Electron density change

The SPR response on electron density change in gold film is simulated as follows:

First, when the voltage is applied on the system, the surface electron density change of the gold film can be calculated from

$$\Delta \sigma = cV \tag{1}$$

where c is the interfacial capacitance per unit area (~47 µF/cm2 for the bare gold), V is the applied voltage. The initial dielectric constant of gold film ε_m can be calculated with Drude model

$$\varepsilon_m(f) = 1 - \frac{n_e e^2}{\varepsilon_0 m_e 4\pi^2 f^2}$$
⁽²⁾

where *e*, *m_e*, and *n_e* are the electron charge, mass, and density $(5.9 \times 10^{-28} m^{-3})$, respectively, *f* is the frequency of the incident light (wavelength ~635 nm), and ε_0 is the absolute dielectric constant. Then we can get the dielectric constant change of gold film $\Delta \varepsilon_m$ according to

$$\Delta \sigma = -\frac{ed_m n_e}{\varepsilon_m - 1} \Delta \varepsilon_m \tag{3}$$

where d_m is the thickness of gold film (~42 nm). The dielectric constant of prism is unchanged (~1.734²). With the voltage applied, the dielectric constant of gold film changes to $\varepsilon_m + \Delta \varepsilon_m$. Then through Fresnel equations we can get the reflection ratios of s-polarized components r_s and p-polarized components r_p under different voltages

$$r_{m} = \frac{r_{1,2}^{m} + r_{2,3}^{m} e^{2idk_{z2}}}{1 + r_{1,2}^{m} r_{2,3}^{m} e^{2idk_{z2}}} (m = p, s)$$
(4)

where

$$r_{j,j+1}^{m} = \frac{\frac{\varepsilon_{j+1}}{k_{zj+1}} - \frac{\varepsilon_{j}}{k_{zj}}}{\frac{\varepsilon_{j+1}}{k_{zj+1}} + \frac{\varepsilon_{j}}{k_{zj}}} (j = 1, 2)$$
(4-a)

$$k_{zj} = \sqrt{\left(\frac{\omega}{c}\right)^2 \varepsilon_j - k_{1x}^2} \ (j = 1, 2, 3)$$
 (4-b)

$$k_{1x} = \frac{\omega}{c} \sqrt{\varepsilon_1 \sin \theta} \tag{4-c}$$

 $(r_{1,2} \text{ and } r_{2,3} \text{ are the reflectance of the prism-gold film interface and the gold film-solution interface, respectively. <math>\omega$ is the angular frequency of incident light and c is the speed of light. ε_1 , ε_2 and ε_3 are the dielectric constants of prism, gold film and solution, respectively. θ is the angle between polarized direction and *x* coordinate ~53.49°.) Finally, according to the definition of SPR response, we can get the SPR signal change to voltage and dielectric constant of solution

$$SPR \ response = \frac{2r_s r_p \cos \theta \sin \theta \cos \left(\varphi_p - \varphi_s\right)}{r_s^2 \cos \theta^2 + r_p^2 \sin \theta^2}$$
(5)

where φ_s and φ_p are phase retardances of s-polarized components and p-polarized components, respectively (45°). And the refractive index relative factor (F) is defined as the unit of SPR signal.

EDL rearrangement

According to previous studies^{1, 2}, we got the modified PNP equation set as

$$\frac{\partial c}{\partial t} = a \cdot \frac{\partial}{\partial x} \cdot \left(\frac{\partial c}{\partial x} + \rho \cdot \frac{\partial \phi}{\partial x} + \frac{vc}{1 - vc} \cdot \frac{\partial c}{\partial x} \right)$$
(6)

$$\frac{\partial \rho}{\partial t} = a \cdot \frac{\partial}{\partial x} \cdot \left(\frac{\partial \rho}{\partial x} + c \cdot \frac{\partial \phi}{\partial x} + \frac{v\rho}{1 - vc} \cdot \frac{\partial c}{\partial x} \right)$$
(7)

$$-a^2 \cdot \frac{\partial^2 \phi}{\partial x^2} = \rho \tag{8}$$

$$\frac{c_{+} + c_{-}}{2c_{0}} = \frac{c_{+} - c_{-}}{2c_{0}}$$

In the equation set, $c = \frac{2c_0}{1}$ is the normalized local ions concentration, and $\rho = \frac{2c_0}{2}$ is the normalized local charge density, where c_+ and c_- are the concentrations of cations and anions respectively and c_0 is the mean ions concentration. $\Phi = \frac{zeU}{kT}$ is the normalized local electrostatic voltage, where U is the local electrostatic voltage, z is the ions

valence and e is the electron charge, k is the Boltzmann constant and T is the absolute λ_D

temperature. The parameter $a = \overline{L}$, is the ratio of the Debye length to the system size L. The parameter v is the effective volume fraction of the ions, with 1/v equal to the highest salt concentration in the compact layer that neither the

concentration c nor the charge density ρ ever overcome the steric limit 1/v.

The equation (6) and (7) respectively represent the ion diffusion caused by concentration gradient and the ion migration induced by electric field gradient in the vertical direction of the interface (the coordinate x in Fig. 2). The equation (8) expresses the relation between the local electrostatic potential and ionic charge density.

According to the blocking electrode assumption with no redox current, the boundary conditions at $x = \pm 1$ are as follows

$$\frac{\partial c}{\partial x} + \rho \cdot \frac{\partial \phi}{\partial x} + v \cdot \frac{c}{1 - vc} \cdot \frac{\partial c}{\partial x} = 0$$
(9)

$$\frac{\partial \rho}{\partial x} + c \cdot \frac{\partial \phi}{\partial x} + v \cdot \frac{\rho}{1 - vc} \cdot \frac{\partial c}{\partial x} = 0$$
(10)

$$\phi \pm a \cdot b \cdot \frac{\partial \phi}{\partial x} = \pm V \tag{11}$$

The solution is determined by two dimensionless parameters: $V = \overline{kT}$, the ratio of the applied

voltage to thermal voltage which approximately equals to $\frac{U_0}{25mV}$; and $b = \frac{\lambda_s}{\lambda_p}$, the ratio of the Stern length to the Debye length. We decided the boundary condition for the potential by accounting for the presence of a thin insulating layer. This leads to a mixed boundary condition. The equation (11) describes the effect of the surface Stern layer on the electrostatic voltage results, where $\pm V$ is the applied potential at the electrode which is reduced by the linear electric field of insulating layer to \emptyset at the surface of the electrolyte,

$$a \cdot b = \frac{\lambda_D}{L} \times \frac{\lambda_S}{\lambda_D} = \frac{\lambda_S}{L}$$

where MPNP starts to be applied. ${}^{L} {}^{\lambda}{}_{D} {}^{L}$ is a measure of the thickness of Stern layer.

And the initial conditions are set as

$$c(x)|_{t=0} = 1 \tag{12}$$

$$\rho(x)|_{t=0} = 0 \tag{13}$$

$$\left. \phi(x) \right|_{t=0} = bx \tag{14}$$

Solving the equation with spatial step of 1nm and temporal step of 0.05tc (tc is the generalized time,

 $tc = \frac{t}{\tau} = \frac{t}{\lambda_D L/D}$, *D* is the ions diffusion parameter), we can get the distribution of the ions concentration c(x,t).

References

1 M.Z. Bazant, K. Thornton and A. Ajdari, *Physical review E*, 2004, 70, 21506. 2 M.S. Kilic, M.Z. Bazant and A. Ajdari, Physical review E, 2007, 75, 21503.