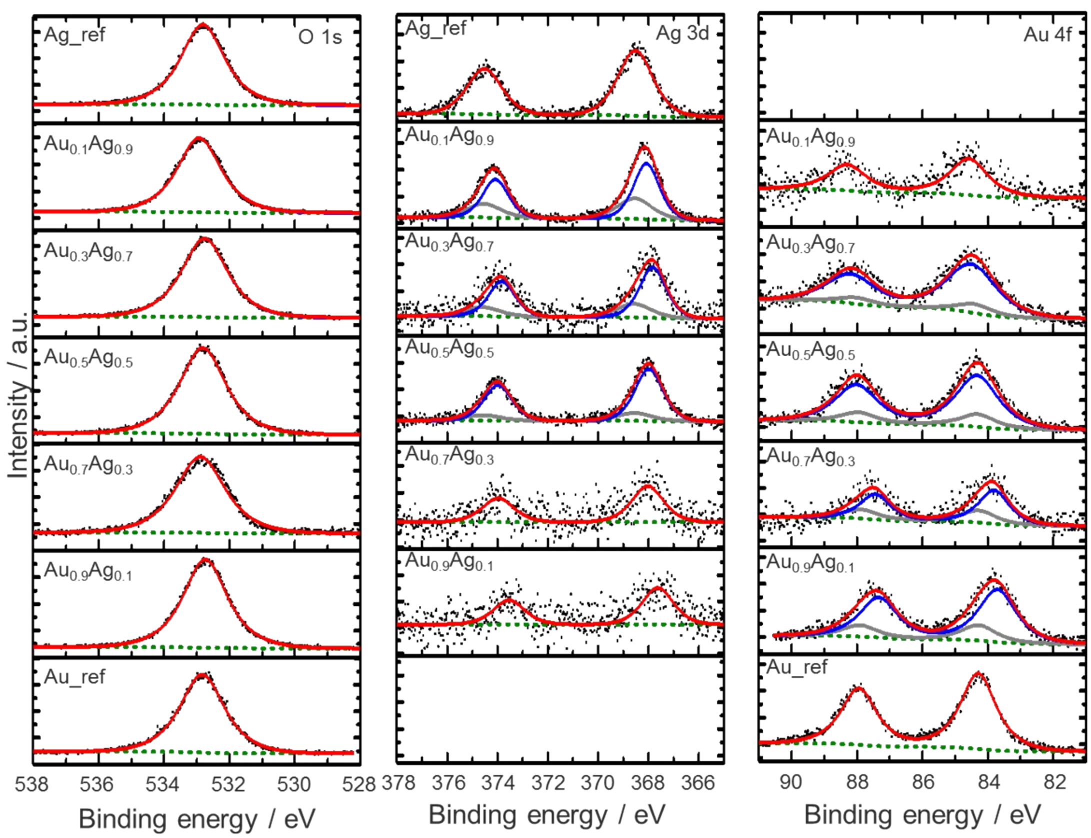

Figure S4. O 1s, Ag 3d and Au 4f XPS spectra of the Au_xAg_{1-x} BNPs on SiO_2 wafers from x = 0.9 to 0.1. The green dash lines are the shirley backgrounds, the blue lines are pure phase of Au and Ag and the grey lines are the Au-Ag alloy phases.

