Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Engineering High Refractive Index Sensitivity through the Internal and External Composition of Bimetallic Nanocrystals

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Experimental Details

Chemicals and Supplies

L-ascorbic acid ($C_6H_8O_6$, L-AA, 99%), palladium (II) chloride ($PdCl_2$, 99.98%), chloroauric acid ($HAuCl_4 \bullet 3H_2O$, 99.9%), cetyltrimetylammonium bromide (CTAB, > 99.0% LOT # BCBK3869V), and sodium borohydride ($NaBH_4$ 98.5%) were purchased from Sigma Aldrich. Concentrated hydrochloric acid (HCl, 12.1M) was purchased from Mallinckrodt. Sodium Bromide (NaBr, 99.50%) and Dimethyl sulfoxide (DMSO) was purchased from J. T. Baker. Poly(styrene sulfonic acid) sodium salt (Na-PSS, MW = 700K) was purchased from Alfa Aesar. Nanopure water (18.2 MΩ•cm) was used in all experiments. An aqueous 10 mM H_2PdCl_4 solution was prepared by stirring dissolved $PdCl_2$ (44.6 mg) in 25 mL of HCl (pH 1.69) for 1 h while heating at ~70 °C.

Synthesis of Pd and Au Cubic Seeds

Synthesis of small cubic Pd seeds was adapted from previously published literature protocol.[1,2] To synthesize NCs, 0.5 mL H_2PdCl_4 (10 mM) was added to 10 mL CTAB (12.5 mM) and stirred in a 95°C oil bath for 5 minutes. Next, 0.08 mL L-AA (100 mM) was added. The solution was stirred for 30 minutes in the 95°C oil bath and stored at 40°C. Prior to use for co-reduction, the solution was centrifuged at 3,900 RPM for 30 minutes and diluted to 3 mL.

Synthesis of large cubic Pd seeds was adapted from previously published literature protocol.[1,2] To synthesize NCs, 0.125 mL H_2PdCl_4 (10 mM) was added to 5 mL CTAB (50 mM) in a 40°C oil bath. Next, small Pd seeds (unwashed) were injected (0.2, 0.05, 0.03 mL for 35±3, 52±3, and 60±3 nm cubes), followed by 0.025 mL L-AA (100 mM). Solutions were mixed by shaking and left undisturbed 14 hours in a 40°C oil bath. The solution was centrifuged at 3,900 RPM for 30 minutes and diluted to 3 mL.

The synthesis of Au nanocubes is adapted from a previous literature protocol.[3] Gold seeds were initially prepared. To synthesize seeds, 0.25 mL $HAuCl_4•3H_2O$ (10 mM) and 7.5 mL CTAB (0.1 M) were mixed together. Next, 0.6 mL freshly prepared $NaBH_4$ (0.01 M) was added and the solution was mixed by inversion for 2 min and aged one hour in an oil bath set to 25°C. After one hour, seeds were diluted 10:1. Into a separate vial, 0.2 mL $HAuCl_4•3H_2O$ (10 mM), 8 mL nanopure water and 1.6 mL CTAB (0.1 M) were added and mixed by inversion. Next, 0.95 mL L-AA (0.1 M) was added. Last, 5 µL seed was added. The reaction vial was capped and allowed to sit undisturbed in a 25°C oil bath for 1 hour. Particles were collected by centrifugation for 30 minutes at 3,900 RPM and diluted with water to a total volume of 3 mL.

