Analyte Transport to Micro- and Nano-Plasmonic Structures

Supplementary Information

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Abstract

This document contains information to supplement the data in the main manuscript, specifically, additional material regarding the *microwire*- (section 1), *nanodisk*- (section 3), and *nanorod*-based experiments (section 5). Furthermore, this document provides schematics, methods, and parameters to predict analyte transport to *microwire*- (section 2), *nanodisk*- (section 4), and *nanorod*-based experiments (section 6). Finally, we include data showing the independence of initial guesses on the fitted parameters for a selected sensorgram (section 7).

1. Additional Material Regarding Microwire Experiments

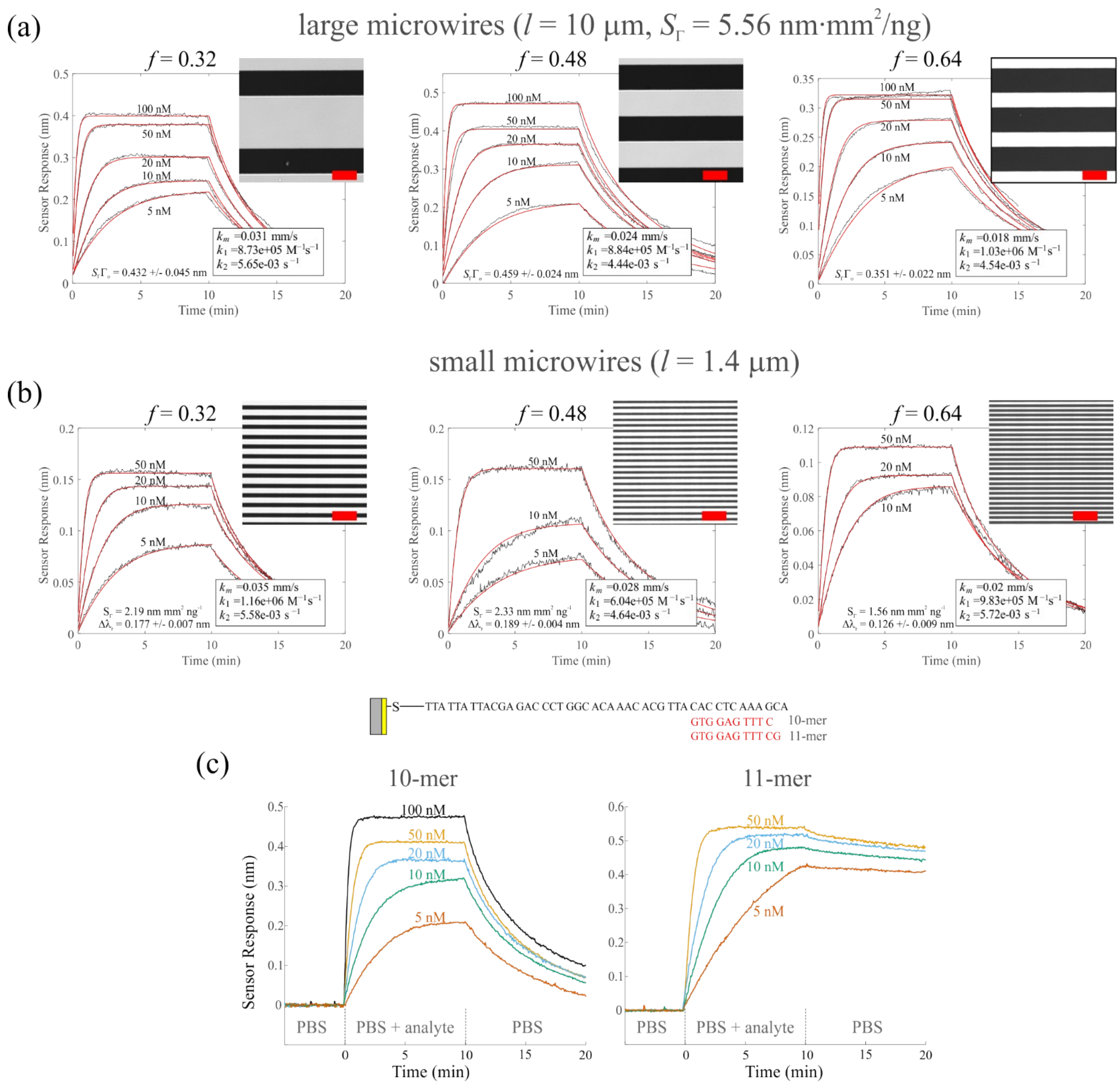

Figure S1. Fitted sensorgrams for (a) l = 10 μm and (b) l = 1.4 μm microwire substrates at three different fill fractions. The respective insets are microscope images (60× objective) for each substrate (scale bar 10 μm). Extracted values for global (k_m, k_1, k_2) and local parameters (Γ_o, averaged) are shown for each sensorgram. The sensitivity (S_Γ) for each fit is shown for the small microwires, which was calculated for each sensorgram as $S_\Gamma = \Delta\lambda_r/\Delta\lambda_{r,SPR}\cdot S_{\Gamma,SPR}$. (c) Sensorgrams taken using a microwire substrate (l = 1.4 μm, f = 0.48) for the analysis of both 10-mer (left) and 11-mer (right) target analytes.

2. Prediction of Analyte Transport to Microwire Substrates

