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Revisiting the Effect of Air-Water Interface of Ultrasonically Atomized Water Microdroplets on H$_2$O$_2$ Formation

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ABSTRACT: Studying chemical processes at air-water interface is always challenging. A recent report claimed that H$_2$O$_2$ was formed spontaneously on the surface of condensed water microdroplets. However, a newer report concluded that the detected H$_2$O$_2$ in the previous report could originate in part from the water vapor source that involved ultrasonic atomization of liquid water. Here, this phenomenon is reinvestigated regarding the influence of ultrasonic cavitation, surface modification of droplets and solutes in the bulk liquid on the H$_2$O$_2$ production. When the droplet surfaces were modified by surfactants, the H$_2$O$_2$ production did not change, whereas adding gases or inorganic compounds to the bulk solution caused significant changes in H$_2$O$_2$ production. These results confirm that H$_2$O$_2$ formation originates from cavitation in the bulk solutions. It is concluded that the air-water interface of water microdroplets itself does not generate H$_2$O$_2$.

INTRODUCTION

Air-water interfaces are expected to favor some chemical processes, as compared to the bulk solution[1-3], yet gathering more experimental evidence is still challenging. Recently, Zare and coworkers reported that H_2O_2 was formed spontaneously when condensing water vapor from the air onto inert substrates to form water droplets, and a strong electric field existing at the air-water interface of the droplets was suggested as the origin of H_2O_2 formation.[4] Shortly afterwards, Mishra and coworkers pointed out that the H_2O_2 production in the previous experiment was an experimental artifact.[5] They contrasted the H_2O_2 detection for water droplets produced from condensing two separate sources of water vapor: one generated by an ultrasonic humidifier as similarly used in the Zare et al study[4], and another created by gently heating water. The droplets condensed from the former did contain H_2O_2 while the later did not.

Scheme 1. Platforms for studies of H_2O_2 formation from water droplets.
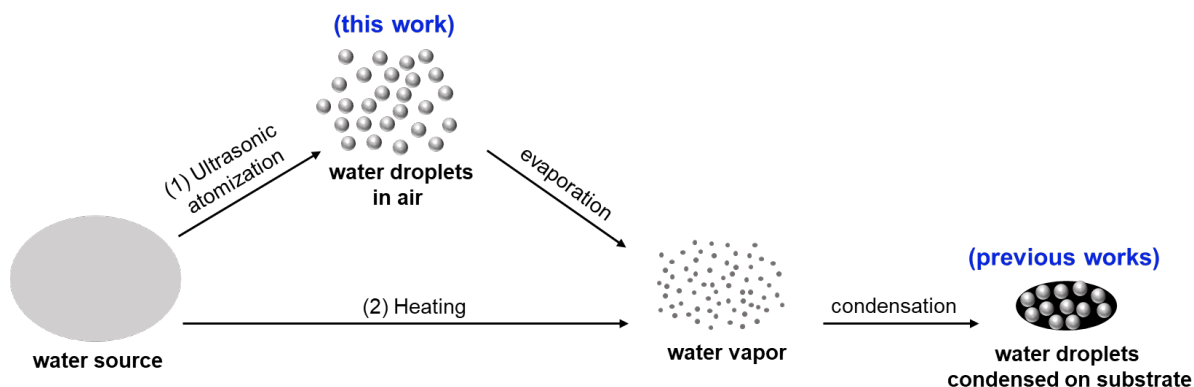
While there are discrepancies in detected amount of H_2O_2 between these two early studies, the observed phenomenon deserves more confirmation from different approaches and considerations. In this paper, the production of H_2O_2 by the ultrasonic mist maker (also known as humidifier) was studied and discussed relative to the two previous works (Scheme 1). More importantly, the H_2O_2 formation was reinvestigated as to whether it originates from the air-water

interface of the water droplets. Unlike the previous experiments, wherein the ultrasonic humidifier created water droplets, which in turn were allowed to evaporate at room temperate to provide water vapor for later condensation, our experiments directly utilized these droplets to avoid any potential side effects from the substrates or environmental contaminations (Scheme 1 and Figure 1a). The water droplet surfaces were then modified by adding surfactants to the bulk solution, and the effect of surface modification on the H_2O_2 formation was examined.

