

Revealing Light-Driven Dynamics at Nanostructured Solid–Liquid Interfaces with In-Situ SHG

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Abstract

Light and heat are key drivers of interfacial chemistry at solid–liquid boundaries, governing fundamental processes in sustainable energy conversion systems such as photoelectrochemical and hydrovoltaic devices. However, non-invasive probing of light-induced surface-potential dynamics at these interfaces remains challenging due to limited surface sensitivity. Here, we introduce a nanophotonic approach that amplifies second harmonic generation (SHG) from nanostructured solid–liquid interfaces by over two orders of magnitude, providing real-time, all-optical access to light-driven interfacial phenomena. Using in-situ SHG at silicon–oxide–electrolyte interfaces, we uncover two concurrent pathways for light-mediated modulation: (i) low-intensity illumination induces photocharging via carrier generation and trapping, while (ii) high-intensity excitation leads to photothermal heating that modifies surface group dissociation through temperature-dependent reaction equilibria. We further show that nanostructured semiconductor interfaces deviate markedly from the monotonic electrolyte-concentration dependence predicted by Gouy–Chapman theory. Instead, the surface potential exhibits a pronounced non-monotonic behavior governed by interfacial geometry—consistent with prior device-level observations. Importantly, SHG measurements reveal that this concentration-dependent modulation of surface potential directly alters the electronic polarizability of silicon, exposing the underlying ion-electronic coupling at the solid–liquid boundary. By combining nanophotonic design, in-situ SHG probing, and quantitative modeling, this work establishes an experimentally validated framework for actively manipulating interfacial charge distributions to advance the performance of solid–liquid energy conversion technologies.

Keywords: Second Harmonic Generation, Nanostructured Silicon, Surface Charge, Photocharging, Photothermal

1 Introduction

In the face of an escalating energy crisis, the prospect of energy conversion and storage from renewable natural resources, such as water and sunlight, without reliance on external mechanized inputs is incredibly appealing. Hydrovoltaic, photo-electrochemical systems, and light-enhanced blue energy technologies represent a key opportunity in energy conversion, providing a pathway for sustainable energy solutions. At the core of these systems lies the formation of a charged interface when liquid closely interacts with a solid surface, resulting in the development of an electrical double layer (EDL) [1–3]. This EDL consists of a Stern layer firmly anchored to the solid surface, accompanied by a diffusion layer enriched with counter-ions. These create substantial interfacial electrical fields that govern the selectivity of essential photo-chemical processes, such as CO₂ reduction [4], surface charges in hydrovoltaic[5], and blue energy devices [6] for enhancing ionic conductance, and the double-layer capacity of electrochemical supercapacitors [7]. Under low electrolyte concentration in contact with a planar solid electrode, the ion dynamics can be well described by the Debye, Gouy-Chapman-Stern models [8–10]. However, for practical relevance, the deployments of hydrovoltaic and blue energy devices operating at high ion concentrations are particularly advantageous due to the vast availability of saline water. Additionally, most practical electrochemical reactions typically involve high concentrations and surface charges induced by external electrical potential. Furthermore, due to the advancements of micro-nanotechnology, all the aforementioned systems have shown enhanced performance by using nanostructured electrodes, and therefore, planar electrodes are seldom used. Importantly, these systems predominantly utilize metal and semiconducting materials; thus, interfacial electrical fields are highly dependent on the electronic properties of the solid electrode [11, 12], and can be substantially modulated under light stimuli through the photocharging and thermal effects of light [6, 13, 14], resulting in high tunability of charged species near the aqueous interface. Yet, a thorough understanding of these nanostructured interfaces and their light-driven dynamics is still lacking.

Notably, in these systems, the surface charge is not constant, as the interfacial chemical equilibrium between the liquid and solid phases regulates it through the dissociation of surface groups in the presence of local ionic species. The surface charges can be controlled either passively via changes to the bulk electrolyte environment [15, 16] or actively via external heat and light stimuli [2, 17–19]. Light, in particular, is typically used to power these devices sustainably, and it is expected to exert a multi-faceted impact on the interfacial equilibria. In semiconductors, for instance, photon absorption generates electron-hole pairs, and subsequent charge trapping can significantly boost surface charge [20]. Concurrently, light can induce local heating through photothermal effects [21], influencing both surface charges and reaction kinetics. Furthermore, any temperature increase can modify the optical properties of nanostructured electrodes due to the thermo-optical effect, altering light absorption [22]. Thus, while being convoluted, light-induced effects play a crucial role in the interfacial dynamics underlying both electrokinetic interactions and (photo)electrochemical reactions. However, going beyond device-scale measurements, in-situ monitoring of light-driven dynamic changes

in surface charge and surface potential, as well as local temperature and optical properties, remains challenging, due to the need for highly sensitive probes that do not disrupt the local environment while providing accurate readings of interfacial fields. As these interfaces are not perfectly sharp, techniques such as atomic force microscopy (AFM) and other tip-based methods often interfere with the surrounding area [23, 24], producing a convolution of the tip and surface that perturbs the surrounding region and causes spatial averaging. Overall, achieving a microscopic understanding of light-driven charging and thermal effects at nanostructured interfaces is essential for the rational design of light-driven electrochemical systems, but significant methodological advances are still needed [25].

Second harmonic generation (SHG) [26–28], a nonlinear optical spectroscopy technique, offers a unique pathway for sensitivity to interfacial effects without the need for invasive probes. Due to the inherent symmetry-breaking selection rule, which occurs at the interfaces between two media [29–34], SHG has been repeatably established as an exceptional tool for examining surface charge, potential, and molecular organization across a diverse array of solid–liquid systems [27, 35–37]. SHG is governed by the effective surface nonlinear susceptibility, which encodes both the surface’s intrinsic properties and its electrostatic environment. While the vast majority of studies focus on oxide–liquid interfaces, energy devices rely on metal or semiconductor–oxide interfaces. For oxide surfaces, such as silica, the purely solid surface contribution to the nonlinear susceptibility is typically weak [27, 38], leading to a dominant SHG contribution from interfacial water. In contrast, at metal–electrolyte and semiconductor–electrolyte interfaces, the intrinsic surface contribution [27, 39], which is influenced by the interfacial charges and potential in the liquid phase, becomes important. Overall, this approach offers a robust quantitative framework for monitoring changes in the interfacial electrostatic environment and carrier dynamics within semiconducting solids. However, weak signal intensity challenges in situ monitoring, leading to the loss of subtle interfacial changes.

This work introduces a unique nanophotonic-enhanced, in-situ SHG platform that, for the first time, enables real-time probing and understanding of how light and heat independently and jointly modulate nanostructured solid–liquid interfaces. By employing a periodic array of silicon nanodisks immersed in a water-based electrolyte, thereby forming a semiconductor–oxide–liquid interface, we can enhance the SH signal by more than 200 times, enabling the detection of subtle changes in interfacial susceptibility despite its very small absolute value. Firstly, this allows us to observe a second-harmonic spectral shift of approximately 1.3 nm as the electrolyte concentration varies, showing a strong correlation with the extracted surface potential and uncovering the coupling between ions and electrons. This effect can be associated with changes in the surface polarizability of silicon as the electrolyte concentration changes. Secondly, by using a separate optical pump as a controlled stimulus, we directly observe reversible, intensity-dependent shifts in interfacial susceptibility arising from two distinct mechanisms: below threshold intensity, light drives photocharging of the solid, reducing the interfacial susceptibility by $\sim 5\%$, and above threshold intensity, light drives dominant photothermal heating, which increases the interfacial susceptibility

by $\sim 7\%$. Notably, we can control the threshold intensity by optimizing the nanodisk geometry. Crucially, our nanostructure design and probing strategy enable the unambiguous separation of true photothermal effects from inevitable thermo-optical modulation in optically resonant systems, demonstrating that the dominant mechanism can be switched simply by adjusting the illumination intensity. Beyond providing quantitative, time-resolved signatures of these processes, our approach constitutes a sensitive diagnostic tool that can be extended to monitor and manipulate light-driven electrochemical and catalytic phenomena at aqueous interfaces. Together, these capabilities open a path toward actively controlling the carrier dynamics and interfacial chemistry with light — a capability with broad implications for photoelectrochemistry, hydrovoltaic, and nanophotonic device engineering.

2 Boosting SHG Sensitivity with Nanophotonically-informed Nanostructuring

Second harmonic (SH) generation entails a nonlinear optical process in which two photons of frequency ω interact with materials, leading to the generation of a single photon at the frequency of 2ω (Fig. 1 A). In our system (Fig. 1 B and SI S1, Fig. S1), optical excitation is driven by a fundamental-wave (FW) pulsed laser beam centered at 1030 nm (linearly polarised and normal incidence), which leads to the coherent generation of a SH beam centered around 515 nm. An additional laser, centered at 633 nm (also linearly polarised and normal incidence), is used for light-driven modulation. The SH intensity $I_{\text{SH}}(2\omega)$ is directly proportional to the square of the non-linear polarization $P_{\text{nl}}(2\omega)$. This, in turn, is equal to the product of the electric field on the surface $E(\omega)$ and the surface second-order effective susceptibility $\chi_{\text{eff}}^{(2)}$. While a complete analytical derivation can be found in [31], for mathematical simplicity, we have dropped the proportionality constant terms and written:

$$P_{\text{nl}}(2\omega) = E(\omega)^2 \chi_{\text{eff}}^{(2)} = \sqrt{I_{\text{SH}}(2\omega)} \quad (1)$$

Unlike SHG in non-centrosymmetric materials—where the response is governed by a bulk susceptibility—in a centrosymmetric solid-liquid system, $\chi_{\text{eff}}^{(2)}$ is an interfacial property jointly defined by both phases and can vary when either is modified (Fig. 1 C). In aqueous systems, liquid contributions arise from both the alignment of water molecules within the Stern layer ($\chi_{\text{Stern}}^{(2)}$) and the third-order susceptibility of water, $\chi_{\text{H}_2\text{O}}^{(3)'$, due to the coupling of the electrical double-layer (EDL) field with the FW oscillating electromagnetic field. For oxide surfaces, the solid contribution is weak and largely invariant; however, for metal–electrolyte and semiconductor–electrolyte interfaces, the intrinsic solid surface contribution ($\chi_{\text{solid}}^{(2)}(\omega)$, Eq. S1) becomes dominant and can vary with the electrostatic environment. This variation stems from the polarizability of free and bound electrons in metals [31], and from the space charge layer (band-bending) in semiconductors [40].

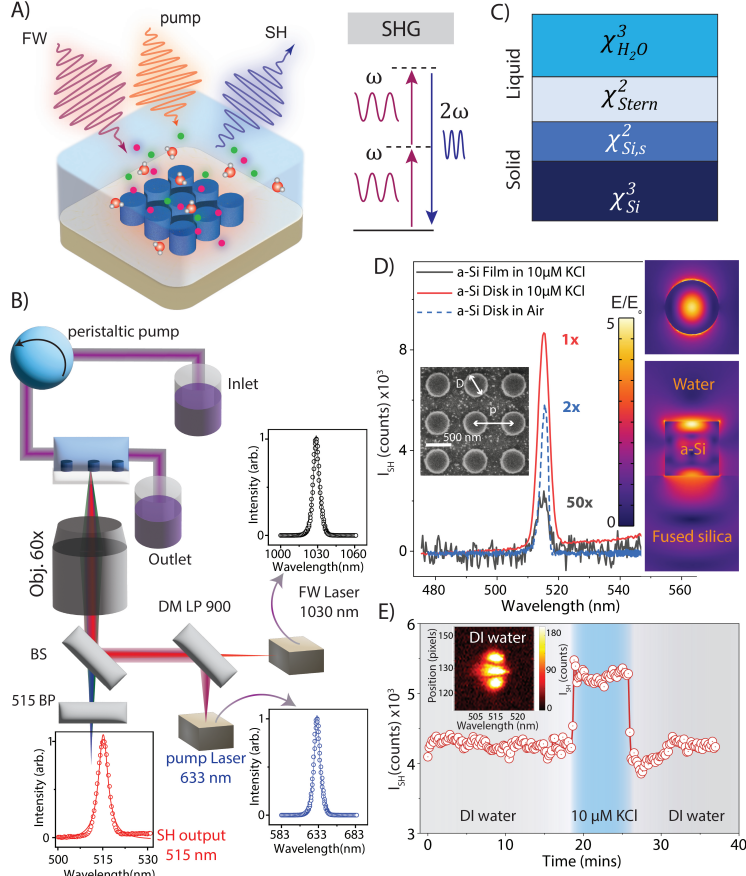


Fig. 1 Second harmonic generation modulation and in-situ monitoring at nanostructured electrochemical interface. A) Overview of the device structure for the SHG experiment, highlighting the periodic disk array positioned in the electrolyte medium, excited by both fundamental (FW) and pump laser beams. The FW facilitates probing of interfacial dynamics via SHG, while the pump beam modulates interfacial charges/potential and temperature. The inset shows that the nonlinear optical process (SHG) occurs when a high-intensity fundamental (FW) beam at frequency ω is excited. B) The compression cell is mounted on an inverted microscope, showing the excitation path featuring the FW (centered at 1030 nm with a bandwidth of 6 nm), and a pump laser (centered at 633 nm with a bandwidth of 10 nm). BS is the beam splitter; BP is the band pass filter. The bottom graph shows an output SH intensity (centered at 515 nm with a bandwidth of 4.3 nm) detected by the collection path for a representative case. C) This illustration depicts the interfaces between semiconductors, oxide, and electrolyte, highlighting that the susceptibility is made up of four distinct contributions. D) SH enhancement in the disk array (red line) is approximately 200 times greater than in the planar film (black line) under identical conditions, with the dashed blue line indicating SH intensity for the disk array without electrolyte, underscoring the significant change due to the solid-liquid interface. As $I_{SH} \propto E(\omega)^4$, the inset shows the FW electric field enhancements in a periodic nanodisk array. The maximum electric field enhancement on the surface is ≈ 5 , and the scanning electron microscopy (SEM) image of the nanostructured array. E) In-situ SHG recorded at a 10 seconds acquisition time, illustrating the change in SH intensity due to the transition of the electrolyte from DI water (gray shaded region) to 0.01 mM KCl (blue shaded region) and back, demonstrating the concentration dependence of SH intensity. The inset shows the SH image obtained in DI water, which shows pronounced enhancements in nonlinear polarization around the disk.

