

## Supporting Information – Distance-Dependent RI Sensitivity

The goal of the fit regime described herein is to provide an analytical approximation that provides the distance-dependent RI sensitivity  $S(r)$  for a nanorod of arbitrary dimensions. This is accomplished by fitting experimental  $S(r)$  data, identifying the geometric dependence of the fits, and generating expressions to reproduce a theoretical  $S(r)$  for a nanorod of arbitrary geometry.

First, a fit is applied to the experimentally determined response curves,  $\lambda^*$  versus adsorbed polyelectrolyte thickness. To determine the form that this equation should take, we examine the underlying physical process. Since light energy is driving the detection system, it is reasonable to assume that the proper weighting factor for the distance-dependent response is proportional to the light intensity at that point<sup>1</sup>. The light intensity is the electric field strength squared, and for planar SPR, it has been shown that the field decays with distance  $r$  from the surface. Thus, the distance-dependent response can be modeled to follow the form  $\exp(-2 \cdot r / l_d)$  where  $l_d$  is some characteristic decay length<sup>2</sup>. The overall sensor response can then be calculated as the depth integral of the local RI weighted by the electric field intensity. For a system composed of a single adlayer in the surrounding medium, the response can be written as<sup>1</sup>:

$$\text{Eq. S1} \quad R(r) = S_0 \cdot (n_a - n_s) [1 - \exp(-2r / l_d)]$$

where  $n_a$  and  $n_s$  are the refractive indices of adlayer and solvent respectively,  $S_0$  is the bulk RI sensitivity, and  $l_d$  is the decay length characteristic of a particular SPR geometry. This equation has also been shown to be reliably extended to modeling LSPR response of individual nanoparticles<sup>3,4</sup>.

In order to provide an analytic form of equation S1 in terms of nanoparticle geometry, the overall bulk RI sensitivity  $S_0$  must first be determined in regard to nanoparticle length and diameter. The value of  $S_0$  is in units of nm/RIU and it is a measure of how much  $\lambda^*$  will shift (in nm) upon a given RI increase of the entire medium surrounding the nanorod.  $S_0$  can be approximated by taking advantage of the linear correlation in visible wavelength range between  $S_0$  and  $\lambda^*$  for nanoparticles of similar composition described by Miller et al<sup>5</sup>. For single-component nanoparticles, the bulk sensitivity  $S_0$  is given by:

$$\text{Eq. S2} \quad S_0 = \frac{2}{n} \left( \lambda_0 + \frac{\epsilon_0}{m} \right)$$

where  $n$  is the RI of the ambient environment,  $\lambda_0$  is the LSPR peak in vacuum, and  $m$  is the slope of is a linear fit to the real part of the metal's dielectric function ( $\epsilon' \approx m\lambda_0 + \epsilon_0$ ). This function describes nanoparticle sensitivity behavior for particles that are in a surrounding medium of homogenous RI. Recently Miller et al. have shown that the correlation can be extended to accommodate particles in intimate contact with a substrate by introducing a scaling factor by replacing  $n$  with  $\beta n$  giving:

$$\text{Eq. S3} \quad S_0 = \frac{2}{\beta n} \left( \lambda_0 + \frac{\epsilon_0}{m} \right)$$

where  $\beta$  depends on the nanoparticle geometry and substrate RI. For nanorods on glass, they have shown that  $\beta n = 1.75$  provides excellent agreement with experimental results. Using  $\lambda_0$  determined from the simulated scattering spectra, the bulk sensitivity  $S_0$  can be approximated for a nanorod of arbitrary dimensions. For example, utilizing Equation S3 with  $\beta n = 1.75$  predicts a bulk RI sensitivity of 268.7 nm/RIU for 74.1 x 33.2 nm (length

x diameter) nanorods on glass with  $\lambda^*$  of 720 nm, which is in good agreement with the experimentally determined bulk RI sensitivity of 261.7 nm/RIU<sup>6</sup>.

Now  $S_0$  has been determined as a function of nanorod geometry and  $n_a$  and  $n_s$  are known, only the decay length  $l_d$  is yet to be determined to produce an analytical expression for  $R(r)$ . Mathematically, this decay length determines the rate at which the response curve approaches its asymptote. Physically, this represents the confinement of sensitivity to the nanorod surface. So for lower values of  $l_d$ , the response curve approaches its asymptote more quickly, simulating nanorods where the sensing volume is confined closer to the surface. Because  $l_d$  is a function describing electric field enhancement, we assume its dependence on nanorod geometry is of the same form as the shape parameter,  $e$ , employed in the Gans<sup>7</sup> extension of Mie theory<sup>8</sup> describing the scattering cross section of elliptical gold nanoparticles.

$$\text{Eq. S4} \quad l_d(l, d) \equiv l_d(e) = l_d \left( \sqrt{1 - \left(\frac{d}{l}\right)^2} \right)$$

To determine the correlation between  $l_d$  and  $e$ , Eq. S3 was fit to the experimental response curves of twelve experiments, two each for six different nanorod geometries. Plotting  $l_d$  versus  $e$  for the range of nanorods used, a linear correlation is observed. A linear fit to this plot yields equation 15 with an R-squared value of 0.941. Residuals from the linear fitting exhibit no clear shape.

$$\text{Eq. S5} \quad l_d(e) = 228 \cdot e - 176$$

This expression provides an approximation for describing  $l_d$  in units of nm based on the geometry of the nanorod. Now that the response curve  $R$  can be determined for arbitrary nanorod geometries, the distance-dependent sensitivity  $S(r)$  and the total sensing volume  $V_S$  are defined. As discussed above, the response is proportional to the square of the decaying electric field strength. Thus, it will be of the form:

$$\text{Eq. S6} \quad S(r) \equiv A \cdot \exp(-2r/l_d)$$

The normalization constant  $A$  is chosen to normalize  $S(r)$  such that its average value over the detection range is equal to the bulk sensitivity,  $S_0$ . This normalization is solved when  $A = 3S_0$ , which is then substituted into equation S6 yielding the following.

$$\text{Eq. S7} \quad S(r) \equiv 3S_0 \cdot \exp(-2r/l_d)$$

The sensing volume  $V_S$  is defined as the volume of a cylinder with hemispherical endcaps circumscribed by extending a distance  $r_s$  from the nanorod, where  $r_s$  is the distance at which  $S(r)$  drops to 5% of its maximum value. This distance occurs at 1.5 decay lengths. For nanorods on a substrate, the volume occupied by substrate within the circumscribed cylinder is subtracted to yield the effective  $V_S$ .

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