

Supporting Information

Facile Synthesis of Tadpole-Like Nanostructures Consisting of Au Heads and Pd Tails

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Experimental

Chemicals and Materials. Ethylene glycol (EG, J. T. Baker, 99.9%), sodium palladium(II) chloride (Na_2PdCl_4 , Aldrich, 99.998%), potassium bromide (KBr, Fisher), sodium chloride (NaCl, J. T. Baker), poly(vinyl pyrrolidone) (PVP, MW \approx 55,000, Aldrich), and ethanol (AAPER Alcohol and Chemical Co., 200 proof) were all used as received.

Synthesis of Pd Nanorods. In a typical synthesis, 5 mL of EG was added to a 25-mL three-neck flask equipped with a reflux condenser and a Teflon-coated magnetic stirring bar. This system was heated at 140 °C in air under magnetic stirring for 1 h. Meanwhile, 0.0486 g of Na_2PdCl_4 and 0.2574 g of KBr were dissolved in 3 mL of water, and 0.0916 g of PVP was dissolved in 3 mL of EG at room temperature. These two solutions were then injected simultaneously into the flask using a two-channel syringe pump (KDS-200, Stoelting, Wood Dale, IL) at a rate of 45 mL per hour. The reaction mixture was heated at 140 °C in air for another 3 h before the product was collected by centrifugation and washed with acetone once and with ethanol three times to remove most of the EG and excess PVP.

Galvanic Replacement Reactions. In a typical synthesis, a fixed amount (15 mM, 200 μL) of Pd nanorods was dispersed in 5 mL of water containing PVP (1 mg/mL) in a 50-mL flask under magnetic stirring. This system was heated at 100 °C for 10 min. A specific amount (as indicated in the text) of 0.4 mM HAuCl_4 was added to the flask through a syringe pump at a rate of 45 mL per hour under magnetic stirring. The solution was heated for another 10 min and then cooled down to room temperature. After that, the solution was centrifuged and washed with saturated NaCl solution to ensure that all Pd(II) species were in the form of $[\text{PdCl}_4]^{2-}$ to avoid the precipitation of PdCl_2 . Finally, the sample was centrifuged and washed with water several times to remove PVP and NaCl before characterization.

Instrumentation. Transmission electron microscopy (TEM) studies were performed with a Phillips CM100 microscope operated at 100 kV. The TEM images were obtained with a Gatan digital camera. High-resolution TEM images (HRTEM) were taken on a JEOL field-emission transmission electron microscope (2100F) operated at 200 kV. Filtered images were generated by inverse FFT with a Gatan Digital Micrograph program. The STEM/EDS measurements were collected using a Vacuum Generator HB501 STEM microscope equipped with an EDS - Oxford

ISIS 30mm ATW detector. Samples for TEM and HRTEM studies were prepared by drying drops of the aqueous suspension of the nanostructures on carbon-coated copper grids (SPI, West Chester, PA) under ambient conditions. UV-visible (UV-vis) absorption spectra were taken on a Hewlett-Packard 8452A spectrometer using quartz cuvettes with an optical path length of 1 cm.

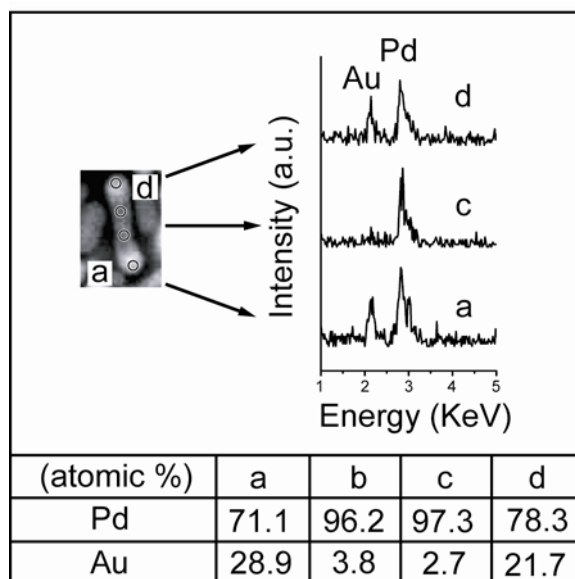


Figure S1. STEM/EDS analysis at 4 different sites (*a-d*) along the Pd-Au hybrid nanostructure shown in Figure 1B. It is clear that Au was mainly deposited on both ends of the Pd nanorod. The enclosed table presents the EDS atomic percentages for Pd and Au at sites *a-d*, confirming that Au was mainly localized to the ends (while the middle segment contains essentially all Pd). The EDS spectra taken from *a*, *c* and *d* are also included.