We focus on a semiconductor–oxide–electrolyte interface, specifically a silicon–silicon oxide–water system, due to its relevance for both hydrovoltaic and photoelectrochemical devices [14, 40–43]. In this case, the susceptibility consists of 4 different contributions (Fig. 1 C)—the third-order contributions from the EDL’s diffuse layer and the space charge layer of silicon, and the second-order contributions from the Stern layer and silicon’s surface polarizability. A phenomenological framework for total susceptibility can account for both second- and third-order contributions from both solid and liquid phases (SI S2 and Eq. S1). This approach explicitly links the measured SH signal with the surface potential, Φ_0 , which can be controlled by the electrostatic environment across the interface (Fig. S2). While in the Methods section we present the complete mathematical framework (SI S2), here we only report the final expression for the non-linear polarization, $P_{\text{nl}}(2\omega)$, simplified by assuming flat-band conditions on the semiconductor side (consistent with the absence of an externally applied electric field [20, 44]) [37, 45, 46]:

$$P_{\text{nl}}(2\omega) = E(\omega)^2 \left[\chi_{\text{Si}}^{(2)}(\omega) + \chi_{\text{Stern}}^{(2)} - \chi_{\text{H}_2\text{O}}^{(3)'} \Phi_0 (\cos(\phi_{\text{DC}}) e^{i\phi_{\text{DC}}} + 1.5i) \right] \quad (2)$$

with, $\tan(\phi_{\text{DC}}) = \frac{\Delta k_z}{\lambda_D^{-1}}$ and $\Delta k_z = |2\tilde{k}_\omega - \tilde{k}_{2\omega}| = 2.43 \times 10^7 \text{ m}^{-1}$ is the wave-vector mismatch in the reflection setup with fused silica substrate, and λ_D is the Debye length (Eq. S3). Importantly, we note that, contrary to $\chi_{\text{Stern}}^{(2)}$ and $\chi_{\text{H}_2\text{O}}^{(3)'}$, $\chi_{\text{Si}}^{(2)}(\omega)$ is frequency-dependent. In fact, silicon’s non-linear susceptibility can be expressed in terms of its linear dielectric response, which has a strong frequency dispersion (see Fig. S3). In deionized water, $\cos(\phi_{\text{DC}}) \approx 0$ due to the large Debye length, and hence the second and third-order contributions to the susceptibility are 90° out of phase. For clarity, we will henceforth denote the total solid and liquid second-order contribution as $\chi_s^{(2)}$. The modulus of the total susceptibility in Eq. 2 further simplifies to:

$$\sqrt{I_{\text{SH}}(2\omega)} = E(\omega)^2 \sqrt{\left[\chi_s^{(2)} \right]^2 + \left[1.5 \chi_{\text{H}_2\text{O}}^{(3)'} \Phi_0 \right]^2} = E(\omega)^2 \chi \quad (3)$$

When employing SHG as a probing technique to explore interfacial phenomena, we focus on monitoring variations in $\chi_{\text{eff}}^{(2)}$ (or χ , in DI water condition) [11, 39, 47]. However, due to its low typical values, $\text{O}(10^{-21} \text{ m}^2 \text{V}^{-2})$, sensitivity is often an issue. From Eqns. 1–3 it is clear that $E(\omega)$ acts as a SH signal amplifier, enhancing the ability to detect subtle local changes without disturbing the interfacial dynamics.

While for planar interfaces, intense pulsed lasers are typically employed to increase $E(\omega)$, and hence $I_{\text{SH}}(2\omega)$, metasurfaces, i.e., engineered arrays of optical nano-resonators, can constitute an excellent platform for interfacial SHG studies, thanks to their unique capacity to locally amplify electromagnetic near fields [48–50]. We performed electromagnetic calculations of the optical response of hydrogenated amorphous silicon (a-Si:H) nanodisks (SiND) as a function of diameter, thickness, and periodicity (SI S3). We observed significant variations in the local electric field enhancement with geometry, resulting in substantial changes in the expected SH response (Fig. S4A, B). For a SiND diameter of 520 nm, a periodicity of 800 nm,

and a thickness of 440 nm, we predicted an optimum 5-fold $E(\omega)$ enhancement at the solid-liquid interface (Fig. 1D, and SI S3 for details).

We subsequently fabricated a-Si:H nanodisks on a fused silica substrate using e-beam lithography (SI S4). Linear optical characterization of the fabricated structures (SI S6 and Fig. S4A) demonstrates consistent trends with the electromagnetic simulations (Fig. S4B). Most remarkably, as shown in Fig. 1D, for the optimized SiND array immersed in a 10 μ M KCl solution, we obtain an increase in $I_{\text{SH}}(2\omega)$ of the factor > 200 compared to a flat a-Si:H film under identical conditions. While increased surface area for the disk array can account for only $\sim 2\text{--}3\times$ enhancement, the dominant contribution arises from the strong local field amplification, owing to the fourth-power dependence of SHG on $E(\omega)$. As a further validation of the key role of the electric near field enhancement at the FW in amplifying the SH response, we measured $I_{\text{SH}}(2\omega)$ as a function of the SiND diameter at a fixed periodicity (Fig. S4C). It shows that the SH intensity enhancement follows the trend predicted by electromagnetic simulations, with a maximum observed at a diameter of approximately 520 nm (Fig. S4D).

Continuous SHG measurements were also performed in a reflection configuration using a compression flow cell (Fig. 1B and SI S1) that is connected to a peristaltic pump for continuous electrolyte circulation. As shown in Fig. 1E, the spectroscopic signal is stable during electrolyte pumping at optimized flow rates, and the increased signal sensitivity (SI S5) enables continuous monitoring of SH intensity transitions as the bulk electrolyte environment is altered.

Overall, nanostructuring enabled by nanophotonics provides exceptional sensitivity for SHG probing interfacial processes, which is essential for detecting light-induced dynamic changes at solid-liquid interfaces. Interestingly, as shown in the inset of Fig. 1E and Fig. S5, the SH enhancement achieved with our optimal SiND array already allows SH imaging within the FW beam irradiation spot using an inexpensive CMOS camera and an industrial-grade FW pump laser (SI S1).

In the following, we employ this SHG experimental set-up and the described well-established theoretical framework to study SiND arrays in contact with aqueous electrolytes. We first monitor the change in total susceptibility under varying electrolyte conditions, validating the methodology and demonstrating that $\Delta\chi$ sensitivity in SiND is more than two orders of magnitude improved compared to planar film (i.e. $(\Delta\chi)_{\text{SiND}} \approx 0.005(\Delta\chi)_{\text{film}}$), enabling detection of subtle changes in interfacial potential and charges (SI S5). Subsequently, we apply it, to the best of our knowledge, for the first time to the investigation of light-driven changes in the interfacial chemical equilibrium, revealing the coupled influence of charge and heat contributions at nanostructured solid-liquid interfaces.

3 Concentration- and Geometry-Dependent Surface Potentials Modulate Solid-Liquid Interfacial Susceptibility

Estimating interfacial potentials is crucial because they affect the magnitude of surface charges and the local ionic environment, both of which play significant roles in most electrochemical processes at interfaces. Having established the mathematical link

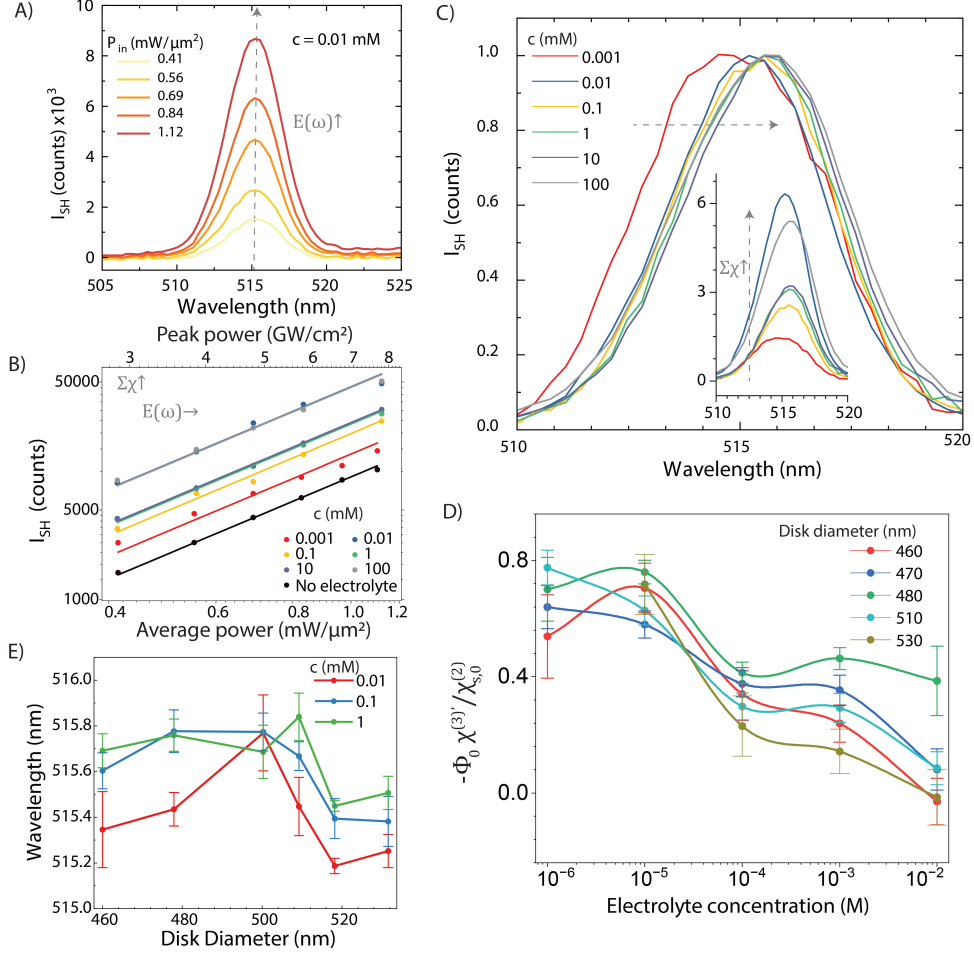


Fig. 2 Interfacial potential and susceptibility changes as a function of electrolyte concentration and SiND geometry. A) SH spectra at 0.01 mM electrolyte concentration across different FW powers, demonstrating that while the spectrum position remains constant, the peak height increases with incident power. B) SH intensity plotted against FW light intensity across different electrolyte concentrations, with data fitted to a straight line exhibiting a slope of 2. C) Normalized SH spectra for various electrolyte concentrations, highlighting a noticeable red shift with increasing concentration. The inset shows the non-normalized spectra, highlighting that both peak intensity and spectra positions vary with electrolyte concentration. D) Interfacial potential estimated from SH measurements for varying disk diameters and electrolyte concentrations. E) Spectra positions obtained as a function of SiND diameters for various electrolyte concentrations.

between surface potential (resulting from solid-liquid chemical equilibrium) and SH intensity (Eq. 2), we now present a direct approach to experimentally estimate the surface potential as a function of electrolyte concentration and SiND geometry. In these measurements, no pump laser is used; only the FW beam is used for SHG. SH intensities were measured from arrays with disk diameters ranging from 460 to 535 nm

(pitch: 800 nm; height: 440 nm) fabricated on the same substrate. Measurements were first performed in air and subsequently repeated in electrolyte solutions with concentrations spanning six orders of magnitude (0.001 to 100 mM). Fig. 2A shows the SH spectra for a 520 nm SiND array at 0.01 mM electrolyte concentration for varying FW intensities (0.41–1.12 mW/ μm^2). As expected, the spectral position remains invariant with FW intensity, while the peak intensity increases following a quadratic power dependence. In Fig. 2B, SH intensity is plotted as a function of FW intensity for a wide range of electrolyte concentrations, as well as for the purely solid contribution (no electrolyte). The quadratic scaling (slope fixed at 2) confirms the second-order nonlinear origin of the signal (Eqns. 1 and 2) while systematic changes in the fitted intercept highlight electrolyte-dependent modifications of the effective susceptibility. Analytically, this can be easily appreciated because $\log(I_{\text{SH}}) \propto 2\log(\chi) + 2\log(I_{\text{FW}})$. Thus, when I_{SH} is plotted as a function of I_{FW} in a log-log scale, it gives a slope of 2, while the intercept changes with electrolyte concentration, indicating that χ changes, establishing the interfacial origin of the SH response in different electrolyte environments. However, it doesn't prescribe the change in interfacial potential, as it arises from the third-order contribution; however, the total magnitude can change due to both second- and third-order contributions.

Thanks to the amplification of the SH intensity, we can capture extremely subtle changes in the measured SH spectra. Detailed spectral analysis reveals that the SH peak redshifts up to ~ 1.3 nm with increasing electrolyte concentration (Fig. 2C). To the best of our knowledge, such shifts have not been reported previously, likely because most prior liquid–solid SHG studies focused on planar systems, with very limited work on semiconductor interfaces. These subtle spectral changes are detectable here due to the strong nanophotonic enhancement of the SHG signals. Notably, the observed spectral shift cannot be attributed to changes in the susceptibility magnitude of the liquid phase, which remains spectrally invariant under the nonresonant probing conditions (1030 nm excitation does not couple to water vibrational modes). Furthermore, the FW laser is non-invasive, as confirmed by the prior FW power-dependent measurements (fixed peak position for a given concentration, consistent quadratic power dependence, Fig. 2A, B). Instead, the redshift arises from concentration-dependent dispersion of the second-order susceptibility of the a-Si:H, $\chi_{\text{Si}}^{(2)}(\omega)$, which is intrinsically sensitive to interfacial surface charge density. Notably, first-principles DFT studies of metal–electrolyte junctions have reported analogous charge-induced spectral shifts in $\chi_s^{(2)}(\omega)$ for metal–electrolyte systems [31, 39]. Therefore, our results show that the silicon susceptibility must change as the electrolyte concentration tunes the interfacial potential.

