

Supporting Information

Film Preparation. 45-nm gold films were deposited on clean glass slides using a 5-nm chromium adhesion layer with an electron beam evaporator (CHA Industries). LBL deposition of poly(allylamine) hydrochloride (PAH, $M_w = 70$ kDa, Aldrich) and polystyrene sulfonate (PSS, $M_w = 70$ kDa, Aldrich) was used to create dielectric spacers to controllably separate gold NPs from gold films. For each adsorption step the gold-coated slides were immersed in 0.003 moles-of-monomer/L (monomol/L) polyelectrolyte and 1 M NaCl for 30 min, rinsed thoroughly with a gentle stream of ultra-pure water (18 M Ω , used in all experiments), and immersed in fresh ultra-pure water for 1 min, after which the substrates were either immersed in 1 M NaCl for 30 s before repeating the same steps for deposition of the oppositely charged PE or dried with a stream of nitrogen for analysis.

LBL film thicknesses were measured, in air, with a J.A. Woollam Co., Inc., M-88 spectroscopic ellipsometer and WVASE32 software (version 3.460). Variable-wavelength scans (277.5 – 763 nm) were performed at 65°, 70°, and 75°. Ellipsometry data was analyzed by a 2-layer model, similar to previously reported methods (1-4), that is comprised of a bulk gold layer underneath an organic layer composed of the PEs. The optical parameters of each gold-coated slide were determined prior to LBL deposition. After deposition, each slide containing PE layers was modeled using the previously determined gold optical parameters for the bulk gold layer along with the Cauchy expression for a normal dispersion to represent the PE layers. The thickness of the film and optical parameters of the Cauchy expression were optimized to give the lowest mean standard error in the minimization algorithm used by the WVASE software. In addition to the thickness, these models also provided an independent estimate of the refractive index for the layers of PAH and PSS of 1.58 at 633 nm, which lies in the previously reported range of 1.45 – 1.65 (2, 4-6). All LBL depositions were initiated and terminated with a cationic PAH layer to facilitate both the attachment of the first PEL layer to the gold film through amine-gold interactions (7) and the electrostatic immobilization of the negatively charged gold NPs to the top layer of

the LBL. Thus, the minimum step height between PEL layers of increasing thickness was a bi-layer of PSS and PAH. The average PE bi-layer thickness of 4.1 nm was obtained from ellipsometry measurements and agrees with previously reported results from LBL depositions performed under similar conditions (8, 9). The dry thickness measurements of the PE layers were reported as estimates of the thickness of the PE in the experiment done in water. Preliminary AFM characterization of PE layer thickness changes upon water submersion indicates that swelling of as much as 15% of the thickness at ambient humidity occurs. Further characterization is required; however, previous studies have shown that similar PE layers can swell up to 40% of the thickness at ambient humidity when submerged (3, 4, 10, 11).

Gold colloids with a nominal diameter of 60 nm and a coefficient of variation of $< 8\%$ (BB International) were electrostatically immobilized on the top surface of the PE multi-layer film by exposure to a 1:10 dilution (in ultra-pure water) of the stock solution of the NPs for 30 s at room temperature. The gold NPs were also deposited onto bare gold slides by incubation of the gold surface for 45-min in the undiluted colloid solution. After NP deposition all slides were rinsed with ultra-pure water and dried with compressed air. These sample preparation conditions resulted in a well spaced population of single gold NPs dispersed either on the surface of the top PE layer at a predictable distance above the gold film (as determined by the number of PE layers deposited) or directly on the gold film in the case where no PE layers were deposited.

Additional Data:

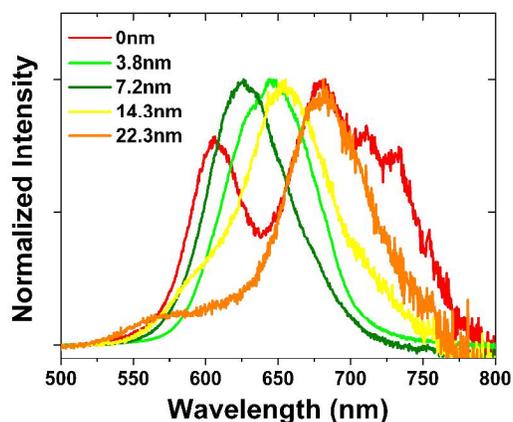


Figure 7C: Single NP plasmon resonant scattering spectra (water environment) with increasing polyelectrolyte (PE) spacer layers between NP and gold film. The gold film was placed on a dove prism and illuminated with TIR at 73 degrees. A coverslip is placed over the sample with 10- μ l droplet of water and the scattering from the single NPs (5 at each layer) on the gold film (NP-film) at various spacer thicknesses are collected by a 100 \times oil immersion objective. The spectra were amplitude normalized to ease comparison between distances.

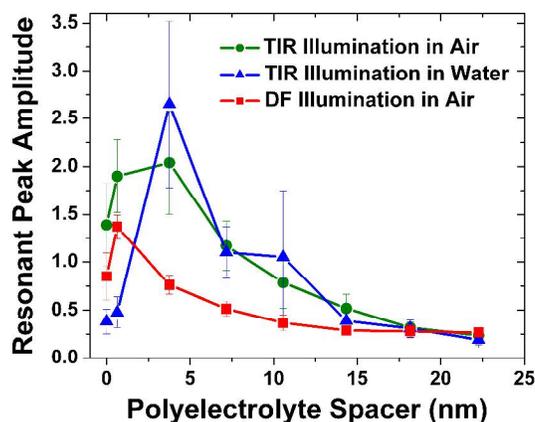


Figure 8: Spectral peak scattering amplitudes for all NP measurements displaying the change in brightness of the NPs with respect to the distance above the gold film. In the case for the water data, we use the ellipsometric measurements (in air) to estimate the PE spacer distance. However, as discussed above, we expect there to be some swelling of the polymer.

References

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