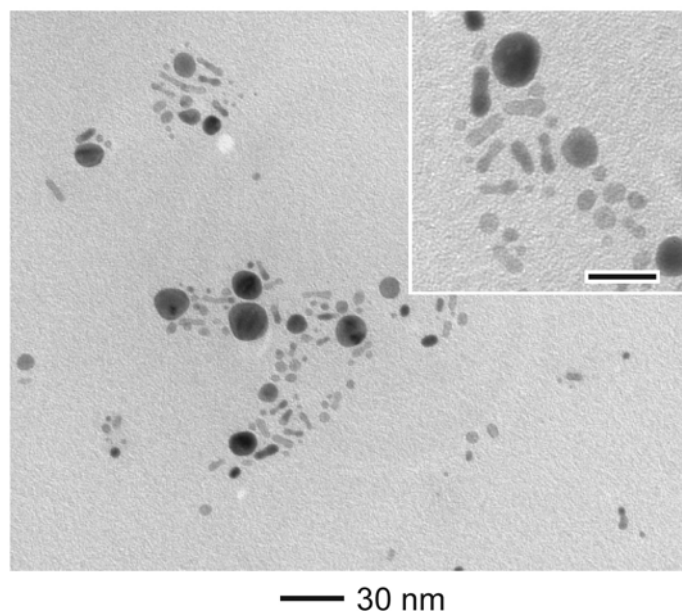


Figure S2. Titration of Pd nanorods with 10 mL of 0.4 mM HAuCl_4 . In this case, the Pd-Au tadpoles were dismantled into round Au nanoparticles and smaller/shorter Pd fragments. The scale bar in the inset corresponds to 20 nm.

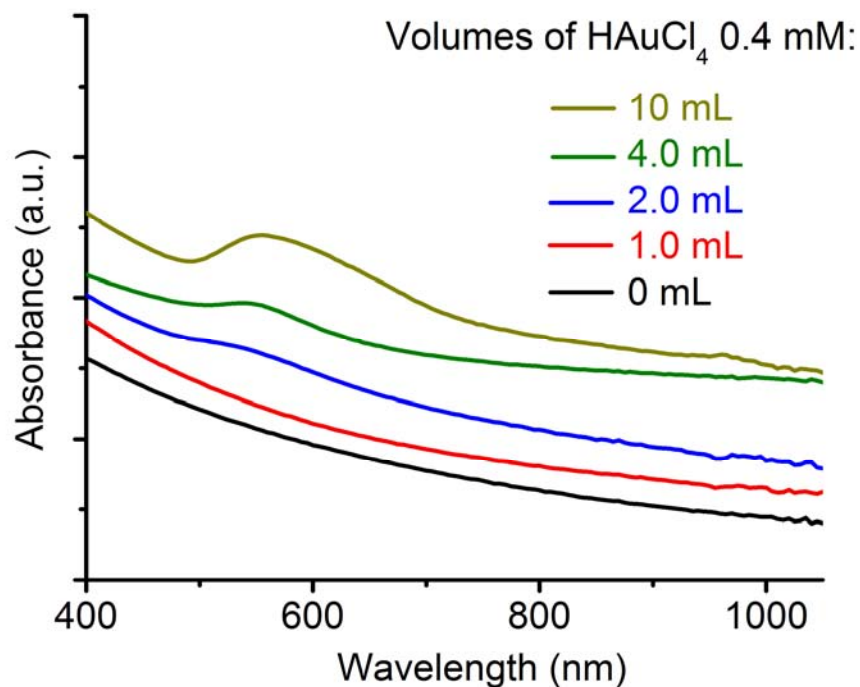


Figure S3. UV-vis spectra taken from a suspension of Pd nanorods after they had been titrated with 1, 2, 4 and 10 mL of 0.4 mM HAuCl₄. A broad peak around 560 nm developed as the volume of HAuCl₄ was increased from 2 to 10 mL, clearly showing the evolution of a localized surface plasmon resonance (LSPR) mode associated with the Au nanoparticles either located at the tips of the Pd-Au tadpoles (Au heads) or de-attached from the Pd segments.