To extract the interfacial potential from the measured SH intensities, we first normalized the nonlinear polarization of the SiND array in electrolyte to that in air, correcting for Fresnel coefficients associated with the refractive index change between air and water. We indicate with α the ratio of the norm of the electric fields at the fundamental frequency, which relates to the Fresnel coefficient in the two conditions: $\alpha = \frac{|E^0(\omega)|}{|E(\omega)|} \approx 0.97$. The resulting non-linear polarization ratio (R_{SH}) was then analyzed in terms of the second-order susceptibility and interfacial potential Φ_0 (SI S7), combining Eqns. 1 and 2, we obtain the ratio of the square root of the SH intensity

(also equal to R_{SH}) Eq. S5. Further simplifying, we get an explicit equation that can be solved analytically (Eq. S6), and using the notation of '0' to indicate measurements in air, we get:

$$-\Phi_0 \frac{\chi_{H_2O}^{(3)'}}{\chi_{s,0}^{(2)}} = \frac{\chi_s^{(2)}}{\chi_{s,0}^{(2)}} \left[\frac{-A^2 \pm \sqrt{A^4 + \left[\left(\alpha^2 \frac{\chi_{s,0}^{(2)}}{\chi_s^{(2)}} R_{SH} \right)^2 - 1 \right] (A^2 + 3AB + 2.25)}}{(A^2 + 3AB + 2.25)} \right] \quad (4)$$

With the definitions: $\cos(\phi_{DC}) = A$ and $\sin(\phi_{DC}) = B$

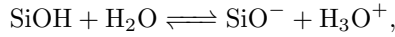
Phase-resolved SHG measurements can be used to estimate how the second-order susceptibility varies with electrolyte concentration [46]. However, a complete separation of the second-order contributions from the Stern layer and from the intrinsic polarizability of silicon remains an open challenge, requiring additional investigation—for example, wavelength-dependent SH measurements. Nevertheless, our analytical expression for Φ_0 as a function of electrolyte concentration allows the determination of surface potential by assuming that the concentration dependence of the interfacial second-order susceptibility follows the empirical relation $\frac{\chi_s^{(2)}}{\chi_{s,0}^{(2)}} = 1.81 + 0.130 \log[c_0(\text{M})]$, where c_0 denotes the bulk electrolyte concentration [46]. The resulting Φ_0 concentration curves for different electrolyte concentrations, as well as disk diameters, consistently exhibit non-monotonic behavior with a secondary peak around ~ 1 mM (Fig. 2D). These findings closely match prior device-scale, open circuit voltage measurements [42], supporting the notion of an interfacial origin. This indicates that, at the nanoscale, surface potentials are influenced by both concentration and geometry. The measured surface potential across different concentrations and pH for silica surface lies in the range of -0.2 to -1 V [51, 52]. Therefore, the factor $\chi_{H_2O}^{(3)'}/\chi_{s,0}^{(2)}$ in the Eq. 4 and Fig. 2 D must be of the order of 1 V^{-1} , which is consistent with the values of second-order surface susceptibility of silicon ($\chi_{s,0}^{(2)} \sim 10^{-21} \text{ m}^2 \text{ V}^{-1}$) [53], as $\chi_{H_2O}^{(3)'} \sim 10^{-21} \text{ m}^2 \text{ V}^{-2}$. Furthermore, the diameter-dependent spectral shifts across various concentrations (Fig. 2E) show a strong correlation with the extracted surface potential. Specifically, for different SiND diameters, the spectra display a red shift with increasing surface potential, revealing that the solid-liquid interface exerts a measurable influence on silicon's polarizability.

Taken together, these results highlight the essential but often overlooked role of interfacial chemical equilibria in governing electrostatic potentials at nanostructured solid-liquid interfaces. Beyond fundamental insights, this phenomenon has direct implications for electrochemical, catalytic, and sensing platforms where interfacial charge plays a central role. More broadly, our findings establish SHG as a sensitive, surface-selective optical voltmeter for probing local surface potentials in SiND systems. Notably, the observed deviations from conventional Gouy-Chapman predictions

underscore the importance of considering electronic polarizability and geometric effects in modeling interfacial electrostatics.

4 Photocharging Shifts Solid–Liquid Equilibria

In an electrochemical system with a semiconducting electrode, light can trigger photocharging at the solid surface, thereby modifying the surface charge at the liquid–solid interface. Understanding how light influences the semiconductor–oxide–electrolyte interface requires a quantitative description of the solid–liquid equilibrium that governs surface charging (Fig. S2). As schematically illustrated in Fig. 3A, the SiND interface acquires charge through dissociation reactions of the native oxide layer upon wetting. This process typically generates a net negative surface charge, σ , in silicon-based interfaces due to the dissociation of silanol groups (yellow circles), which is compensated by adsorption of counter-ions (pink circles), leading to the formation of an electrical double layer (EDL) in the electrolyte. The resulting potential drop spans both the EDL and the space-charge region in silicon (Fig. S2). For common oxide–aqueous interfaces such as silica (SiO_2), titania (TiO_2), and alumina (Al_2O_3), this dissociation is well described by the surface complexation model. For instance, the SiO_2 layer, which naturally forms on silicon-based surfaces, undergoes the equilibrium reaction [16, 54]



governed by the equilibrium constant K_a . The total surface charge density can thus be expressed as:

$$\sigma = \frac{-e\Gamma}{1 + \frac{[\text{H}^+]_s}{K_a}} \quad (5)$$

where, Γ is the density of total reactive surface sites ($\Gamma = [\text{SiO}^-] + [\text{SiOH}]$), and $[\text{H}^+]_s$ denotes the local interfacial proton concentration (SI S8) [14, 42]. Importantly, σ increases with temperature, due to the temperature dependence of K_a (SI S8), and with the bulk pH ($-\log([\text{H}^+]_{\text{bulk}})$), but can also vary dynamically with $[\text{H}^+]_s$ at constant temperature and pH due to local interfacial changes [14]. The surface potential depends on surface charge given by the relation $\Phi_0 = \frac{2k_B T}{e} \sinh^{-1}(\sigma / \sqrt{8000\varepsilon_0\varepsilon_r c_0 k_B T}) + \sigma / C_{\text{Stern}}$, where k_B is the Boltzmann constant, T is the absolute temperature, e is the electronic charge, $\varepsilon_0\varepsilon_r$ is the dielectric permittivity of the electrolyte and c_0 is the bulk electrolyte concentration in moles/L, and C_{Stern} is the stern layer capacitance [16]. The surface potential is related to the interfacial electrostatic field E_{DC} by: $\Phi_0 = \int_0^\infty (\mathbf{E}_{\text{DC}} \cdot \hat{n}) dn$ where, $\hat{n}$ is the surface normal.

Under low-irradiance conditions and in the absence of external heating, temperature variations can be neglected, and changes in chemical equilibrium arise primarily from photocharging. At the silicon–oxide interface, equilibration of the Fermi level across the junction establishes the band bending in the dark. Upon illumination, photogenerated carriers accumulate at the semiconductor surface, altering the electrostatic potential within the space-charge region. Through capacitive coupling across the oxide, these electronic changes induce a redistribution of interfacial protons, thereby modifying σ . In this way, light dynamically shifts the surface chemical equilibrium, generating

a photovoltage that reflects the capacitive rather than faradaic response of the interface. Specifically, for p-type silicon, the initial band bending is downward (Fig. 3A, left panel), leading to electron accumulation at the interface and attraction of hydronium ions via capacitive coupling. This reduces the net surface charge, consistent with Eq. 5, and produces a negative photovoltage [13, 20]. For example, defining the open circuit voltage (OCV) as the potential difference between bulk silicon and the electrolyte (Fig. S2A), OCV typically decreases under illumination for p-type silicon [13, 14].

To experimentally probe this effect, we analyzed dynamic SH spectra from two SiND arrays in DI water (diameters: 490 nm and 510 nm), while periodically switching the 633 nm pump laser (intensity: $7.5 \mu\text{W}/\mu\text{m}^2$) between on- and off-states every 100 s, acquiring SH spectra every 20 s. The raw data are presented in Fig. S6. After baseline normalization, the results are expressed as the fractional change in susceptibility, $(\Delta\chi/\chi_0)$, shown in Fig. 3B. For both samples, the negative sign for $\Delta\chi$ confirms the expected decrease in surface potential for p-type silicon.

To establish a quantitative relationship between the observed change in susceptibility $\Delta\chi$ and the light-induced variation in potential Φ_0 , we can reference Eq. 3. However, obtaining a precise estimate requires detailed information on the pump-induced spectral variation of $\chi_s^{(2)}$, which has yet to be reported in the literature. Despite this gap, our measurements across various disk geometries provide real-time monitoring of changes in total susceptibility. Our findings indicate that light-induced photocharging leads to a decrease in surface charge and the associated potential, ultimately reducing the total susceptibility (Fig. 3B) of $\approx 5\%$ and $\approx 2.5\%$ for 490 nm and 510 nm SiNDs, respectively, under $7.5\mu\text{W}/\mu\text{m}^2$ pump intensity. This demonstrates that optical excitation is a unique method for actively manipulating interfacial charge and potential in SiND arrays, complementing traditional passive control approaches based on bulk ionic strength or pH.

5 Photothermal Effect Modulates Interfacial SHG

At high irradiation intensities with the same 633 nm pump, silicon nanoresonators can heat. This leads to localized temperature changes that influence chemical equilibrium and alter both the surface charge and interfacial chemistry (Fig. 3A, right panel). Notably, this heating can also affect the electrode's optical properties, as the refractive indices of silicon and water are strongly temperature-dependent, thereby altering the SH response. In Fig. S7, we show the ellipsometry data for the silicon's refractive indices across various wavelengths (from 280 to 2400 nm) at different temperatures (up to 200 °C). These measurements allow us to calculate the thermo-optical (TO) coefficients (dn/dT and dk/dT). At the fundamental wave excitation (1030 nm), the TO coefficient is positive, with a magnitude of $2 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$. This coefficient is substantial enough to shift the resonance peak from 1017 nm at 25 °C to 1022 nm at 75 °C (Fig. S8). Moreover, as temperature increases, the refractive index of water slightly decreases, characterized by a negative thermo-optic coefficient of around $-10^{-4} \text{ }^\circ\text{C}^{-1}$ in the 1030 nm spectral region. Overall, light-induced heating can lead to two main effects on the interfacial SH response of the solid-liquid system (Eq. 2). First, it can

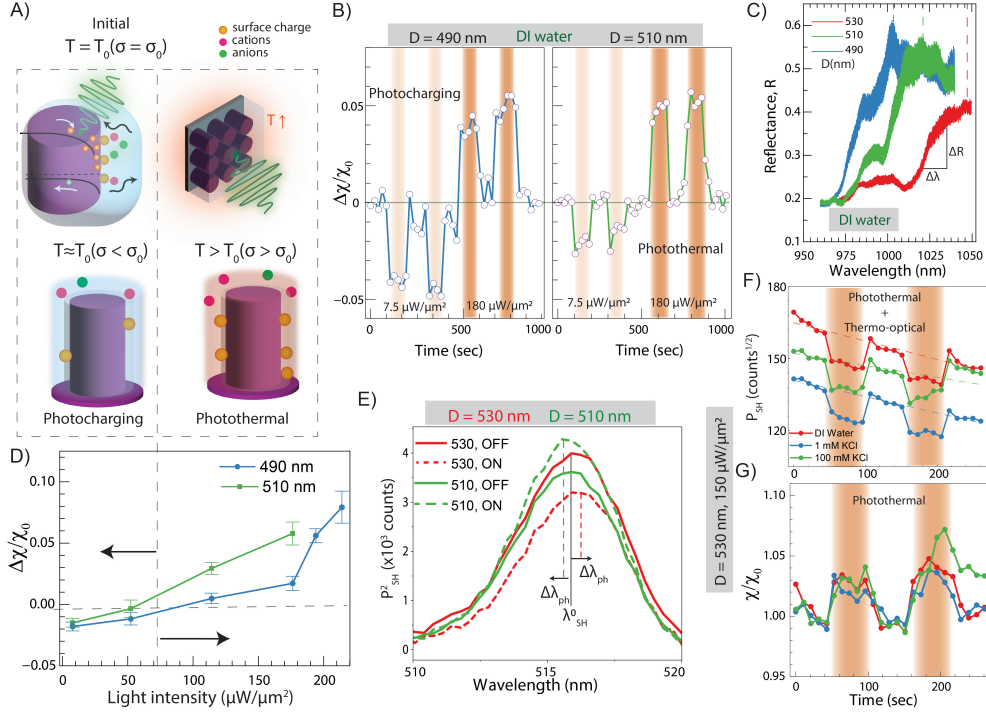


Fig. 3 Photocharging and photothermal modulation of the interfacial susceptibility probed by second harmonic generation. A) Schematic illustration of the light-induced (right) heating and (left) changes in the capacitive interface, affecting surface charge and potential. The inset on the top highlights the initial surface charge conditions at ambient temperature T_0 . B) Time traces of the light-induced fractional change in effective susceptibility ($\Delta\chi$), normalized to the initial value in the dark (χ_0), for SiNDs with $D = 490$ nm and $D = 510$ nm in DI water under 633 nm pump irradiation. Two distinct regimes, depending on the pump laser intensity, are observed. At low intensity, the photocharging effect is observed; at high power, the photothermal effect dominates due to light-induced heating of the structures. C) The reflectance spectra for the SiND arrays in DI water with diameters of 490, 510, and 530 nm. D) Fractional change is total susceptibility as a function of light intensity for the two SiNDs, showing photocharging and photothermal regimes, with transition points at distinct light intensities. E) SH spectra recorded using deionized (DI) water for disk arrays with diameters $D = 510$ nm (red lines) and $D = 530$ nm (blue lines) under 633 nm pump laser irradiation (dashed lines) and subsequent pump turn-off (solid lines). F) The time-trace of non-linear polarization P_{SH} during 633 nm excitation for a sample with disk diameter $D = 530$ nm, showcasing variations under different electrolyte conditions, with dashed lines indicating the decay of the non-linear polarization baseline. G) Corresponding to the measurements in panels F, the normalized susceptibility values obtained by decoupling the TO effect induced change in $E(\omega)^2 \propto R$.

change the total susceptibility (χ), as the third-order susceptibility of water and surface charges (and Φ_0) change with temperature (SI S8 and Eq. S7). Additionally, the polarizability of silicon is related to the dielectric function [55] and is therefore temperature-dependent (Fig. S3). Secondly, the electric field enhancement factor ($E(\omega)$) may also change due to TO effects, which induce shifts of the nanostructure optical resonances. The latter contribution can be positive, negative, or nearly zero

depending on the initial reflectance peak’s position, whether it blueshifts or redshifts, or if it appears broad and flat within the TO spectral transition, because reflectance is an experimental measure of near-field enhancements as discussed in Section 2. Thus, to explore the changes in chemical equilibrium induced by photothermal effects at the solid-liquid interface, it’s crucial to separate the TO carefully.