Synthesis of Octopodal Au and Au-Pd Nanocrystals

For branched nanocrystal growth on Pd cores typically, 2 mL CTAB (0.2 M) was added to a reaction vial. Next 0.05 mL of H_2PdCl_4 (10 mM) and $HAuCl_4$ (0.1 M) solutions were added followed by 1.5 mL L-AA (0.1 M) solution. Then 21.35 mL of water was added, followed by 1 mL of seed solution. These reaction vials were gently shaken then capped and allowed to sit undisturbed in a 25 °C oil bath for 24 hours. For branched nanocrystal growth on Au cores typically, 2 mL CTAC (0.2 M) and 2 mL NaBr (50 mM) was added to a reaction vial. Next 2.0 mL of H_2PdCl_4 (0.750 mM) and 0.1 mL of $HAuCl_4$ (0.15 M) solutions were added followed by 1.5 mL L-AA (0.1 M) solution. Then 17.4 mL of water was added, followed by 1 mL of seed solutions. These reaction vials were gently shaken then capped and allowed to sit undisturbed in a 25 °C oil bath for 2-24 hours. The resulting NCs were centrifuged at 3,900 RPM for 30 minutes and stored in water. Reaction conditions were optimized for the size study and RI study.

Synthesis of Au octopods was achieved using the seed-mediated method adapted from previous literature protocols.[4] For branched nanocrystal growth typically, 2 mL CTAC (0.2 M) solution and 2.5 mL NaBr (50 mM) were added to a reaction vial. Next, 0.1 mL of $HAuCl_4•3H_2O$ (0.1 M) solution was added followed by 1.5 mL L-AA (0.1 M) solution. Then, 18.9 mL of water was added, followed by 1 mL cubic Au seed solution. These reaction vials were gently shaken then capped and allowed to sit undisturbed in a 25 °C oil bath for 2.5 hours. NCs were centrifuged at 3,900 RPM for 30 min.

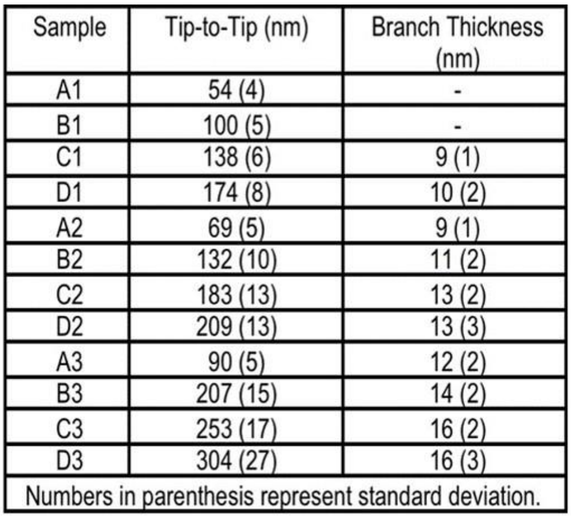
Synthesis of Pd@Au octopods was achieved using a seed-mediated method. For branched nanocrystal growth typically, 2 mL CTAB (0.2 M) solution was added to a reaction vial. Next, 0.1 mL of $HAuCl_4 \bullet 3H_2O$ (0.1 M) solution was added followed by 1.5 mL L-AA (0.1 M) solution. Then, 21.4 mL of water was added, followed by 1 mL cubic Pd seed solution. These reaction vials were gently shaken then capped and allowed to sit undisturbed in a 25 °C oil bath for 2 hours. NCs were centrifuged at 3,900 RPM for 30 min.

Octopod Size Study

For the octopod size study the concentration of cubic Pd seeds added was kept constant by UV-visible spectroscopy. The absorbance at 200 nm was held at 0.178±0.002. When growing nanocrystals using seed mediated co-reduction the amount of H_2PdCl_4 was varied (0.025, 0.05, and 1 mL) resulting in Rows 1-3 in Figure S1.

For the refractive index study each synthesis was altered slightly to get the proper LSPR location and size control. For the Pd core octopod the synthesis followed the typical one mentioned above and the concentration of cubic Pd seeds was not changed. For the Au core octopods with size 145 nm, 1.5 mL of Au cubic cores was added instead of 1 mL. The amount of water added was reduced to 19.15 mL to keep the reaction volume at 25 mL.

Table S1. Measurements of tip-to-tip length and tip thickness of branched NCs.