Figure S2 shows a schematic of the flow cell used in the experiments for the microwire substrates. For purposes of prediction we assume transport in a straight rectangular channel having width W and length L. Values of W are taken as the full width in the center of the flow cell, and L is taken as the distance between inlet and outlet ports. We also disregard the height of each wire, and assume that the array is composed of embedded strips of length l in the direction of flow; this assumption is based on the large difference between the height h (50 nm) and the size of each microwire. The flow cell width is much larger than its height, thus the problem is reduced to a two-dimensional problem (transport is homogenous along the direction perpendicular to flow), and we can estimate rates of transport via the results of Newman:[1]

$$k_p = \frac{D}{H}\left(0.808Pe_s^{1/3} + 0.706Pe_s^{-1/6} - 0.808Pe_s^{-1/3}\right) \quad \text{(S1)}$$

where $\mathrm{Pe}_s = 6\eta^2\mathrm{Pe}$ is the sensor Péclet number, which is calculated from both the channel Péclet number Pe = Q/WD and the sensor aspect ratio (the ratio of the sensing region length to the channel height).

Table S1 lists the dimensional and dimensionless parameters related to the prediction of both k_p and k_{np} for microwire arrays. We calculated the analyte diffusivity via the Stokes-Einstein equation. The size of the 10-mer target analyte (molecular weight M_w = 3153 g/mol) was used to calculate a hydraulic length via the results of Kalwarczyk et al.[2] as $r_h = 0.024M_w^{0.57}$, resulting in a size of r_h = 2.37 nm. The viscosity of PBS buffer (25°C) was estimated to be 0.88×10^{-3} g/mm/s. Due to the power law dependence of k_p on Pe (Eqn. S1), similar results as those in Tab. S1 will be obtained by using the size of the 11-mer analyte (M_w = 3482 g/mol).

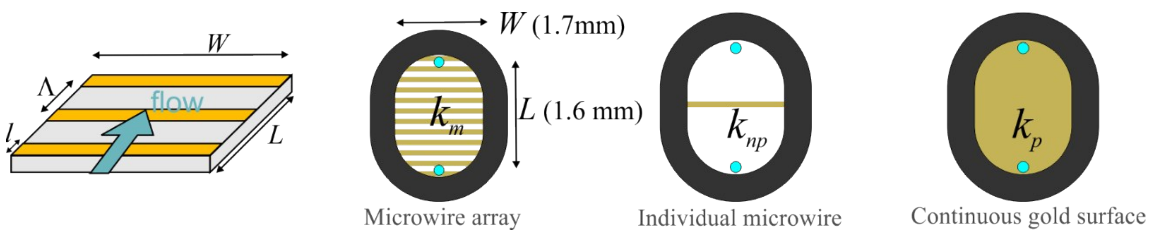

Figure S2. Schematic and dimension of the flow cell used for the prediction of analyte transport to microwire substrates.

