Supporting Information

Halide-Assisted Metal Ion Reduction: Emergent Effects of Dilute Chloride, Bromide, and Iodide in Nanoparticle Synthesis

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Ligand	Concentration	Volume	Ratio		
Added	(mM)	(µL)	(X ⁻ : Pd ²⁺)		
	10	25	1:10		
		25	1:1		
NaCl	100	50	2:1		
IvaCi	100	75	3:1		
		100	4:1		
	500	80	16:1		
	1	1 25			
	1	125	1:20		
NaPu	10	25	1:10		
INUDI [*]		25	1:1		
	100	50	2:1		
		75	$(X^-: Pd^{2+})$ $1:10$ $1:1$ $2:1$ $3:1$ $4:1$ $16:1$ $1:100$ $1:20$ $1:10$ $1:10$ $1:1$ $2:1$ $3:1$ $1:1000$ $1:250$ $1:100$ $1:25$ $1:100$ $1:100$ $1:100$		
		2.5	1:1000		
	1	10	1:250		
NaI	1	25	1:100		
		100	1:25		
	10	25	1:10		
	1	2.5	1:1000		
NaSCN or NaN ₃	1	25	1:20 1:10 1:1 2:1 3:1 1:1000 1:250 1:100 1:25 1:10 1:1000 1:100 1:100 1:100 1:100 1:100		
	10	25	1:10		

Table S1. Reaction Conditions for Palladium Nanoparticles in Halide-Free Surfactant

Table S2. Reaction Conditions for Silver-Assisted Synthesis of Gold Nanoparticles with Added

 Halide

_			500 µL Au	40 µL Ag	100 µL Ag
Ligand Added	Conc. (mM)	Volume (µL)	Ratio (X ⁻ : Au ³⁺)	Ratio (X ⁻ : Ag ⁺)	Ratio (X ⁻ : Ag ⁺)
NaBr 10	25	1:20	1:1.6	1:4	
	50	1:10	1:0.8	1:2	
NaI 1	25	1:200	1:16	1:40	
		50	1:100	1:8	1:20



Figure S1. Graph of reduced palladium (palladium nanoparticle formation) over a one-hour reaction period with different chloride to palladium ion ratios.



Figure S2. SEM images of palladium nanoparticles formed in the absence of halide with an average size of 42.2 ± 10 nm. Scale bars: 500 nm and 200 nm (inset).



Figure S3. SEM and TEM images of palladium nanoparticles with the following ratios of chloride to palladium: (A) 1:10 with an average size of 40.2 ± 4 nm, (B) 1:1 with an average size of 38.9 ± 8 nm, (C) 2:1 with an average size of 36.3 ± 11 nm, (D) 3:1 with an average size of 35.8 ± 11 nm, (E) 4:1 with an average size of 39.9 ± 9 nm, and (F) 16:1 with an average size of 47.7 ± 12 nm. Scale bars: 500 nm and 200 nm (inset).



Figure S4. Graph of reduced palladium (palladium nanoparticle formation) over a one-hour reaction period with different bromide to palladium ion ratios.



Figure S5. TEM and SEM images of palladium nanoparticles with the following ratios of bromide to palladium: (A) 1:100 with an average size of 27.6 ± 5 nm, (B) 1:20 with an average size of 22.3 ± 5 nm, (C) 1:10 with an average size of 18.3 ± 4 nm, (D) 1:1 with an average size of 17.5 ± 5 nm, (E) 2:1 with an average size of 16.7 ± 7 nm, and (F) 3:1 with an average size of 56.5 ± 18 nm. The large deviation in size in (F) is due to particle anisotropy including rods, bipyramids, and spheres. Scale bars: (A-E) 200 nm and 50 nm (inset) and (F) 500 nm and 200 nm (inset).



Figure S6. Graph of reduced palladium (palladium nanoparticle formation) over a one-hour reaction period with different iodide to palladium ion ratios.



Figure S7. TEM images of palladium nanoparticles with the following ratios of iodide to palladium: (A) 1:1000 with an average size of 17.3 ± 4 nm and (B) 1:250 with an average size of 5.4 ± 2 nm. Scale bars: 100 nm and 20 nm (inset).