To understand the significant role of light-induced local heating on SH intensity, we performed a thorough SHG probing of three SiND arrays with diameters of 490, 510, and 530 nm. Their linear reflectance spectra around the FW, in deionized (DI) water, shown in Fig. 3C, reveal important differences. The 530 nm SiNDs display a pronounced reflectance peak at 1047 nm, to the right of the FW (red dashed line). In contrast, the 490 nm and 510 nm SiNDs exhibit much flatter spectra across the 1000–1050 nm range. As a result, we expect that the TO effect for the 490 nm and 510 nm SiNDs will be minimal within the temperature range of 25-100 °C employed in our experiments, while the 530 nm SiND will show a significant temperature-dependent effect. In fact, the slopes of the reflectance curves around 1030 nm in DI water ($\Delta R/\Delta \lambda$) are almost zero for 490 nm and 510 nm. Instead, a significant slope of 0.008 nm^{-1} is obtained for the 530 nm SiNDs. Since the temperature-induced variation in $E(\omega)^2$ is proportional to reflectance (R), this analysis effectively separates the TO effects from the photothermal changes in susceptibility.

First, we analyze the SH response for the 490 nm and 510 nm SiNDs (Fig. 3D), as in these cases the modulation in interfacial SHG arises solely from the susceptibility term (negligible TO effects). As mentioned earlier, at low pump intensities, the surface potential tends to decrease, while at higher intensities, it increases. Using SHG as a probe, we can observe these effects through corresponding decrease and increase in interfacial susceptibility. Notably, by carefully tuning the geometry of the SiND, we can effectively control the threshold pump intensity required to switch between regimes dominated by photothermal or photocharging effects. The variation in interfacial susceptibility as a function of light intensity for two SiNDs (Fig. 3D and S6) clearly shows that the threshold intensity is $100 \mu\text{W}/\mu\text{m}^2$ for the 490 nm SiND, whereas it drops to just $65 \mu\text{W}/\mu\text{m}^2$ for the 510 nm SiND. This difference stems from our ability to optimize light absorption through nanophotonic design, as supported by the reflectance spectra, which reveal an optical mode near the pump wavelength (Fig. S9). This indicates higher absorption for the 510 nm SiND, which correlates with the lower threshold pump intensity.

To explore the contribution of the TO effect in the interfacial SHG, we irradiated the samples with a 633 nm pump, applying a high laser intensity of $150 \mu\text{W}/\mu\text{m}^2$ for the 530 nm SiND and $180 \mu\text{W}/\mu\text{m}^2$ for the 510 nm SiNDs. This power limitation was crucial in keeping local temperatures below 100 °C, thus avoiding any phase change to a liquid-vapor state that might significantly affect SH intensity. The results, illustrated in Fig. 3E, clearly show that, compared to the dark case (Pump OFF), under photoexcitation (pump ON), a change in SH intensity and a shift in the SH-peak position occur for both 510 nm and 530 nm SiNDs. Interestingly, the 510 nm SiND exhibits an increase in SH intensity, accompanied by a notable blueshift, which directly corresponds to the expected increase in surface potential resulting from temperature changes as discussed above. In contrast, the SH spectrum for the 530 nm SiNDs shows

a decrease in peak amplitude and a redshift. When we examine the SH response under cyclic pump laser-on and off conditions, we consistently observe a decrease in nonlinear polarization during irradiation (Fig. 3F). This trend holds across a range of electrolyte concentrations, underscoring that the behavior has a non-electrochemical origin. Therefore, as noted earlier, TO effects can be convoluted and alter the SH response in a non-intuitive manner.

To separate the thermo-optical effects, we estimate the change in $E(\omega)$ from the reflectance spectra. For instance, for the 530nm SiNDs, a spectral shift of approximately 4 nm (Fig. S8) and $(\Delta R/\Delta\lambda) = 0.008 \text{ nm}^{-1}$ were previously noted (Fig. 3C) and we can estimate $(\Delta R/R) \approx 0.09$. As $E(\omega)^2 \propto R$, we can normalize the SH signal with the reflectance, and extract the sole variation of χ , which clearly shows the increase in χ with an increase in temperature (Fig. 3G), as expected based on the discussion of the temperature dependence of solid-liquid chemical equilibrium.

Together, these results indicate that light can trigger charge trapping or thermal effects, thereby influencing surface charges and the equilibrium at the solid-liquid interface. When dealing with nanostructures that also exhibit optical resonances, it is crucial to be aware of thermo-optical modulation, as this can produce convoluted effects on the SH signal. The insights from this work, based on nanostructuring and probing, enable us to effectively disentangle these effects by carefully controlling optical resonances at targeted wavelengths.

Importantly, by fine-tuning the SiND geometry, we can achieve reversible switching between the photocharging effect of light and a photo-thermal dominated regime simply by adjusting the light intensity. This phenomenon, evidenced by both intensity and spectral changes in the SH response, introduces a novel mechanism for all-optically driven interfacial control, going beyond the conventional methods of tuning via pH or electrolyte concentration. This dynamic response, which depends on geometry, opens up new possibilities for actively modulating electrochemical processes, enhancing nonlinear optical responses, and improving sensing capabilities at semiconductor-electrolyte interfaces.

6 Conclusion

Overall, this work introduces nanophotonic-driven electromagnetic design as a powerful approach for in-situ probing of interfacial phenomena. By achieving unprecedented SHG sensitivity to surface potential and local fields, optimized nanostructured interfaces enable real-time readout of interfacial charge and potential. We find that the surface potential is strongly geometry-dependent and exhibits a non-monotonic dependence on electrolyte concentration. These variations on the electrolyte side directly modulate silicon polarizability—a coupling that is important for photo-electrochemical and hydrovoltaic devices employing metals or semiconductor electrodes.

By further controlling light absorption at the pump wavelength, also enabled by nanophotonic design principles, we intentionally drive and differentiate between two interacting pathways that dynamically modulate solid-liquid interfaces: light-induced charge carrier-driven capacitive coupling (photocharging) and light-induced heating (photothermal effects). These pathways influence surface charge through variations

in the local ionic environment and temperature, respectively. Notably, in cases of optical heating, a significant temperature gradient at the interface can complicate its monitoring, as temperature can equilibrate quickly over short distances from the surface. However, second harmonic generation is inherently surface sensitive, offering a unique optical perspective on the temperature-dependent shifts in equilibrium (and consequently surface charge) that would typically be masked in aqueous systems. Importantly, we present an effective method to adjust and mitigate the unavoidable thermo-optical contributions at nanostructured interfaces, allowing us to isolate and accurately quantify the true photothermal effects on surface charge and potential.

Crucially, we demonstrate that light-driven modulation effects are reversible and controllable: by adjusting the illumination intensity, we can toggle between dominant photocharging and dominant photothermal responses, thereby providing dynamic control over the interfacial state of the system. Together, these results provide a coherent, experimentally validated framework — combining nanophotonic design, SHG sensing, and modeling — that altogether elucidates light–matter interactions at electrochemical interfaces for actively controlling surface charge towards high performance solid–liquid energy conversion systems.

References

- [1] Li, D.: *Electrokinetics in Microfluidics*. Interface science and technology, vol. v. 2. Academic, Oxford (2004)
- [2] Memming, R.: *Semiconductor Electrochemistry*, 2nd edition edn. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2015)
- [3] Wu, J.: Understanding the electric double-layer structure, capacitance, and charging dynamics. *Chemical Reviews* **122**(12), 10821–10859 (2022) <https://doi.org/10.1021/acs.chemrev.2c00097> <https://doi.org/10.1021/acs.chemrev.2c00097>. PMID: 35594506
- [4] How local electric field regulates C–C coupling at a single nanocavity in electrocatalytic CO₂ reduction | *Nature Communications*. <https://www.nature.com/articles/s41467-024-51397-4> Accessed 2025-09-25
- [5] Wang, X., Lin, F., Wang, X., Fang, S., Tan, J., Chu, W., Rong, R., Yin, J., Zhang, Z., Liu, Y., Guo, W.: Hydrovoltaic technology: from mechanism to applications. *Chemical Society Reviews* **51**(12), 4902–4927 (2022) <https://doi.org/10.1039/D1CS00778E>. Publisher: Royal Society of Chemistry. Accessed 2024-12-07
- [6] Graf, M., Lihter, M., Unuchek, D., Sarathy, A., Leburton, J.-P., Kis, A., Radenovic, A.: Light-Enhanced Blue Energy Generation Using MoS₂ Nanopores. *Joule* **3**(6), 1549–1564 (2019) <https://doi.org/10.1016/j.joule.2019.04.011>. Publisher: Elsevier. Accessed 2025-08-26
- [7] Burt, R., Birkett, G., Zhao, X.S.: A review of molecular modelling of electric

- double layer capacitors. *Physical Chemistry Chemical Physics* **16**(14), 6519–6538 (2014) <https://doi.org/10.1039/C3CP55186E> . Publisher: The Royal Society of Chemistry. Accessed 2025-09-25
- [8] DEBYE, V.: Zur Theorie der Electrolyte. *Physikalische Zeitschrift*. **0**, 185–206 (1923). Accessed 2025-08-29
- [9] Stern, O.: Zur Theorie Der Elektrolytischen Doppelschicht. *Zeitschrift für Elektrochemie und angewandte physikalische Chemie* **30**(21-22), 508–516 (1924) <https://doi.org/10.1002/bbpc.192400182> . eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/bbpc.192400182>. Accessed 2025-09-01
- [10] Helmholtz, H.: Studien über electrische Grenzsichten. *Annalen der Physik* **243**(7), 337–382 (1879) <https://doi.org/10.1002/andp.18792430702> . eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/andp.18792430702>. Accessed 2025-08-29
- [11] Nagy, G., Roy, D.: Surface charge dependence of second harmonic generation from a Ni electrode. *Chemical Physics Letters* **214**(2), 197–202 (1993) [https://doi.org/10.1016/0009-2614\(93\)90081-B](https://doi.org/10.1016/0009-2614(93)90081-B) . Accessed 2025-08-15
- [12] Z.Bazant, M.: Unified quantum theory of electrochemical kinetics by coupled ion–electron transfer. *Faraday Discussions* **246**(0), 60–124 (2023) <https://doi.org/10.1039/D3FD00108C> . Publisher: Royal Society of Chemistry. Accessed 2025-09-25
- [13] Li, J., Long, Y., Hu, Z., Niu, J., Xu, T., Yu, M., Li, B., Li, X., Zhou, J., Liu, Y., Wang, C., Shen, L., Guo, W., Yin, J.: Kinetic photovoltage along semiconductor–water interfaces. *Nature Communications* **12**(1), 4998 (2021) <https://doi.org/10.1038/s41467-021-25318-8> . Publisher: Nature Publishing Group. Accessed 2024-07-01
- [14] Anwar, T., Tagliabue, G.: A Unified Framework for Harnessing Heat and Light with Hydrovoltaic Devices. *arXiv*. arXiv:2412.08953 [physics] (2025). <https://doi.org/10.48550/arXiv.2412.08953> . <http://arxiv.org/abs/2412.08953> Accessed 2025-08-28
- [15] Kosmulski, M.: pH-dependent surface charging and points of zero charge. IV. Update and new approach. *Journal of Colloid and Interface Science* **337**(2), 439–448 (2009) <https://doi.org/10.1016/j.jcis.2009.04.072> . Accessed 2024-07-02
- [16] Behrens, S.H., Grier, D.G.: The charge of glass and silica surfaces. *The Journal of Chemical Physics* **115**(14), 6716–6721 (2001) <https://doi.org/10.1063/1.1404988> . Accessed 2022-08-03
- [17] Azam, M.S., Cai, C., Gibbs, J.M., Tyrode, E., Hore, D.K.: Silica Surface Charge

