Reactivity of Monolayer-Protected Gold Nanoclusters at Dye-Sensitized Liquid|Liquid Interfaces

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Supporting Information

Mathematical development of photocurrent density as a function of time (Equation 16)

The photocurrent responses involve contributions from the electron transfer, charge recombination and back electron transfer processes, i.e., equations 3-11, can be described as:

$$\frac{j}{F} = -k_1^{\mathrm{et}}\Gamma_{\mathrm{S}^*} + k_2^{\mathrm{et}}\Gamma_{\mathrm{S}^*} + k_1^{\mathrm{rec}}\Gamma_{\left[\mathrm{S}^+\cdots\mathrm{MPC}^{Z\text{-}1}\right]} - k_2^{\mathrm{rec}}\Gamma_{\left[\mathrm{S}^-\cdots\mathrm{MPC}^{Z+1}\right]} + k_1^{\mathrm{b}}\Gamma_{\mathrm{S}^+} + k_2^{\mathrm{b}}\Gamma_{\mathrm{S}^-} \quad \text{(s1)}$$

where Γ_{X} ($\mathrm{X} = \mathrm{S}^*$, $\left[\mathrm{S}^+\cdots\mathrm{MPC}^{Z\text{-}1}\right]$, $\left[\mathrm{S}^-\cdots\mathrm{MPC}^{Z+1}\right]$, $\left[\mathrm{S}^+\right]$ and $\left[\mathrm{S}^-\right]$) denote surface concentrations.

Equation s1 can be expressed in the Laplace plane:

$$\frac{\overline{j}}{F} = -k_1^{\mathrm{et}}\overline{\Gamma_{\mathrm{S}^*}} + k_2^{\mathrm{et}}\overline{\Gamma_{\mathrm{S}^*}} + k_1^{\mathrm{rec}}\overline{\Gamma_{\left[\mathrm{S}^+\cdots\mathrm{MPC}^{Z\text{-}1}\right]}} - k_2^{\mathrm{rec}}\overline{\Gamma_{\left[\mathrm{S}^-\cdots\mathrm{MPC}^{Z+1}\right]}} + k_1^{\mathrm{b}}\overline{\Gamma_{\mathrm{S}^+}} + k_2^{\mathrm{b}}\overline{\Gamma_{\mathrm{S}^-}} \quad \text{(s2)}$$

The differential equations for the concentrations of species involved in the heterogeneous electron transfer process can be written as follows:

$$\frac{\mathrm{d}\Gamma_{\mathrm{S}^*}}{\mathrm{d}t} = I_0\sigma\Gamma_{\mathrm{S}} - k_{\mathrm{d}}\Gamma_{\mathrm{S}^*} - k_1^{\mathrm{et}}\Gamma_{\mathrm{S}^*} - k_2^{\mathrm{et}}\Gamma_{\mathrm{S}^*} = 0 \quad \text{(s3)}$$

$$\frac{\mathrm{d}\Gamma_{\left[\mathrm{S}^+\cdots\mathrm{MPC}^{Z\text{-}1}\right]}}{\mathrm{d}t} = k_1^{\mathrm{et}}\Gamma_{\mathrm{S}^*} - k_1^{\mathrm{rec}}\Gamma_{\left[\mathrm{S}^+\cdots\mathrm{MPC}^{Z\text{-}1}\right]} - k_1^{\mathrm{ps}}\Gamma_{\left[\mathrm{S}^+\cdots\mathrm{MPC}^{Z\text{-}1}\right]} \quad \text{(s4)}$$

$$\frac{\mathrm{d}\Gamma_{\left[\mathrm{S}^-\cdots\mathrm{MPC}^{Z+1}\right]}}{\mathrm{d}t} = k_2^{\mathrm{et}}\Gamma_{\mathrm{S}^*} - k_2^{\mathrm{rec}}\Gamma_{\left[\mathrm{S}^-\cdots\mathrm{MPC}^{Z+1}\right]} - k_2^{\mathrm{ps}}\Gamma_{\left[\mathrm{S}^-\cdots\mathrm{MPC}^{Z+1}\right]} \quad \text{(s5)}$$

$$\frac{\mathrm{d}\Gamma_{\mathrm{S}^+}}{\mathrm{d}t} = k_1^{\mathrm{ps}}\Gamma_{\left[\mathrm{S}^+\cdots\mathrm{MPC}^{Z\text{-}1}\right]} - k_1^{\mathrm{b}}\Gamma_{\mathrm{S}^+} \quad \text{(s6)}$$

$$\frac{\mathrm{d}\Gamma_{\mathrm{S}^-}}{\mathrm{d}t} = k_1^{\mathrm{ps}}\Gamma_{\left[\mathrm{S}^-\cdots\mathrm{MPC}^{Z+1}\right]} - k_1^{\mathrm{b}}\Gamma_{\mathrm{S}^-} \quad \text{(s7)}$$

