SUPPORTING INFORMATION

Microscopic Investigation of Chemoselectivity in Ag-Pt-Fe₃O₄ Heterotrimer Formation: Mechanistic Insights and Implications for Controlling High-Order Hybrid Nanoparticle Morphology

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Additional Experimental Details

Differential Magnetic Catch and Release (DMCR). DMCR is a magnetic nanoparticle separation technique^{1,2} that was used to purify each aliquot (as described in the main text) in order to obtain samples for microscopy that were enriched in targeted fractions containing magnetic Fe₃O₄ domains. A typical DMCR fractogram for the purification of the 14-hour Ag-Pt-Fe₃O₄ sample is shown below. The first peak elutes while the magnetic flux is held at 1.8 T, and it consists of non-magnetic material, such as excess surfactants, Pt, Ag, and Pt-Ag particles. After 800 seconds the field was dropped from 1.8 T to 0 T in order to elute the population containing the magnetically targeted Ag-Pt-Fe₃O₄ particles.



Synthesis of Pt nanoparticle seeds. Following a previously reported procedure,³ Pt(acac)₂ (200 mg), OLAC (2 mL) and OLAM (2 mL) were mixed with ODE (20 mL) in a 50-mL 3-neck round bottom flask equipped with a thermocouple, gas flow adapter, rubber septum, and magnetic stir bar. The reaction solution was heated to 120 °C and held under vacuum for 30 minutes to remove any dissolved air or water. The system was then exposed to an Ar blanket, and heated to 185 °C followed by rapid injection of Fe(CO)₅ (0.02 mL) dissolved in ODE (0.2 mL). The system was then heated to 190 °C and held for one

hour, before being cooled to room temperature. The Pt particles were precipitated by adding 2propanol and then isolated using centrifugation. The precipitated particles were redispirsed in hexanes with 0.5% OLAM and 0.5% OLAC by volume, precipitated again with ethanol, and isolated by centrifugation. This washing procedure was repeated one more time with ethanol, and the final nanoparticle samples were redispersed in hexanes with 0.5% OLAM and 0.5% OLAC by volume. The resulting Pt nanoparticles were cubic in shape with an average length of 8.1 ± 1.1 nm, measured from corner to corner, diagonally across the particle.

Synthesis of Pt-Fe₃O₄ nanoparticle seeds. Following a previously reported procedure,⁴ OLAC (0.45 mL) was mixed with ODE (10 mL) in a 50-mL 3-neck round bottom flask equipped with a thermocouple, condensing column, gas flow adapter, rubber septum, and magnetic stir bar. The reaction solution was heated to 120 °C and held under vacuum for 15 minutes to remove any dissolved air or water, before being exposed to an Ar blanket. Fe(CO)₅ (35 μ L) dissolved in ODE (125 μ L) was then injected rapidly. After five minutes, OLAM (0.5 mL) and Pt nanoparticle seeds (10 mg dissolved in 1mL ODE) were injected. The reaction solution was then heated to 310 °C at a rate of 3 °C min⁻¹ and held at this temperature for 30 minutes. The resulting solution was cooled to 100 °C, and then air was bubbled through the solution for 16 hours to ensure complete oxidation of the iron to form Fe₃O₄. The solution was then cooled to room temperature, the particles were precipitated from the product mixture by adding 2-propanol, and then isolated using centrifugation. The precipitated particles were redispersed in hexanes with 0.5% OLAM and 0.5% OLAC by volume, precipitated again with ethanol, and isolated by centrifugation. This washing procedure was repeated one more time with ethanol, and the final nanoparticle samples were redispersed in hexanes with 0.5% OLAM and 0.5% OLAC by volume. The final product was composed of a mixture distinct dimer structures with spherical Fe_3O_4 domains (16.8 ± 2.0 nm) and cubic Pt domains, as well as unreacted Pt seed particles.

Synthesis of Bimodal Pt-Fe₃O₄. In order to generate Pt-Fe₃O₄ nanoparticle seeds with a wider size distribution, a modified procedure of Wu et al.⁵ was followed. Pt nanoparticle seeds were synthesized as described above. To generate Pt-Fe₃O₄ dimers with an Fe₃O₄ domain size of 15 ± 2.0 nm, Pt nanoparticle seeds (5 mg) were mixed with OLAM (6 mL) OLAC (4 mL) and Fe(acac)₃ (70 mg) in a 50-mL 3-neck round bottom flask equipped with a thermocouple, condensing column, gas flow adapter, rubber septum, and magnetic stir bar. The reaction solution was held under vacuum for 5 minutes, to remove any dissolved water or air, and then introduced to an Ar blanket and heated rapidly to 310 °C, where it was held for 30 minutes. The resulting solution was cooled to 100 °C, and air was bubbled through the solution for 16 hours to ensure complete oxidation of the iron to form Fe₃O₄. The solution was then cooled to room temperature, and precipitated through the same 2-propanol/ethanol rinse cycles as described above. The final particles were redispersed in hexanes with with 0.5% OLAM and 0.5% OLAC by volume.