- Enhancement at Elevated Temperatures Revealed by Interfacial Water Signals. *Journal of the American Chemical Society* **142**(2), 669–673 (2020) <https://doi.org/10.1021/jacs.9b11710> . Publisher: American Chemical Society. Accessed 2024-06-06
- [18] Joutsuka, T., Morita, A.: Electrolyte and Temperature Effects on Third-Order Susceptibility in Sum-Frequency Generation Spectroscopy of Aqueous Salt Solutions. *The Journal of Physical Chemistry C* **122**(21), 11407–11413 (2018) <https://doi.org/10.1021/acs.jpcc.8b02445> . Publisher: American Chemical Society. Accessed 2024-06-10
- [19] Charge regulation at semiconductor-electrolyte interfaces. *Journal of Colloid and Interface Science* **449**, 409–415 (2015) <https://doi.org/10.1016/j.jcis.2014.12.058> . Publisher: Academic Press. Accessed 2023-12-18
- [20] Mönch, W.: *Semiconductor Surfaces and Interfaces*, 3rd, rev. ed edn. Springer series in surface sciences, vol. 26. Springer, Berlin ; New York (2001)
- [21] Cui, X., Ruan, Q., Zhuo, X., Xia, X., Hu, J., Fu, R., Li, Y., Wang, J., Xu, H.: Photothermal Nanomaterials: A Powerful Light-to-Heat Converter. *Chemical Reviews* **123**(11), 6891–6952 (2023) <https://doi.org/10.1021/acs.chemrev.3c00159> . Publisher: American Chemical Society. Accessed 2025-09-25
- [22] Naef, A., Mohammadi, E., Tsoulos, T.V., Tagliabue, G.: Light-Driven Thermo-Optical Effects in Nanoresonator Arrays. *Advanced Optical Materials* **11**(20), 2300698 (2023) <https://doi.org/10.1002/adom.202300698> . eprint: <https://advanced.onlinelibrary.wiley.com/doi/pdf/10.1002/adom.202300698>. Accessed 2025-09-25
- [23] Collins, L., Jesse, S., Kilpatrick, J.I., Tselev, A., Varenky, O., Okatan, M.B., Weber, S.A.L., Kumar, A., Balke, N., Kalinin, S.V., Rodriguez, B.J.: Probing charge screening dynamics and electrochemical processes at the solid–liquid interface with electrochemical force microscopy. *Nature Communications* **5**(1), 3871 (2014) <https://doi.org/10.1038/ncomms4871> . Publisher: Nature Publishing Group. Accessed 2025-09-25
- [24] Kobayashi, N., Asakawa, H., Fukuma, T.: Nanoscale potential measurements in liquid by frequency modulation atomic force microscopy. *Review of Scientific Instruments* **81**(12), 123705 (2010) <https://doi.org/10.1063/1.3514148> . Accessed 2025-09-25
- [25] Cortés, E., Grzeschik, R., Maier, S.A., Schlücker, S.: Experimental characterization techniques for plasmon-assisted chemistry. *Nature Reviews Chemistry* **6**(4), 259–274 (2022) <https://doi.org/10.1038/s41570-022-00368-8>
- [26] Phase-referenced nonlinear spectroscopy of the α -quartz/water interface | *Nature Communications*. <https://www.nature.com/articles/ncomms13587> Accessed

- [27] Corn, R.M., Higgins, D.A.: Optical second harmonic generation as a probe of surface chemistry. *Chemical Reviews* **94**(1), 107–125 (1994) <https://doi.org/10.1021/cr00025a004> <https://doi.org/10.1021/cr00025a004>
- [28] Yan, E.C.Y., Liu, Y., Eisenthal, K.B.: New Method for Determination of Surface Potential of Microscopic Particles by Second Harmonic Generation. *The Journal of Physical Chemistry B* **102**(33), 6331–6336 (1998) <https://doi.org/10.1021/jp981335u> . Publisher: American Chemical Society. Accessed 2025-08-31
- [29] Dadap, J.I., Xu, Z., Hu, X.F., Downer, M.C., Russell, N.M., Ekerdt, J.G., Aktsipetrov, O.A.: Second-harmonic spectroscopy of a Si(001) surface during calibrated variations in temperature and hydrogen coverage. *Physical Review B* **56**(20), 13367–13379 (1997) <https://doi.org/10.1103/PhysRevB.56.13367> . Accessed 2025-03-21
- [30] Nagy, G., Roy, D.: Surface charge dependence of second harmonic generation from a Ni electrode. *Chemical Physics Letters* **214**(2), 197–202 (1993) [https://doi.org/10.1016/0009-2614\(93\)90081-B](https://doi.org/10.1016/0009-2614(93)90081-B) . Accessed 2025-08-16
- [31] Mizrahi, V., Sipe, J.E.: Phenomenological treatment of surface second-harmonic generation. *JOSA B* **5**(3), 660–667 (1988) <https://doi.org/10.1364/JOSAB.5.000660> . Publisher: Optica Publishing Group. Accessed 2025-03-31
- [32] Guyot-Sionnest, P., Shen, Y.R.: Local and nonlocal surface nonlinearities for surface optical second-harmonic generation. *Physical Review B* **35**(9), 4420–4426 (1987) <https://doi.org/10.1103/PhysRevB.35.4420> . Accessed 2025-03-21
- [33] Falasconi, M., Andreani, L.C., Malvezzi, A.M., Patrini, M., Mulloni, V., Pavesi, L.: Bulk and surface contributions to second-order susceptibility in crystalline and porous silicon by second-harmonic generation. *Surface Science* **481**(1), 105–112 (2001) [https://doi.org/10.1016/S0039-6028\(01\)01004-4](https://doi.org/10.1016/S0039-6028(01)01004-4) . Accessed 2025-07-14
- [34] Lu, X., Pasternak, R., Park, H., Qi, J., Tolk, N.H., Chatterjee, A., Schrimpf, R.D., Fleetwood, D.M.: Temperature-dependent second- and third-order optical nonlinear susceptibilities at the Si/SiO_2 interface. *Physical Review B* **78**(15), 155311 (2008) <https://doi.org/10.1103/PhysRevB.78.155311> . Publisher: American Physical Society. Accessed 2025-02-25
- [35] Mifflin, A.L., Musorrafti, M.J., Konek, C.T., Geiger, F.M.: Second Harmonic Generation Phase Measurements of Cr(VI) at a Buried Interface. *The Journal of Physical Chemistry B* **109**(51), 24386–24390 (2005) <https://doi.org/10.1021/jp055174n> . Publisher: American Chemical Society. Accessed 2025-08-14
- [36] Dreier, L.B., Bernhard, C., Gonella, G., Backus, E.H.G., Bonn, M.: Surface Potential of a Planar Charged Lipid–Water Interface. *What Do Vibrating Plate*

- Methods, Second Harmonic and Sum Frequency Measure? The Journal of Physical Chemistry Letters **9**(19), 5685–5691 (2018) <https://doi.org/10.1021/acs.jpcclett.8b02093> . Publisher: American Chemical Society. Accessed 2025-08-29
- [37] Ma, E., Ohno, P.E., Kim, J., Liu, Y., Lozier, E.H., Miller, T.F.I., Wang, H.-F., Geiger, F.M.: A New Imaginary Term in the Second-Order Nonlinear Susceptibility from Charged Interfaces. The Journal of Physical Chemistry Letters **12**(24), 5649–5659 (2021) <https://doi.org/10.1021/acs.jpcclett.1c01103> . Publisher: American Chemical Society. Accessed 2025-07-14
- [38] Kulyuk, L.L., Shutov, D.A., Strumban, E.E., Aktsipetrov, O.A.: Second-harmonic generation by an SiO₂–Si interface: influence of the oxide layer. JOSA B **8**(8), 1766–1769 (1991) <https://doi.org/10.1364/JOSAB.8.001766> . Publisher: Optica Publishing Group. Accessed 2025-03-20
- [39] Guyot-Sionnest, P., Tadjeddine, A., Liebsch, A.: Electronic distribution and nonlinear optical response at the metal-electrolyte interface. Physical Review Letters **64**(14), 1678–1681 (1990) <https://doi.org/10.1103/PhysRevLett.64.1678> . Accessed 2025-08-15
- [40] Water flipping and the oxygen evolution reaction on Fe₂O₃ nanolayers | Nature Communications. <https://www.nature.com/articles/s41467-025-58842-y> Accessed 2025-08-16
- [41] Gao, R.-T., Truong Nguyen, N., Nakajima, T., He, J., Liu, X., Zhang, X., Wang, L., Wu, L.: Dynamic semiconductor-electrolyte interface for sustainable solar water splitting over 600 hours under neutral conditions. Science Advances (2023) <https://doi.org/10.1126/sciadv.ade4589> . Publisher: American Association for the Advancement of Science. Accessed 2025-10-01
- [42] Anwar, T., Tagliabue, G.: Salinity-dependent interfacial phenomena toward hydrovoltaic device optimization. Device **2**(5), 100287 (2024) <https://doi.org/10.1016/j.device.2024.100287> . Accessed 2024-05-29
- [43] Qin, Y., Wang, Y., Sun, X., Li, Y., Xu, H., Tan, Y., Li, Y., Song, T., Sun, B.: Constant Electricity Generation in Nanostructured Silicon by Evaporation-Driven Water Flow. Angewandte Chemie **132**(26), 10706–10712 (2020) <https://doi.org/10.1002/ange.202002762> . eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/ange.202002762>. Accessed 2021-07-26
- [44] Zhao, F., Xu, Z., Suo, S., Lin, L., Hill, C.L., Musaev, D.G., Lian, T.: A contactless in situ EFISH method for measuring electrostatic potential profile of semiconductor/electrolyte junctions. The Journal of Chemical Physics **161**(9), 094703 (2024) <https://doi.org/10.1063/5.0226128> . Accessed 2025-10-01

- [45] Gonella, G., Lütgebaucks, C., Beer, A.G.F., Roke, S.: Second Harmonic and Sum-Frequency Generation from Aqueous Interfaces Is Modulated by Interference. *The Journal of Physical Chemistry C* **120**(17), 9165–9173 (2016) <https://doi.org/10.1021/acs.jpcc.5b12453> . Publisher: American Chemical Society. Accessed 2024-09-16
- [46] Ohno, P.E., Chang, H., Spencer, A.P., Liu, Y., Boamah, M.D., Wang, H.-f., Geiger, F.M.: Beyond the Gouy–Chapman Model with Heterodyne-Detected Second Harmonic Generation. *The Journal of Physical Chemistry Letters* **10**(10), 2328–2334 (2019) <https://doi.org/10.1021/acs.jpcllett.9b00727> . Publisher: American Chemical Society. Accessed 2025-08-12
- [47] Fischer, P.R., Daschbach, J.L., Gragson, D.E., Richmond, G.L.: Sensitivity of second harmonic generation to space charge effects at Si(111)/electrolyte and Si(111)/SiO₂/electrolyte interfaces. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **12**(5), 2617–2624 (1994) <https://doi.org/10.1116/1.579080> . Accessed 2025-08-16
- [48] Makarov, S.V., Petrov, M.I., Zywiets, U., Milichko, V., Zuev, D., Lopanitsyna, N., Kuksin, A., Mukhin, I., Zograf, G., Ubyivovk, E., Smirnova, D.A., Starikov, S., Chichkov, B.N., Kivshar, Y.S.: Efficient Second-Harmonic Generation in Nanocrystalline Silicon Nanoparticles. *Nano Letters* **17**(5), 3047–3053 (2017) <https://doi.org/10.1021/acs.nanolett.7b00392> . Publisher: American Chemical Society. Accessed 2025-03-20
- [49] Tonkaev, P., Lai, F., Kruk, S., Song, Q., Scalora, M., Koshelev, K., Kivshar, Y.: Even-order optical harmonics generated from centrosymmetric-material metasurfaces. *Physical Review Research* **6**(3), 033073 (2024) <https://doi.org/10.1103/PhysRevResearch.6.033073> . Publisher: American Physical Society. Accessed 2025-08-30
- [50] Choudhury, B.D., Sahoo, P.K., Sanatinia, R., Andler, G., Anand, S., Swillo, M.: Surface second harmonic generation from silicon pillar arrays with strong geometrical dependence. *Optics Letters* **40**(9), 2072–2075 (2015) <https://doi.org/10.1364/OL.40.002072> . Publisher: Optica Publishing Group. Accessed 2025-08-31
- [51] Macias-Romero, C., Nahalka, I., Okur, H.I., Roke, S.: Optical imaging of surface chemistry and dynamics in confinement. *Science* **357**(6353), 784–788 (2017) <https://doi.org/10.1126/science.aal4346> . Publisher: American Association for the Advancement of Science. Accessed 2024-03-04
- [52] Alghamdi, A.O., Gonzalez, N.M., Geiger, F.M.: Temperature Dependence of Proton Coverage and the Total Potential at Fused Silica:Water Interfaces from Phase-Resolved Nonlinear Optics. *Journal of the American Chemical Society* **147**(17), 14308–14315 (2025) <https://doi.org/10.1021/jacs.4c18310> . Publisher: American Chemical Society. Accessed 2025-07-07

- [53] Gavrilenko, V.I., Rebentrost, F.: Nonlinear optical susceptibility of the surfaces of silicon and diamond. *Surface Science* **331-333**, 1355–1360 (1995) [https://doi.org/10.1016/0039-6028\(95\)00296-0](https://doi.org/10.1016/0039-6028(95)00296-0) . Accessed 2025-10-03
- [54] Sposito, G.: On the surface complexation model of the oxide-aqueous solution interface. *Journal of Colloid and Interface Science* **91**(2), 329–340 (1983) [https://doi.org/10.1016/0021-9797\(83\)90345-4](https://doi.org/10.1016/0021-9797(83)90345-4) . Accessed 2024-12-08
- [55] Mendoza, B.S., Mochán, W.L.: Exactly solvable model of surface second-harmonic generation. *Physical Review B* **53**(8), 4999–5006 (1996) <https://doi.org/10.1103/PhysRevB.53.4999> . Accessed 2025-08-16
- [56] Dzhavakhidze, P.G., Kornyshev, A.A., Liebsch, A., Urbakh, M.: Theory of second-harmonic generation at the metal-electrolyte interface. *Physical Review B* **45**(16), 9339–9346 (1992) <https://doi.org/10.1103/PhysRevB.45.9339> . Accessed 2025-08-16

Acknowledgments

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Author contributions

T.A. and G.T. conceptualized the study; T.A. developed the experimental platform, performed all the experiments, numerical calculations, and modeling, and investigated and visualized the results under the supervision of G.T.; D.D.A. fabricated the samples; M.S. and D.D.A. contributed to the setup development.

Supplementary Information

This section provides methods and additional figures.

