A Controlled, and Reproducible Pathway to Dye-Tagged, Encapsulated Silver Nanoparticles as Substrates for SERS Multiplexing

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Supporting Information

Particle tagging procedure. Ag nanoparticles (500 mL, 110 pM) are placed in a plastic vial without a stir bar. (Although the particles are stable in glass, plastic is selected in order to minimize competing interactions with the silane / silicate.) MPTMS (25 µL, 25 µM) is added and rapidly mixed. After standing for at least two minutes (particles are stable in the presence of small amounts of MPTMS for hours to days), the chosen dye is added (variable amount – typically 50 µL, 2.8 µM), followed by NaCl as an aggregation agent (variable amount – typically 20 to 120 µL, 170 mM). The NaCl can be added stepwise to investigate the effect of [NaCl] on SERS intensity. Aggregation may be fast or slow depending on the amount of NaCl added, and the identity of the dye. Over-aggregated samples flocculate and fall out of solution; samples that remain stable for > 12 hours are usually stable enough to undergo SiO_2-coating. Coating with SiO_2 is performed by adding excess sodium silicate (60 µL, 22 mM) and allowing the solution to sit for ~1 week. The resultant SiO_2 coating is thin (see **Error! Reference source not found.**), but provides sufficient stability for purification. Leaving the nanoparticle aggregates in the presence of sodium silicate for extended periods tends to result in the formation of isolated silica structures, and highly networked aggregates of nanoparticle aggregates, rather than a thicker SiO_2 shell. Shorter time periods tend to result in insufficient deposition of SiO_2. Particle aggregate purification is by centrifuge: typically 6×35 min @ $14,500 \times g$. We have also used the centrifuge to concentrate nanoparticle aggregates up to ~25 nM with no discernable issues of stability.

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Optimization of [NaCl] and [Nile blue]. Samples were prepared as described above – using differing amounts of NaCl or Nile blue – without adding sodium silicate after NaCl aggregation. UV-Vis-NIR spectra, and SERS spectra were recorded after 3 days. For SERS, multiple acquisitions were obtained on each sample (as shown in Figure 1) – these datasets were processed into the data shown in main text Figures 3b and 4b. The example datasets show the relatively consistent intensities obtained from under-aggregated (2.9 mM NaCl) and optimally aggregated (7.1 mM) samples, as well as the highly variable intensities obtained from over-aggregated (21 mM) samples.
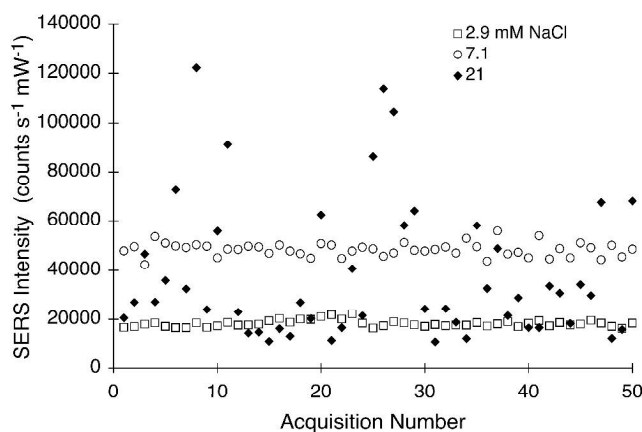

Figure 1. Three example datasets contributing to Figure 3b in the main text. Each dataset consists of 50 SERS spectrum acquisitions (532 nm excitation) of 110 pM Ag nanoparticles treated with MPTMS (1.2 µM prior to further additives), Nile blue (230 nM final), and NaCl (final concentrations listed in figure). All data points are corrected for background, particle concentration, integration time, and excitation power at the sample. The average intensity from each series gives a data point in main text Figure 3b, while the standard deviation of the series gives the error bars.