Parameter	Variable/Equation	Parameter	Variable/Equation
Experimental Parameters		*Individual microwire*	
Channel height	H = 50 µm	Sensor aspect ratio	
Channel width	W = 1.7 mm	l = 1.4 µm	$\eta = l/H = 0.028$
Channel length	L = 1.6 mm	l = 10 µm	$\eta = l/H = 0.2$
Flow rate	Q = 0.3333 mm³/s	l = 100 µm	$\eta = l/H = 2$
Analyte Diffusivity	$D = 1.048\times10^{-4}$ mm²/s	Mass transfer coefficient (Eqn. S2)	
Channel Peclet number	Pe = Q/WD = 1871	l = 1.4 µm	k_{np} = 0.154 mm/s
		l = 10 µm	k_{np} = 0.067 mm/s
Continuous gold surface		l = 100 µm	k_{np} = 0.030 mm/s
Sensor aspect ratio	$\eta = L/H = 32$		
Sensor Peclet number	$\mathrm{Pe}_s = 6\eta^2\mathrm{Pe} = 1.15\times10^7$	*Microwire array*	
Mass transfer coefficient	k_p = 0.0119 mm/s	Mass transfer ratio ($R_k = k_{np}/k_p$)	
		l = 1.4 µm	R_k = 12.93
		l = 10 µm	R_k = 5.63
		l = 100 µm	R_k = 2.53

Table S1. List of dimensional and dimensionless parameters used for the prediction of analyte transport to the microwire substrates used herein. For the individual microwires, the sensor Peclet number is calculated in a similar fashion as the continuous gold surface ($\mathrm{Pe}_s = 6\eta^2\mathrm{Pe}$); values of Pes for individual microwires are omitted for clarity.

