

Supporting information for:

# Controlling the Growth Kinetics of Nanocrystals via Galvanic Replacement: Synthesis of Au Tetrapods and Star-shaped Decahedra

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## **S1. Expanded Experimental Details**

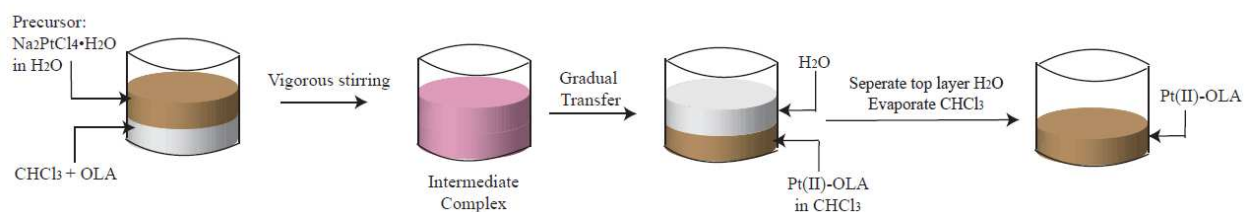
### **S1-a. Synthesis of Branched Au Nanocrystals**

In the optimized synthesis represented by Figure 1, Au and Pt precursors were dispersed in 0.05 mM oleylamine and hexane at a 1-to-1 Au-to-Pt mole ratio, with final Au(I) and Pt(II) concentrations both being 5mM. Neither AuCl nor Na<sub>2</sub>PtCl<sub>4</sub> are directly soluble in hexane. Thus, a phase transfer procedure was developed (Step 1). The Au and Pt precursors were then combined for the synthesis of branched Au nanocrystals (Step 2).

#### **Step 1: Solubilization of Pt(II) and Au(I) precursors**

In preparation for the optimized synthesis, 0.4mmol of oleylamine and 0.03mmol AuCl were dissolved in 3mL chloroform. The chloroform was then removed by rotary evaporation, yielding a viscous yellow solution of Au(oleylamine)Cl in excess oleylamine.<sup>1</sup> For Pt, 0.03 mmol of Na<sub>2</sub>PtCl<sub>4</sub>•XH<sub>2</sub>O was first dissolved in 3mL of Millipore H<sub>2</sub>O, yielding a brown-yellow

aqueous solution. Separately, 0.4mmol oleylamine was dissolved in 3mL chloroform, which was subsequently added to the Pt(II) aqueous solution to create a biphasic mixture. For experiments represented by Figure 5, the oleylamine concentration was varied during Step 1. The mixture was vigorously vortexed for 10 minutes to facilitate coordination of the Pt(II) with oleylamine and its transfer into organic phase. The emulsion was then allowed to settle back into two phases, with the organic layer containing Pt(II) settling on the bottom and the aqueous layer on top. This process was monitored visually with the initially brown solution turning pink when being emulsified with the oleylamine/chloroform phase. Upon settlement, the aqueous layer appeared colorless while the organic layer was now a transparent brown-yellow color. Upon completion of the phase transfer process, the bottom organic layer was isolated. The chloroform was then removed via rotary evaporation, yielding a solution containing  $\text{Pt(oleylamine)}_2\text{Cl}_2$  and excess oleylamine. This process is represented by Figure S1.

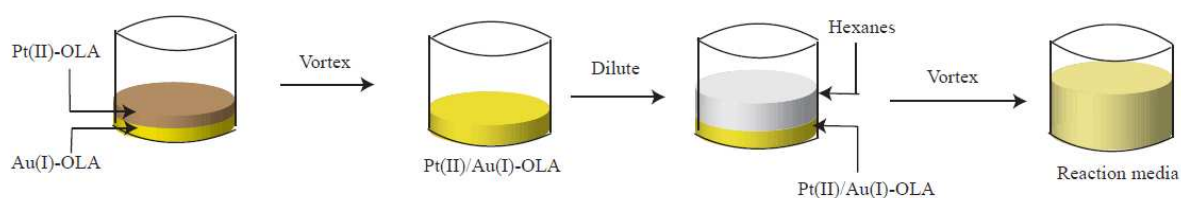


**Figure S1.** Scheme of stepwise phase transfer technique for the solubilization of Pt(II) into organic solvent.

## Step 2: Synthesis of branched Au nanocrystals

For the optimized synthesis of branched Au nanocrystals, the phase-transferred Au and Pt precursors were combined as prepared and mixed by vortexing for 5 minutes. The solution was then diluted with hexanes for a total volume of 6 mL (Figure S2). The solution was then

transferred to a 3-neck, 25 mL flask, which was sustained in a silicone oil bath at a constant temperature of 60°C for 52 hours with stirring at 400 rpm. The reaction temperature was modified for studies described in Figure 3. The 3-neck flask was equipped with a cold-water condenser and modified septa to allow gas flow into and out of the reaction vessel. The solution was saturated with N<sub>2</sub>/H<sub>2</sub> gas (95% N<sub>2</sub> and 5% H<sub>2</sub>) by sparging it for the initial 30 minutes of the reaction while cold water (15 °C) flowed through a condenser for 1 hour. The product was collected as described in the manuscript body.

