

Free Radical Generation from High-Frequency Electromechanical Dissociation of Pure Water

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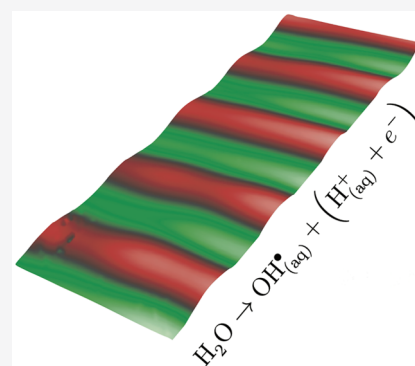
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ABSTRACT: We reveal a unique mechanism by which pure water can be dissociated to form free radicals without requiring catalysts, electrolytes, or electrode contact by means of high-frequency nanometer-amplitude electromechanical surface vibrations in the form of surface acoustic waves (SAWs) generated on a piezoelectric substrate. The physical undulations associated with these mechanical waves, in concert with the evanescent electric field arising from the piezoelectric coupling, constitute half-wavelength “nanoelectrochemical cells” in which liquid is trapped within the SAW potential minima with vertical dimensions defined by the wave amplitude (~ 10 nm), thereby forming highly confined polarized regions with intense electric field strengths that enable the breakdown of water. The ions and free radicals that are generated rapidly electromigrate under the high field intensity in addition to being convectively transported away from the cells by the bulk liquid recirculation generated by the acoustic excitation, thereby overcoming mass transport limitations that lead to ion recombination.



The search for a more efficient means for the production of free radical species such as H^\bullet , OH^\bullet , and OOH^\bullet , among others,¹ for the breakdown of perfluorinated substances, textile dyes, and other pollutants^{2,3} as a means for environmental remediation, and hydrogen as a renewable and sustainable energy source as an alternative to fossil fuels⁴ has motivated renewed interest in the dissociation of water. The free energy required to cleave the H–O–H bonds can be drawn from various means, including electrochemical,⁵ photocatalytic,⁶ or sonochemical⁷ reactions. Electrochemical reactions, i.e., water electrolysis,⁵ remains the most widely used of these techniques. Besides requiring a suitable catalyst, high electrolyte concentrations, and, in some cases, high temperatures or pressures,⁸ the necessity for the electrodes to be in contact with the bulk solution, which typically comprises highly concentrated acids/bases, make them susceptible to corrosion over time. While electrical breakdown of deionized (DI) water has been explored to directly dissociate water molecules, this typically necessitates the use of extremely large DC voltages (hundreds of kilovolts) to generate sufficiently high electric fields to induce the process (>0.3 V/Å).⁹

In a recent attempt to overcome some of these issues, Wang et al.¹⁰ proposed driving the electrolysis of pure (DI) water at substantially lower voltages by locally confining the electrochemical cell within a nanogap with a separation down to 37 nm that is considerably smaller than the Debye length (around 300 nm for DI water). By eliminating the existence of an electroneutral bulk Ohmic region, they were able to exploit two effects. The first is the significantly larger 10^7 V/m electric field arising from the overlapping electric double layers within

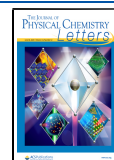
the nanogap (the so-called “deep-sub-Debye-length” region) to drive ionization of the water molecules. This is because dissociation occurs at a lower threshold electric field (i.e., a so-called “virtual breakdown” process) significantly below that for pure water where there is a dearth of ions (i.e., 0.3 V/Å) given that there is a significantly greater ion concentration in this region by several orders of magnitude. Second, such an enhancement in the polarization is accompanied by a corresponding increase in conductivity within this region, which overcomes mass transport limitations associated with ion diffusion and electromigration across the electrodes. However, their complex nanoscale electrode and nanochannel setup requires elaborate fabrication. Moreover, their throughput is considerably limited owing to the confined nanoscale region where the reaction occurs. Further, the authors themselves readily admit problems associated with bubble generation that spans the nanogap across the electrodes and their tendency to corrode, which suppresses the reaction and leads to a sharp degradation in performance.