3. Additional Material Regarding Nanodisk Experiments

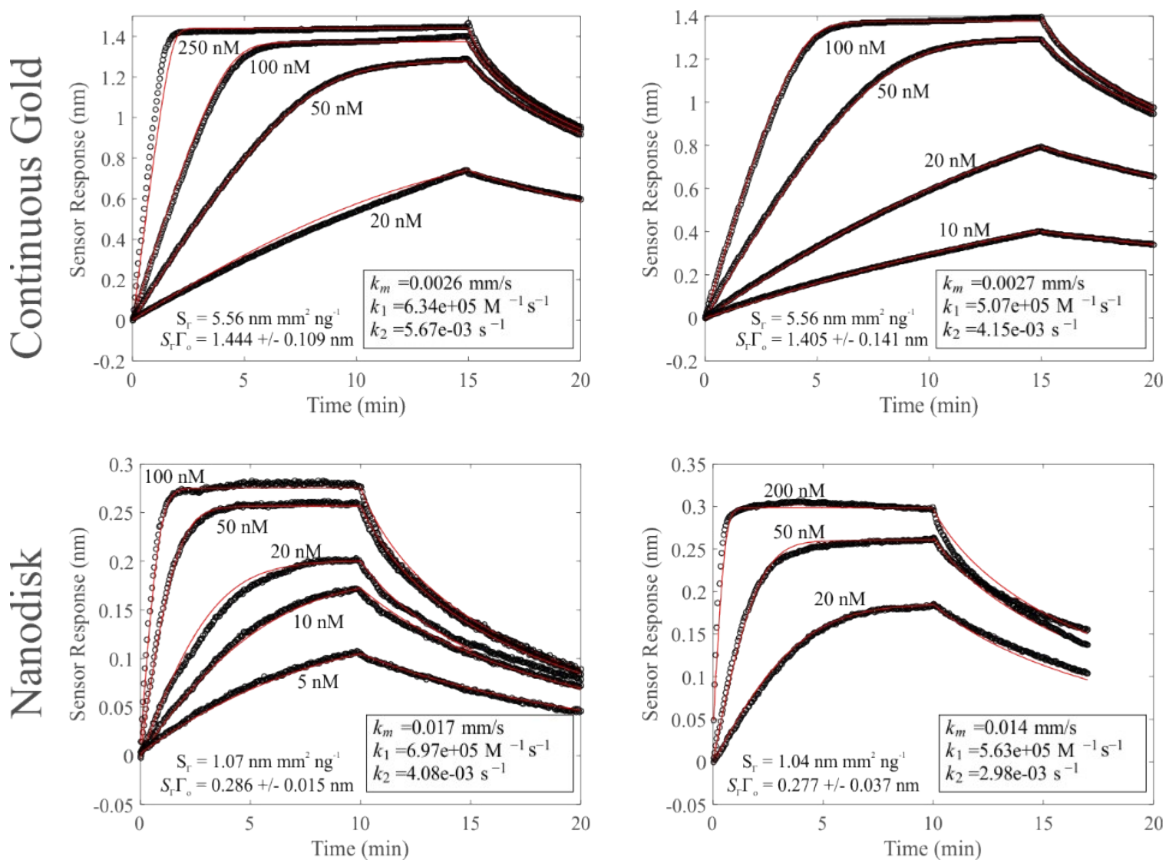

Figure S3. Fitted sensorgrams and extracted parameters for the nanodisk experiments used herein. The top row pertains to data taken using a continuous gold substrate, and the bottom row pertains to data taken from the nanodisk substrate (Fig. 4, main text). All data were taken with a flow cell having geometry as shown in Fig. S4.

4. Prediction of Analyte Transport to Nanodisk Substrates

Figure S4 shows a schematic of the flow cell used in the experiments using the nanodisk substrates. For purposes of prediction we assume transport in a straight rectangular channel, where values of W are taken as the full width of the center of the experimental microchannel. In the experimental setup the nanodisks were only interrogated in a 4 mm long portion near the center of the microchannel. Due to this arrangement, predictions of k_p via Eqn. S1 are not possible, and we must use a microscopic approach. In dimensional terms, the microscopic mass transport coefficient as a function of the distance z from the inlet can be calculated as[3]

$$k_p = \frac{D}{H}\left[\left(\frac{H\mathrm{Pe}}{z}\right)^{5/3} + 2.5^5\right]^{1/5}. \qquad \text{(S2)}$$

Equation S2 is plotted in Fig. S4 using the conditions used in the nanodisk experiments. We calculate k_p as the average value of Eqn. S2 over the range pertaining to the illumination zone ($5 < z < 9$ mm). To predict the mass transport coefficient to a single nanodisk we use the results of our previous study,[4] where the characteristic length (l_o) of a nanodisk/nanorod can be calculated as

$$l_o = a\left(fo + 6\alpha^{3/4} + (2.157 + 0.525\alpha^{3/5})\gamma^{17/20}\right), \qquad \text{(S3)}$$

where a is the nanodisk radius, and we use a value of $f_o = 4.0$. Pertaining to a nanodisk, the term $\alpha = h/2a$ is the dimensionless height, and $\gamma = 0$ is a dimensionless aspect ratio. This characteristic length can then be used to calculate a nanodisk aspect ratio as $\eta = l_o/4H$, which is then used to calculate Pe_s. Using the results of Phillips et al.,[5] this value of Pe_s can be used to estimate the mass transfer coefficient to a single nanodisk as

$$k_{np} = \frac{D}{\eta H}\left(\frac{4 - 0.123\mathrm{Pe}_s^{3/2}}{1 - 0.203\mathrm{Pe}_s^{1/2}}\right). \tag{S4}$$

Table S2 lists the dimensional and dimensionless parameters related to the prediction of both k_p and k_{np} for nanodisk substrates. The diffusivity of the analyte was calculated as that in the microwire experiments, where the molecular weight of the 13-mer RNA oligiomer ($M_w = 4301$ g/mol) leads to a hydraulic length of $r_h = 2.83$ nm.