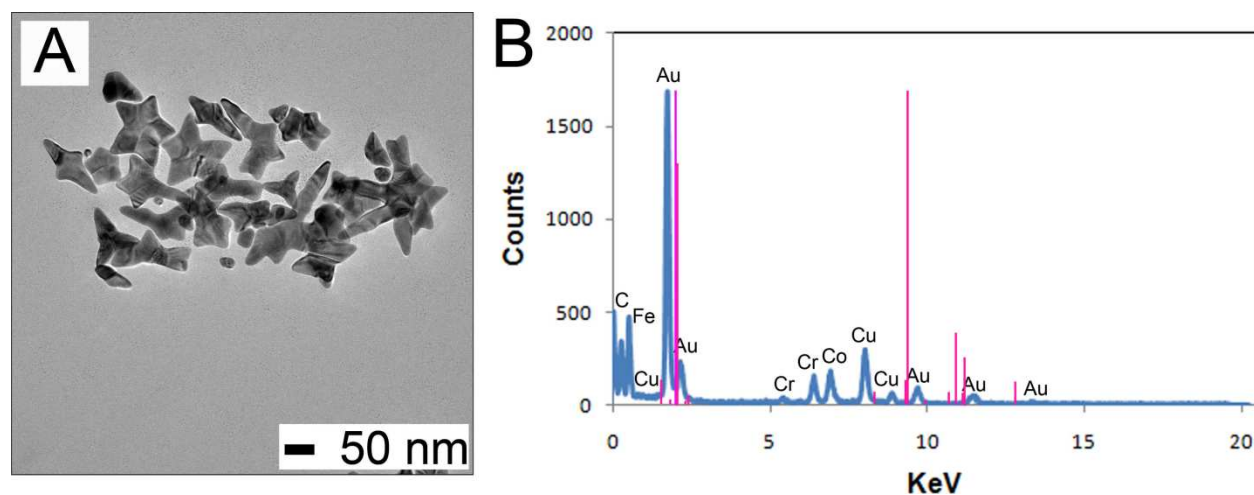


**Figure S2.** Final steps involved in reaction preparation.

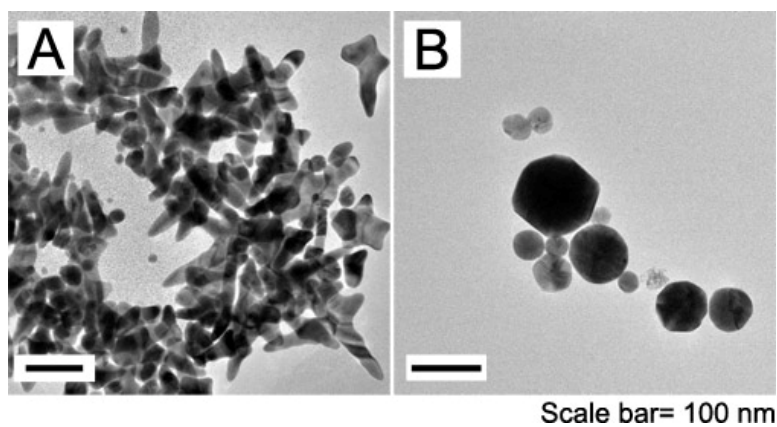
#### **S1-b. Sample Preparation Procedure for ICP-OES Analysis**

1.0 mg of sample was digested in 50 mL of freshly prepared aqua regia (1:3 HNO<sub>3</sub>:HCl). For this metal analysis, a Perkin Elmer Optima 2000 Dual-View ICP-OES was used which constructs a calibration curve by first running a blank, a standard, then the sample.