Sample	Tip-to-Tip (nm)	Branch Thickness (nm)
A1	54 (4)	-
B1	100 (5)	-
C1	138 (6)	9 (1)
D1	174 (8)	10 (2)
A2	69 (5)	9 (1)
B2	132 (10)	11 (2)
C2	183 (13)	13 (2)
D2	209 (13)	13 (3)
A3	90 (5)	12 (2)
B3	207 (15)	14 (2)
C3	253 (17)	16 (2)
D3	304 (27)	16 (3)

Numbers in parenthesis represent standard deviation.

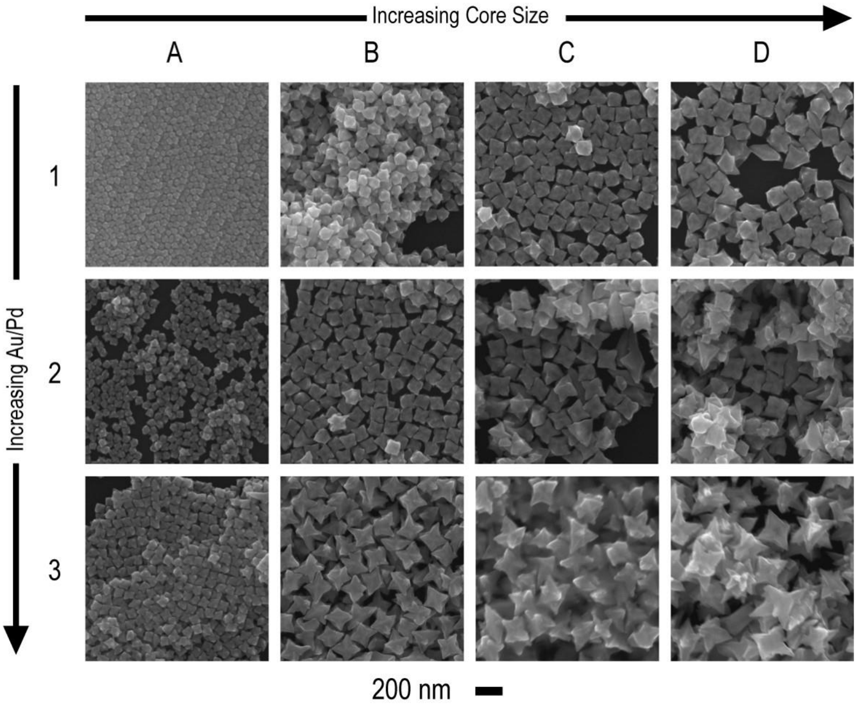


Figure S1. SEM images of NCs built from nanocubes with average edge lengths of 15±3, 35±3, 52±3, and 60±3 nm (columns A-D), in the presence of 25, 50, 100 µL Au and Pd precursor (rows 1-3).

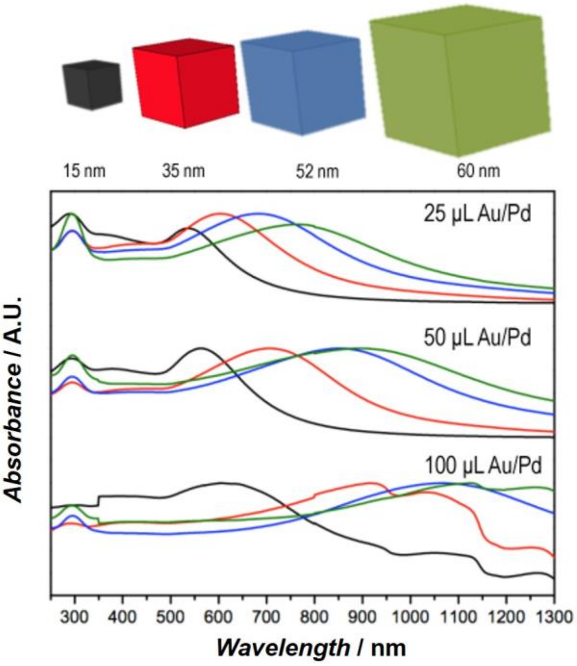


Figure S2. Plot of normalized absorption spectra for all 12 samples. NCs built from 15 nm seeds are represented by black lines, 35 nm seeds by red lines, 52 nm seeds by blue lines and 60 nm seeds by green lines.