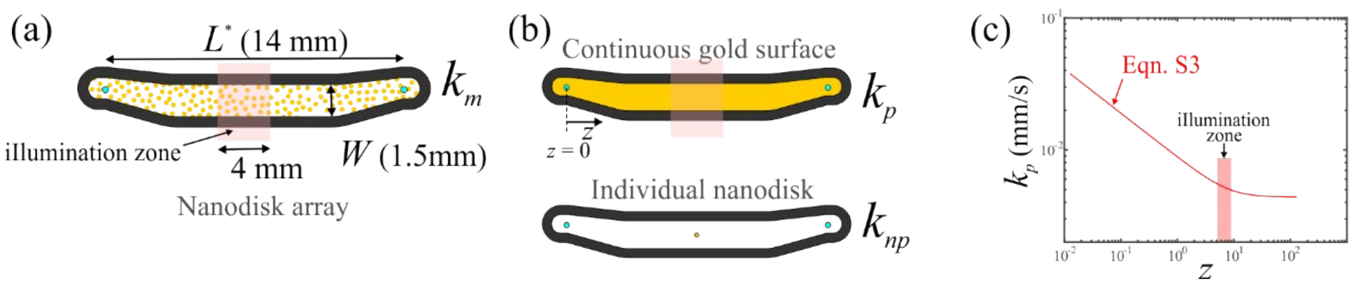

Figure S4. (a) Schematic and dimension of the flow cell used in nanodisk experiments. (b) Schematic of the flow cell considered for the prediction of both k_p and k_{np}. The light source is made incident only onto the center portion of the channel. (c) Microscopic mass transport behavior in a rectangular channel, used to predict k_p (via Eqn. S2).

Parameter	Variable/Equation	Parameter	Variable/Equation
Experimental Parameters		*Individual nanodisk*	
Channel height	$H = 50$ µm	Nanodisk diameter	$a = 44$ nm
Channel width	$W = 1.5$ mm	Dimensionless height	$\alpha = 0.341$
Flow rate	$Q = 0.3333$ mm^3/s	Dimensionless length	$\gamma = 0$
Analyte Diffusivity	$D = 8.78\times10^{-5}$ mm^2/s	Characteristic length (Eqn. S3)	$l_o = 294$ nm
Channel Peclet number	$\mathrm{Pe} = Q/WD = 2531$	Nanodisk aspect ratio	$\eta = l_o/4H = 0.0015$
		Nanodisk Péclet number	$\mathrm{Pe}_s = 0.0328$
Continuous gold surface		Mass transfer coefficient (Eqn. S4)	$k_{np} = 1.862$ mm/s
Mass transfer coefficient (Eqn. S2)	$k_p = 0.0052$ mm/s	*Nanodisk array*	
		Fill fraction	$f = 0.200$
		Mass transfer coefficient (Eqn. 3)	$k_m = 0.0258$ mm/s
		Mass transfer ratio ($R_k = k_{np}/k_p$)	$R_k = 358.1$

Table S2. List of dimensional and dimensionless parameters used for the prediction of analyte transport to the nanodisk substrates used herein.