In this work, we report a surprising discovery wherein high-frequency (10 MHz) nanometer-amplitude vibrations in the form of Rayleigh surface acoustic waves (SAWs) (electro-

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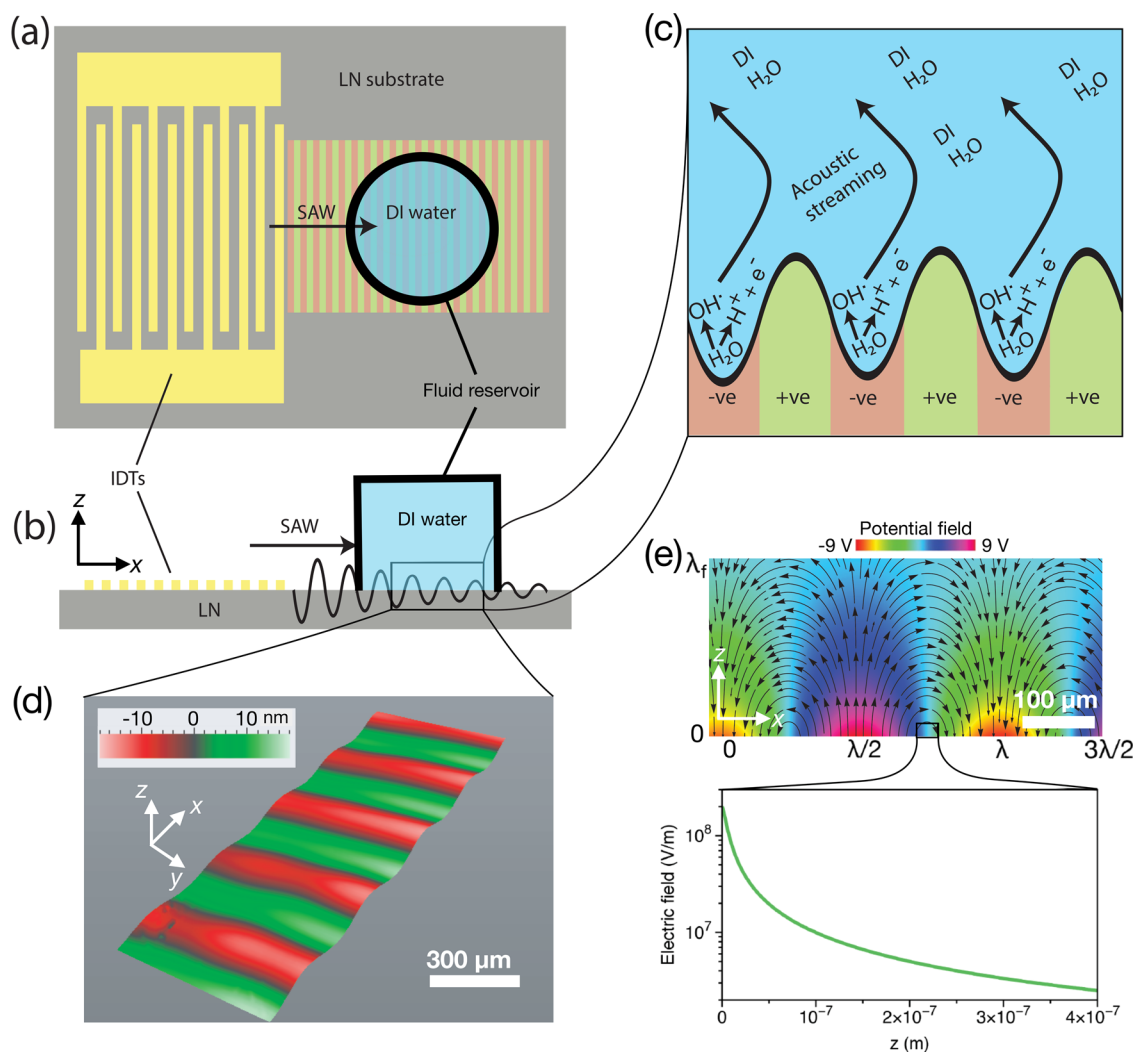


