

Supporting Information

Pt Nanocrystal Evolution in the Presence of Au(III)-Salts at Room

Temperature: Spontaneous Formation of AuPt Heterodimers

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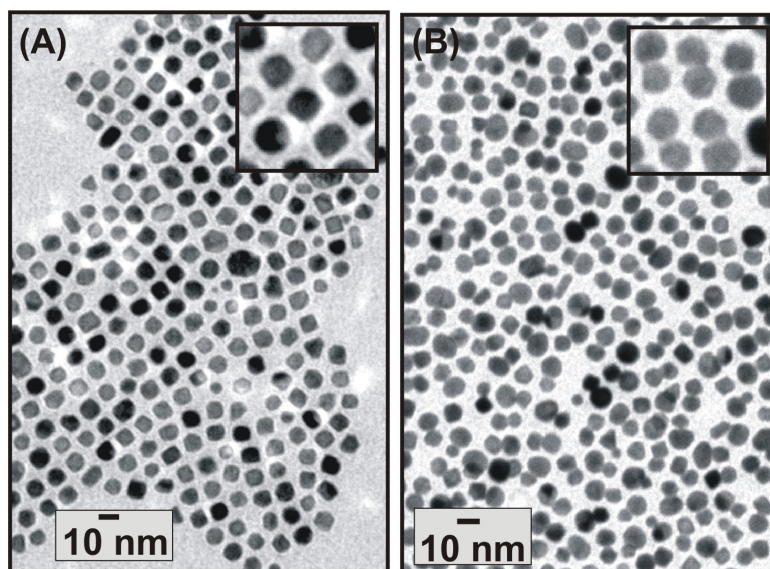


Fig. S1. TEM images illustrating the Pt NC shape and size change (A) before and (B) after the formation of the AuPt heterodimers. While there are still some cubic Pt NCs in (B), the majority of Pt domains in the heterodimers are more spherical in shape due to the etching of the vertex atoms.

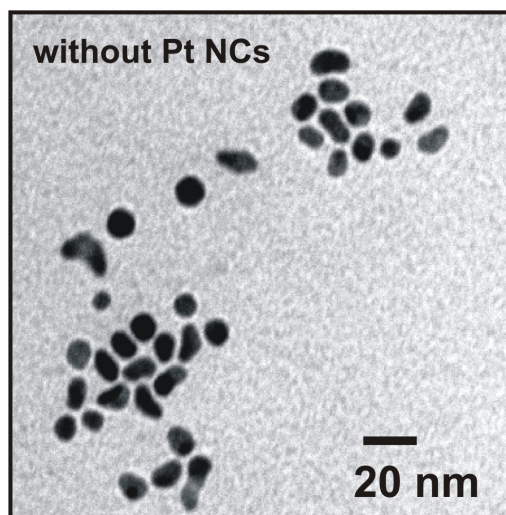


Fig. S2. TEM image of polydispersed Au NCs synthesized in the absence of Pt NCs. This solution contains 3 mL of AuCl_4^- (0.79 mM stock solution prepared in 5% UD) and 3 mL of DCB (containing 1% OAM) mixed and stirred for 196 h in a darkened environment. The final fractions of OAM and UD in the solution were 0.45% and 2.5%, respectively.

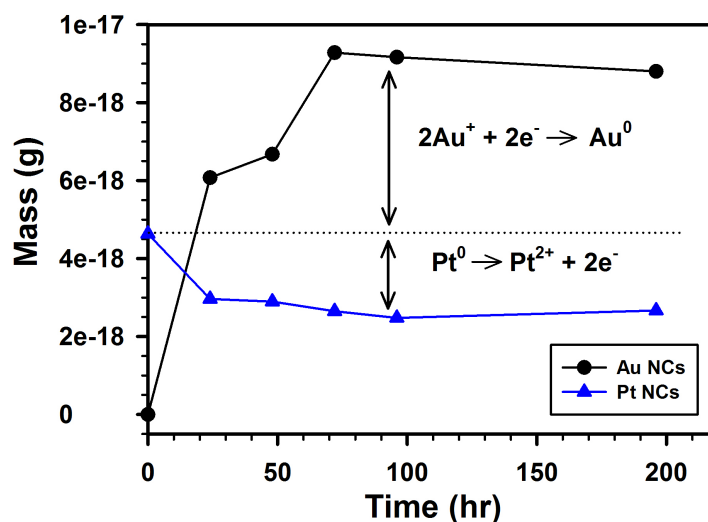


Fig. S3. Plot of mass vs. time to compare the mass change as the size of the Pt and Au NCs evolved.

The masses were obtained using the densities: $d_{(\text{Au})} = 19.3 \text{ g/cm}^3$; $d_{(\text{Pt})} = 21.45 \text{ g/cm}^3$. When looking at the mass balance between the Pt losses and the growth of the Au in the heterodimers, it seems that for each released (oxidized) platinum, there are two Au ions reduced. Assuming that the history of all Pt NC seeds and AuPt heterodimers are the same, a possible mechanism may involve the reduction of Au^{3+} to Au^+ by the traces of oleylamine. Assuming that the weak reducer/capping agents cannot further reduce the Au^+ , the Pt NCs become the electron suppliers, which reduce the Au^+ to Au^0 . Similarly, it is known that ascorbic acid reduces Au^{3+} to Au^+ , where the Au NC seeds are needed to catalyze further growth.

Sample	Pt NC	AuCl ₄ ⁻ (5% UD) (0.79 mM)	DCB (1% OAM)
A	0.3 mL	0.1 mL	5.60 mL
B	0.3 mL	0.5 mL	5.20 mL
C	0.3 mL	1.0 mL	4.70 mL
D	0.3 mL	2.0 mL	3.70 mL
E	0.3 mL	3.0 mL	2.70 mL
F	30 μL	1.0 mL	4.97 mL

Table S1. Summary of the amount of Pt NCs, AuCl₄⁻ and DCB used for each AuPt heterodimer synthesis in Figure 5. The stock solution of AuCl₄⁻ contains 5% of UD to ensure the complete dissolution of the Au ions, and the DCB solution contains 1% of OAM. After mixing together, the final concentration of the UD ranges from 0.024 to 0.72 mmol, and that of the OAM ranges from 0.082 to 0.17 mmol.

	2θ at different hkl			
	(111)	(200)	(220)	(311)
Au, syn JCPDS no. 004-0784	38.19	44.39	64.58	77.55
Pt, syn JCPDS no. 004-0802	39.77	46.24	67.46	81.29
Au NCs (experimentally)	38.22	44.34	64.65	77.63
Pt NCs (experimentally)	40.04	46.51	67.77	81.61
AuPt heterodimers (experimentally)	38.24 (Au) 39.79 (Pt)	44.42 (Au) 46.30 (Pt)	64.64 (Au) 67.89 (Pt)	77.72 (Au) 81.82 (Pt)

Table S2. Table comparing Au NCs, Pt NCs and heterodimer crystalline structures after 114 h of reaction at room temperature.

Note that the concentration of the Au(III) precursor was increased three-fold compared to the normal concentration range to allow the growth of larger sized Au NCs for XRD analysis. Using the normal concentration (i.e. 3 mL of 0.79 mM AuCl₄⁻), XRD spectrum of heterodimers showed broadening of the Au peaks.