5. Additional Material Regarding Nanorod Experiments

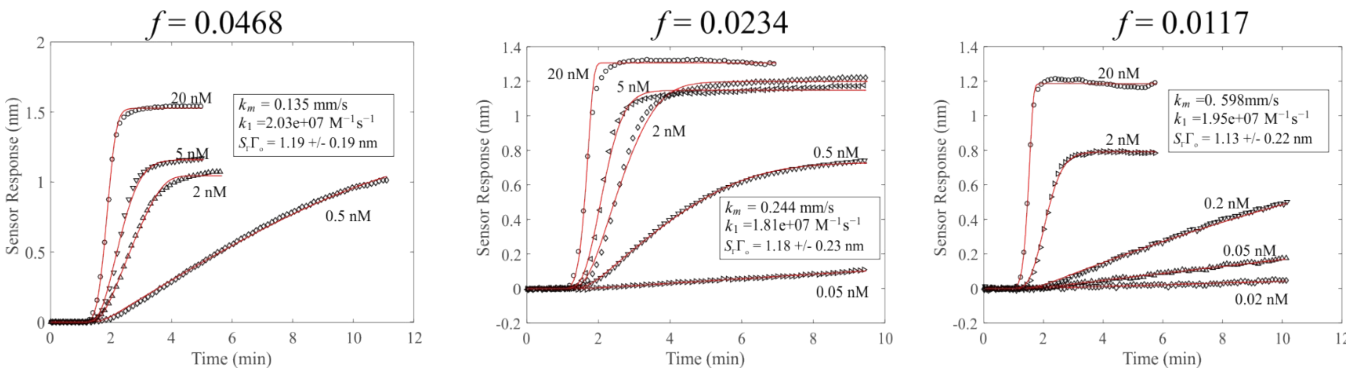

Figure S5. Fitted sensorgrams and associated extracted parameters for three representative nanorod experiments used herein.

6. Prediction of Analyte Transport to Nanorod Substrates

Figure S6 shows a schematic of the flow cell used in the experiments using the nanorod substrates. For purposes of prediction we assume transport in a straight rectangular channel, where values of *W* are taken as the full width of the center of the experimental channel, and *L* is taken directly from the length of the experimental array. For the continuous gold surface we used Eqn. S1 to predict k_p. For estimates of mass transport to an individual nanorod we used Eqn. S3 to calculate the characteristic length, which was then used in a similar fashion as the previous section to calculate k_{np}.

Table S3 lists the dimensional and dimensionless parameters related to the prediction of both k_p and k_{np} for nanorod substrates. The diffusivity of the analyte was calculated as that in the microwire experiments, where the molecular weight of the 20-mer DNA oligiomer (M_w = 6281 g/mol) leads to a hydraulic length of r_h = 3.51 nm.

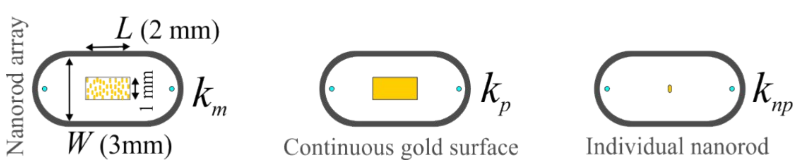

Figure S6. Schematic and dimension of the flow cell used for nanorod substrates.

Parameter	Variable/Equation	Parameter	Variable/Equation
Experimental Parameters		*Individual nanorod*	
Channel height	$H = 50$ µm	Nanorod diameter	$a = 15$ nm
Channel width	$W = 3$ mm	Dimensionless height	$\alpha = 1$
Channel length	$L = 2$ mm	Dimensionless length	$\gamma = 2.67$
Flow rate	$Q = 0.3333$ mm^3/s	Characteristic length (Eqn. S3)	$l_o = 252$ nm
Analyte Diffusivity	$D = 6.99\times10^{-5}$ mm^2/s	Nanodisk aspect ratio	$\eta = l_o/4H = 0.0013$
Channel Peclet number	$\mathrm{Pe} = Q/WD = 1588$	Nanodisk Péclet number	$\mathrm{Pe}_s = 0.0151$
		Mass transfer coefficient (Eqn. S4)	$k_{np} = 1.544$ mm/s
Continuous gold surface		*Nanodisk array*	
Sensor aspect ratio	$\eta = L/H = 40$	Mass transfer ratio ($R_k = k_{np}/k_p$)	$R_k = 220.4$
Sensor Péclet number	$\mathrm{Pe}_s = 1.52\times10^7$		
Mass transfer coefficient (Eqn. S2)	$k_p = 0.007$ mm/s		

Table S3. List of dimensional and dimensionless parameters used for the prediction of analyte transport to the nanorod substrates used herein.

