Supporting Information

Synthesis of Platinum Cubes, Polypods, Cuboctahedrons and Raspberries Assisted by Cobalt Nanocrystals

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Experimental Procedures

Chemicals. Platinum (II) acetylacetonate (Pt(acac)₂, 98%) was purchased from Strem Chemicals and used as received. Oleylamine (OAM, 70%), 1,2-dichlorobenzene anhydrous (DCB, 99%), oleic acid (OA, 99%), 1,2-hexadecanediol (HDD, 90%), cobalt (II) acetylacetonate (Co(acac)₂, 97%), cobalt carbonyl moistened with 5-10% hexane (Co₂(CO)₈, 90-95%), cobalt (II) chloride (CoCl₂, 98%) and super-hydride[®] lithium triethylborohydride (in 1M THF) were purchased from Sigma-Aldrich and used as received. All chemicals were stored and prepared for synthesis in a UNIlab MBraun glovebox unless otherwise stated. The synthesis of Co NCs [Puntès, V. F.; Krishnan, K. M.; Alivisatos, A. P. *Science* **2001**, *291*, 2115] and Au NCs [Hiramatsu, H.; Osterloh, F. E. *Chem. Mater.* **2004**, *16*, 2509] follow the previously reported procedures and the NC purification was performed in the presence of methanol or acetone followed by dispersion in DCB or toluene, respectively.

Instrumentation. Transmission electron microscopy (TEM) analysis was performed on a JEOL 1010 with an accelerating voltage of 80 kV. High resolution TEM (HRTEM) analysis was performed on a JEOL 2100 with an accelerating voltage of 200 kV equipped with an energy-dispersive X-ray spectroscopy (EDX) detector. The Pt NCs were drop-cast onto a carbon coated grid and allowed to air dry under ambient conditions. X-ray diffraction (XRD) data were collected on a PANalytical X'Pert diffractometer using a Cu K α radiation source ($\lambda=1.541$ Å). In a typical experiment, the 2 θ diffraction (Bragg) angles were measured by scanning the goniometer from 25° to 100° at a speed of 0.021° s⁻¹. The samples were prepared by precipitating the Pt NCs in the presence of methanol or ethanol followed by brief centrifugation to ensure that all the NCs precipitated. The supernatant was discarded and the samples were dried under nitrogen before smearing onto (510) silicon wafers (3° off axis) for XRD analysis. Estimates of nanocrystal size were obtained using the Scherrer equation ($d = (K \lambda) / \beta \cos \theta$) where d is the mean crystallite dimension, K is the shape factor (0.9), λ is the X-

ray wavelength, β is the line broadening at full width half maximum (FWHM) (radians) and θ is the Bragg angle. The peak positions were determined using the X'Pert HighScore program and compared before and after baseline correction. Vegard's law of alloy nanocrystals was considered for a slight shift in the 2θ Bragg peaks when compared to those for bulk Pt. Induced coupled plasma-mass spectroscopy (ICP-MS) was performed using an ICP-MS Agilent instrument (Model: 7500cx) with a detection limit of 0.02386 ppb. For each sample, the as-synthesized NCs, the purified NCs and the supernatant from the purification were all subjected to ICP-MS analysis. Aliquots of the Pt NC samples were dissolved in concentrated aqua regia, which was then heated to ensure complete dissolution of all the metals, and diluted to an optimal concentration for ICP-MS analysis. Ga was used as the internal standard and the integration time/point and time/mass were 0.1 sec and 0.3 sec, respectively with a 3x repetition.

Synthesis.

Scheme S1. A general synthesis procedure where the only variable is the different traces added to the synthesis.

General Synthesis: Unless otherwise stated, all syntheses were performed under an argon atmosphere using the standard Schlenk-line setup. In a typical synthesis, a solution containing 92 mg of HDD (0.36 mmol), 45 μL of OAM and 10 mL of DCB was added to a 3-neck round-bottom flask equipped with a condenser. The solution temperature was increased to 180 $^{\circ}\text{C}$ using a glycerol oil bath over a time period of ~ 30 -60 min. Once the boiling temperature of DCB was reached, a 3 mL solution of DCB containing 45 mg of Pt(acac)_2 (0.11 mmol) was added drop-wise to the solution at a rate of 0.5 mL/min. 100 μL of trace (0.0018 mmol) was then added immediately to the solution. The solution was refluxed at 180 $^{\circ}\text{C}$ for 20 min and gradually cooled down to room temperature before being transferred to an argon filled vial. In order to remove the excess capping/reducing agent or ions, the Pt NCs were purified by precipitation in methanol (or ethanol), followed by brief centrifugation and redispersion in DCB.

