Supporting Information

Controlled Synthesis of Sponge-like Porous Au-Ag Alloy Nanocubes for Surface-Enhanced Raman Scattering Property

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Synthesis of Monodispersed Au@Ag Nanorods

The Au@Ag nanorods (NRs) were synthesized by a previous method developed by our group.⁵⁷ For a typical synthesis of Au@Ag NRs with aspect ratio of 2.3, 0.015 mL of 1 M HAuCl₄ aqueous solution, 1.2 mL of PDDA and 0.057 mL of 2 M AgNO₃ aqueous solution were introduced into 58.8 mL of EG solution in a brown glass vial. The mixture solution was vigor ously stirred for about 1 min at room temperature and ambient conditions. The final concentrations of $[AuCl_4]^-$ ions, AgNO₃, and PDDA were 0.25, 1.9, and 25 mM, respectively. The as-prepared mixture solution was subsequently reacted at 200 °C for 60 h in air in an oil bath. The final product was collected by centrifugation at 14 500 rpm and washed repeatedly with pure water for 2 times. The Au@Ag NRs were redispersed in 1 mL water for further use after centrifugation.

Synthesis of Au@Ag@SiO₂ NRs

Typically, 0.3 mL of FSDNA (5 mg/mL) and 0.045 mL of MPY (1×10^{-5} M) were dropped into 0.04 mL of the Au@Ag NRs aqueous solution. The mixture was vigorously shaken for 10 s and undisturbed for another 45 min. After centrifugation, the products were mixed with 0.2 mL of ethyl alcohol, 0.06 mL of TEOS (1 vol % in ethyl alcohol), and 0.014 mL of NH₃·H₂O under stirring. After 6 h, Au@Ag@SiO₂ NRs were collected by centrifugation and washed with ethanol and water for 3 times, respectively.

Synthesis of Sponge-like Au-Ag alloy NRs

The above Au@Ag@SiO₂ NRs were dried in vacuum and annealed in a tube furnace at 700 °C in nitrogen for 2 h, forming fully alloyed Au-Ag@SiO₂ NRs. After cooling down to room temperature, the products were sonicated and redispersed in 20 mL of 0.1 M NaOH at 70 °C for 3 h. The Au-Ag alloy NRs with an ultrathin silica shell were obtained. Then, sponge-like Au-Ag alloy NRs were fabricated through chemical dealloying, which exposed the solid Au-Ag alloy NRs to 2 M HNO₃ at room temperature.

Synthesis of Sponge-like Au-Ag Alloy Nanospheres (NSs)

The Au@Ag NSs were synthesized by a slightly modified method.³⁶ The spongelike Au-Ag alloy NSs were fabricated following the same method with NCs. The size of sponge-like Au-Ag alloy NSs was ca. 50 nm.



Fig. S1 XRD pattern of sponge-like Au-Ag alloy NCs.



Fig. S2 EDS for fully alloyed sponge-like Au-Ag NCs on the copper grid. The percentage of Au and Ag was 57.5% and 42.5%, respectively.



Fig. S3 Typical XPS spectra of Au and Ag in the sponge-like Au-Ag alloy NCs.



Fig. S4 TEM images of sponge-like Au-Ag alloy NSs. The percentage of Au and Ag was 56.9% and 43.1%, respectively.



Fig. S5 Raman spectra on the sponge-like Au-Ag alloy NSs with different concentrations of 10^{-6} M to 10^{-9} M 4-ATP.



Fig. S6 (a) Raman signal obtained by dropping 10 μ l 4-ATP ethanol solution (10-7 M) on sponge-like Au-Ag alloy NCs substrate. (b) Normal Raman signal of 10 μ l of 10-1 M 4-ATP solution dropped on the Si substrate.



Fig. S7 TEM (a) and HAAD-STEM (b) images of single Au@Ag core-shell NC. (c-d)

EDS elemental mapping of Ag and Au, respectively.



Fig. S8 TEM (a), HRTEM (b), and HAADF-STEM (c) images of solid Au-Ag alloy NCs. (d-e) EDS elemental mapping of Ag and Au, respectively. (f) EDS for solid Au-Ag alloy NCs on the copper grid.



Fig. S9 XRD pattern of solid Au-Ag alloy NCs.



Fig. S10 Size distribution of sponge-like Au-Ag alloy NCs with different etching time of 20, 30, and 40 min.



Fig. S11 Raman spectra on the sponge-like Au-Ag alloy NCs with different dealloying time of 20, 30, and 40 min.



Fig. S12 EDS for sponge-like Au-Ag alloy NRs on the copper grid. The percentage of Au and Ag was 21.3 % and 78.7 %, respectively.



Fig. S13 TEM images of Au@Ag core-shell NRs (a) and Au@Ag@SiO₂ NRs (b).



Fig. S14 (a) FESEM image of solid Au-Ag alloy NRs. (b) HAAD-STEM image of single solid Au-Ag alloy NR. (c-d) EDS elemental mapping of Ag and Au, respectively.



Fig. S15 EDS for solid Au-Ag alloy NRs on the copper grid. The percentage of Au and Ag was 15.5 % and 84.2 %, respectively.