7. Sensorgram Analysis: Sensitivity to Initial Guesses

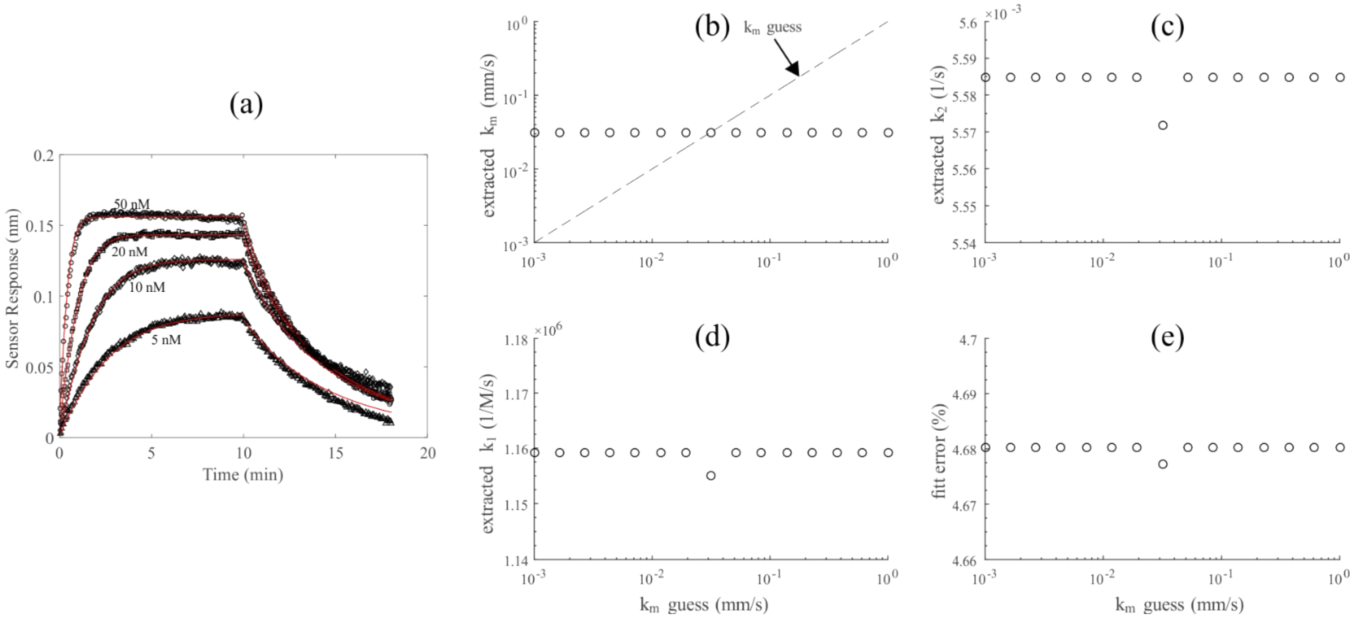

Figure S7: Sensitivity of the initial guesses on the fitted parameters of k_m, k_1, and k_2. **(a)** Sensorgram under consideration was taken from a microwire sensor (l = 1.4 µm, f = 0.32). Initial guesses were $k_1 = 9\times10^4$ 1/M/s, $k_2 = 4\times10^{-4}$ 1/s, and $S_\Gamma\Gamma_o$ = 0.2 nm. Note that the guess for k_1 was an order of magnitude lower than the final fitted value. Initial guesses of k_m varied by three orders of magnitude. **(b)-(e)** Fitted values of parameters, and the error of fit, plotted vs. the initial guess of k_m. It can be seen that there is little to no sensitivity to the initial guess of k_m. Similar results were observed when varying initial guesses for all other parameters.

8. References

(1) Newman, J. *Electroanalytical Chemistry* **1973**, *6*, 279-297.
(2) Kalwarczyk, T.; Tabaka, M.; Holyst, R. *Bioinformatics* **2012**, *28*, 2971-2978.
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(4) Lynn Jr, N. S.; Homola, J. *Chemistry–A European Journal* **2018**, *24*, 12031-12036.
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