Supporting Information for

A New Imaginary Term in the 2nd Order Nonlinear Susceptibility from Charged Interfaces

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Fig. S1. Square root of the square modulus of the SHG amplitude and phase.

Fig. S2. a) SHG Phase and amplitude obtained from the sine fits as a function of bulk solution pH at constant 0.5 M NaCl (filled black and purple circles) and constant 50 mM NaCl (empty black and purple circles). The SHG phases are referenced to the one obtained at pH 2.5 at 0.1 M NaCl. The amplitudes are normalized to the one obtained at 0.5 M at pH 5.8. b) Point estimates of $\chi^{(2)}$ and $\Phi(0)$ obtained from eqn. 10 as a function of pH at 50 mM [NaCl]. Shaded areas indicate 10% uncertainties. Dashed lines are the X-ray spectroscopic surface potentials for silica colloids suspended in a liquid jet at 50 mM [NaCl] reported by Brown et al.¹
Fig. S3. Point estimates of $\chi^{(2)}$ and $\Phi(0)$ obtained from eqn. 10 as a function of bulk ionic strength at constant pH 5.8. Shaded areas indicate 10% uncertainties, for full pH range studied.
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Supporting Information Note S1. The 3rd-order silica contribution in eqn. 4 is derived via

\[
\chi^{(2)}_{dc} = \int_{-\infty}^{0} \chi^{(3)} E_{DC}(z) e^{i \Delta k z} dz = \int_{-\infty}^{0} \chi^{(3)} \frac{d\Phi(z)}{dz} e^{i \Delta k z} dz = \int_{-\infty}^{0} \chi^{(3)} e^{i \Delta k z} d\Phi(z) \tag{S1}
\]

where we apply a linearly decaying potential into the bulk silica according to \( \Phi(z) = a(z + b) \) (for \(-b \leq z \leq 0\)) and \( \Phi(z) = 0 \) (for \( z \leq -b \)). We then obtain

\[
\chi^{(2)}_{dc} = \int_{-b}^{0} \chi^{(3)} e^{i \Delta k z} dz = \frac{1}{i \Delta k z} \frac{\chi^{(3)} a}{i \Delta k z} (e^{-i \Delta k z b} - 1) \tag{S2}
\]

\[
= \frac{a \chi^{(3)}}{i \Delta k z} (\cos \Delta k z b - 1 - i \sin \Delta k z b) \tag{S3}
\]

\[
= - \frac{a}{\Delta k z} [(\sin \Delta k z b) - i(1 - \cos \Delta k z b)] \chi^{(3)} \tag{S4}
\]

\[
= - \frac{a}{\Delta k z} \sqrt{(\sin \Delta k z b)^2 + (1 - \cos \Delta k z b)^2} \chi^{(3)} e^{-i \varphi_{DC}} \tag{S5}
\]

\[
= - \frac{a}{\Delta k z} \sqrt{2 \times (1 - \cos \Delta k z b)} \chi^{(3)} e^{-i \varphi_{DC}} \tag{S6}
\]

\[
= - \frac{a}{\Delta k z} \sqrt{2 \times 2 \left( \frac{\sin \Delta k z b}{2} \right)^2} \chi^{(3)} e^{-i \varphi_{DC}} = - \frac{2a}{\Delta k z} \left| \frac{\Delta k z b}{2} \right| \chi^{(3)} e^{-i \varphi_{DC}} \tag{S7}
\]

\[
= - \frac{2a}{\Delta k z} (\sin \frac{\Delta k z b}{2}) \chi^{(3)} e^{-i \varphi_{DC}} \tag{S8}
\]

Since \( \Phi(0) = ab \), \( a = \frac{\Phi(0)}{b} \). We therefore obtain

\[
\chi^{(2)}_{dc} = - \frac{2}{\Delta k z} \frac{\Phi(0)}{b} \left( \frac{\sin \frac{\Delta k z b}{2}}{2} \right) \chi^{(3)} e^{-i \varphi_{DC}} = - \frac{\Phi(0)}{\Delta k z b} \left( \frac{\sin \frac{\Delta k z b}{2}}{2} \right) \chi^{(3)} e^{-i \varphi_{DC}} \tag{S10}
\]

where \( \varphi_{DC} = \arctan \left( \frac{1 - \cos \Delta k z b}{\sin \Delta k z b} \right) = \arctan \left( \tan \frac{\Delta k z b}{2} \right) = \frac{\Delta k z b}{2} \).

