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Supporting information

Bimetallic Janus Nanostructures via programmed shell growth

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EXPERIMENTAL DETAILS

Materials

All materials were used as received without any further purification. Cetyltrimethylammonium bromide (CTAB), gold chloride (HAuCl₄.4H₂O), sodium borohydride (NaBH₄), ascorbic acid, 1,4-benzenedithiol (BDT), sodium chloride (NaCl), silver nitrate (AgNO₃) were purchased from Sigma Aldrich (St. Louis, MO, USA). Hydrochloric acid (HCl) was obtained from EMD (Gibbstown, NJ). Cetyltrimethylammonium chloride (CTAC) was obtained from TCI (Portland, OR, USA). The fromvar/carbon coated copper TEM grids were acquired from Ted Pella Inc. (Redding, CA, USA). Nanopure water (>18.0 MΩ-cm) was used for all experiments.

Methods

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Synthesis of nanostructures

20 nm Gold nanoparticles synthesis

Gold nanoparticles were synthesized in three steps. In the first step, seed solution was prepared by vigorous mixing of 5 ml of aqueous CTAC solution (0.2 M), 4.5 ml of nanopure water and 515 μ l of HAuCl₄ (4.86 mM) with 450 μ l of ice-cold NaBH₄ solution. The seed solution was aged for 1 hr at 30°C in a hot bath. In the second step, the growth solution was prepared by mixing 4.5 ml of nanopure water, 5 ml of aqueous CTAC solution (0.2 M), 515 μ l of HAuCl₄ (4.86 mM), and 75 μ l of ascorbic acid (0.04 M). To this colorless solution, 25 μ l of seed solution was added with vigorous stirring and kept undisturbed for two days to obtain highly uniform spherical nanoparticles with LSPR at 521 nm. The size of the nanoparticles obtained at this stage was 20 nm.

Core-shell structure synthesis

Au core-shell nanostructures were synthesized by employing 20 nm Au nanoparticles as cores. Prior to adding these nanoparticles to the growth solution, the nanoparticles were modified with BDT. 5 μ l of BDT solution (1 mM) was added to 1 ml of 20 nm core nanoparticles (50 nM) under vigorous sonication for 10 minutes. These modified cores were centrifuged twice at 12,500 rpm for 10 minutes to remove unabsorbed BDT. Growth solution was prepared by mixing 862 μ L of CTAC (0.1 M), 43 μ L HAuCl₄ (4.86 mM), and 54 μ L ascorbic acid (0.04 M). Subsequently, 43 μ L of the BDT-modified cores were added to growth solution, which yields ~1 mL of Au core-shell nanostructures with BDT trapped in between the core and shell.

Core-semishell nanostructures synthesis

For synthesis of core-semishell nanostructures, Au cores were first modified with BDT. 5 μ l of BDT solution (1 mM) was added to 1 ml of 20 nm core nanoparticles (50 nM) under vigorous sonication for 10 minutes. These modified cores were centrifuged twice at 12,500 rpm for 10 minutes to remove unabsorbed BDT. For forming the semishell on these BDT modified cores they were introduced into the growth solution comprised of Au precursor, ascorbic acid (reductant) and CTAC (capping agent). The growth solution was prepared by mixing 620 μ L CTAC (0.1M), 31 μ L HAuCl₄ (4.86 mM), and 39 μ L ascorbic acid (1.0 M) . 310 μ L of the BDT modified cores suspended in solution. The core-semishell structures were left undisturbed for three days.

Au/Ag Bimetallic core-Janus shell nanostructures

Following the synthesis of core-semishell nanostructures, exposed regions of the BDT-modified cores was passivated with PEG to facilitate preferential growth of Ag on the opposite hemisphere. For that, core-semishells were centrifuged two times at 8000 rpm to completely remove the free CTAC from the reaction and dispersed with SH-PEG solution (10 μ M). The resultant solution was sonicated for 30 minutes and left on natauting mixer for 12 hours. Silver growth solution was prepared by mixing of 620 μ L of CTAC (0.1 M), 31 μ L of AgNO₃ solution (4.86 mM), and 39 μ L of ascorbic acid (1.0 M). We then added 310 μ L of the PEG-passivated core-semishell nanostructures to form core-Janus shell nanostructures.

Au/Ag Bimetallic Core/Shell nanostructures

Following the synthesis of core-semishell structures as described above, the nanostructures were centrifuged and resuspended in 0.9 mM polyvinylpyrrolidone (PVP) solution followed by

ultrasonication for 3-5 min. Silver growth solution was prepared by mixing 567 μ L of CTAC (0.1M), 113 μ L of AgNO₃ solution (4.86 mM), and 35 μ L of ascorbic acid (1.0 M). We then added 283 μ L of core-semishell structures to the silver growth solution. The particles were left undisturbed for 2-4 days.

Characterization

TEM images were obtained using either field emission TEM (JEM-2100F, JEOL) operating at an accelerating voltage of 200 kV or FEI sprint Lab6 with an accelerating voltage of 120 kV. UV/vis extinction spectra were collected using a Shimadzu 1800 spectrophotometer. Raman spectra were collected using a Renishaw inVia confocal Raman spectrometer mounted on a Leica microscope with 50× objective (NA = 0.90) in the range of 100 -3200 cm⁻¹ with one accumulation and 10 sec exposure time.