Characterization

Images of the nanoparticles were taken via a FEI Quanta 600F Environmental Scanning Electron Microscope (SEM) operated at 30 kV and a spot size of 3. Routine transmission EM (TEM) was conducted with a JEOL JEM 1010 TEM operating at 80 kV. Images were acquired with a ROM CCD camera. Scanning TEM (STEM) and high-resolution TEM (HR-TEM) images were taken on a JEOL JEM 3200FS TEM at 300 kV and a spot size of 1 with a Gatan 4k x 4k Ultrascan 4000 camera. EDS spectra were obtained with an Oxford INCA dispersive X-ray system interfaced to the JEM 3200FS TEM, operating at 300 kV. STEM-EDS analysis shows no Pd deposition on the exterior of the Pd@Au octopods (Figure S3). SPR measurements were measured with a Varian CARY 5000 Bio UV-visible spectrophotometer, using a disposable cuvette and a background scan of water. Samples for TEM analysis were prepared by washing a carbon-coated copper grid with chloroform to remove Formvar then drop-casting a dispersed particle solution onto the grid. Grids were rinsed with methanol. SEM samples were prepared by drop-casting a dispersed particle solution onto a silicon wafer and then washing the wafer with methanol after initial solvent evaporation. Atomic %Pd was determined with an Agilent 7700 inductively coupled plasma – mass spectrometer (ICP-MS).

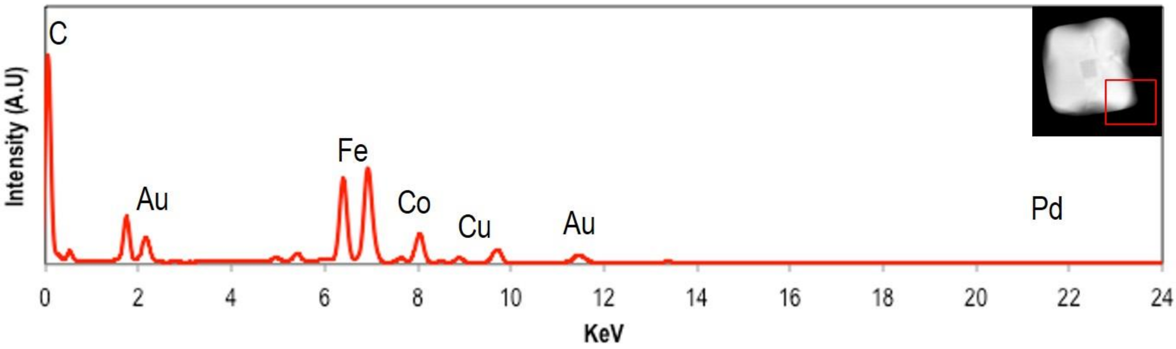


Figure S3. STEM-EDS elemental analysis of the branch (boxed in inset) of a Pd@Au octopod. There is no Pd deposition onto the exterior of the octopod. The additional elements identified by STEM-EDS correspond to those from the sample holder.

Refractive Index Sensitivity Measurements

Refractive Index Sensitivity Measurements: Water/DMSO solutions with a percentage of DMSO ranging from 0 to 50% at 12.5% intervals were used to change the RI experienced by the Au-Pd octopods. The Lorentz-Lorenz equation was used to calculate the RI of the various water-DMSO solutions[5]:

$$\frac{n_{12}^2 - 1}{n_{12}^2 + 2} = \varphi_1 \frac{n_1^2 - 1}{n_1^2 + 2} + \varphi_2 \frac{n_2^2 - 1}{n_2^2 + 2}$$