Therefore, \( \chi^{(2)}_{dc} = - \frac{\sin \varphi_{DC}}{\varphi_{DC}} \chi^{(3)} \Phi(0) e^{-i \varphi_{DC}} \), where \( \varphi_{DC} = \Delta k z \frac{b}{2} = \Delta k z \lambda_D \).
Supporting Information Note S2. The one-dimensional Poisson equation was numerically solved for an oxide in contact with ionic water of 0.1 mol L\(^{-1}\) NaCl using the Newton-Raphson iteration method:\(^2\)

\[
\frac{d^2\Psi(x)}{dx^2} = \left\{ \begin{array}{ll}
-\frac{e[\delta(x_p)-\delta(x_n)]}{\epsilon_{ox}\epsilon_0} & \text{if } x < L_{ox} \\
-\frac{e\rho_b}{\epsilon_w\epsilon_0} [e^{-e\beta\Psi} + e^{e\beta\Psi}] & \text{if } L_{ox} < x < L
\end{array} \right. 
\]  

(eqn. S11).

Here, \(\Psi(x)\) is the one-dimensional electrostatic potential, and \(L(=220\text{ nm})\) is the total length of the system, including a 200 nm thick oxide and a 20 nm thick water region. The water-oxide interface is located at \(x = L_{ox} = 200\text{ nm}\). The vacuum permittivity is \(\epsilon_0 = 8.854 \times 10^{-12}\text{ Fm}^{-1}\), the relative dielectric permittivities are \(\epsilon_{ox} = 4\) for the oxide and \(\epsilon_w = 78\) for the ionic water, \(e\) is the elementary charge, and \(\beta = (k_BT)^{-1}\) with \(T\) being the temperature (300 K) and \(k_B\) being the Boltzmann constant. The bulk ion density in the ionic water is \(\rho_b = 0.1\text{ mol L}^{-1}\) with monovalent cations and anions whose thermal motion is incorporated using the Boltzmann factor.

The oxide is modeled to include a pair of positively and negatively charged point defects that decrease the electric field inside the oxide. A positively charged defect \((x = x_p)\) is randomly placed inside the oxide region, followed by a random insertion of a negatively charged defect \((x = x_n)\) according to a Poisson distribution having an average of 100 nm, so the distance between the defects is 100 nm on average to recapitulate the 100 ppm defect density in commercially available silica.

Three boundary conditions are applied in our model using the fact that the oxide surface in contact with water is lightly charged and both the oxide and water boundaries are electrically grounded. We employ (i) the Dirichlet condition with \(\Psi(x = 0) = 0\) at the oxide end, (ii) the Dirichlet condition with \(\Psi(x = L) = 0\) at the water end, and (iii) the Neumann condition at the aqueous oxide interface \((x = L_{ox})\) as follows:
where $Q_s (-0.015 \text{ C m}^{-2})$ is the oxide surface charge density. The differential equation is solved by discretizing the space with finite elements whose size is 0.01 nm along the x-axis. Note that 0.01 nm is short enough to properly recapitulate the Debye screening length (0.39 nm at 1 mol L$^{-1}$ NaCl) in the water region. The iteration is terminated once $L^2$-norm of the solution is less than $10^{-6}$. The electric potential and the associated electric field is averaged over $10^6$ realizations with the random insertion of defects inside the oxide. We also confirmed that the result is insensitive to the spatially varying relative dielectric permittivity in the aqueous region.$^2$

The two-dimensional linearized Poisson-Boltzmann equation was numerically solved for rough oxide:water interfaces (See Fig. S4), modeled by a small dendrite of height (H) and length (L):

$$
\left( \frac{d^2}{dx^2} + \frac{d^2}{dy^2} \right) \Psi(x, y) = \begin{cases} 
0, & \text{in the oxide region} \\
\kappa^2 \Psi(x, y), & \text{in the water region}
\end{cases} \quad (\text{eqn. S13}),
$$

where $\kappa = \left( \frac{2e^2 \beta \rho_b}{\epsilon_w \epsilon_0} \right)$ is the inverse of Debye screening length and $\Psi(x, y)$ is the two-dimensional electrostatic potential. Here, the length of each region is fixed with a 10 nm thick oxide and a 20 nm thick water region. The height of the oxide region varies according to the height of the dendrite: $H_{\text{oxide}} = 2H$. Other parameters are kept the same as in the one-dimensional model above.