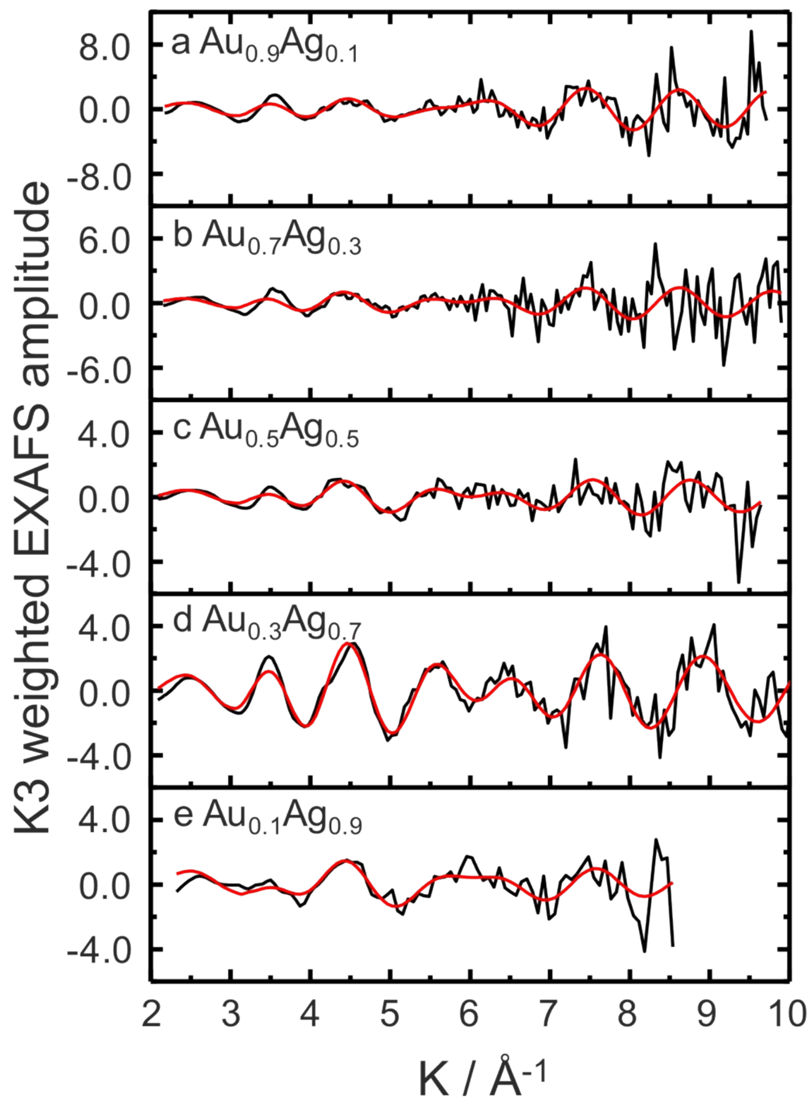

Figure S5. k^3 weighted XAFS spectra of the Au_xAg_{1-x} BNPs on SiO_2 wafers from x = 0.9 to 0.1. The corresponding phase-corrected Fourier transformed EXAFS spectra is shown in main text Figure 2a.

Table S1. Summary of structural results of Ag K-edge XAFS refinements of the Au-Ag BNPs on SiO_2 wafer measured in full reflection and fluorescence-detection mode.

	Shell	Coordination number N	Bond distance R (Å)	Debye-Waller factor A (Å^2)	E_f (eV)
$Au_{0.9}Ag_{0.1}$	Ag-Ag	0.9 (1)	2.91 (3)	0.03 (2)	0.0(9)
	Ag-Au	3.6 (5)	2.84 (2)	0.013 (4)	
	Ag-O	0.4 (1)	2.23 (2)	0.008 (4)	
$Au_{0.7}Ag_{0.3}$	Ag-Ag	1.0 (4)	2.89 (3)	0.012 (5)	-0.4(9)
	Ag-Au	1.7 (4)	2.88 (3)	0.012 (6)	
	Ag-O	0.2 (1)	2.22 (6)	0.01 (1)	
$Au_{0.5}Ag_{0.5}$	Ag-Ag	1.0 (1)	2.85 (2)	0.010 (3)	-1.2(9)
	Ag-Au	1.1 (1)	2.88 (2)	0.011 (4)	
	Ag-O	0.4 (1)	2.23 (3)	0.022 (6)	
$Au_{0.3}Ag_{0.7}$	Ag-Ag	4.0 (2)	2.83 (1)	0.016 (1)	-1.6(6)
	Ag-Au	3.0 (2)	2.88 (1)	0.013 (2)	
	Ag-O	0.4 (1)	2.24 (2)	0.019 (6)	
$Au_{0.1}Ag_{0.9}$	Ag-Ag	1.2 (2)	2.83 (3)	0.020 (8)	2.6(9)
	Ag-Au	1.6 (3)	2.86 (2)	0.017 (6)	
	Ag-O	1.2 (2)	2.20 (2)	0.02 (1)	

E_f = contribution of the wave vector of the zero photoelectron relative to the origin of k [eV]

N = number of atom in the shell

R = radial distance of atoms in the shell [Å]

A = Debye-Waller term of the shell ($A=2\sigma^2$ with σ = Debye-Waller factor)[Å^2]

R factors were ranging from 39 to 73 %.

