Supporting Information

Learning from Nature: Introducing an Epiphyte-Host Relationship in the Synthesis of Alloy Nanoparticles by Co-Reduction Methods

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Materials and Methods

Materials

Palladium (II) chloride ($PdCl_2$, Sigma Aldrich, 98%), silver nitrate ($AgNO_3$, Merck, 99.8%), Chloroplatinic (IV) acid (H_2PtCl_6, Sigma Aldrich, 98%), hydrogen tetrachloroaurate (Ш) hydrate ($HAuCl_4.xH_2O$, Alfa Aesar, 49.87% Au), cetyltrimethylammonium bromide (CTAB, Sigma Aldrich, ≥98%) and L-ascorbic acid (Sigma Aldrich, 99%) were used as received. Ultrapure

Millipore water (18.2 MΩ) was used as the solvent throughout. 5 mM H_2PdCl_4 solution was prepared by dissolving 22.25 mg $PdCl_2$ in 25 mL 10 mM HCl solution.

Synthesis of Ag-Pd alloy nanoparticles (NPs). For the synthesis of Ag-Pd alloy NPs, a given volume of 5 mM $AgNO_3$ and 0.155 mL 38.8 mM ascorbic acid were added to 3 mL 16 mM CTAB solution. After thorough mixing, 90 μL 5 mM H_2PdCl_4 was introduced. The solutions were mixed well and left on the shaker overnight. 10 μL, 22.5 μL, 38.6 μL, 60 μL, 90 μL, 135 μL, and 210 μL of 5 mM $AgNO_3$ were used to prepare precursor mixtures with Ag atom% of 10%, 20%, 30%, 40%, 50%, 60% and 70% respectively.

Synthesis of Au-Pt alloy NPs. The preparation of Ag-Pt alloy NPs was similar to the preparation of Ag-Pd NPs except that H_2PdCl_4 in the growth solution was replaced by H_2PtCl_6, and the reaction time was extended to one week. In particular, a given volume of 5 mM $AgNO_3$ and 0.155 mL 38.8 mM ascorbic acid were added to 3 mL 16 mM CTAB solution. After thorough mixing, 90 μL 5 mM H_2PdCl_4 were added. The solutions were well mixed and left on the shaker overnight. 10 μL, 22.5 μL, 38.6 μL, 60 μL, 90 μL, 135 μL, and 210 μL of 5 mM $AgNO_3$ were used to prepare precursor mixtures with a Ag atom% of 10%, 20%, 30%, 40%, 50%, 60% and 70% respectively.

Materials characterizations.

The structures of the alloy NPs were analyzed by transmission electron microscopy (TEM), high-resolution TEM (HRTEM) on a JEM-2010 and a JEM-2100F (JEOL) microscopes operating at 200 kV accelerating voltage. Field emission scanning electron microscopy (FESEM) (on a JEOL JSM-6700F equipped with scanning TEM (STEM) function operating at 25 kV) was used to evaluate overall particle morphology and product uniformity. EM samples were typically prepared by dispensing a drop of the washed product on a copper grid followed by drying in air at room temperature.

Electrochemical measurements. Electrochemical measurements were carried out in a standard 3-electrode cell under the control of a Metrohm Autolab type III potentiostat/galvanostat. The working electrode was a polished and cleansed glassy carbon electrode (diameter 5 mm). A Pt gauze and a Ag|AgCl (3 M KCl) electrode were used as the counter electrode and the reference electrode respectively. The Ag precursor solution was a 0.15 mM $AgNO_3$ in 16 mM CTAB solution. Electrochemical measurements by cyclic voltammetry were carried out at 10 mV/s.

