Engineering versatile SERS-active nanoparticles by embedding reporters between Au-core/Ag-shell through layer-by-layer deposited polyelectrolytes

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Supporting Information

Polyelectrolytes and Raman reporters used in this work: poly(allylamine hydrochloride) (PAH, MW=15000), poly(acrylic acid) (PAA, MW=1800), meso-tetra(4-carboxyphenyl) porphine (TCPP), and Rose Bengal (RB).
Figure S1. (a) Fluorescence emission spectra of Au@I@Ag after adding NaCN, excited at 520 nm. (b) Calibration curve of RB emission at 570 nm vs. [RB]. (c) SERS spectra of Au@I@Ag. (d) Raman spectra of 10 mM RB solution collected under the same conditions as (c).

Figure S2. TEM images of Au@I@Ag NPs. Scale bar is 50 nm.
Figure S3. Particle size distribution of Au-cores (a) and Au@1@Ag NPs (b).

Figure S4. UV-vis extinction spectra of TCPP, Au core, Au@2 and Au@2@Ag.
Figure S5. (a) Fluorescence emission spectra of Au@2@Ag after adding NaCN, excited at 416 nm. (b) Calibration curve of TCPP solution with emission intensity at 650 nm as y-axis and [TCPP] as x-axis. (c) SERS spectra of Au@2, Au@2@Ag. (d) Raman spectra of 10 mM TCPP solution collected under the same conditions as (c). The 1235 cm⁻¹ peak of TCPP is used to calculate the SERS EFs of all samples containing TCPP molecules. Following the procedures described previously and data shown here, the EFs of Au@2 and Au@2@Ag were calculated to be 9×10³ and 8.1×10⁵, respectively.

Figure S6. A) EFs of Au@1@Ag NPs coated with different amounts of 1 mM AgNO₃ in the deposition step. B) Fluorescence emission spectra of NaCN-treated Au@1@Ag NPs coated with different amounts of 1 mM AgNO₃ in the deposition step. a) 100 uL. b) 200 uL. c) 300 uL. d) 400 uL. e) 500 uL. The results indicate that, throughout the Ag deposition process and the removal of both Ag and Au, the amounts of RB in each sample remain essentially the same.
Figure S7. Fluorescence emission spectra of NaCN-treated Au@1-2@Ag. Excited at 520 nm (RB); Excited at 416 nm (TCPP). The EFs of Au@1-2@Ag are calculated to be $5.7 \times 10^5$ for RB and $6.6 \times 10^5$ for TCPP, respectively.

Figure S8. Fluorescence emission spectra of NaCN treated Au@1-(PAH-PAA)$_2$@Ag, Au@(PAH-PAA)-1-(PAH-PAA)@Ag and Au@(PAH-PAA)$_2$-1@Ag. Excited at 520 nm. EFs of the three nanoparticles, Au@1-(PAH-PAA)$_2$@Ag, Au@(PAH-PAA)-1-(PAH-PAA)@Ag and Au@(PAH-PAA)$_2$-1@Ag, are calculated to be $2.8 \times 10^5$, $2.3 \times 10^5$ and $5.0 \times 10^5$, respectively.
Figure S9. SERS spectra of Au@1, and Ag@1 under the same experimental conditions.

Figure S10. SERS spectra of Au@1@Ag and Au@1@Ag@MHA under the same experimental conditions.