# Simultaneous SERS and surface-enhanced fluorescence from dye-

# embedded metal core-shell nanoparticles

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Figure S1. Schematic illustration of the dye-embedded core-shell nanoparticles.

# Experimental

## Chemicals

Polyacrylic acid (PAA, MW=1800), polyallylamine hydrochloride (PAH, MW=15000), toluidine Blue O (TBO), sodium citrate, hydroquinone, sodium cyanide, hydrogen tetrachloroaurate (HAuCl<sub>4</sub>, 99.99%), 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride (EDC), and *N*hydroxysuccinimide (NHS), were obtained from Sigma-Aldrich. All chemicals, unless specified, were of reagent grade. Reagents and solvents were obtained commercially and used without further purification. All glassware were cleaned with freshly prepared aqua regia and rinsed thoroughly with DI water prior to use. All solutions were prepared using deionized (DI) water (18 MΩ-cm).

#### Synthesis of citrate stabilized AuNPs

Gold nanoparticles of ~40 nm were synthesized according to the procedures in the literature.<sup>[S1]</sup> Briefly, in a 100-mL glass flask, 50 mL of a 0.01% aqueous HAuCl<sub>4</sub> solution was heated to boil under magnetic stirring. Upon boiling, 0.5 mL of 1% sodium citrate was rapidly injected. Within seconds, the pale yellow solution turned into deep purple and quickly progressed to red. The colloid was kept boiling for 15 min to ensure complete reduction, before left to cool to room temperature. Excessive ions were removed from the solution by centrifugation, and the AuNPs were redispersed in 50 mL of DI water. The AuNPs solution was kept at 4 °C until later use.

#### Synthesis of PAA-TBO

EDC (1.9 mg) and NHS (1.2 mg) were added subsequently to PAA solution (40 mg in 10 mL DI water) under stirring for 20 min. Then 100  $\mu$ L of TBO solution (10 mM) was added, and the solution was stirred overnight in the dark. Note that only a small fraction of the amino groups on PAA were labeled by the TBO molecules.

#### Synthesis of Au@PAH-(PAA-TBO) nanoparticles

The layer-by-layer assembly procedure was adapted from the method in the literature with slight modification.<sup>[S2]</sup> In a typical run, 10 mL of prepared AuNP solution were added dropwise under vigorous stirring to PAH aqueous solution (40 mg in 10 mL DI water), which had been sonicated and stirred for 2 hr. The mixture was kept under stirring at room temperature in the dark for ~4 hr. Then the solution was centrifuged for 10 min at 14,000 rpm, supernatant removed and precipitates re-dispersed in DI water. This washing process was repeated one more time to remove the excess PAH. The total re-dispersion volume after the second centrifugation was adjusted to 10 mL, and added dropwise under vigorous stirring to 10 mL PAA-TBO solution, which had been sonicated and stirred for 2 hr. The mixture was again kept under stirring at room temperature in the dark for ~4 hr. Then same washing process was repeated three times to remove the excess PAA as well as any free TBO. After washing, the total re-dispersion volume was adjusted to 10 mL. Hereafter, the layer assembly PAH-(PAA-TBO) is denoted as "1".

### Synthesis of Au@1@Ag nanoparticles

Deposition of silver shell onto the polyelectrolyte-coated AuNPs was similar to the method in the literature with slight modification.<sup>[S3]</sup> Hydroquinone (30  $\mu$ L, 10 mM in water) and AgNO<sub>3</sub> (300  $\mu$ L, 1 mM in water) were added in sequence to a 1 mL of Au@1 solution under vigorous stirring. The mixture was incubated at room temperature for 12 hr to allow for the completion of the reaction.

The solution was then centrifuged for 10 min at 14,000 rpm to collect the precipitate, which was redispersed in DI water until later use.