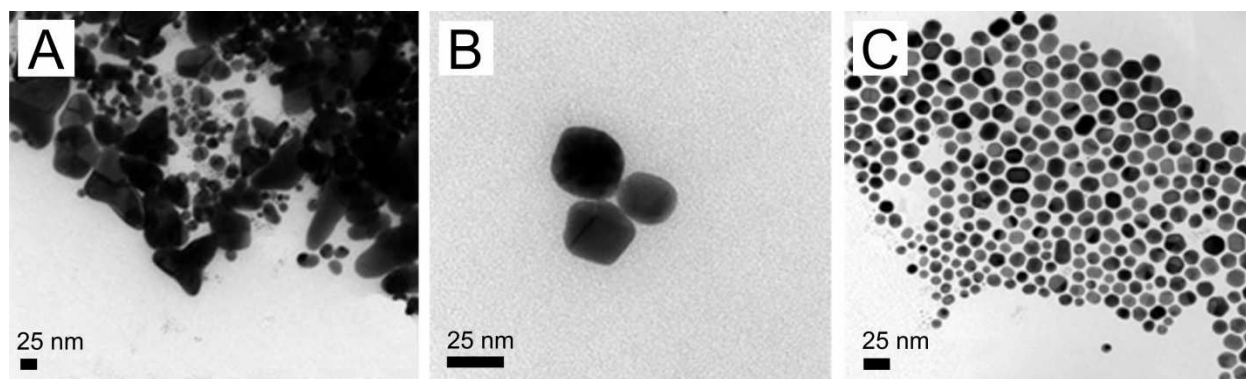
## S2. Additional Characterization and Results from Control Experiments



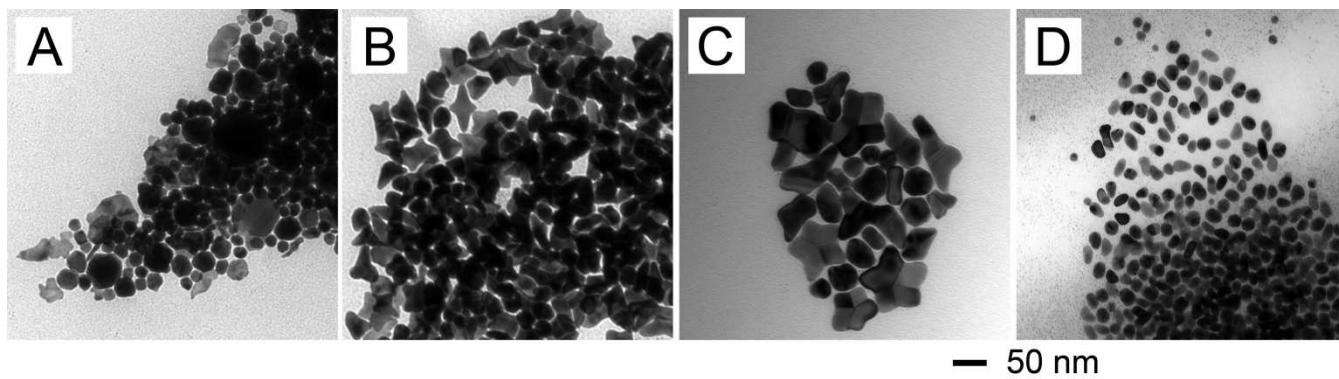
**Figure S3.** (A) TEM image of branched gold particles and (B) corresponding EDX spectrum. Detection of Fe, Cr, and Co arise from high-tilt sample holder and Cu peaks from TEM grid. There is no indication of Pt in the sample, with the expected positions for signature Pt peaks labeled pink.



**Figure S4.** TEM image of branched Au nanocrystals (A) after one year of storage in hexanes at room temperature and (B) subsequent prolonged heating (130 °C, 22 hours) in oleylamine.



**Figure S5.** TEM images of products obtained from control experiments, which indicate that both Au(I) and Pt(II) are required for branched Au nanocrystal formation. In (A), the results obtained when Pt(II) was omitted from the synthesis but all other experimental parameters held constant with the optimized conditions. In (B), the results obtained when Au(I) was omitted from the synthesis but all other experimental parameters held constant with the optimized conditions. In (C), the results obtained when Au(I) was replaced with Au(III) for the Au precursor.



**Figure S6.** TEM images of the results obtained when the Pt(II) complex was replaced with the analogous Pd(II) complex. The Au:Pd mole ratio is (A) 1:0.1, (B) 1:1, (C) 1:1.2, and (D) 1:1.6.

## References

- (1) Lu, X.; Yavuz, M. S.; Tuan, H.-Y.; Korgel, B. A.; Xia, Y. *J. Am. Chem. Soc.* **2008**, *130*, 8900-8901.