Electronic Supplementary Information

Colloidal Core-Shell Materials with ‘Spiky’ Surfaces Assembled from Gold Nanorods

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Experimental Section

Synthesis and Characterization of Gold Nanorods. All reagents were used as received. A 50-mL glass round bottom flask and stir bar were first cleaned with aqua regia for 15 min and rinsed with >200 mL of deionized water (18.2 MΩ-cm, Barnstead Nanopure Diamon water filtration system) before further use. The aqua regia solution was prepared from a 3:1 (v/v) solution of hydrochloric acid (36.5 – 38.0%, Anachemia Canada Inc., Richmond, BC) and nitric acid (68-70%, Anachemia Canada Inc., Richmond, BC). CAUTION: Aqua regia solutions are extremely corrosive. This solution should be handled with extreme care. This cleaning and rinsing process was repeated using a piranha solution prepared from a 7:2 (v/v) mixture of sulfuric acid (95-98%, Anachemia Canada Inc., Richmond, BC) and a 30 % by volume aqueous solution of hydrogen peroxide (VWR International, Mississauga, ON). CAUTION: Piranha solution is a strong oxidizing agent and reacts violently with organic compounds. This solution should be handled with extreme care. The cleaned and rinsed flask and stir bar were dried in an oven at 120°C for 2 h prior to use in the synthesis of AuNRs.

An aqueous solution of gold seeds was prepared by first mixing chloroauric acid trihydrate (5 mL of 0.5 mM; HAuCl₄·3H₂O, 99.0%, Sigma-Aldrich, St. Louis, MO) with hexadecyltrimethylammonium bromide, (5 mL of 0.2 M; CTAB, ≥96.0%, Sigma-Aldrich, St. Louis, MO). An ice-cold freshly prepared solution of sodium borohydride (0.6 mL of 0.01 M; NaBH₄, 98.0%, Fisher Scientific Canada, Ottawa, ON) was injected into the mixture with vigorous stirring. The mixture was aged for 30 min with continuous stirring before use. In preparation for the synthesis of AuNRs, a CTAB solution (50 mL of 0.1 M) was prepared in a polystyrene vial (100 mL, Dynalab Corp., Rochester, NY. catalog number 2637-0010). To this CTAB solution, we sequentially added silver nitrate (315.7 µL of 0.01 M; AgNO₃, ≥99.0%, Sigma-Aldrich, St. Louis, MO), HAuCl₄·3H₂O (2.1 mL of 0.01 M) and L-ascorbic acid (336 µL of 0.1 M; LAA, ≥99.0%, Sigma-Aldrich, St. Louis, MO) with a gentle swirling after the addition of each reagent. After adding freshly prepared gold seed solution (420 µL), the mixture was left
undisturbed for 24 h at 30°C. The extinction spectra of the AuNRs were characterized by monitoring the position and intensity of their plasmon bands using a Varian Cary 300 Bio spectrophotometer. The shape and size of the nanorods were determined by transmission electron microscopy (TEM) operating at 200kV (Hitachi 8000). The TEM grids were copper grids coated with Formvar/carbon (300 mesh size, Electron Microscopy Sciences, PA) for analysis of the AuNRs. The AuNRs used in these studies had an aspect ratio of ~10:3 (length:width). These AuNRs had lengths of ~46 nm and widths of ~14 nm. The lengths of these AuNRs were equivalent to approximately one-tenth the diameter of the PS spheres.

*Surface Modification of Gold Nanorods.* Prior to the exchange of CTAB with polyvinylpyrrolidone (PVP, 55,000 average molecular weight, Sigma-Aldrich, St. Louis, MO), the newly synthesized AuNRs were purified to remove excess CTAB by three times of centrifugation (13500 rpm, 30 min). The purified nanorods were suspended in a CTAB solution (1 mM) for the first two times, and at the end of the third purification, the AuNRs were suspended in a phosphate buffered solution (PB, pH 8, 10 mM) with sodium dodecyl sulfate (3%; SDS, Sigma-Aldrich, St. Louis, MO). A solution was prepared with PVP (2 g) dissolved in ethanol (18 mL; EtOH, 99.9%, Commercial Alcohols Inc., Mississauga, ON). Purified AuNRs (5 mL) were mixed with the PVP solution (5 mL) in a glass scintillation vial (20 mL) and stirred (40 °C for 48 h).