Cl [−] : Pd ²⁺	[Pd(H ₂ O) ₄] ²⁺	$[PdCl(H_2O)_3]^+$	$[PdCl_2(H_2O)_2]$	[PdCl ₃ (H ₂ O)] ⁻	[PdCl ₄] ²⁻
1:10	91%	9%	0%	0%	0%
1:1	26%	63%	10%	0%	0%
2:1	6%	55%	36%	3%	0%
3:1	2%	38%	52%	8%	0%
4:1	1%	27%	58%	15%	0%
16:1	0%	3%	34%	55%	8%

Table S3. Predicted Solution Speciation of Palladium in the Presence of Chloride

Table S4. Predicted Solution Speciation of Palladium in the Presence of Bromide

Br ⁻ : Pd ²⁺	$[Pd(H_2O)_4]^{2+}$	$[PdBr(H_2O)_3]^+$	[PdBr ₂ (H ₂ O) ₂]	[PdBr ₃ (H ₂ O)] ⁻	[PdBr4] ²⁻
1:100	99%	1%	0%	0%	0%
1:20	95%	5%	0%	0%	0%
1:10	90%	10%	0%	0%	0%
1:1	23%	59%	17%	1%	0%
2:1	2%	33%	52%	12%	0%
3:1	0%	12%	52%	34%	2%

Table S5. Predicted Solution Speciation of Palladium in the Presence of Iodide

I ⁻ : Pd ²⁺	$[Pd(H_2O)_4]^{2+}$	$[PdI(H_2O)_3]^+$
1:1000	100%	0%
1:250	100%	0%
1:100	99%	1%
1:25	96%	4%
1:10	90%	10%



Figure S8. Graph of reduced palladium (palladium nanoparticle formation) over a one-hour reaction period with different azide to palladium ion ratios.



Figure S9. TEM images of palladium nanoparticles with added pseudohalides. (A) 1:1000 $SCN^-: Pd^{2+}$, (B) 1:100 $SCN^-: Pd^{2+}$, (C) 1:1000 $N_3^-: Pd^{2+}$, and (B) 1:100 $N_3^-: Pd^{2+}$. Scale bars: 50 nm. Particles in (A), (C), and (D) are likely aggregates of smaller nanoparticles.



Figure S10. Graph of reduced palladium (palladium nanoparticle formation) over a one-hour reaction period with different thiocyanate to palladium ion ratios.

SCN ⁻ : Pd ²⁺	$[Pd(H_2O)_4]^{2+}$	$[PdSCN(H_2O)_3]^+$
1:1000	100%	0%
1:100	99%	1%
1:10	90%	10%

Table S6. Predicted Solution Speciation of Palladium in the Presence of Thiocyanate



Figure S11. Graphs of reduced gold and silver (bimetallic nanoparticle growth) over a one-hour reaction period with different concentrations of bromide. Top: Reduced gold (A) and silver (B) in the presence of 40 μ L of 10 mM AgNO₃ and 0, 23, or 46 μ M bromide. Bottom: Reduced gold (C) and silver (D) in the presence of 100 μ L of 10 mM AgNO₃ and 0, 23, or 46 μ M bromide.



Figure S12. SEM images of gold and silver nanoparticles with different concentrations of bromide. (A - C) Gold particles grown in the presence of 40 µL added silver with increasing concentrations of added bromide from left to right. (D - F) Gold particles grown in the presence of 100 µL added silver with increasing concentrations of added bromide from left to right. Scale bars: 500 nm.



Figure S13. Graphs of reduced gold and silver (bimetallic nanoparticle growth) over a one-hour reaction period with different concentrations of iodide. Top: Reduced gold (A) and silver (B) in the presence of 40 μ L of 10 mM AgNO₃ and 0, 2.3, or 4.6 μ M iodide. Bottom: Reduced gold (C) and silver (D) in the presence of 100 μ L of 10 mM AgNO₃ and 0, 2.3, or 4.6 μ M iodide.



Figure S14. SEM images of gold and silver nanoparticles with different concentrations of iodide. (A - C) Gold particles grown in the presence of 40 µL added silver with increasing concentrations of added iodide from left to right. (D - F) Gold particles grown in the presence of 100 µL added silver with increasing concentrations of added iodide from left to right. Scale bars: 500 nm.