S1 Experimental

We designed a compression flow cell, as shown in (Fig. S1A), which consists of three essential components: i) a top section with three ports for electrolyte inflow and outflow, along with a reference electrode situated within the bulk electrolyte; ii) a middle spacer available in thicknesses of 0.5 mm or 1 mm; and iii) a bottom section where the sample to be examined can be positioned for back illumination. This flow cell works in conjunction with an external peristaltic pump that continuously circulates the electrolyte during in-situ experiments. To ensure optimal observations, the cell is mounted on an inverted microscope (Nikon Eclipse T2), providing flexibility in sample placement—whether at the bottom for back illumination (Fig. S1B) or at the top for front illumination (Fig. S1C). When the sample is placed on top, a fused-silica substrate is set at the bottom, and this arrangement is reversed for front placement. The variable-coverslip correction of the 0.7 NA 60x objective enables precise focusing of light onto specific planes.

As illustrated in Fig. S1D, the inverted microscope is set up to simultaneously excite and capture optical signals. The excitation pathway features two lasers: i) a 1030 nm, 6 nm full-width-half-maximum, linearly polarized femtosecond laser (NKT origami, 200 fs, 80 MHz) serving as the fundamental beam (FW) for second harmonic generation, and ii) a supercontinuum white light laser (NKT Photonics) used for generating charge carriers and optically modulating the semiconductor. To fine-tune the wavelength and power of the NKT laser, we employ a tunable wavelength filter (SuperK VARIA) spanning 450-840 nm with a 10 nm bandwidth. Both laser beams are *normal incidence* to the sample and are carefully aligned to converge at the same point on the sample through independent paths, as shown in Fig. S1D. The beam diameter for the FW beam is fixed at 4.4 μm , slightly smaller than the pump laser beam's diameter of 4.6 μm (Fig. S10), with precision tuning achieved using collimating lenses.

We conduct SHG measurements in a reflection configuration, in which the emitted SH signal and the reflected fundamental wave (FW) are directed into the collection pathway. This pathway employs a 4F configuration to couple the signal to a grating spectrometer (Princeton Instruments Spectra Pro HRS-500), equipped with a Peltier-cooled 2D CCD detector (Princeton Instruments PIXIS 256). To characterize the system, we first perform SHG measurements without electrolyte in the cell, then introduce the electrolyte via the external pump. Notably, our spectroscopic signal remained stable during electrolyte pumping at optimal rates, enabling us to monitor SH intensity transitions as the bulk electrolyte environment changed. To monitor SH intensity under light stimuli, we switched the pump laser between on and off states using a shutter in the optical path. Notably, the substantial spectral separation between the excitation (1030 nm) and SH emission (515 nm), as well as the pump laser (633 nm) and an additional notch filter in the collection path, ensures that the measured SH intensity is not affected by residual signals from the pump and excitation. In addition,

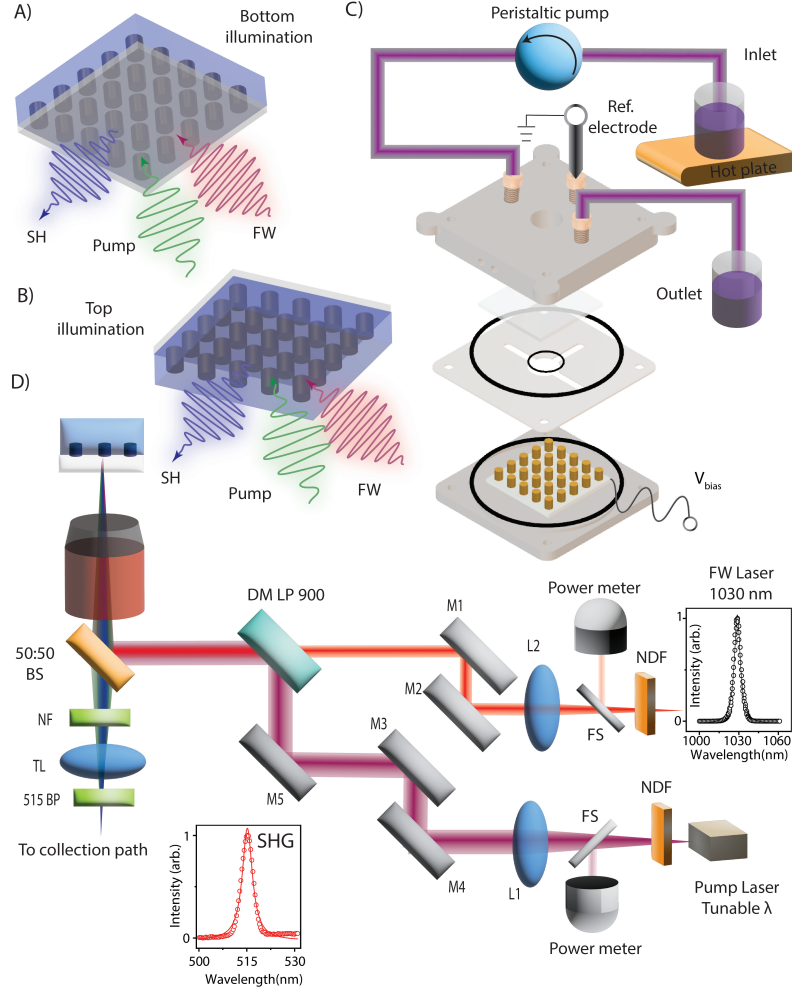


Fig. S1 The operando spectro-photo(electro)-chemical setup. A-B) Sample configuration depicting the (A) bottom and (B) top illumination configuration in the reflection mode. C) An external pump circulates the electrolyte through the designated inlet and outlet ports, and an additional port for a reference electrode is available for precise electrochemical measurements. The nanostructured sample can be arranged either on the top or bottom, based on whether front or back illumination is employed. A hot plate is used to heat the electrolyte for temperature-dependent measurements. D) In the (bottom-right), we have the excitation path featuring the FW (centered at 1030 nm with a bandwidth of 6 nm), and a tunable wavelength pump laser (wavelength, power, and bandwidth can be varied). At the (top-left), an inverted microscope is mounted with the flow cell as shown in panel C. On the (bottom left), the $4F$ collection path facilitates the signal, which then travels through the spectrometer and is monitored via a CCD camera. The various critical elements in this setup are as follows: M1-M5 signify mirrors; L1, L2 are collimating lenses; TL denotes the tube lens; DM LP900 is the long pass dichroic mirror; FS consists of 0.17 mm thin fused silica substrates for reflecting a small percentage for real-time power monitoring; NDF is a neutral density filter for controlling the power level; BS is the beam splitter; NF is a notch filter designed to eliminate the pump excitation wavelength from the collection path; SP is the short pass filter; and BP is the band pass filter. The bottom graph shows an SH intensity (centered at 515 nm with a bandwidth of 4.3 nm) detected for a representative case.

our in-situ setup is adapted for measurements that require an external electrical bias or an increase in bulk temperature, using the equipped reference electrode and hot plates beneath the inlet reservoir.

S2 Extracting interfacial susceptibility from the SH intensity

The non-linear surface polarisation is given according to Eq. S1, which depends on the non-linear second-order susceptibility of the surface of interest.

$$\mathbf{P}_{\text{nl}}(2\omega) = \chi_{\text{eff}}^{(2)} : \mathbf{E}(\omega) \mathbf{E}(\omega).$$

In a semiconductor-oxide-electrolyte system, it is essential to consider the effective second-order susceptibility that originates not only from the inherent semiconductor surface but also from the interfacial contributions of the electrical double layer and the space charge layer [40, 45, 56]. This relationship can be expressed as

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{solid}}^{(2)} + \chi_{\text{Stern}}^{(2)} - \chi_{\text{H}_2\text{O}}^{(3)'} \Phi_0(e^{i\alpha} \cos \alpha + 1.5i) + \chi_{\text{solid, sc}}^{(3)'} (V - V_{\text{FB}}) e^{i\beta} \cos \beta. \quad (\text{S1})$$

where $\chi_{\text{solid}}^{(2)}$ is the second-order susceptibility of the electrode, which is frequency dependent.

For the case of an aqueous electrolyte, $\chi_{\text{Stern}}^{(2)}$, the second-order susceptibility is that of oriented water molecules in the Stern layer. $\chi_{\text{H}_2\text{O}}^{(3)'}$ and $\chi_{\text{solid, sc}}^{(3)'}$ is the effective third-order susceptibility of interfacial water, which results in net orientation due to the interaction of the electrical double-layer electrostatic field, and the space charge layer in the semiconductor due to interfacial band bending. V and V_{FB} are the applied potential and flat-band potentials of the semiconductor-oxide-electrolyte. Please note that the minus sign in the third term is included solely to ensure consistency with other works in the literature. In the above equation, it is clear that the contributions from the electrical double layer and the space charge layer stem from a third-order effect, necessitating the interaction of DC electric fields. For mathematical convenience, this third-order contribution has been effectively transformed into a second-order term by applying an exponential decay of the electric fields in the two interfacial regions [45]. This strategic simplification leads to the emergence of phase terms $e^{i\alpha} \cos \alpha$ and $e^{i\beta} \cos \beta$ for the electrical double layer and the space charge layer, respectively. The parameters α and β are precisely defined based on the wave-vector mismatch and the exponential decay length of the electric field in these two layers.

$$\tan \alpha = \frac{\Delta k_z}{\kappa_{\text{EDL}}}, \quad \tan \beta = \frac{\Delta k_z}{\kappa_{\text{SC}}}. \quad (\text{S2})$$

where Δk_z are the wave-vector mismatch between the fundamental and the second harmonic frequency, and κ_{EDL} and κ_{SC} are the inverse Debye length (Eq. S3) in the electrical double layer and the space charge layer, respectively.

$$\lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{\sum_{i=1}^N n_{0,i} z_i^2 e^2}} \quad (\text{S3})$$

S3 Numerical simulation

All simulations in this study were conducted using the finite element method in COMSOL Multiphysics 6.3. The primary objective was to optimize the SHG efficiency of a silicon nanodisk embedded on a fused silica substrate, surrounded by either water or air as the top layer. A three-dimensional unit cell model was established, with the unit cell dimensions precisely adjusted to reflect the periodicity of the array $p = 800$ nm. The silicon nanodisk's height and diameter were systematically varied to identify configurations that maximize SHG output. A detailed description of the simulation approach is as follows.

Linear Simulation: The simulation process began with a linear analysis to obtain the electric field distribution under the excitation of a fundamental planar wave (FW). To create a realistic representation of an infinite array, periodic boundary conditions were applied to the lateral surfaces of the unit cell model.

1. **Excitation Configuration:** At the bottom boundary of the unit cell, a port boundary condition was defined with excitation activated, simulating back illumination by a normal incident plane wave. The electric field polarization was oriented along a predetermined axis to generate the desired excitation conditions.
2. **Boundary Conditions:** The upper boundary of the model employed a second port boundary condition without excitation, allowing for the transmission of the excited wave through the structure. To mitigate the influence of artificial reflections that could skew the simulation results, perfectly matched layers (PML) were implemented at both the top and bottom boundaries of the simulation area.
3. **Reflectance and Transmittance Calculation:** To evaluate the optical performance of the structure, the reflectance and transmittance were calculated by integrating the Poynting vectors over planes parallel to both the substrate and superstrate. This integration enabled a thorough assessment of the energy flow in and out of the nanostructure.
4. **Material Properties:** The refractive index for silicon was sourced from experimental ellipsometry measurements (Fig. S7A), ensuring accuracy in the simulation parameters.

Non-Linear Simulation: Having acquired the electric field distribution from the linear simulation, the next phase involved computing the nonlinear surface polarization responsible for SHG, as expressed in Equation 4.1.

$$\mathbf{P}_{\text{nl}}^{(2)}(2\omega) = \varepsilon_0 \left[\chi_{nnn}^{(2)} E_n(\omega) E_n(\omega) + \chi_{ntt}^{(2)} E_t(\omega) E_t(\omega) \right] \hat{\mathbf{n}} + \varepsilon_0 \left[\chi_{tnt}^{(2)} E_t(\omega) E_n(\omega) \right] \hat{\mathbf{t}} \quad (\text{S4})$$

In the above equation, the subscripts stand for the direction tangential (t) and normal (n) to the surface of the nanodisk. $E_n(\omega)$ and $E_t(\omega)$ are the normal and tangential components of the FW electric field on the surface. $\chi_{nnn}^{(2)}$, $\chi_{ntt}^{(2)}$, and $\chi_{tnt}^{(2)}$ are different tensor components of the second-order surface susceptibility of silicon. $\hat{n}$ and $\hat{t}$ are unit vectors normal and tangential to the disk. ε_0 is the free space electrical permittivity.

1. Surface Polarization Calculation: The field profile obtained earlier was used to derive the nonlinear surface polarization, incorporating the material nonlinearity as a source term for subsequent simulations.
2. Second harmonic generation analysis: A linear simulation at the second harmonic (SH) wavelength was then executed, with the nonlinear surface polarization acting as the radiation source. This setup enabled the derivation of the SH signal strength.
3. Non-linear reflectance and transmittance: The SH signal strength was calculated similarly to the linear case, by integrating the Poynting vectors on planes parallel to the substrate. This method enabled a comprehensive understanding of how the SHG signal evolves with varying disk dimensions and environmental conditions.

In summary, this dual-step simulation process, combining linear and nonlinear analyses, provided an in-depth study of the silicon nanodisk's optical properties, ultimately aimed at optimizing SH intensity.