where n_{12} is the RI of the mixture, n_1 (1.33) and n_2 (1.48) are the RIs of water and DMSO, respectively, and φ_1 and φ_2 are their volume fractions. For RI sensitivity measurements, nanoparticle samples were collected via centrifugation, decanted to 3 mL, and then dispersed with 12 mL of a 2 mg/mL Na-PSS aqueous solution. Next, the samples were concentrated via centrifugation and fractioned into five samples. An additional 0.800 mL of Na-PSS was added to avoid aggregation following the protocol reported by Desantis *et al.*[6] Then, each sample was dispersed to 3 mL in the desired DMSO/water solution for analysis by UV-visible spectroscopy (Figure S4). The lack of LSPR band width changes in the varying DMSO/water ratios indicates that the octopods remain stabilized.[7] Furthermore, the concentration of Na-PSS in all Water/DMSO solutions was kept constant such that the contribution to the differential index of refraction remains constant in all solutions;[8] Na-PSS has a RI of 1.3875 at 20 °C. In addition, the reversibility of the LSPR red-shift when suspended back into lower RI media was demonstrated (Figure S5).

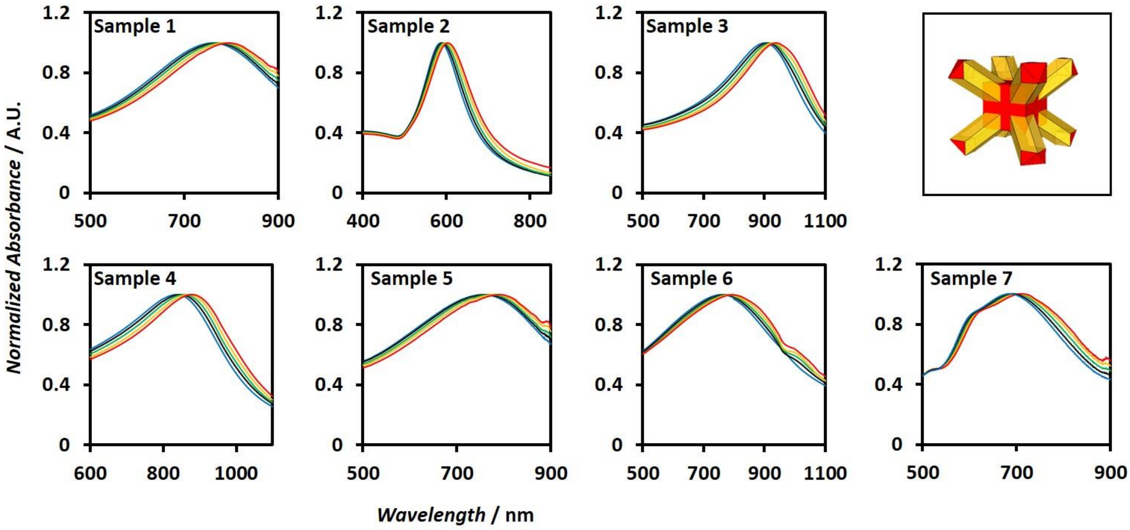


Figure S4. Normalized absorption spectra of Samples 1-7, listed in Table 1, in increasing RI media. The RI values are 1.33 (blue), 1.35 (black), 1.37 (green), 1.39 (orange), and 1.4 (red).

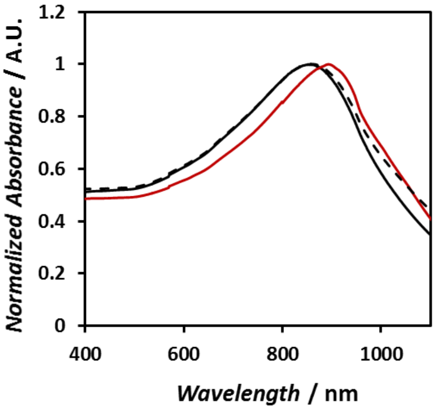


Figure S5. Plot of normalized absorption spectra of Au-Pd octopods in water media (black solid), 50/50 DMSO/water solution (red), then suspended back into water media (black dash). The LSPR of the octopods is reversible when removed from the 50/50 DMSO/water solution (RI = 1.4) and suspended in water (RI = 1.33).