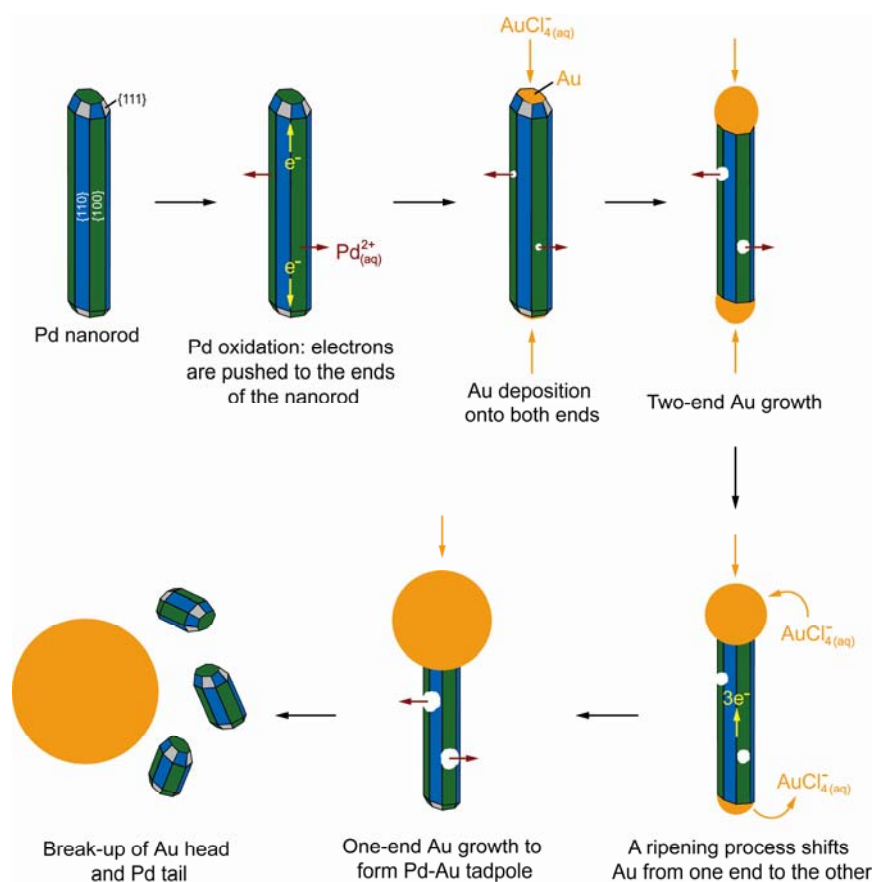


Figure S4. Schematic detailing all major steps involved in the galvanic replacement reaction between a Pd nanorod and AuCl_4^- ions. In the first step, Pd atoms are oxidized from certain sites on the nanorod, producing electrons that are quickly pushed to the ends of the nanorod due to the strong repulsion between them. AuCl_4^- ions are reduced by the electrons and epitaxially deposited onto both ends (two-end growth). As more Pd oxidation and AuCl_4^- reduction take place, the Au tips grow and reach a critical size at which a ripening process shifts Au from one end to the other, leading to a transition from two-end to one-end growth and production of a Pd-Au tadpole. The driving force for this ripening process comes from the stabilization of one Au head relative to the other one on each nanorod when the size difference between these two Au heads becomes sufficiently large as the tips grow and reach a critical size. In this scenario, the difference in surface energy favors the growth of larger particles at the expense of smaller ones. The Pd nanorod can provide a conductive path for electron migration from one tip to the other. As Pd oxidation further continues, more Au atoms will be deposited onto the Au head, and this growth can continue until the Pd-Au tadpoles are dismantled into short Pd fragments and a Au nanoparticle.