Figure 1. (a) Top and (b) side view schematics (not to scale) illustrating the experimental setup in which a SAW, generated along the piezoelectric LiNbO₃ substrate (LN) by applying an oscillating electrical signal to the IDT, is coupled into a 10 μL fluid reservoir (microchamber) of pure (DI) water. We note that the IDT is *not* in contact with the fluid or chamber at all times. (c) Magnified schematic (not to scale) showing the confined regions defined by the SAW substrate displacement—approximately 10 nm, as shown in the laser Doppler vibrometer (LDV) scan in panel d—which constitute nanoscale “electrochemical cells” with high field intensities ($O(10^8)$ V/m) where the water dissociation reaction occurs. These high field intensities are supported by (e) the numerical simulation (see the [Supporting Information](#) for details) of the electric potential (top) and calculation of a representative electric field profile immediately adjacent to the SAW substrate surface at $z = 0$ (bottom). λ and λ_f denote the wavelength of the SAW and the sound wave in water, respectively; we note that the dimensions of the call-out box in the contour plot are not to scale. The ions and free radicals that are generated are rapidly swept into the bulk of the fluid by electromigration effects as well as the accompanying acoustic streaming flow. Concomitantly, fresh water molecules are also continuously convected into the nanoelectrochemical cell region where they dissociate to produce more free radicals.

mechanical waves that are confined to and which propagate along the surface of a piezoelectric substrate) are able to drive catalyst-free dissociation of pure (DI) water at low voltages *without* the need for electrodes that are physically in contact with the water, therefore addressing many of the challenges associated with the preceding technologies. In particular, when a 10 μL DI water (resistivity 18.2 MΩ.cm; Milli-Q, Merck Millipore, Bayswater, VIC, Australia) sample, housed in a closed (sealed to minimize gas dissolution) cylindrical glass microchamber, is exposed to the acoustic excitation, i.e., the SAW, by placing it on a single-crystal piezoelectric (128° Y-X LiNbO₃; Roditi Ltd., London, UK) substrate along which the SAW propagates (Figure 1a,b; see the [Supporting Information](#) for details on the fabrication of the device, which was carried out in-house), we observe from the current–voltage (I – V)

curves in Figure 2 an increase in the current beyond a voltage of approximately 2.6 V, as measured through a voltage sweep using a two-wire probe station (10 μm tungsten needle tips) connected via a BNC cable to a sourcemeter (2450; Keithley Instruments, Cleveland, OH, United States). The larger the input power applied to the SAW device, the larger the electrolytic current observed, indicating almost an order of magnitude enhancement in the electrical conductivity. We note the placement of the reservoir 5 mm from the interdigitated transducer (IDT) electrodes (Figure 1a,b) to which an oscillating AC signal with potentials across the range 3–10 V_{rms} was applied in order to generate the SAW, whose amplitude and profile is measured using a laser Doppler vibrometer (UHF-120; Polytec GmBH, Waldbronn, Germany) as seen from the scan in Figure 1d. The reservoir is thus

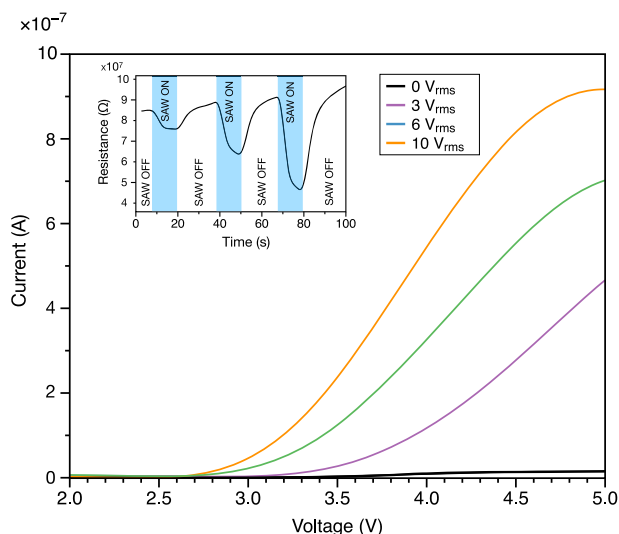
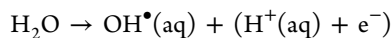