Laplace transformation of equations s3-s7 yields:

$$\overline{\Gamma_{\mathrm{S}^*}} = \frac{I_0\sigma\Gamma_{\mathrm{S}}}{s\left(k_{\mathrm{d}} + k_1^{\mathrm{et}} + k_2^{\mathrm{et}}\right)} \quad \text{(s8)}$$

$$\overline{\Gamma_{\left[S^{+}\cdots MPC^{Z-1}\right]}}=\frac{k_1^{\mathrm{et}}\overline{\Gamma_{S^*}}}{s+k_1^{\mathrm{rec}}+k_1^{\mathrm{ps}}}=\frac{I_0\sigma\Gamma_S}{s\left(k_{\mathrm{d}}+k_1^{\mathrm{et}}+k_2^{\mathrm{et}}\right)}\cdot\frac{k_1^{\mathrm{et}}}{\left(s+k_1^{\mathrm{rec}}+k_1^{\mathrm{ps}}\right)} \tag{s9}$$

$$\overline{\Gamma_{\left[S^{-}\cdots MPC^{Z+1}\right]}}=\frac{k_2^{\mathrm{et}}\overline{\Gamma_{S^*}}}{s+k_2^{\mathrm{rec}}+k_2^{\mathrm{ps}}}=\frac{I_0\sigma\Gamma_S}{s\left(k_{\mathrm{d}}+k_1^{\mathrm{et}}+k_2^{\mathrm{et}}\right)}\cdot\frac{k_2^{\mathrm{et}}}{\left(s+k_2^{\mathrm{rec}}+k_2^{\mathrm{ps}}\right)} \tag{s10}$$

$$\overline{\Gamma_{S^{+}}}=\frac{k_1^{\mathrm{ps}}\overline{\Gamma_{\left[S^{+}\cdots MPC^{Z-1}\right]}}}{s+k_1^{\mathrm{b}}}=\frac{I_0\sigma\Gamma_S}{s\left(k_{\mathrm{d}}+k_1^{\mathrm{et}}+k_2^{\mathrm{et}}\right)}\cdot\frac{k_1^{\mathrm{et}}}{\left(s+k_1^{\mathrm{rec}}+k_1^{\mathrm{ps}}\right)}\frac{k_1^{\mathrm{ps}}}{\left(s+k_1^{\mathrm{b}}\right)} \tag{s11}$$

$$\overline{\Gamma_{S^{-}}}=\frac{k_2^{\mathrm{ps}}\overline{\Gamma_{\left[S^{-}\cdots MPC^{Z+1}\right]}}}{s+k_2^{\mathrm{b}}}=\frac{I_0\sigma\Gamma_S}{s\left(k_{\mathrm{d}}+k_1^{\mathrm{et}}+k_2^{\mathrm{et}}\right)}\cdot\frac{k_2^{\mathrm{et}}}{\left(s+k_2^{\mathrm{rec}}+k_2^{\mathrm{ps}}\right)}\frac{k_2^{\mathrm{ps}}}{\left(s+k_2^{\mathrm{b}}\right)} \tag{s12}$$

where s is the Laplace variable. Then equation s2 can be rewritten as:

$$\frac{\overline{j}}{F}=\left(-\frac{k_1^{\mathrm{et}}I_0\sigma\Gamma_S}{k_{\mathrm{d}}+k_1^{\mathrm{et}}+k_2^{\mathrm{et}}}\right)\frac{\left(s+k_1^{\mathrm{b}}+k_1^{\mathrm{ps}}\right)}{\left(s+k_1^{\mathrm{rec}}+k_1^{\mathrm{ps}}\right)\left(s+k_1^{\mathrm{b}}\right)}+\left(\frac{k_2^{\mathrm{et}}I_0\sigma\Gamma_S}{k_{\mathrm{d}}+k_1^{\mathrm{et}}+k_2^{\mathrm{et}}}\right)\frac{\left(s+k_2^{\mathrm{b}}+k_2^{\mathrm{ps}}\right)}{\left(s+k_2^{\mathrm{rec}}+k_2^{\mathrm{ps}}\right)\left(s+k_2^{\mathrm{b}}\right)} \tag{s13}$$

The inverse Laplace transform of equation s13 gives **equation 16** describing the photocurrent density as a function of time:

$$j=g_1F\cdot\left\{\frac{k_1^{\mathrm{ps}}\exp\left(-k_1^{\mathrm{b}}t\right)+\left(k_1^{\mathrm{rec}}-k_1^{\mathrm{b}}\right)\exp\left[-\left(k_1^{\mathrm{rec}}+k_1^{\mathrm{ps}}\right)t\right]}{\left(k_1^{\mathrm{rec}}+k_1^{\mathrm{ps}}-k_1^{\mathrm{b}}\right)}\right\}+$$
$$+g_2F\cdot\left\{\frac{k_2^{\mathrm{ps}}\exp\left(-k_2^{\mathrm{b}}t\right)+\left(k_2^{\mathrm{rec}}-k_2^{\mathrm{b}}\right)\exp\left[-\left(k_2^{\mathrm{rec}}+k_2^{\mathrm{ps}}\right)t\right]}{\left(k_2^{\mathrm{rec}}+k_2^{\mathrm{ps}}-k_2^{\mathrm{b}}\right)}\right\}$$