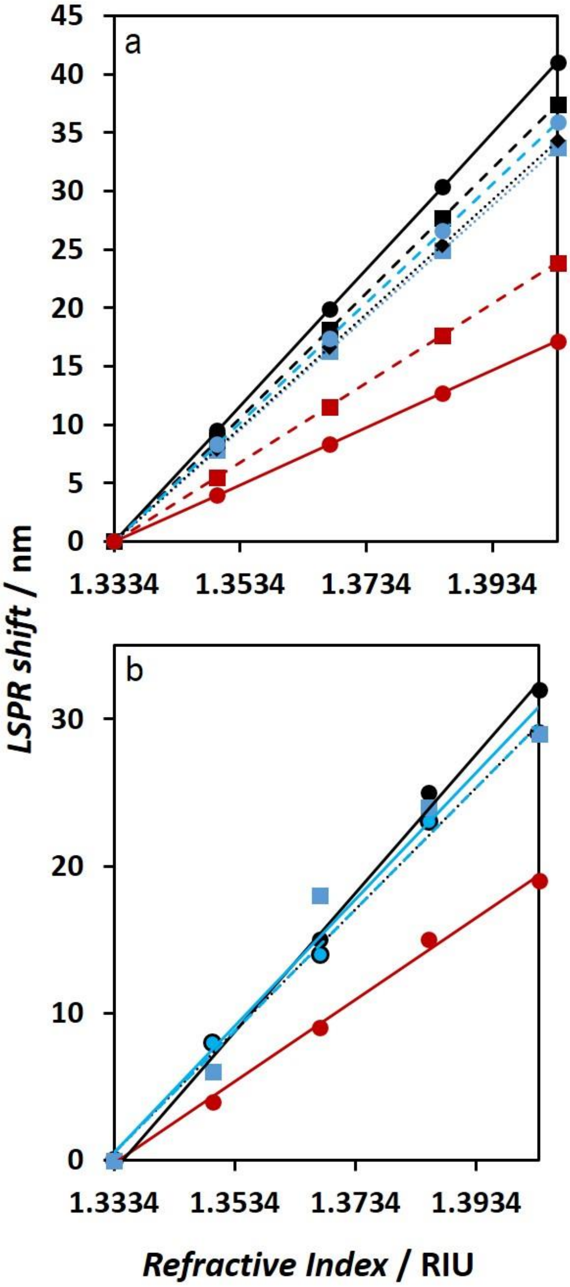


Figure S6. Plot of RIS for a) experimental samples: Sample 1-all-Au (red circle), Sample 2-Au core with 4.2% Pd tip (black diamond), Sample 3-Au core with 5.8% Pd tip (black square), Sample 4-Au core with 6.4% Pd tip (black circle), Sample 5-30 nm Pd core with 4% Pd tip (blue circle), Sample 6-60 nm Pd core with 1.2 % Pd tip (blue square), and Sample 7-60 nm Pd core with Au tips (red square) octopods. Plot of RIS for b) models: Simulation A-all-Au (red circle), Simulation B-Au core with 4% Pd tip (black open circle), and Simulation D-4% Pd core with 4% Pd tip (blue circle), Simulation E-32% Pd core and 4% Pd tip (blue square), and Simulation C-Au core with 8% Pd tip (black circles) octopods.

Hydrogen Sensing, Dynamic Light Scattering, and Morphology

As prepared Au-Pd octopods were divided into two 1.5 ml aliquots. One sample was sealed with a septa through which hydrogen gas was delivered to the headspace for 1 minute followed by a 2 minute bubbling directly into the Au-Pd colloidal suspension. UV-visible spectra were acquired for the control and hydrogen sensing samples after 2 hours. This process was repeated with all Au octopods, and no LSPR shift was detected (Figure S7-a). Furthermore, this process was repeated for Au-Pd octopods with nitrogen gas as a control; no shift in LSPR found (Figure S7-b).