Figure 2. I – V curves for a pure (DI) water sample measured using a two-wire probe station. The current flow was monitored through a voltage sweep from 0 to 5 V, in the absence of the SAW and during SAW excitation for three different input voltages. The inset shows the in situ and reversible behavior associated with the change in electrical resistance in the fluid when the SAW is triggered on and off at the same input voltage as that used to generate the results in the main figure.

sufficiently far from the IDT to prevent any electrode contact with it although within reach of the SAW transmission (Figure 1d) given that the SAW attenuation length in the substrate is approximately 12 mm along its propagation direction for the 10 MHz frequency employed.¹¹ We also note the measurement probe wires, inserted into the reservoir as described in the Supporting Information, were in contact with the sample only to monitor the current enhancement. The separation distance between the probes was approximately 2 mm, such that any electric field generated across it is weak, thus eliminating the possibility of the participation of the probes in the breakdown of the pure water sample. Heat effects are also negligible given the short exposure durations of the sample to the acoustic radiation (typically 10 s), thus limiting the temperature increase to below 5 °C even for the highest input voltage to the device, as measured using an infrared camera (Trotec EC060 V; Emona Instruments Pty. Ltd., Melbourne, VIC, Australia).

The enhancement in the current above a voltage of approximately 2.6 V observed in Figure 2, which is close to the theoretical limiting potential of 2.38 V for a one-electron water oxidation reaction¹



while not ruling out the likelihood of other oxidation reactions (e.g., the two- and four-electron water oxidation reactions) taking place, suggests that the increase in the electrolytic current can be attributed to a concomitant increase in the electrical conductivity of the solution as a consequence of H^+ ion production upon irradiation of the water with the SAW. This was independently verified from measurement of the solution pH with a methyl red assay against a standard solution of 0.1 M sodium acetate/acetic acid buffer, wherein an increase in the acidity from pH 6.8–7 to 5.4 over a mere 10 s of SAW exposure, corresponding to an H^+ concentration of 4.2 μM , was observed (Figure S4 in the Supporting Information).

Further, we note the reversibility of the process by which the SAW modulates the conductivity of the DI water in the inset of Figure 2, wherein the conductivity can be seen to decay exponentially upon relaxation of the SAW excitation because of H^+ ion recombination. We observe though that the conductivity does not decrease to its baseline value each time, but slightly decreases on each cycle, possibly because of incremental H_2 gas production that leads to progressive trapping of bubbles at the measurement probes; such an increase in the resistance can also be seen in the onset of saturation at high voltages (10 V_{rms}) in Figure 2. Additionally, hydrogen peroxide (H_2O_2)—generated in the other half (water reduction) reaction via consumption of the electrons produced in the one-electron water oxidation reaction above—at a concentration of approximately 15 μM , comparable to the concentration of free radicals that were produced (see below), was observed through colorimetric detection (PeroxiDetect Kit, Sigma-Aldrich Pty. Ltd., Castle-Hill, NSW, Australia).

OH^\bullet free radical generation is supported by electron paramagnetic resonance (EPR) measurements. DI water samples, to which 5,5-dimethyl-1-pyrroline *N*-oxide ((DMPO) 100 μM ; Sigma-Aldrich Pty. Ltd., Castle Hill, NSW, Australia) radical traps were added, were exposed to the SAW and immediately pipetted into a 55 mm \times 10 mm \times 0.2 mm quartz flat cell, and the spectra recorded (E500 X-Band Spectrometer equipped with a ER4122 SHQ Resonator; Bruker BioSpin GmbH, Rheinstetten, Germany). OH^\bullet radicals were then observed following their reaction with DMPO. As can be seen in Figure 3, the intensity of each of the four peaks associated with the DMPO– OH^\bullet adduct increases with longer exposure times of the fluid to the SAW to at least 17 μM after 10 s.