# Synthesis of Au@1-(PAH-PAA)<sub>2</sub>@Ag, Au@(PAH-PAA)-1-(PAH-PAA)@Ag and Au@(PAH-PAA)<sub>2</sub>-1@Ag nanoparticles

The synthesis of these nanoparticles was similar to that of Au@1@Ag. The PAA-TBO layer was included as the second, fourth and sixth layer in the layer-by-layer assembly, respectively. There were a total of six layers of PAH and PAA for each type of nanoparticles.

# Characterization

UV-vis extinction spectra were recorded on a USB 4000 spectrophotometer (Ocean Optics, USA) using a 1-cm path length quartz cell at room temperature. TEM measurements were performed on a Biotwin 12 transmission electron microscope (FEI). A drop of suspension containing nanoparticles was deposited on a Formvar-covered carbon-coated copper grid (Electron Microscopy Sciences, PA) and let dried at room temperature. Raman measurements were done on a Renishaw InVia Raman microscope system. The dye-embedded Au-core/Ag-shell nanoparticles were dispersed thoroughly in DI water by sonication. A drop of the dispersion was transferred into a small quartz tube of ~1 mm I.D. The tube was placed on the stage of the microscope for Raman measurements. Laser intensity at the samples was ~0.96 mW from the 633 nm line of a HeNe laser or ~11 mW from the 785 nm line of a diode laser for all measurements. Exposure time for all Raman measurements was 10s. Between different Raman sessions, the 520.7 cm<sup>-1</sup> peak of a silicon wafer was used to calibrate the spectrograph.

## **SERS EFs calculation**

The concentration of TBO in the TBO-embedded Au-core/Ag-shell nanoparticle solution was determined by measuring the fluorescence intensity of the NaCN-treated samples and comparing it to a standardization curve. We have tested that NaCN itself has little effect on the intensity of TBO fluorescence. SERS EF values were then calculated by comparing the Raman intensity of these nanoparticle solutions with those from a pure TBO solution, both excited at 785 nm and measured under the same experimental conditions.

Take Au@1@Ag as an example to illustrate the calculation. The 1620 cm<sup>-1</sup> peak of TBO was used to calculate the SERS EFs of all samples containing TBO molecules. The calculation was based on the following equation:

# $EF = (I_{SERS} \times C_{bulk})/(I_{bulk} \times C_{SERS})$

where  $I_{SERS}$  and  $I_{bulk}$  are the Raman intensities of the 1620 cm<sup>-1</sup> peak for Au@1@Ag and a pure TBO solution (10 mM),  $C_{SERS}$  and  $C_{bulk}$  are the concentrations of TBO in Au@1@Ag and the TBO solution.

After the SERS measurements with the results shown in Figure S2c, 50  $\mu$ L of 100 mM NaCN solution was added to the 1 mL Au@1@Ag dispersion to completely dissolve both Au and Ag out of the nanoparticles. Fluorescence spectrum of the resulting solution was measured and shown in Figure S2a. By comparing the integrated fluorescence intensity of TBO of this sample to a calibration curve shown in Figure S2b, the concentration of TBO in the original Au@1@Ag dispersion was determined to be  $6.4 \times 10^{-7}$  M. The Raman spectra for the 10 mM TBO solution was measured under the same conditions as those for Au@1@Ag, and shown in Figure S2d. SERS EF was then calculated to be  $3.0 \times 10^5$  for Au@1@Ag and  $8.3 \times 10^3$  for Au@1, based on the spectra in Figure S2c. The same method was applied to calculate SERS EFs for other samples. Figure S3 is the Raman spectrum of Au@PAH-PAA@Ag excited by 633 nm laser, showing essentially no Raman or fluorescence signal from the Au@polyelectroytes@Ag nanostructures without TBO.



excited by 633 nm laser. (b) Calibration curve of pure TBO solution with integrated fluorescence intensity (640 -780 nm) as y-axis and [TBO] as x-axis. (c) SERS spectra of Au@1, Au@1@Ag

excited at 785 nm. (d) Raman spectra of 10 mM TBO solution collected under the same conditions as (c).



Figure S3. Raman spectrum of Au@PAH-PAA@Ag excited by 633 nm laser.

References

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