S4 Nanofabrication of a-Si:H Nanopillar Arrays

Hydrogenated amorphous silicon (a-Si:H) nanopillar arrays were fabricated on fused silica substrates using electron-beam lithography (EBL) and reactive-ion etching. Fused silica wafers were first cleaned in piranha solution, followed by deposition of a 430 nm-thick a-Si:H layer via plasma-enhanced chemical vapor deposition (PECVD, Corial D250L) at a substrate temperature of 280 °C. The wafers were diced into 20 × 20 mm chips, each of which was plasma-cleaned (Tepla 300, 2 min) and hard-baked at 180 °C (5 min). A bilayer resist stack was spin-coated using a Sawatec SM-150 system: ZEP 520A (50 %, 2000 rpm, 150 nm thickness) was applied and baked, followed by Electra 92 conductive polymer at 1000 rpm, which was left to air dry without post-bake. Nanopillar arrays were patterned by exposing the surrounding regions to negative exposure using a Raith EBPG5000+ EBL system operating at 100 keV, with exposure doses between 150 and 300 $\mu\text{C}/\text{cm}^2$. The resist was developed in amyl acetate at room temperature (90 s), rinsed in 90:10 methyl isobutyl ketone (MIBK):isopropanol, and dried under nitrogen. Pattern transfer into the a-Si:H layer was performed by inductively coupled plasma etching (AMS 200, 0 °C, 3.5 min). The etch selectivity was >10:1 between ZEP and a-Si:H, and >20:1 between a-Si:H and fused silica, enabling complete etching of the silicon layer. The residual resist was removed by high-power plasma ashing (Tepla Gigabatch, 5 min). The final structures consisted of nanopillars arranged in a square lattice with 800 nm pitch, 500 nm diameter, and 430 nm height. The dose sweep during EBL allowed systematic tuning of the pillar diameter. Structural quality and fidelity were verified using scanning electron microscopy (SEM), with samples grounded by surrounding copper tape to minimize charging effects.

S5 Enhancing sensitivity for monitoring interfacial susceptibility

The second harmonic intensity is expressed as:

$$I_{\text{SH}} = E(\omega)^4 \chi^2$$

Taking the logarithm on both sides, we get,

$$\log I_{\text{SH}} = 4 \log E(\omega) + 2 \log \chi$$

Using the method of differential, we can write the fractional change in second harmonic intensity due to the changes in susceptibility. We have assumed that the electric field enhancement $E(\omega)$ does not change with a change in susceptibility.

$$\frac{\Delta I_{\text{SH}}}{I_{\text{SH}}} = 2 \frac{\Delta \chi}{\chi}$$

By substituting the expression for second harmonic intensity in terms of electric field enhancement, we obtain an expression for the change in susceptibility as follows:

$$\Delta \chi = \frac{\chi}{2 I_{\text{SH}}} \Delta I_{\text{SH}} = \frac{1}{2 E(\omega)^4 \chi} \Delta I_{\text{SH}}$$

The ratio of change of susceptibility for the silicon nanodisk (SiND) and planar film (film) can be expressed as:

$$\frac{(\Delta \chi)_{\text{SiND}}}{(\Delta \chi)_{\text{film}}} = \left(\frac{1}{2 E(\omega)^4 \chi} \Delta I_{\text{SH}} \right)_{\text{film}} \times \left(\frac{1}{2 E(\omega)^4 \chi} \Delta I_{\text{SH}} \right)_{\text{SiND}}^{-1}$$

As the sensitivity of intensity detection depends on the detector used, the sensitivity of intensity detection is constant. We further note that $\frac{(\chi)_{\text{SiND}}}{(\chi)_{\text{film}}} \sim 1$, so we have:

$$\frac{(\Delta \chi)_{\text{SiND}}}{(\Delta \chi)_{\text{film}}} \approx \left(\frac{E(\omega)_{\text{film}}}{E(\omega)_{\text{SiND}}} \right)^4$$

As the maximum field enhancement in SiND is ≈ 5 , the surface average is slightly lower. From the discussion in the manuscript related to the second harmonic intensity amplification, we can write:

$$(\Delta \chi)_{\text{SiND}} \approx \frac{1}{200} (\Delta \chi)_{\text{film}}$$

Hence, it shows that with the nanostructuring approach, we can enhance the sensitivity of detection of changes in interfacial susceptibility by 200 times.

S6 Linear optical characterisation

To record the linear reflectance and transmittance spectra of the studied structures, we employed the same inverted microscope and spectrometer as for the non-linear measurements. Illumination was achieved using a fiber-coupled, broadband laser-driven white light source (Energetic LDLS), precisely focused onto the back focal plane (BFP) of a long working distance, high numerical aperture (NA) objective lens (Nikon 60x,

NA=0.7). This arrangement allowed for the sample to be illuminated from the bottom with collimated light, ensuring uniform illumination across the area of interest (as depicted in Fig. S11 A). The collected reflected light was then relayed to the spectrometer for spectral analysis. To estimate absolute reflectance, the spectra were normalized against a reference silver mirror (ThorLabs, PF10-03-P01). Additionally, a background correction was systematically applied to all measurements to eliminate noise and interference, thereby refining the acquired spectral data. The reflectance spectra are shown in Fig. S11B for a few representative disk structures with a fixed pitch of 800 nm, height of 440 nm.

S7 Estimating interfacial potential

The ratio of non-linear polarization for measurements in air and water is obtained by combining the following equations. 1 and 2

$$R_{SH} = \frac{|P_{nl}(2\omega)|}{|P_{nl}^0(2\omega)|} = \frac{\sqrt{I_{SH}(2\omega)}}{\sqrt{I_{SH}^0(2\omega)}} = \frac{1}{\alpha^2} \frac{|\chi_s^{(2)} - \chi_{H_2O}^{(3)'} \Phi_0 (\cos(\phi_{DC}) e^{i\phi_{DC}} + 1.5i)|}{\chi_{s,0}^{(2)}} \quad (S5)$$

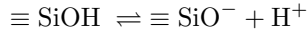
In the above equation, we have used the notation '0' to indicate the measurements carried out in air, i.e., no, electrolyte contribution, and the effective susceptibility contains only the solid contribution. As derived in Eq. 4, the quadratic relation (Eq. S6) yields two mathematical solutions corresponding to in-phase and out-of-phase signal third-order contributions.

$$\begin{aligned} \left[\alpha^2 \chi_{s,0}^{(2)} R_{SH} \right]^2 &= \left(\chi_s^{(2)} \right)^2 + \\ &\quad - 2 \chi_s^{(2)} \chi_{H_2O}^{(3)'} \Phi_0 \cos^2(\phi_{DC}) + \\ &\quad \Phi_0^2 \left(\chi_{H_2O}^{(3)'} \right)^2 \left(\cos^2(\phi_{DC}) + 3 \cos(\phi_{DC}) \sin(\phi_{DC}) + 2.25 \right) \end{aligned} \quad (S6)$$

By solving the above quadratic equation, we can obtain an expression for surface potential as shown in Eq. 4

S8 Temperature dependent equilibrium constant

In our system, the observed linear relationship between temperature and surface charge arises from the thermally driven shift in the equilibrium of surface ionization reactions. Specifically, temperature increases promote the dissociation of surface hydroxyl groups, for example:



This thereby increases the surface charge density. The equilibrium constant can be expressed as

$$K_a = \frac{[\text{SiO}^-][\text{H}^+]}{[\text{SiOH}]} = \frac{\sigma[\text{H}^+]}{I - \sigma}$$

The expression for surface charge in terms of surface proton concentration is given by

$$\sigma = \frac{-e\Gamma}{1 + \frac{[\text{H}^+]_s}{K_a}}$$

We note that the temperature dependence of the ionization equilibrium is central to our analysis. In our study, we relate the temperature-dependent equilibrium constant $K(T)$ to the thermodynamic parameter enthalpy ΔH via the Van't Hoff equation:

$$\ln K_1 - \ln K_2 = -\Delta H \left(\frac{1}{RT_1} - \frac{1}{RT_2} \right)$$

Equivalently, this can be written in the form:

$$K = K_0 \exp \left[-\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (\text{S7})$$

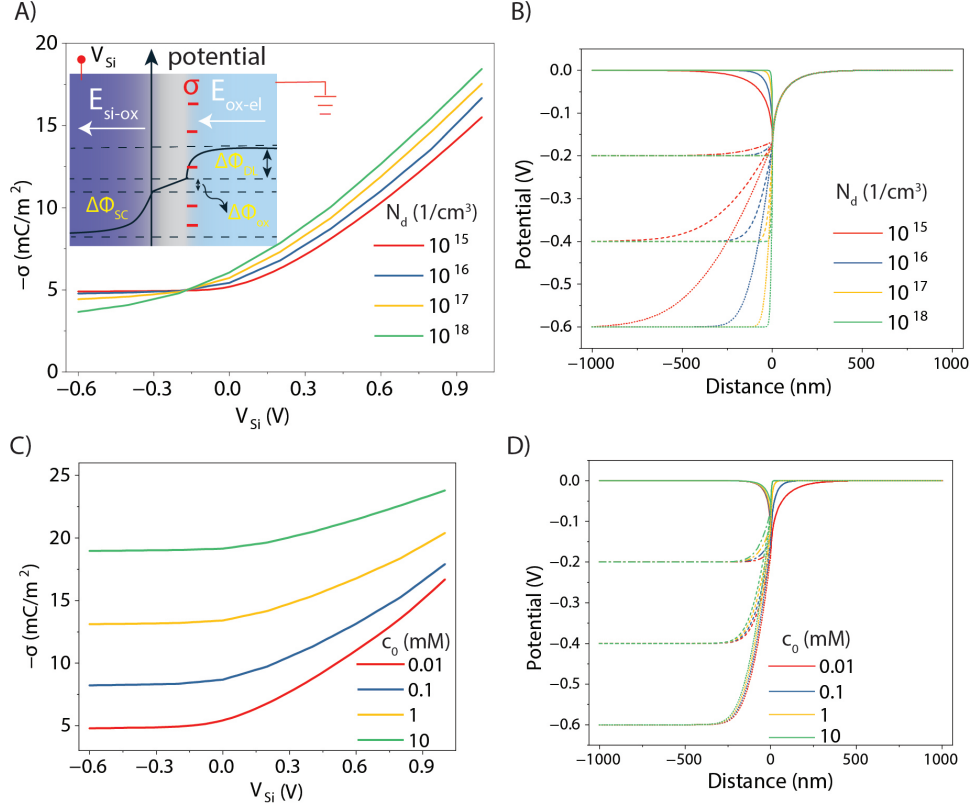


Fig. S2 Influence of band bending at the silicon–oxide side on interfacial charge and electric field regulation. Calculated surface charge at the solid–liquid interface for n-type silicon under different dopant concentrations ($1/\text{cm}^3$). B) The potential profile across the semiconductor–oxide electrolyte system for various bulk potentials of silicon and dopant concentrations. The inset illustrates how changes in band bending modify the interfacial potential profile, thereby shifting the chemical equilibrium on the electrolyte side. C) Surface charge variation as a function of bulk potential of silicon for various electrolyte concentrations. D) Corresponding potential profile for various bulk potentials of silicon and electrolyte concentrations.

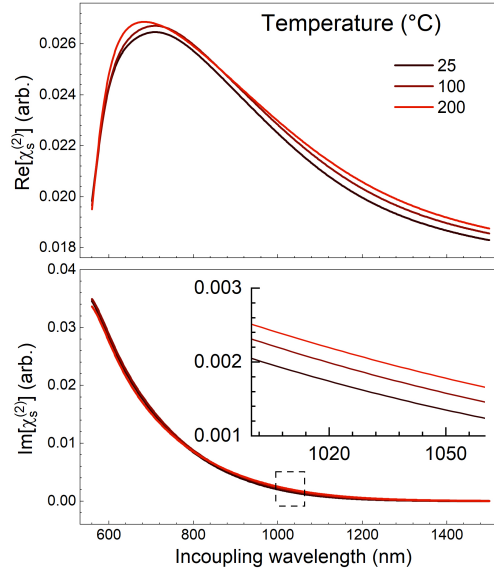


Fig. S3 Real and imaginary parts of the surface second-order susceptibility for different temperatures obtained from the linear refractive index shown in S7 based on the analytical formulation of surface second harmonic generation [55].

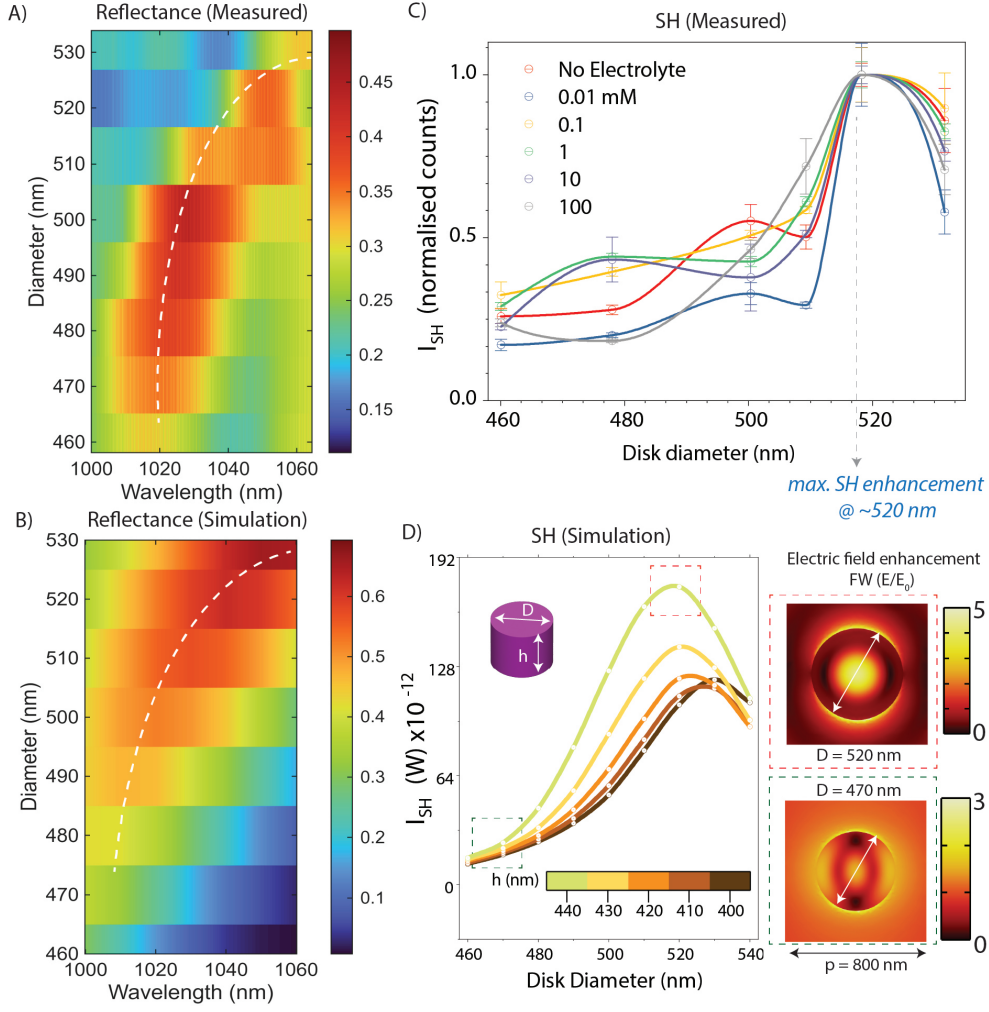


Fig. S4 Characterization of SH intensity and linear reflectance in the nanodisk array. (A) Linear optical characterization showcasing measured reflectance spectra for different nanodisk diameters at a fixed pitch of 800 nm, with Ag mirror reflectance as a reference. (B) Corresponding Comsol linear reflectance simulation for a square lattice with a pitch of 800 nm and height of 440 nm across various nanodisk diameters. (C) Measured second harmonic (SH) intensity as a function of nanodisk diameters under varying KCl electrolyte concentrations (0.01 mM to 100 mM) in DI water, normalized to the peak intensity observed for the 520 nm diameter disks. (D) Comsol simulation of SH intensity as a function of disk diameter, focusing on surface contributions to nonlinear polarization, revealing a peak enhancement at a diameter closely matching experimental trends as a function of disk diameter for a disk height of 440 nm. The red and green rectangles show the electric field enhancement for disk diameters of 520 nm and 470 nm, respectively.