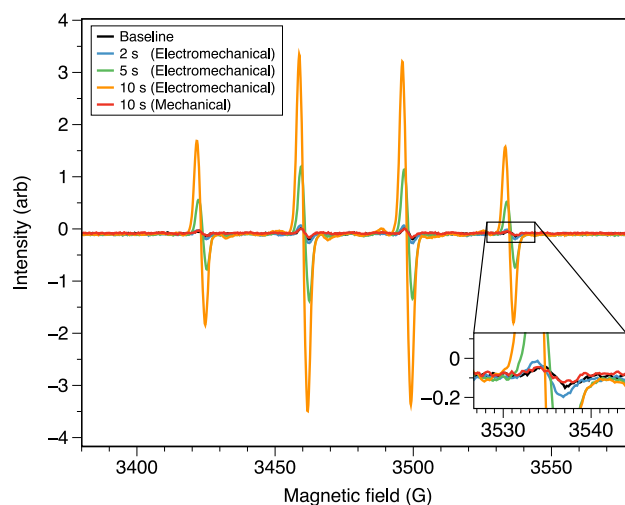


Figure 3. Electron paramagnetic resonance (EPR) measurements monitoring the concentration of the OH^\bullet radicals formed following exposure of water to the SAW (electromechanical wave) over a duration of 2, 5, and 10 s, compared to water that was only exposed purely to its mechanical component (the electrical field associated with the SAW is shielded with a thin gold layer deposited on the SAW substrate) for 10 s in which no free radicals were produced, as compared to the baseline reading. The EPR signal observed is that of the DMPO– OH^\bullet adduct, which allows the short-lived OH^\bullet radical to be quantified. The EPR settings are as follows: microwave frequency, 9.8 GHz; power, 4.74 mW; magnetic field modulation frequency, 100 kHz; and magnetic field modulation amplitude, 0.5 G.

Further indirect evidence of free radical generation by the SAW was obtained from methylene blue dye breakdown experiments given that OH^\bullet free radicals are known to oxidize the dye, leading to its decomposition.¹² Repeated exposure of the aqueous dye solution (6.75 mg/L methylene blue (1428008; Sigma-Aldrich Pty. Ltd., Castle-Hill, NSW, Australia) in 2 mL DI water) to the SAW irradiation can be seen to progressively break down the dye, as seen from its discoloration (Figure 4a), which was monitored using a UV–