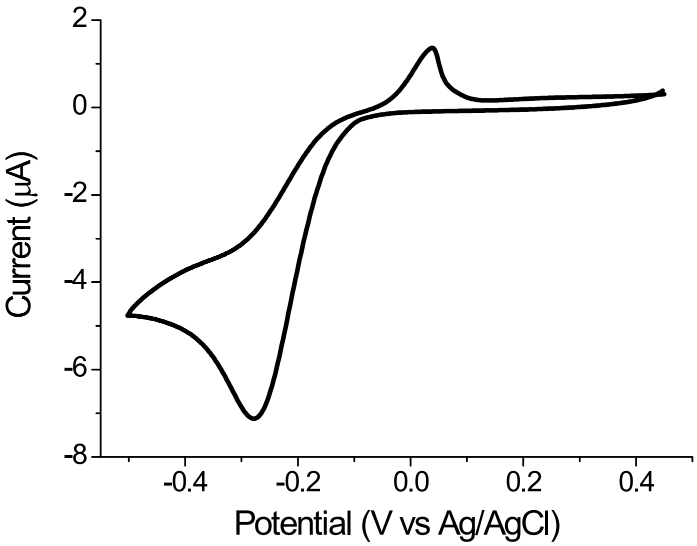

Figure S1. Cyclic voltammetry of Ag reduction in a 0.15 mM $AgNO_3$ solution with 16 mM CTAB (pH value of 5.0). The electrode potential was estimated to be -0.12 V vs Ag|AgCl (0.385 V vs SHE). The interception of the line adjoining the Ag^+/Ag reduction and oxidation peaks on the potential axis as the proxy of the reduction potential of Ag^+.

Table S1. Underpotential shifts ΔE_{UPD} and Standard electrode potentials

Underpotential shift ΔE_{UPD}			Standard electrode potential (V)	
Substrate/UPD metal ion	ΔE_{UPD} (V)	References		
Pd/Ag^+	0.296	7	$PdBr_4^{2-}/Pd$	0.49
Pt/Ag^+	0.336~0435	6, 7, 12	$PtBr_6^{2-}/Pt$	0.613
Au/Ag^+	0.505~0.55	7, 12	$AuBr_4^-/Au$	0.854

Table S2. Compositions (Ag atom%) of Ag-Pt and Ag-Pd NPs as determined by EDX and XPS measurements.

Ag atom% in the precursor mixture	Ag atom% in **Ag-Pt** alloy NPs		Ag atom% in **Ag-Pd** alloy NPs	
	EDX	XPS	EDX	XPS
10	16.98	15.81	5.39	4.06
20	24.09	23.22	11.49	8.26
30	33.57	32.32	17.89	16.46
40	44.05	43.68	23.98	24.23
50	52.11	50.63	29.92	33.36
60	55.24	54.84	34.78	37.72
70	55.78	55.84	36.10	40.83

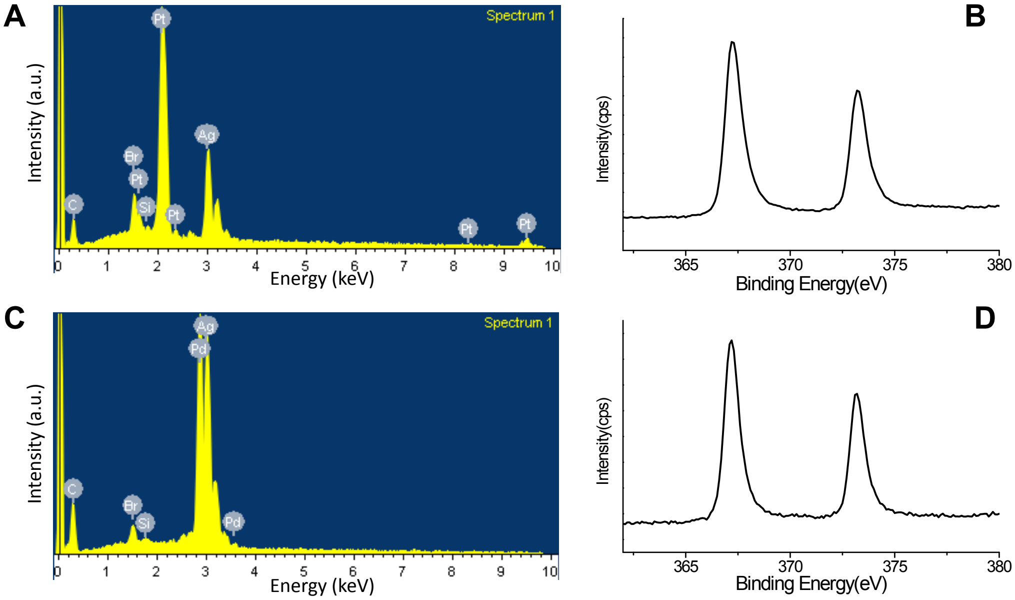

Figure S2. Representative EDX (A and C) and Ag 3d XPS spectra (B and D) of Ag-Pt alloy NPs (A and B) and Ag-Pd alloy NPs (C and D). The NPs were prepared with 50 atom% of Ag in the precursor mixture.