*Loading of Gold Nanorods onto Polystyrene Colloids.* The polystyrene microspheres (Polysciences Inc., Warrington, PA, catalog number 07763-5) were first purified by centrifugation (13500 rpm, 5 min) followed by suspension in EtOH. The PVP/SDS-coated AuNRs (8 mL) were added to a 20 mL vial and stirred (48 h at 55 °C) with EtOH solution (1 mL) containing purified PS (50 µL) and HCl (100 µL of a 1% solution). The resulting solution was purified twice by centrifugation (6000 rpm, 30 min) to remove excess PVP and SDS and suspended in EtOH. The assemblies were characterized by extinction
spectroscopy (as described above), dynamic light scattering measurements, TEM and scanning electron microscopy (SEM), and Raman spectroscopy. Analyses by TEM of PS@AuNRs assemblies were performed on drop-cast samples prepared on copper grids coated with carbon only (300 mesh size, Electron Microscopy Sciences, PA). The average number of AuNRs per PS sphere was calculated from at least five independent PS spheres and the errors reported as one standard deviation of the variance within each sample. The SEM analysis was performed using an FEI Dual Beam Strata 235 operating between 5 and 30 kV. The dynamic light scattering data was obtained using a Zetasizer Nano ZS from Malvern Instruments by dispersing the sample (50 µL) into deionized water (950 µL). Zeta potential measurements were performed at 22°C using the same instrument, and the samples were prepared by dilution into water or ethanol. For these measurements, folded capillary cells (Malvern, Westborough, MA, USA) with a volume of 0.75 mL were cleaned by flushing ~4 mL of ethanol through the cell. This rinse solution was removed before loading the samples into the cells. These assemblies were stored either in an ethanol solution or as a powder isolated from solution by evaporation from ethanol.

*Preparation of Samples for SERS Analysis.* A polished silicon substrate was cleaved into ~0.25 cm² pieces. These pieces were cleaned with piranha solution as described above. Following this cleaning step, the silicon substrate was rinsed thoroughly with water and subsequently dried under a stream of filtered nitrogen gas. These pieces of polished silicon wafer were used as substrates for all subsequent Raman analyses. A portion of the test solution (e.g., ~2 mL containing PS@AuNRs assemblies) were drop cast onto the cleaned silicon substrate and dried under ambient conditions. This process of depositing sample (e.g., PS@AuNRs assemblies or control samples) onto the silicon substrate was repeated several times. Subsequently, a solution of 1,4-benzenedithiol (1.0x10⁻⁵ M; 1,4-BDT) was prepared in ethanol. Through control experiments, we observed that without the use of an enhancing agent, the Raman signal associated with a pure sample of 1,4-BDT is below the detection limit of
our instrument at a concentration of $10^{-5}$ M. We estimated the final concentration of 1,4-BDT on our assemblies to be well below this concentration. The silicon substrate with multiple layers of PS@AuNRs assemblies was immersed into the 1,4-BDT solution (~500 uL) for ~48 h; control samples were prepared from films containing the PS spheres, but in the absence of the gold nanorods. The immersed samples were rinsed with excess ethanol and dried under ambient conditions. Raman spectra were acquired with a Renishaw inVia Raman microscope using a 50x LWD lens (0.5 NA) and a 785 nm laser excitation at 1% laser power (~4.2 mW/μm²) with an exposure time of 20 s. Acquired spectra resulted from the co-addition of three sequential accumulations. The laser power was measured at the sample using a Spectra-Physics laser power meter (model 407A) from Newport Corporation.
**Fig. S1** Representative transmission electron microscopy (TEM) image of gold nanorods capped with polyvinylpyrrolidone (PVP) and sodium dodecyl sulfate (SDS). The scale bar (white bar, lower left corner) is 50 nm in length.
Fig. S2 Transmission electron microscopy images of a mixture of gold nanorods capped with PVP/SDS and carboxylic acid functionalized PS spheres. This mixture did not form PS@AuNRs assemblies after a period of 2 days.
The long-term stability of the PS@AuNRs assemblies could have important implications in the potential applications of these particles. Our ability to reversibly and repeatedly disperse the PS cores may be altered when AuNRs are assembled onto the PS surfaces, such as through the formation of gold-gold contacts.\(^1\) The acidity of the associated suspensions may also alter the chemistry of and interactions between the AuNRs and PS. These processes could be more pronounced if the samples are stored as an isolated powder rather than in solution. We investigated the influence of pH on the long-term stability of the surface topography and colloidal properties of the PS@AuNRs assemblies stored as either a powder or in solution. We determined that the optimal conditions for storing the PS@AuNRs assemblies were either suspended in an ethanol solution at a pH of ~6 or as an isolated powder. Products stored at room temperature over a period of one year maintained their surface topography (Fig. S3a,b). In addition, the number of AuNRs freely dispersed in solution and the surface coverage of AuNRs on the PS spheres remained relatively constant over this period of time. The assemblies also maintained their spherical shape, suggesting the PS cores are a stable support material under these storage conditions. The PS@AuNRs, whether stored in ethanol or as a powder, could be readily dispersed into solution (ethanol or another alcohol) with gentle agitation. The resulting dispersion had a uniform appearance with coloration similar to that of bismuth subsalicylate (or pink bismuth) and identical to that of the originally prepared PS@AuNRs assemblies. These dispersions could be repeatedly isolated from solution and subsequently dispersed into solution with no apparent instability of the assemblies. Alterations to the storage pH of the PS@AuNRs containing suspensions do, however, have a dramatic influence on the stability of the particles regardless of whether the assemblies had been stored for one year or freshly prepared. A more acidic environment (i.e., pH 1, achieved using HCl) altered the surface topography of the assemblies within as little time as one day (Fig. S3c), after which these colloidal assemblies appeared to have smoother surfaces with fewer 'spikes' or AuNRs with their longitudinal axis oriented perpendicular to the surfaces of the PS cores. Analysis of the TEM results determined that the average diameter of the PS@AuNRs assemblies decreased by ~48 nm after storage in ethanol at pH 1 for 24 h. This decrease corresponds to approximately the length of a typical AuNR, which further suggests the nanorods have reoriented themselves relative to the surfaces of the PS cores. At the other extreme, we altered the basicity of these solutions to pH 12 through addition of sodium hydroxide (NaOH). After a period of 24 h at pH 12, the surface topography of these assemblies was maintained and the relative number of spike-like features of AuNRs was approximately the same as before the addition of NaOH. This sample did, however, have visible aggregates in the suspension that we were not able to disperse by agitation of the solution. Storing these samples at pH 12 for periods >24 h resulted in further degradation of the assemblies through deformation of the PS cores. The isolated product contained aggregated AuNRs and deformed PS residues (Fig. S4). Although the PS@AuNRs assemblies were not stable at a pH of 1 or 12 for prolonged periods of time, the original assemblies can be stored for periods >1 year either as a powder or at pH 6 in ethanol without noticeable degradation of the samples.
Fig. S3 Effects of pH on PS@AuNRs after assembly and their long-term stability. (a,b) Analysis by TEM of as-prepared PS@AuNRs and those maintained at pH 6 for a period of one year, respectively. After this period of incubation, solution pH was adjusted again by further addition of hydrochloric acid or sodium hydroxide. (c,d) Adjusting the pH of samples resulted in slight alterations in the surface topography of the AuNRs in these assemblies. Scale bars in each TEM image are 200 nm in length.
Fig. S4 Transmission electron microscopy images following the progression in changes to PS@AuNRs assemblies after dispersion in a solution at pH 12 up to a period of 2 days. These samples were stored at room temperature, and samples were obtained for TEM analysis at the times designated on each of the images (e.g., 10 min up to 48 h).
**Fig. S5** Extinction spectra of gold nanorods capped with PVP and SDS and dispersed in ethanol.
**Fig. S6** Extinction spectra of PS@AuNRs assemblies dispersed in ethanol.
Table S1. Raman Spectral Assignments and Relative Spectral Intensities for 1,4-Benzenedithiol on Samples of PS@AuNRs.2-4