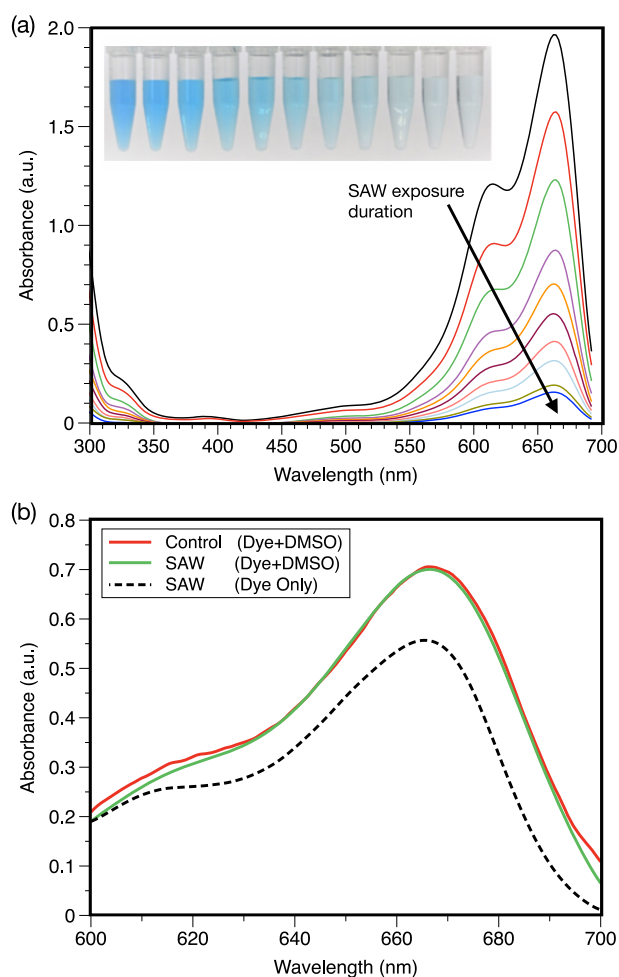


Figure 4. (a) UV–vis spectra for methylene blue dye absorption showing progressive signal reduction and hence breakdown of the dye upon continued exposure to the SAW (94.3% after 40 min), as depicted by the images in the inset which show visual discoloration of the dye as it is progressively decomposed by the SAW. (b) Absorbance measurements showing the effect of adding a free radical scavenger (DMSO) on the dye breakdown process in which the influence of the SAW in generating the free radicals which leads to breakdown of the dye is suppressed.

vis spectrophotometer (UV2700; Shimadzu Corp., Kyoto, Japan). The extent of dye decomposition $[(A_0 - A)/A_0] \times 100\%$ was found to be approximately 94.3% after $t = 40$ min and follows first-order kinetics $\ln[A] = \ln[A_0] - kt$ (Figure S5 in the Supporting Information); A_0 and A are the absorbance values measured for the untreated and treated samples, respectively, and k the reaction rate constant. To verify that the decomposition occurs through a free radical pathway due to OH^\bullet radicals generated as a consequence of the SAW-induced electrolysis of the water matrix, we repeated the

decomposition experiments in the presence of dimethyl sulfoxide ((DMSO) 102952 (>99%); Merck Millipore, Bayswater, VIC, Australia), which is a known free radical scavenger. No change in the absorption and hence decomposition of the dye was observed between the unexcited control and the sample exposed to the SAW (Figure 4b). We thus parenthetically note the potential of the SAW platform for pollutant remediation in textile effluents and other industrial wastewater samples, especially because it does not involve the addition of photocatalysts such as TiO_2 nanoparticles that necessitate their post-treatment removal.

While bulk ultrasonic waves have been known to drive sonolytic water splitting, resulting in the formation of free radicals (H^\bullet and OH^\bullet) and molecular products such as H_2 and H_2O_2 , the physical mechanism by which this occurs is primarily via acoustic cavitation in which the large energy required to break the H–O–H bonds is supplied by that released during the violent implosion of the cavitation bubbles during which extreme temperatures ($>10^4$ K) and pressures (>1 GPa) are generated.¹³ Indeed, acoustic cavitation has also long been invoked for a wide range of sonochemical reactions.^{14,15} Nevertheless, there is a significant fundamental distinction between conventional bulk ultrasonic waves (typically driven at frequencies that are in the 10–100 kHz order and no greater than 3 MHz) and the SAW (typically 10 MHz and beyond) employed in the present work. Besides existing as a *surface* wave that is confined within a depth of several wavelengths (typically $O(100 \mu\text{m})$ order) along the surface of the substrate in contrast to a *bulk* wave that is distributed and propagates throughout its thickness, cavitation is usually extremely difficult to generate at the higher ($O(10$ MHz)) SAW frequency because the threshold sound intensity needed to trigger cavitation events increases rapidly with increasing frequency^{16–18}—all the more given the considerably lower SAW powers employed, particularly in the water dissociation experiments in this work (~ 0.4 W), compared to that required for ultrasound (~ 20 W).¹⁹