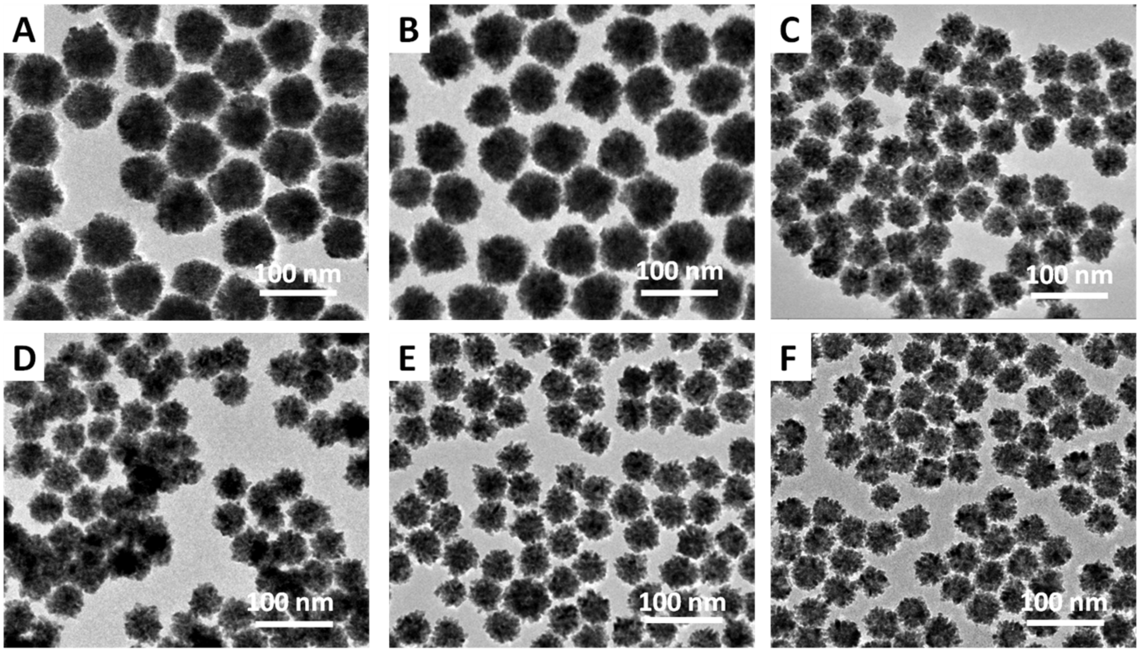

Figure S3. TEM images of Ag-Pt alloy NPs prepared with different Ag contents in the precursor solution. (A) to (F) were prepared with 10, 20, 30, 40, 50 and 60 atom% of Ag respectively in the precursor solution. The Ag-Pt NPs were dendritic with rough surface similar to those prepared in the CTAB-AA system.[1,2]

Table S3. Compositions (Ag atom%) of Ag-Pt and Ag-Pd NPs before and after the addition of Pt(IV) or Pd(II) ions, as measured by EDX analysis. The as-synthesized alloy NP solution was centrifuged to remove the unreacted ascorbic acid and redispersed in aqueous CTAB. The H_2PtCl_6 or H_2PdCl_4 concentrations were 9 μM for alloy NPs with a Ag atom% of ~24% and 16 μM for alloy NPs with a Ag atom% of ～34%.

Alloy	Ag content in growth solution	Ag atom % in alloy NPs by EDX before and after reaction with Pt(IV) or Pd (II) ions		% decrease in Ag content
		before	after	
Ag-Pt NPs	20 atom% of Ag	24.09	22.74	5.60%
Ag-Pd NPs	40 atom% of Ag	23.98	19.67	17.97%
Ag-Pt NPs	30 atom% of Ag	33.57	30.87	8.04%
Ag-Pd NPs	60 atom% of Ag	34.78	29.15	16.19%

Table S4. Composition (Ag atom%) of Ag-Au NPs as determined by EDX and XPS analyses.

Feeding Ag atom% in solution	Ag atom% in **Ag-Au** NPs	
	EDX	XPS
10	5.39	4.06
20	10.83	29.93
30	13.89	37.42
40	15.79	35.68
50	14.65	36.83
60	15.53	34.63
70	16.91	36.46