Au-Pd octopodal size measurements were acquired before and after exposure to H_2 using a Zetasizer Nano-ZS dynamic light scattering instrument from Malvern Instrument at 25 °C with a 633 nm laser. The size distribution by intensity plot for each sample is shown in Figure S8. Each curve represents the average of three size measurements, and there is no evidence of aggregation. SEM images were also obtained before and after hydrogen exposure (Figure S9); there are no morphological changes after hydrogen exposure.

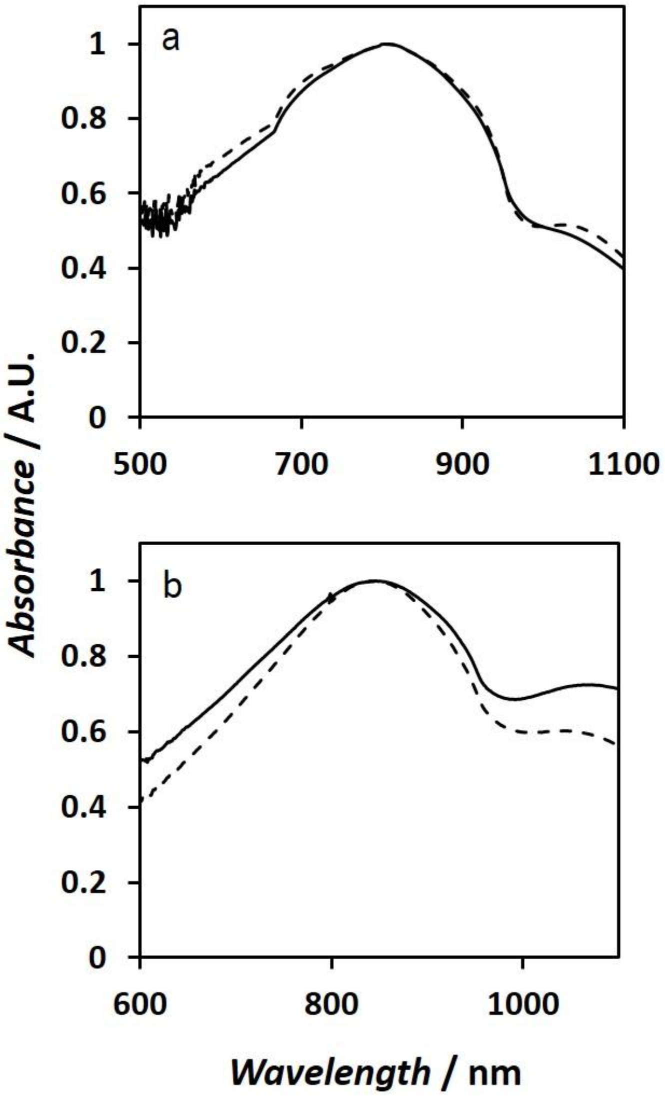


Figure S7. Plot of UV-visible spectra of a) Au octopods before (solid) and after (dash) H_2 exposure for Sample 1 and b) Au-Pd octopods before (solid) and after (dash) N_2 exposure for Sample 4. There is no shift in LSPR.

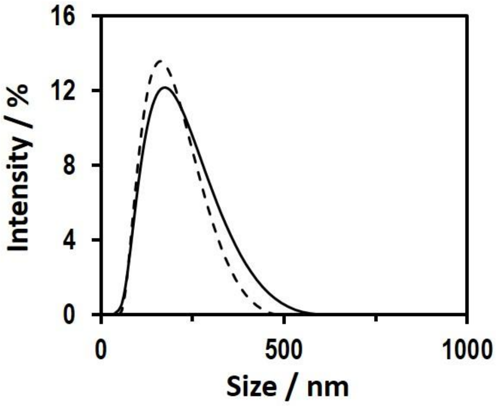


Figure S8. Plot of size distribution before (solid) and after (dash) hydrogen exposure.