<table>
<thead>
<tr>
<th>Raman shift (cm(^{-1}))</th>
<th>assignment</th>
<th>PS@AuNRs-3 versus PS@AuNRs-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1557 (\nu_{\text{ring}}), 8a vibrational mode of (A_g) symmetry</td>
<td>12x higher intensity</td>
<td></td>
</tr>
<tr>
<td>1180 (\nu_{\text{C-H}}), 9a vibrational mode of (A_g) symmetry</td>
<td>7x higher intensity</td>
<td></td>
</tr>
<tr>
<td>1059 overlap from 2 separate vibrational modes*</td>
<td>7x higher intensity</td>
<td></td>
</tr>
<tr>
<td>732 (\gamma_{\text{ring}}), 7a vibrational mode of (A_g) symmetry</td>
<td>13x higher intensity</td>
<td></td>
</tr>
</tbody>
</table>

*Associated with interactions between AuNR surfaces and the \(\pi\)-orbital system of the benzene ring in 1,4-BDT.2-4

The vibrations at 1557 and 732 cm\(^{-1}\) originated from the benzene ring stretching (8a vibrational mode of \(A_g\) symmetry) and benzene ring deformation (7a vibrational mode of \(A_g\) symmetry) of 1,4-BDT, respectively.2-4 In contrast, the C-H stretching vibration of 1,4-BDT at 1180 cm\(^{-1}\) (9a vibration mode of \(A_g\) symmetry) was only enhanced ~7 times more by PS@AuNR-3 in comparison to PS@AuNR-1. The in-plane C-H deformation of the surface bound 1,4-BDT is typically less sensitive to Raman enhancement than the 7a and 8a vibration modes.2 The resulting broad peak at 1059 cm\(^{-1}\) indicates 1,4-BDT molecules bound to the gold surfaces through the formation of two separate Au-S bonds.
Fig. S7 Raman spectra for control samples of PS@AuNRs assemblies. (a) Raman spectrum for PS@AuNRs assemblies with a low concentration of AuNRs per PS core. (b) Raman spectrum of PS spheres after immersion in 1,4-BDT, but without AuNRs. (c) A Raman spectrum of PS@AuNRs assemblies without 1,4-BDT. All Raman spectra were acquired using identical experimental parameters as the samples reported in the manuscript for the SERS experiments.
References