Boundary conditions are applied as in the one-dimensional model. We employ (i) the Dirichlet condition with $\Psi(x, y) = 0$ at both oxide and water ends (blue line in Fig. S4), and (ii) the Neumann condition at the corrugated aqueous oxide interface, $\partial$, (yellow line in Fig. S4) as follows:

$$
\epsilon_{ox} \left( \frac{d}{dx} + \frac{d}{dy} \right) \Psi_{ox}(x, y) \bigg|_{\partial} \cdot \hat{n} - \epsilon_{w} \left( \frac{d}{dx} + \frac{d}{dy} \right) \Psi_{w}(x, y) \bigg|_{\partial} \cdot \hat{n} = \frac{Q_s}{\epsilon_0} \quad (\text{eqn. S14}).
$$
Here, \( \mathbf{n} \) is the unit normal vector pointing the water region from the oxide region. The differential equation is solved by discretizing the space with finite elements whose size is 0.1 nm along both x- and y-axes. Note that 0.1 nm is still short enough to properly recapitulate the Debye screening length (0.39 nm at 0.1 mol L\(^{-1}\) NaCl) in the water region. The linear equation is solved using Jacobi and Gauss-Seidel methods with successive over-relaxation.\(^3\) The relaxation method is terminated once L\(_2\)-norm of the solution is less than 10\(^{-12}\).

![Figure S4. Finite element calculation model for a corrugated oxide:water interface.](image)

The rough oxide:water interface is modeled using a nanoscale dendrite of height \( (H) \) and length \( (L) \), represented by the yellow region. Bright green elements are the dendrite corners where the oxide:water boundary is along both the x- and y-axes.

**Supporting Information Note S3.**

We begin with

\[
\chi_{tot}^{(2)} = \chi^{(2)} + i\chi^{(2)}_{q} - \Phi(0) \chi_{EDL}^{(3)} \cos(\varphi_{DC,EDL}) e^{i\varphi_{DC,EDL}} = E_{sig} \times e^{i\varphi_{sig}} \quad (S15a)
\]

\[
= E_{sig} \times \cos \varphi_{sig} + E_{sig} \times i \times \sin \varphi_{sig} \quad (S15b).
\]

Collection of the real and imaginary parts yields

\[
E_{sig} \times \sin \varphi_{sig} = \chi_{q}^{(2)} - \Phi(0) \chi_{EDL}^{(3)} \cos(\varphi_{DC,EDL}) \sin(\varphi_{DC,EDL}) \quad (S16) \text{ and}
\]
\[ E_{sig} \times \cos \varphi_{sig} = \chi^{(2)} + \Phi(0)\chi_{EDL}^{(3)}(\cos(\varphi_{DC,EDL}))^2 \] (S17).

Therefore,

\[ \Phi(0) = \frac{-E_{sig} \times \sin \varphi_{sig} - \chi_q^{(2)}}{\chi_{EDL}^{(3)}/\cos(\varphi_{DC,EDL})^{\sin(\varphi_{DC,EDL})}} \] (S18) and

\[ \chi^{(2)} = E_{sig} \times \cos \varphi_{sig} + \Phi(0)\chi_{EDL}^{(3)}(\cos(\varphi_{DC,EDL}))^2 \] (S19).

With \( \chi_q^{(2)} = 1.75 \times 10^{-22} \text{ m}^2\text{V}^{-1} \), we find nonphysical results for \( \Phi(0) \) and for \( \chi^{(2)} \).

**Fig. S5.** Point estimates of \( \chi^{(2)} \) and \( \Phi(0) \) obtained from eqn. 8 as a function of bulk ionic strength at constant pH 5.8 for a model containing only an electrical quadrupolar \( \chi_q^{(2)} \) as a new addition to model (1).
Fig. S6. Point estimates of $\chi^{(2)}$ and $\Phi(0)$ obtained from eqn. 8 as a function of bulk ionic strength at constant pH 5.8 for a model containing only an electrical quadrupolar $\chi_q^{(2)}$ as a new addition to model (1).

Fig. S7. SHG Amplitude (filed circles) and phase (empty circles) recorded from fused silica in contact with water maintained at different bulk ionic strengths of Na$_2$SO$_4$ (yellow) and NaCl (green) at constant pH 5.8. The SHG phase is with reference to pH 2.5 at 0.5 M NaCl.
**Fig. S8.** SHG Intensity recorded as a function of local oscillator translational stage position for an air:silica interface (gray circles, and average of five fringes as black line), a water:silica interface held at pH 5.8 and 2 µM ionic strength (blue circles), and at pH 2.5 and 500 mM ionic strength (red circles). Please see text for details.

**Fig. S9.** SHG Intensity recorded for seven replicate measurements from individually assembled silica:ultrapure water interfaces (air-equilibrated overnight, 20 µS cm\(^{-1}\) conductivity, pH 5.8) and seven subsequent replicates from individually assembled silica:α-quartz interfaces (5 mW laser power at the sample).
References


