Electronic Supplementary Information

Silver-Gold Nanotubes Containing Hot Spots on their Surface: Facile Synthesis and Surface-Enhanced Raman Scattering Investigations

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Experimental Procedures

Materials and instrumentation

Analytical grade chemicals $HAuCl_4 \cdot 3H_2O$, (hydrogen tetrachloroaurate trihidrate), $AgNO_3$ (silver nitrate, 99%), PVP (polyvinylpyrrolidone, M.W. 55.000 g/mol), EG (ethylene glycol), CV (crystal violet), sodium borohydride ($NaBH_4$), 9-nitroantracene, and benzo(a)pyrene were purchased from Aldrich or Merck, and were used as received. All solutions were prepared using deionized water (18.2 MΩ). Glassware was cleaned with a piranha solution (3:1 concentrated H_2SO_4 to 30% H_2O_2) aqueous solution before use.

The scanning electron microscopy (FEG-SEM) images were obtained with a JEOL microscope, Mod.: FEG-SEM JSM 6330F operated at 5 kV. The samples for SEM were prepared by drop-casting an aqueous suspension of the nanostructures over a Si wafer, followed by drying under ambient conditions. Energy-dispersive X-ray spectroscopy (EDX, Thermo Electron Corporation) was performed at an acceleration voltage of 15 kV. We used a thick slab (>1 lm) of the NPs deposited onto a silicon wafer in combination with a beam spot of >50 μm^2 for at least three different regions in the sample in order to obtain average and reproducible EDS data from a large NPs ensemble. UV–VIS spectra were obtained with a Shimadzu UVPC-3101 scanning spectrophotometer. Raman spectra were acquired on a Renishaw Raman InVia equipped with a CCD detector and coupled to an Leica microscope that allows a rapid accumulation of Raman spectra with a spatial resolution of about 1μm (micro-Raman technique). The laser beam was focused on the sample by a ×50 lens. Laser power was always kept below 0.7mW at the sample. The experiments were performed at ambient conditions using a back-scattering geometry. The samples were irradiated with the 632.8 nm line of a He–Ne laser (Spectra Physics).

Synthesis of Ag nanowires (Ag NWs)

The synthesis of Ag NWs followed a modified polyol process.[6, 17] In a typical synthesis, 5 mL of ethylene glycol was transferred to a round bottom flask and heated to 160 ºC under stirring for 1 h. Then, 3 mL of a 0.1 M $AgNO_3$ solution in ethylene glycol (EG) and 3 mL of a 0.6 mol L^{-1} PVP solution in EG were added simultaneously, using a peristaltic pump in the rate of 0.4 mL min^{-1}, to the pre-heated EG. The reaction was allowed to proceed at this temperature for 1 h before the product was collected by centrifugation, washed with water three times and re-suspended in water.

Synthesis of Ag-Au Nanotubes (Ag-Au NTs)

For the synthesis of Au-Ag NTs, a suspension containing the Ag nanowires (100 μL) was added to 5 mL of an aqueous PVP solution (1 mg/mL) under magnetic stirring. This system was heated at 100 °C for 10 min. Then, 2 mL of a 0.1 M $HAuCl_4 \cdot 3H_2O$ aqueous solution was added dropwise, causing a changing in color from light brown to violet. The solution was kept at 100 °C for another 10 min and the product was collected by centrifugation, washed with a saturated NaCl aqueous solution and re-suspended in water.

Sample preparation for SERS

The samples were prepared by adding 100 μL of the suspension containing the Ag NWs or the Ag-Au NTs to 50 μL of $1.0 \cdot 10^{-6}$ mol L^{-1} aqueous solutions of crystal violet, 9-nitroanthracene or benzo(a)pyrene. The final concentrations of analyte molecules were calculated as $3.33 \cdot 10^{-7}$ $molL^{-1}$. The SERS spectra were obtained 1 h after the sample preparation, in order to ensure that the adsorption equilibrium of the analytes over the metallic surfaces was reached.

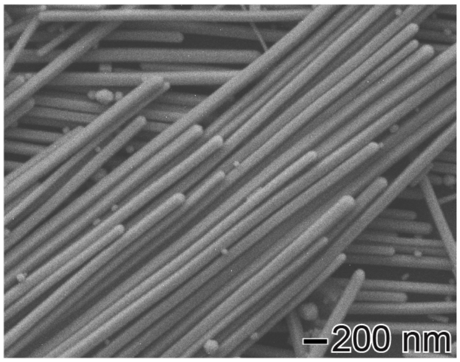

Figure S1. SEM images of Ag NWs obtained by the polyol process. The Ag NWs were 93.5 ± 5.0 nm in width and > 3 mm in length.

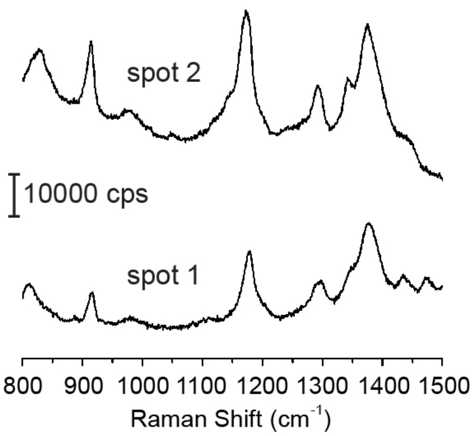

Figure S2. Typical CV SERS spectra obtained from spots 1 and 2 marked in Fig. 4A and B.