Temperature Dependent Synthesis: To study the effect of temperature on the synthesis of Pt NCs, the reaction was performed at 140 $^{\circ}\text{C}$ and 180 $^{\circ}\text{C}$. In a typical synthesis, 92 mg of HDD, 45 μL of OAM and 100 μL of pre-synthesized (unpurified) Co NCs (0.0018 mmol) were added to 10 mL of DCB. The temperature of the solution was increased to 140 $^{\circ}\text{C}$ where 3 mL of

Pt(acac)₂ (45 mg) was added drop-wise at rate of 0.2 mL/min. After adding the Pt(acac)₂, the solution was heated for 30 min at 140 °C after which an aliquot was taken out for TEM analysis. The temperature was then increased to 180 °C where the remaining solution refluxed for another 30 min before gradually cooling down to room temperature.

Different Synthesis Conditions:

Synthesis of Pt NCs in aqueous media: [Pt NCs (Aq)]

The citrate capped Pt NCs were synthesized following the previously reported procedure [Xu, S. L.; Cui, H. *Luminescence* 2007, 22, 77] with some slight modifications (Figure 8A). Briefly, K₂PtCl₄ (0.03 mmol) was added to 100 mL of deionized water in a round bottom flask and boiled at 100 °C. A 5 mL solution of trisodium citrate (1%) was then added all at once and the solution was refluxed for 1 hour before being gradually cooled down to room temperature.

Changing the sequential addition of Pt(acac)₂: [Pt(acac)₂ added at RT]

For the synthesis shown in Figure 8B, the Pt(acac)₂ precursor (45 mg in 3 mL DCB) was added along with OAM and HDD (45 µL OAM and 93 mg HDD) in 10 mL DCB at room temperature. The solution was then heated to 180 °C where 100 µL of Co₂(CO)₈ (0.0018 mmol) was added immediately. The reaction was refluxed for 30 min at 180 °C before being gradually cooled down to room temperature.

Changing the sequential addition of pre-synthesized Co NC and reaction time: [Co NCs added at RT, TEM @ 2hrs]

For the synthesis shown in Figure 8C, the unpurified pre-synthesized Co NCs were added at the beginning of the reaction. In a typical synthesis, 90 mg of HDD, 45 µL of OAM and 100 µL of pre-synthesized Co NCs (unpurified, 0.0018 mmol) were added to 10 mL DCB. The temperature of the solution was increased to 180 °C where 3 mL of Pt(acac)₂ (45 mg) was added drop-wise (0.2 mL/min). The solution was refluxed for 2 hrs at 180 °C and gradually cooled down to room temperature.

Varying the concentration of pre-synthesized Co NC and HDD and reaction time: [[Co NCs] ↑]

For the synthesis shown in Figure 8D, the concentration of the pre-synthesized Co NC trace was increased 10x and added at the beginning of the reaction. In a typical synthesis, 30 mg of HDD and 45 µL of OAM were added to 9 mL DCB and 1 mL of pre-synthesized Co NCs (unpurified, 0.018 mmol). The solution was heated up to 180 °C where 40 mg of Pt(acac)₂ in 3 mL DCB was added drop-wise at a rate of 0.1 mL/min. The solution was refluxed for 2 hrs at 180 °C and gradually cooled down to room temperature.

Varying the concentration of OAM and reaction time: [[OAM] ↑]

For the synthesis shown in Figure 8E, the concentration of OAM was increased 2.2x. In a typical synthesis, 94 mg of HDD and 100 µL of OAM was added to 10 mL DCB. The solution was heated up to 180 °C where 45 mg of Pt(acac)₂ in 3 mL DCB was added drop-wise at a rate of 0.6 mL/min. 100 µL of Co₂(CO)₈ (0.0018 mmol) was added immediately and the solution was refluxed for 50 min at 180 °C and gradually cooled down to room temperature.

Addition of Oleic Acid (OA) and Oleylamine (OAM): [OAM+OA]

For the synthesis shown in Figure 8F, both OA and OAM were added. In a typical synthesis, 93 mg of HDD, 45 µL of OAM and 45 µL of OA were added to 10 mL DCB. The solution was heated up to 180 °C where 45 mg of Pt(acac)₂ in 3 mL DCB was added drop-wise at a rate of 0.4 mL/min. 100 µL of Co₂(CO)₈ (0.0018 mmol) was added immediately and the solution was refluxed for 15 min at 180 °C and gradually cooled down to room temperature.