We support our observations of the absence of any notable cavitation bubbles in the SAW-driven process by measuring the sonoluminescence (or lack thereof) accompanying the SAW excitation of the nondegassed DI water sample in a dark room under the same conditions, albeit in a sessile drop atop the SAW substrate open to the atmosphere as opposed to within a closed microchamber, because intense light emission is well-known to accompany acoustic cavitation events in pure water.^{20,21} The lack of a discernible signal from a typical sonoluminescence detection setup involving a photomultiplier tube ((PMT) Hamamatsu Photonics K.K., Hamamatsu City, Shizuoka Prefecture, Japan) coupled with a high-voltage power supply (Hamamatsu) and oscilloscope (Wavejet 332/334; LeCroy, Chestnut Ridge, NY, United States)^{22–24} again confirms the absence of cavitation within the limits of detection given the likelihood that the presence of dissolved gases in the nondegassed sample act as nucleation sites for cavitation to occur. However, as such a negative observation does not completely rule out the possibility of cavitation in its entirety, we also performed sonochemiluminescence measurements following SAW excitation of the DI water sample containing luminol solution (Sigma-Aldrich Pty. Ltd., Castle Hill, NSW, Australia), whose molecules react with OH^\bullet radicals to emit light.²⁵ The experiments were carried out under various atmospheric (air-saturated, air-depleted, and nitrogen-purged then degassed) conditions; details of the

experimental method and degassing procedure can be found in the [Supporting Information](#). The generation of free radicals in these experiments, albeit in the absence of cavitation, are evident from the sonochemiluminescence signals above the baseline detected using the same PMT setup ([Figure S6](#) in the [Supporting Information](#)), even under air-saturated conditions where sonochemiluminescence from hydroxylated luminol may be partially quenched. Over longer exposure times beyond 1 min, we note the sonochemiluminescence signals associated with the air-depleted and nitrogen-purged conditions to approach that of the air-saturated condition (not shown) as the ambient gases eventually dissolve into the sample.

Together with the dye decomposition results in the presence of DMSO in [Figure 4b](#) (because cavitation is known to also result in breakdown of the dye²⁶), these observations from the sonoluminescence and sonochemiluminescence experiments provide conclusive evidence to rule out the existence of cavitation and hence its role in the generation of free radicals under SAW excitation. Instead, it is possible that the evanescent electric field in the liquid region immediately adjacent to the surface of the substrate, which is associated with the electromechanical coupling of the SAW, plays a role in the dissociation of the DI water. Such fields have already been observed to be responsible for a range of SAW microfluidic actuation^{27–31} phenomena, such as on-chip nanotube or nanowire manipulation, including their alignment and deagglomeration;^{32–39} aerosol charging;⁴⁰ bandgap manipulation and exfoliation of piezoelectric two-dimensional nanomaterials;^{41–43} and molecular orientation of crystal lattices.⁴⁴ Nevertheless, this evanescent electric field alone, which alternates every half wavelength ($\lambda_{\text{SAW}} = 396 \mu\text{m}$ at 10 MHz) and which constitutes the virtual electrodes that drive the electrolytic process ([Figure 1c](#)), is, in itself, inadequate to directly induce the breakdown of pure water.

We thus postulate that the full electromechanical coupling is involved in the water dissociation process. As depicted in [Figure 1c](#), the surface undulation as the SAW traverses the substrate creates “valleys” that constitute “nanoelectrochemical cells” with depths commensurate with the SAW amplitude ($\sim 10 \text{ nm}$) that facilitate the physical trapping of water within highly polarized deep-sub-Debye-length confinement zones. These zones are akin to the nanogap electrochemical cells in [ref 10](#), albeit dynamically created by the SAW, therefore circumventing the need for complex nanofabrication of both the nanoscale electrodes or the nanochannels that separate them. We note that the enhanced evanescent electric field in this region, typically on the order 10^8 V/m (1 V across 10 nm; see, for example, [Figure 1e](#), in addition to [refs 43 and 45](#) where similar values for the intensity of the SAW evanescent electric field are reported), is at least comparable to, if not one order of magnitude larger than the $O(10^7) \text{ V/m}$ electric field across the nanogap electrode in [ref 10](#) sufficient to drive self-ionization of water as a virtual breakdown process.⁹