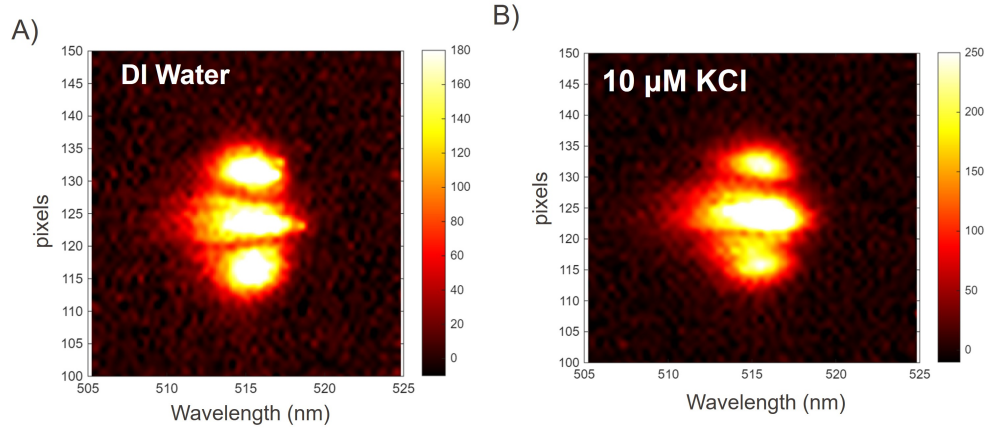


Fig. S5 Spectroscopic image of the SHG from a disk array sample placed in the cell. The electrolyte was changed in situ, and the SH intensity was measured. The time-trace of the SH intensity is shown in Figure 1 E

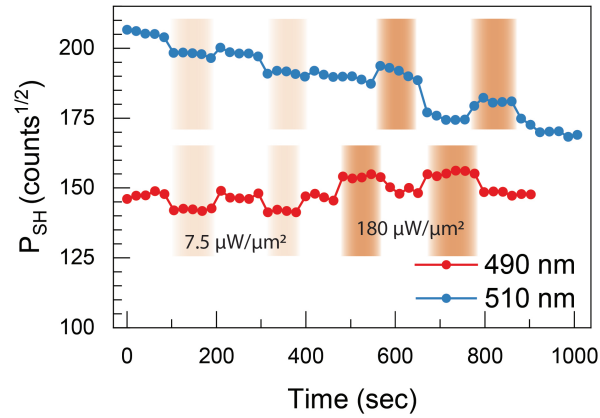


Fig. S6 Non-linear polarization during dynamic light on and off test for two SiNDs with 490 nm and 510 nm diameters under low and high pump (633 nm) irradiation, showing a decrease and an increase in SH amplitude, respectively.

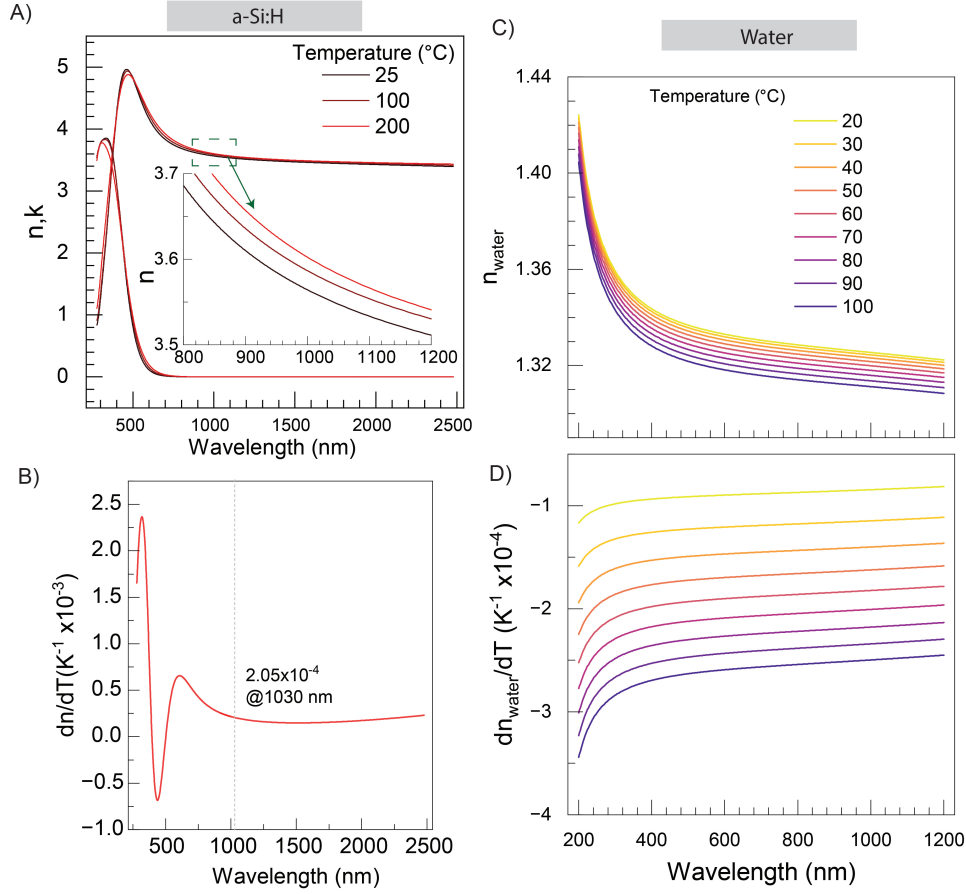


Fig. S7 Thermo-optical coefficients: A) Measured n and k values of a-Si: H films with a thickness of 440 nm under different temperatures. Ellipsometry measurements at different temperatures were carried out using an external heater. B) The real part of the thermo-optical coefficient obtained from the measurements in panel A. C) Refractive index of water at different temperatures. Reproduced from: International Association for the Properties of Water and Steam (IAPWS). Release on the Refractive Index of Ordinary Water Substance as a Function of Wavelength, Temperature, and Pressure; Erlangen, Germany, 1997. Available at: <http://www.iapws.org/relguide/rindex.pdf> D) Corresponding thermo-optical coefficients.

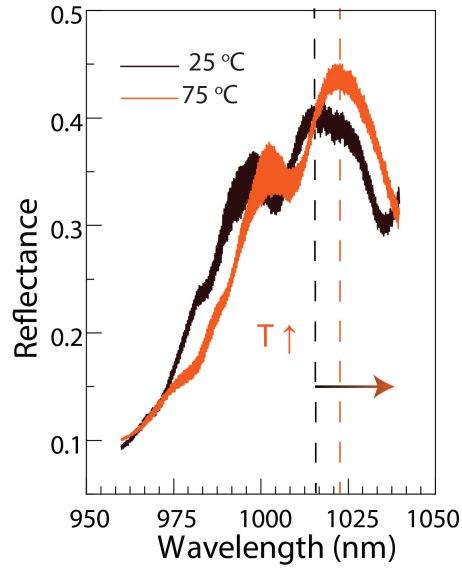


Fig. S8 Reflectance spectra for the 510 nm Silicon Nanodisk (SiND) ref spectra in Air measured at different temperatures according to S11. The temperature was varied using an external heater.

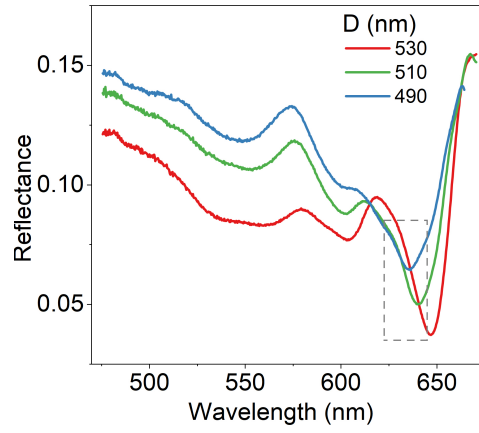


Fig. S9 The reflectance spectra reveal an optical mode near the pump wavelength (633 nm), indicating a higher absorption. The reflectance peak decreases with increasing diameter. The measurements were performed according to S11.

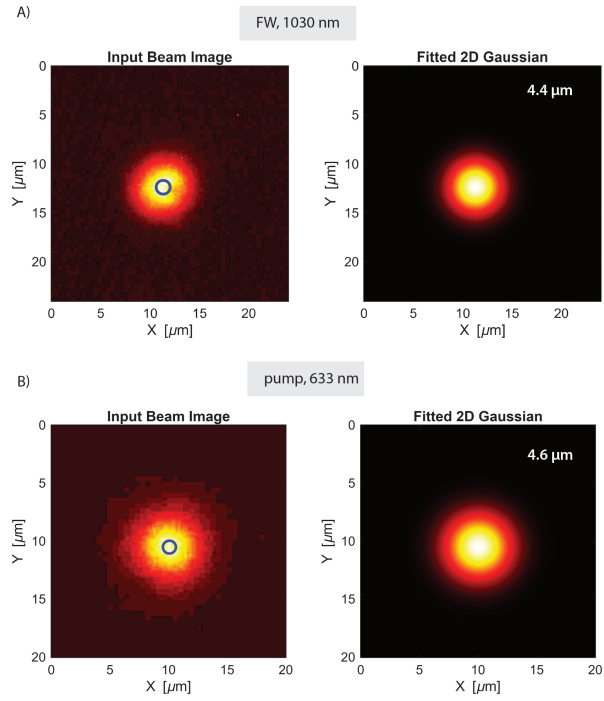


Fig. S10 Beam diameter of the FW (1030 nm) and pump (633 nm) laser obtained by the corresponding 2D Gaussian fit.

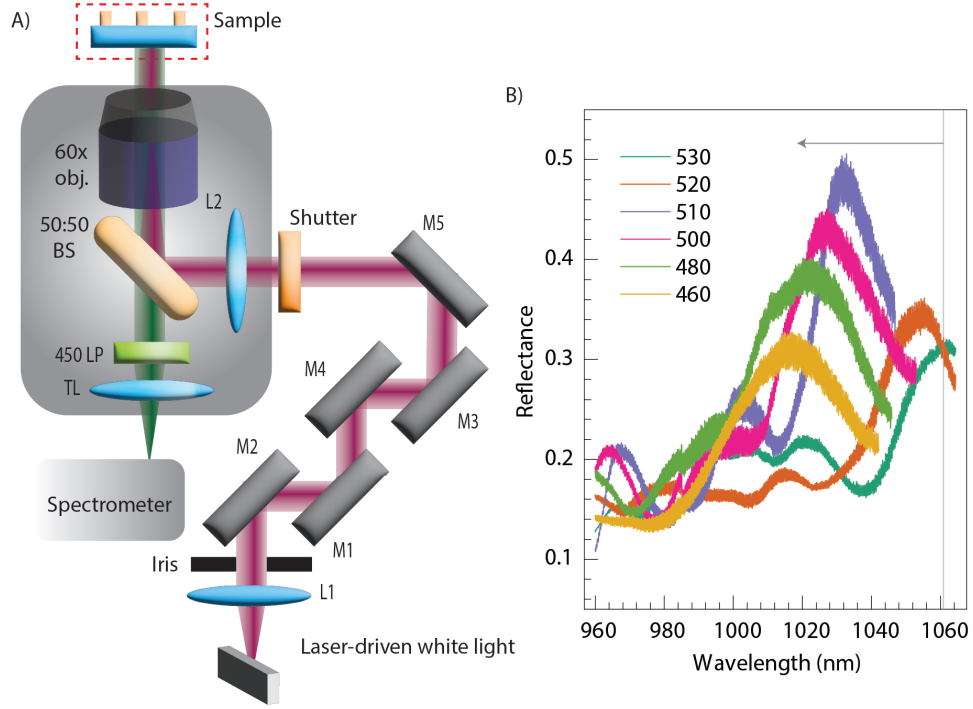


Fig. S11 Optical setup with details of the illumination and the detection paths for reflectance measurements. A) In the setup, the red-shaded beam represents the incident light, and the green-shaded beam represents the reflected light from the sample. BS = BeamSplitter, L = Lens, M=Mirror, LP= Longpass filter. B) Reflectance spectra of the silicon nanodisk array for different diameters. The arrow indicates the blue shift in the spectra with increasing disk diameter.