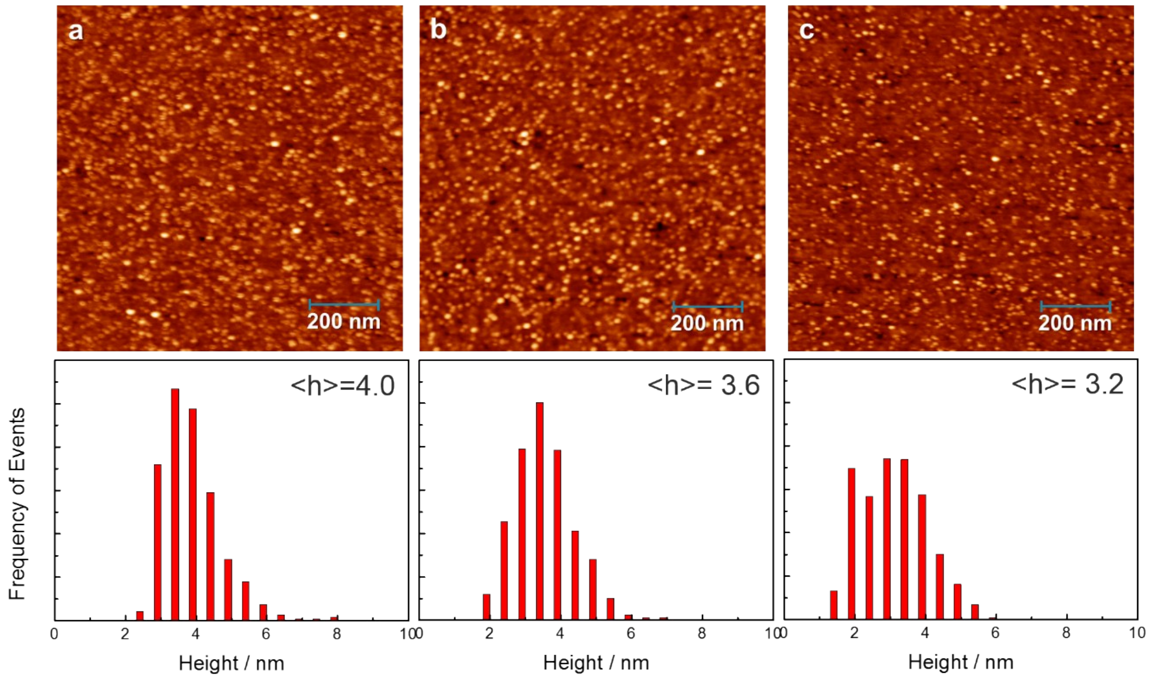

Figure S6. Height histograms of the 0.1 ML Au-Ag BNPs with different composition, $Au_{0.9}Ag_{0.1}$(a), $Au_{0.6}Ag_{0.4}$(b), $Au_{0.2}Ag_{0.8}$(c) deposited on SiO_2 wafers.