Pt-Fe₃O₄ dimer nanoparticles with an average Fe₃O₄ domain size of 10 ± 2.0 nm were synthesized using the same method of Wu et al. mentioned above,⁵ under identical conditions, except 15 mg of Pt nanoparticle seeds were used instead of 5 mg. This increase in the Pt seed: Fe(acac)₃ ratio reduced the total amount of Fe deposited on each Pt seed. It should be noted that a large amount of unreacted Pt was also observed in this synthesis, which is visible in the TEM image shown in Figure 5a of the main text. The presence of free Pt did not influence the outcome of the "bimodal Ag-Pt-Fe₃O₄" control experiment, and Pt-Ag dimer particles are again observed after Ag growth, suggesting the Fe shell encompasses the Pt domain of the Pt-Fe₃O₄ dimers prepared with Fe(acac)₃ as well. Synthesis of Iron Oleate and Bimodal Fe_3O_4 . A modified procedure described by Park et al.⁶ was used to generate monodisperse Fe_3O_4 of controllable size. Iron oleate was first prepared by adding iron(III) chloride hexahydrate (36.5g) and sodium acetate (10.8 g) to a mixture of ethanol (60 mL), distilled deionized water (80 mL), and hexanes (140 mL) and then heated to 70 °C, where it was held overnight. The organic phase of the resulting solution was isolated with a separatory funnel, washed three times with distilled deionized water, and dried by vacuum filtration overnight to yield the waxy, dark-brown iron oleate product. To synthesize the 16 ± 2 nm Fe₃O₄ nanoparticles, iron oleate (2.25g) was added to a solution of OLAC (0.37g) and ODE (12.5 g) in a 50-mL 3-neck round bottom flask equipped with a thermocouple, condensing column, gas flow adapter, rubber septum, and magnetic stir bar. The reaction solution was held under vacuum for 30 minutes at room temperature and then introduced to an Ar blanket. The reaction solution was then heated to 310 °C at a rate of 3.3 °C min⁻¹, and then held at 310°C for 25 minutes. The resulting solution was cooled to 100°C, and then air was bubbled through the solution for 16 hours to ensure complete oxidation of the iron to form Fe_3O_4 . The solution was then cooled to room temperature, the particles were precipitated from the product mixture by adding 2propanol, and then isolated using centrifugation. The precipitated particles were redispersed in hexanes with 0.5% OLAM and 0.5% OLAC by volume, precipitated again with ethanol, and isolated by centrifugation. This washing procedure was repeated one more time with ethanol, and the final nanoparticle sample was redispersed in hexanes with 0.5% OLAM and 0.5% OLAC by volume. The 24 \pm 2nm Fe₃O₄ nanoparticles were synthesized under identical conditions and reactant ratios, but the reaction was held at 310 °C for 1 hour (instead of 25 minutes).

Synthesis of 9-nm spherical Ag nanoparticles. $Ag(C_2H_3O_2)$ (36 mg) and OLAM (3.75 mL) were mixed with toluene (10 mL) in a 50-mL 3-neck round bottom flask equipped with a thermocouple, gas flow adapter, rubber septum, and magnetic stir bar. The reaction solution was held under vacuum for 3 minutes, before being introduced to an Ar blanket and heated to 65 °C, where it was held for 14 hours. The resulting reaction mixture was worked up with the repeated ethanol wash procedure as described for the Ag-Pt-Fe₃O₄ in the Experimental Section of the main text. The final Ag particles were redispersed in hexanes with 0.5% OLAM and 0.5% OLAC by volume. The resulting spherical Ag nanoparticles were 9 ± 3 nm in diameter.

Supplementary Figures







Figure S2: Bright field TEM images for the magnetically purified Ag-Pt-Fe₃O₄ samples of Aliquot #1 (15 minute sample), Aliquot #2(60 minute intermediate sample) and the 14 hour final product.



Figure S3: High resolution TEM images for the (a) Ag-(Pt-Fe₃O₄) 60 minute intermediate sample and (b) the Ag-Pt-Fe₃O₄ 14-hour final product.



Figure S4: Large area HAADF-STEM image for the Ag-(Pt-Fe₃O₄) 60 minute intermediate sample showing multiple Ag domains indiscriminately decorated across the Pt-Fe₃O₄ surface.



Figure S5: (a) HAADF-STEM image and (b) STEM-EDS map for the core shell Pt@Ag nanoparticles.



Figure S6: Additional bright field TEM images for the populations of "Bimodal Ag-Fe₃O₄".



Figure S7: Histograms showing the size distribution of the Fe_3O_4 and corresponding Ag domains for the "Bimodal Ag-Fe₃O₄" sample.



Figure S8: (a) Bright Field TEM image of (a) $Au-Fe_3O_4$ heterodimers, (b) Ag-Au-Fe_3O_4 heterotrimers, (c) Au nanoparticle seeds, and (d) Au-Ag nanoparticles, grown under identical conditions to the Ag-Au-Fe₃O₄ heterotrimers. (e) STEM-EDS map of the same Au-Ag particles from (d), showing overlapping Au and Ag signals.



Figure S9: Optical absorption spectra for the as-made 14-hour Ag-Pt-Fe₃O₄ product, Pt@Ag core-shell sample, and 9-nm spherical Ag nanoparticles.

References

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