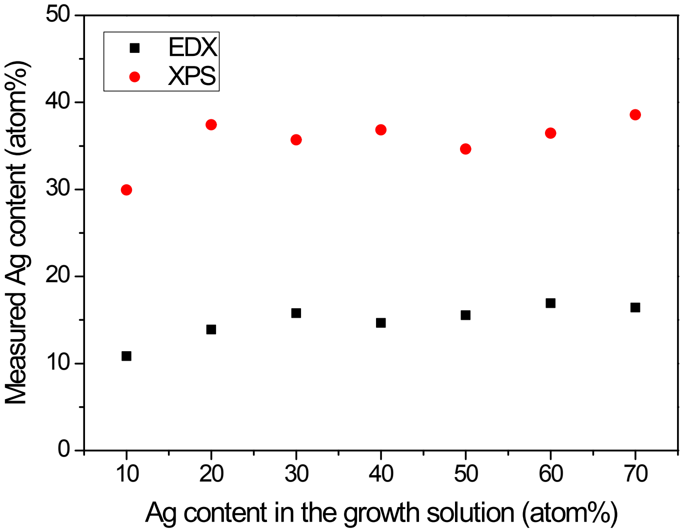

Figure S4. Plot of EDX and XPS measurements of Ag atom% in Ag-Au NPs (the experimentally measured values are also given in Table S4) against the Ag content in the growth solution.. The Ag atom% in the Au-Ag NPs are nearly constant regardless of the Ag^+ concentration in the growth solution. The Ag atom% measured by XPS were higher than those measured by EDX indicating a core-shell structure.

Table S5. Ag atom% measured by EDX in the Ag-Pt and Ag-Pd alloy NPs under different reaction conditions. Reference condition: [CTAB] = 16 mM, [HCl] = 0 mM, [NaBr] = 0 mM, [H_2PdCl_4] (or [H_2PtCl_6]) = 0.15 mM, and [$AgNO_3$] = 64 μM for 30 Ag atom% or [$AgNO_3$] = 150 μM for 50 Ag atom%. The reactant concentrations were the same as the reference condition unless specified.

Reaction conditions	Ag-Pt NPs prepared at 30 atom% of Ag	Ag-Pt NPs prepared at 50 atom% of Ag	Ag-Pd NPs prepared at 30 atom% of Ag	Ag-Pd NPs prepared at 50 atom% of Ag
Reference condition	33.57	52.11	17.89	29.92
[CTAB] = 4 mM	30.69	53.26	16.41	27.78
[CTAB] = 32 mM	32.23	54.05	18.17	29.05
[HCl] = 16 mM	32.98	50.12	15.65	29.66
[NaBr] = 16 mM	32.74	53.03	17.72	26.23

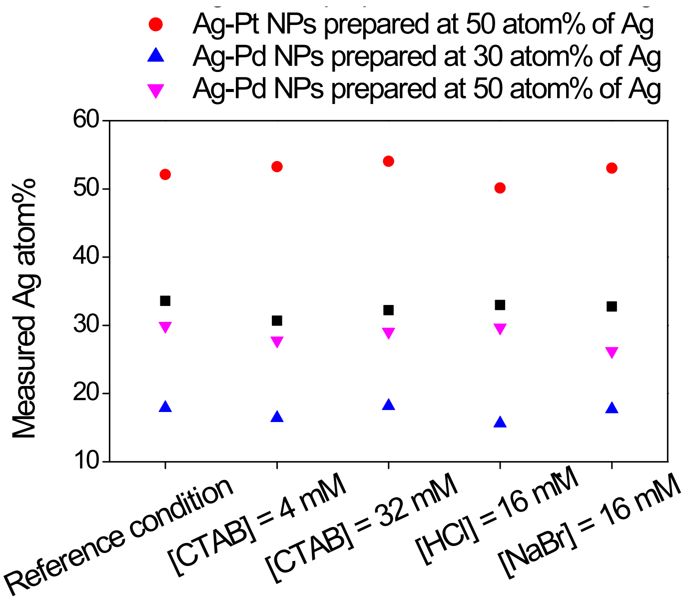

Figure S5. Plot of Ag atom% (measured by EDX) in Ag-Pt and Ag-Pd alloy NPs (the experimentally measured values are also given in Table S5) versus reaction conditions which differed by capping agent or additive concentration. Reference condition: [CTAB] = 16 mM, [HCl] = 0 mM, [NaBr] = 0 mM. All reactant concentrations were the same as the reference condition unless specified.

References

(1) Lee, H.; Habas, S. E.; Kweskin, S.; Butcher, D.; Somorjai, G. A.; Yang, P.: Morphological Control of Catalytically Active Platinum Nanocrystals. *Angew. Chem.* **2006**, *118*, 7988-7992.

(2) Hong, J. W.; Kang, S. W.; Choi, B.-S.; Kim, D.; Lee, S. B.; Han, S. W.: Controlled Synthesis of Pd–Pt Alloy Hollow Nanostructures with Enhanced Catalytic Activities for Oxygen Reduction. *ACS Nano* **2012**, *6*, 2410-2419.