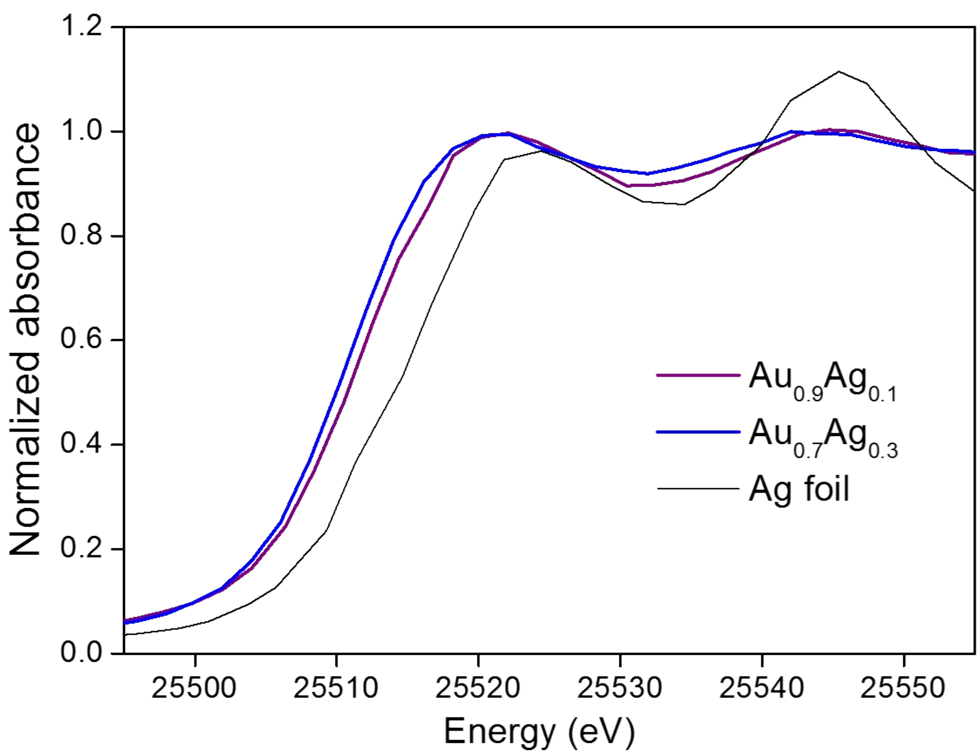

Figure S7. XANES spectra of gold-rich $Au_{0.9}Ag_{0.1}$ and $Au_{0.7}Ag_{0.3}$ BNPs along with Ag foil reference.

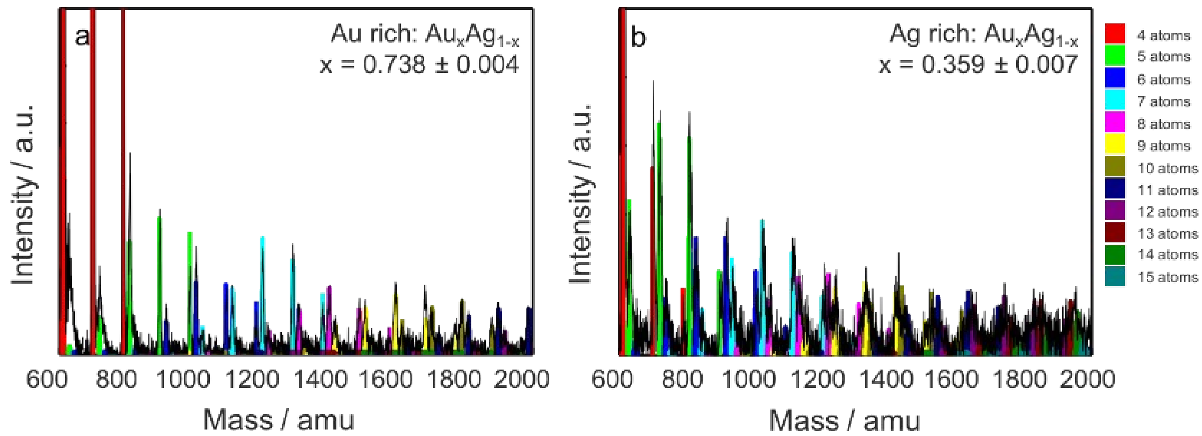

Figure S8. RToF-MS of deposited Au_xAg_{1-x} clusters, (a) and (b) mass spectra of 73.8 ± 0.4 at% Au and 26.2 ± 0.4 at% Ag as well as 35.9 ± 0.7 at% Au and 64.1 ± 0.7 at% Ag combined with simulation spectra.