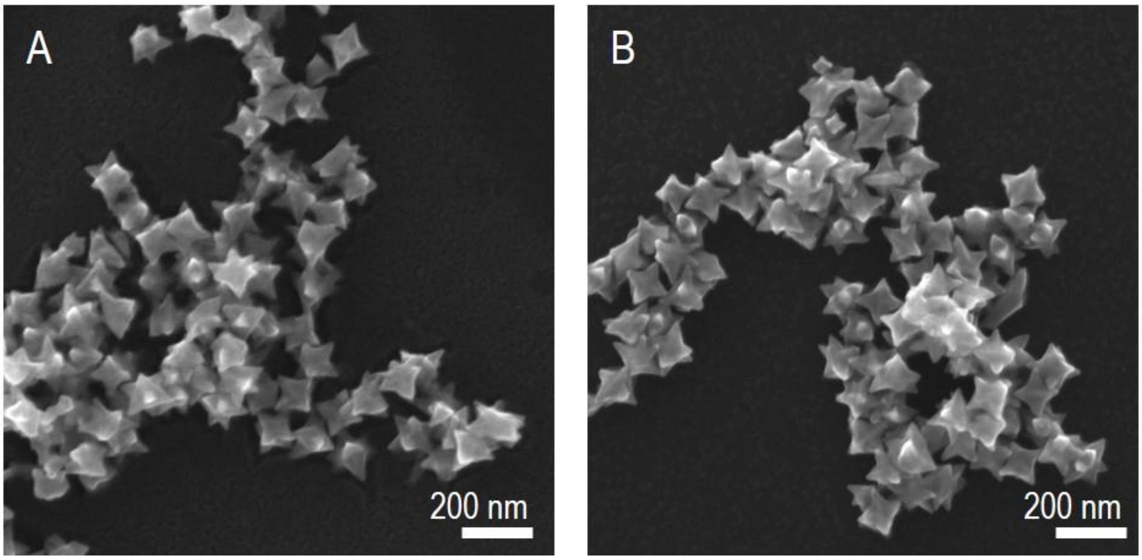


Figure S9. SEMs of (a) Au-Pd octopods before H_2 treatment and (b) after H_2 treatment.

Finite Difference Time Domain Calculations

Finite difference time domain (FDTD) calculations were achieved using Lumerical software. All FDTD models were designed with a FD value of 132 nm and a TW value of 11 nm. Five single octopods with face diagonal lengths of 132 nm and tip widths of 11 nm were modeled varying the core composition. The geometry of the Au octopod was constructed from truncated hexagonal pyramids (THPs) with a base apothem of 55 nm and $(30\ \text{nm})^3$ or $(60\ \text{nm})^3$ cubic seed size. Au-Pd octopods with Pd localized at the tips were constructed in a similar manner with Pd tips modeled as THPs positioned onto the apex of the Au THPs. For the Au core structures, the atomic %Pd located at the tips was set at 0% (for the all Au octopod), 4%, and 8%. For the Pd core structures, the atomic %Pd was set at 4% with the core increasing from (30 nm)^3 to (60 nm)^3. These core dimensions represent 4% and 32% of the total particle volume, respectively. The total FD values of these Pd-tipped Au THPs was kept equivalent with those of Au-only. The scattering spectra of the NCs were calculated using FDTD. The dielectric functions for Au were fitted to optical data from Johnson and Christy,[9] and Pd dielectric functions were fitted to optical data from Palik.[10] The excitation source was a plane wave with a wavelength range of 400-1200 nm, which propagated along the C_4 symmetry axis and through a surrounding medium with a refractive index values of 1.333, 1.3497, 1.3675, 1.3855, and 1.4038 such that five environments were modeled for each of the octopod structures. The mesh values were set to (1 nm)^3.

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