Vegard's Law

The definition of Vegard's law provided by Ashcroft *et al.* [*Phys. Rev. A* **1991**, 43, 3161] is "an approximate empirical rule which holds that a linear relation exists, at constant temperature, between the crystal lattice constant of an alloy and the concentrations of the constituent elements." The lattice parameter (*a*) of Pt and Co NCs used in this calculation are: 3.917 Å for 100% Pt and 3.533 Å for 100% Co NCs [Nam, K. M.; Shim, J. H.; Ki, H.; Choi, S.; Lee, G.; Jang, J. K.; Jo, Y.; Jung, M.; Song, H.; Park, J. T. *Angew. Chem.* **2008**, 120, 9646]. For *a* = 3.905 Å (Pt NCs synthesized in the presence of Co), the % Co was calculated

$$\text{by: } x = \frac{100\%(3.917 - 3.905)}{3.917 - 3.533} \text{ where } x = 3.1\% \text{ Co.}$$

ICP-MS Analysis

<i>TEM Images</i>	<i>Metallic Trace</i>	<i>Sample Description</i>	<i>Co ppm</i>	<i>Pt ppm</i>	<i>% Co</i>	<i>% Pt</i>
Co ₂ (CO) ₈	As synthesized NCs	6.40	1048.0	1.98	98.02
	Co ₂ (CO) ₈	Purified NCs	4.65	559.0	2.68	97.32
	Co ₂ (CO) ₈	Supernatant from purification	0.38	473.8	0.26	99.74
^{a)} Co(acac) ₂	As synthesized NCs	4.90	607.5	2.60	97.40
	^{a)} Co(acac) ₂	Purified NCs	0.10	111.5	0.30	99.70
	^{a)} Co(acac) ₂	Supernatant from purification	4.13	376.3	3.50	96.50
^{b)} Co(acac) ₂	As synthesized NCs	8.15	1007.0	2.61	97.39
	^{b)} Co(acac) ₂	Purified NCs	6.75	449.5	4.74	95.26
	^{b)} Co(acac) ₂	Supernatant from purification	0.13	500.0	0.08	99.92

Table S1. ICP-MS analysis comparing the atomic % Co and % Pt obtained for three different synthesis using Co₂(CO)₈ and Co(acac)₂ as traces. In each batch of syntheses, the as-synthesized NCs, the purified NCs and the supernatant from the purification were subjected to ICP-MS analysis. Two samples from the Co(acac)₂ were chosen for analysis due to the different morphologies observed in TEM. (^a) Co(acac)₂ shows polypod structure and (^b) Co(acac)₂ shows cemented cubes structure). Overall, the experimentally determined compositions are in agreement with the theoretical proportion Co and Pt amounts that were added to a typical synthesis. (theoretical: 2% Co and 98% Pt). The difference in proportion between the added and the measured element concentration is in the solution in ionic form.

Figure S1. HRTEM images of the polypods oriented attached into a multi-crystalline (A) and single-crystalline (B) structure. The FFT pattern in (B) indicates that the (111) planes are perfectly aligned and have a single crystal structure.

Figure S2. A control experiment demonstrating the formation of Co NCs within a 2 min reaction time. The synthesis follows the experimental procedures reported in the paper but in the absence of $\text{Pt}(\text{acac})_2$. For example, upon heating the solution containing DCB, HDD and OAM to 180 °C, 100 μL of $\text{Co}_2(\text{CO})_8$ was added immediately. The solution was heated for 2 min at 180 °C and transferred to an argon filled vial immediately. The background contrast is due to the excess HDD and OAM still remaining at short reaction times.

Figure S3. HRTEM images and their corresponding FFT patterns for the Pt NCs synthesized in the presence of a $\text{Co}_2(\text{CO})_8$ metallic trace. Both examples show that the Pt NC cubes have a preferential orientation along the [100] zone axis, showing facets on the {100} planes.

Figure S4. EDX spectra obtained on different areas of the Pt NC samples synthesized in the presence of a $\text{Co}_2(\text{CO})_8$ metallic trace. The Pt NCs were purified prior to EDX analysis to remove all excess ions and capping agents. Notice that the Co amount varies from 3% to 6% depending on the different areas of the grid. The average content is around 4.5%.