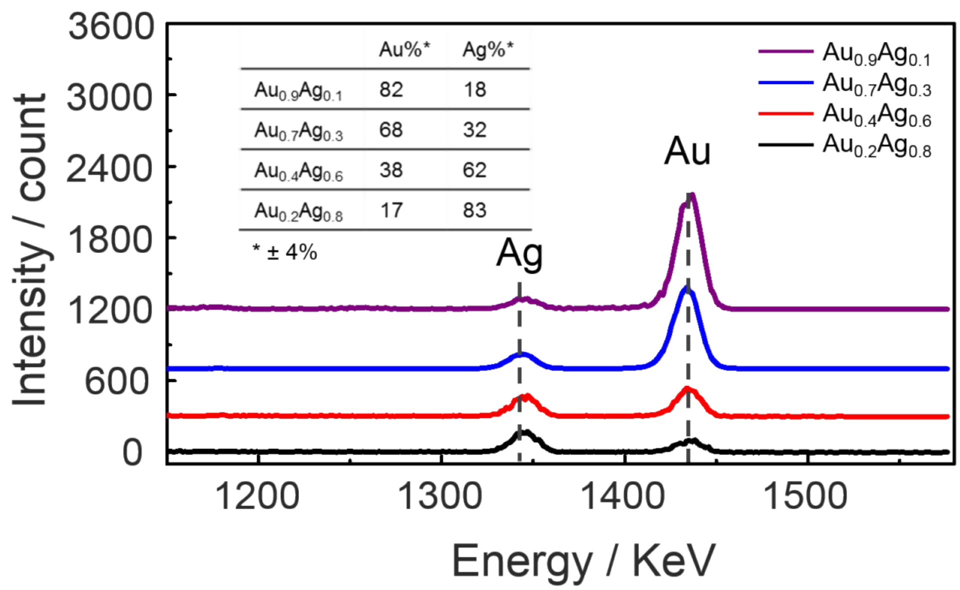

Figure S9. RBS spectra of deposited Au_xAg_{1-x} BNPs from gold rich to silver rich on SiO_2 wafers. The inset table shows the overall composition of deposited clusters as determined by RBS.

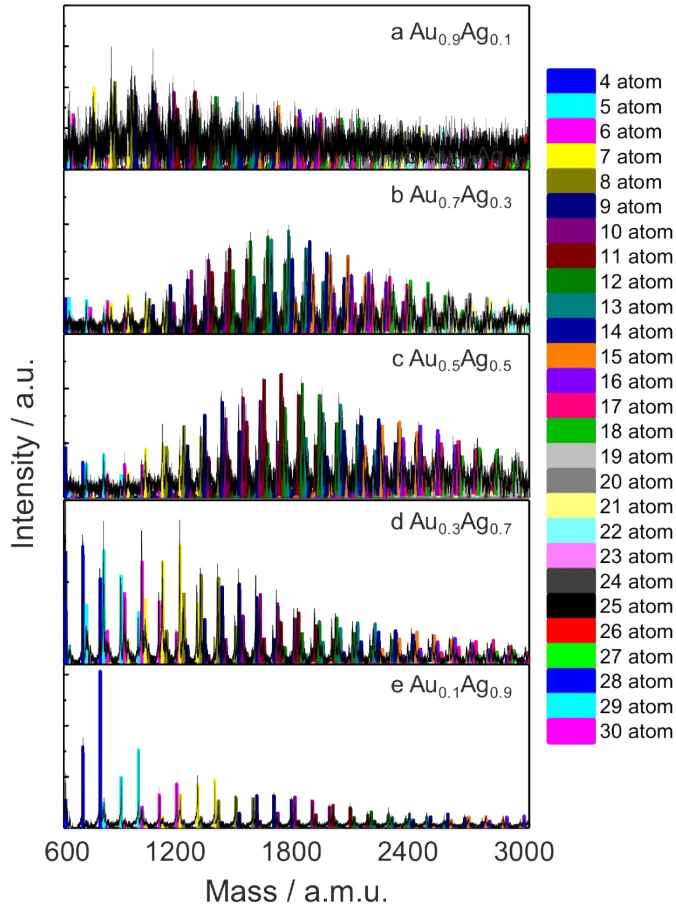

Figure S10. A validation of the fitting based on binomial theorem composition analysis method was done with additionally compositions obtained from the analysis of the mass spectra within the mass range from 600 amu to 3000 amu (4 atoms to 30 atoms) of a series Au_xAg_{1-x} clusters produced from Au_xAg_{1-x} alloy targets of known stoichiometries (x = 0.1, 0.3, 0.5, 0.7 and 0.9). It is showed always a very good agreement with the target composition. The corresponding composition fitting are showned above in the mass range from 600 amu to 3000 amu, x = 0.9 (a), 0.7 (b), 0.5 (c), 0.3 (d) and 0.1 (e).