Moreover, the enhanced local field within the confinement of these nanoelectrochemical cells also drives fast electromigration of the ions and free radicals generated within them during each half AC cycle out into the bulk of the fluid so as to prevent their recombination during the next half cycle when the polarization is reversed, as indicated by the short electromigration time scale $\mathcal{L}_{\text{NRT}}/DFE \approx 10^{-9} \text{ s}$ compared to the typical millisecond to microsecond ion recombination time scale^{46,47} and the typical microsecond to nanosecond

lifetime of the free radicals;⁴⁸ here, $\mathcal{L}_{\text{N}} \approx 10^{-9} \text{ m}$ is the characteristic length scale associated with the depth of the cell out of which the ions have to migrate to reach the bulk, R the molar gas constant, T the absolute temperature, \mathcal{D} the ion diffusivity, F the Faraday constant, and $E \approx 10^8 \text{ V/m}$ the local electric field. This is in contrast to the much longer diffusion time scale $\mathcal{L}_{\text{B}}^2/\mathcal{D} \approx 10^{-3} \text{ s}$ for conventional electrolysis in macroscopic systems in which the electric field is typically screened by the Debye layer, which means that the ions and free radicals that are generated essentially recombine before they are able to diffuse away across the bulk of the fluid to the counterelectrode over a length scale of $\mathcal{L}_{\text{B}} \approx 10^{-3} \text{ m}$. In addition, the acoustic streaming (nonzero time-averaged momentum flux arising from the pressure and viscous fluctuations associated with the sound wave propagation in the fluid)⁴⁹ that arises as a consequence of viscous attenuation of the energy leaked into the water phase by the SAW also plays a role in overcoming the transport limitation of the ions and free radicals generated within the cell. More specifically, the long-range convection facilitated by this acoustically driven recirculatory flow within the fluid transports the ions and free radicals away into the bulk of the fluid while continuously replenishing the nanoelectrochemical cell regions with fresh water molecules where they further dissociate. This is confirmed by suppressing the electric field component of the SAW through the deposition of a thin gold layer on the SAW substrate (thus leaving behind only a pure mechanical wave, i.e., the acoustic component of the SAW), in which case no free radicals (such as that evidenced in [Figure 3](#)) were observed—a result that also provides a further distinction between the present platform and that of cavitation-induced sonolysis where free radicals are generated purely because of the mechanical component associated with the bulk ultrasonic excitation.

In summary, we have discovered a unique mechanism by which pure water can be dissociated via the electromechanical coupling arising from MHz-order surface vibrations in the form of SAWs at low voltages without requiring catalysts or contact with electrodes. The evanescent electric field of the SAW in the water phase and the physical waveform of the SAW on the surface of the piezoelectric substrate act in concert to produce virtual electrodes that give rise to confined regions with alternating polarities over every half wavelength. The nanometer-order vertical dimension of these virtual electrochemical cells, as stipulated by the amplitude of the SAW, is substantially below the Debye length, and therefore constitutes highly polarized regions with high field intensities ($O(10^8) \text{ V/m}$) that drive field-assisted self-ionization and hence virtual breakdown of water. The ions and free radicals that are generated are then transported away from these regions by the long-range convection facilitated by the acoustic streaming that accompanies the SAW excitation of the fluid to prevent their recombination. Given the low costs (typically US\$1/device by exploiting the economies of scale associated with mass nanofabrication) and chipscale dimensions of the devices, we anticipate the possibility for scaling the process to achieve industrial-scale throughput through massive parallelization. Moreover, the free radical generation mechanism reported here could also open up entire new possibilities for cavitation-free sonochemical synthesis that was recently speculated⁵⁰ but which has yet to be demonstrated.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c01227>.

Fabrication and characterization of the SAW device, method for the sonoluminescence and sonochemiluminescence experiments, description of the numerical model used to simulate the SAW evanescent electric field, and supplementary figures (PDF)

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Notes

The authors declare no competing financial interest.

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