EXPERIMENTAL SECTION

In this work, we used a commercial ultrasonic mist maker (1.7 MHz, 12 W) as a source of ultrasound to generate water droplets. We want to clarify that the humidifiers used in previous works[4, 5] and the mist makers used in this work have similar ultrasonic transducers for generating water droplets, but the humidifiers allow the droplets to evaporate to control humidity. However, the "ultrasonic humidifier" and "ultrasonic mist maker" names are usually used interchangeably. To avoid contaminations from air-borne chemicals[6] or the transducer heads, chemical resistance polypropylene tubes containing mili-Q water, sealed by septa, were used as a containers for droplet generation (Figure 1a, sample A). As MHz ultrasound from the transducer propagated through the tube, it continuously created numerous water droplets inside the tubes. When different surfactant solutions were irradiated instead of pure water, these droplets should contain the surfactants, which should change their surface properties.

In a typical experiment (Figure 1a, sample A), a sealed tube containing 3 mL of water was placed at 1 cm above the ceramic disc of the ultrasonic transducer, which was immersed in a 2.5 L water bath (see Figure 1a, Scheme S1 and Movie S1 in the SI). During ultrasonic irradiation, a protuberance (around 1 – 2 cm height) was formed at the water surface, and water droplets were injected from the protuberance. Each droplet had a lifetime of few seconds before it fell back

into the solution. The tube underwent ultrasonic irradiation for 6 hours, allowing sufficient accumulation of H_2O_2 for accurate analysis. Finally, the aliquot from the tube was directly analyzed by peroxide test strips and titration with potassium titanium oxide oxalate (PTO) (see SI for experimental details). We notice that the temperature of the water in the tube rose from room temperature to about 34 °C within 3 minutes, then the water bath kept the sample at that temperature for the rest of the experiment. A 1.28 W acoustic power dissipated into the reaction solution was measured by calorimetry method (See SI, section 1.3 and Figure S4).

In the control sample, sample B in Figure 1a, a polyethylene stopper was placed at the water surface to prevent the formation of the protuberance and water droplets. Sample B was irradiated by the same ultrasound source for 6 hours. Due to a low concentration detected in the tube, the amount of H_2O_2 was then quantified by titration with Amplex® red reagent (see SI for experimental details).

To vary the amount of dissolved oxygen in water in other typical samples (as reported in Figure 3b), the tubes containing 3 mL of water were sealed by septa and purged with either N_2 or O_2 gas for 30 min. Then, the amount of dissolved oxygen in the water was measured by a LaMotte™ dissolved oxygen kit (see results in Table S1).

RESULTS AND DISCUSSION

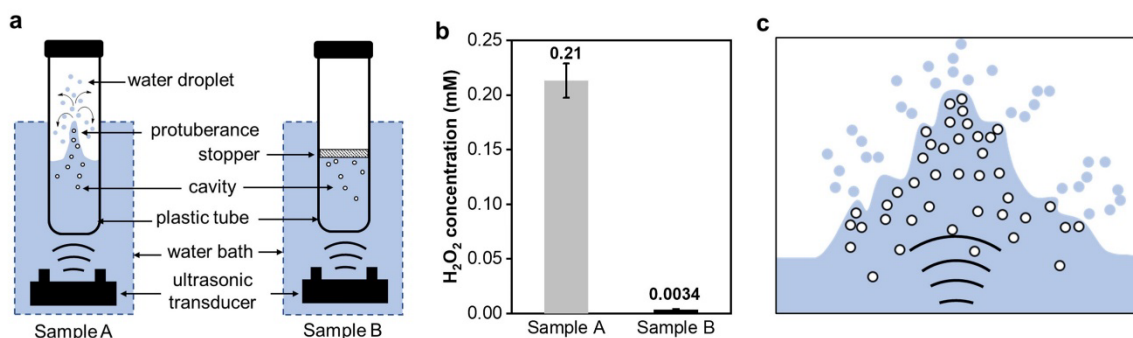### Effect of ultrasound on H_2O_2 formation

Figure 1. Formation of H_2O_2 from ultrasonic irradiation of water. (a) Experimental setup with both open and isolated surface water. (b) Detected H_2O_2 in 3 mL of water in samples A and B after 6 h irradiation by 1.7 MHz ultrasound. The 3 mL water in sample A or B absorbs an ultrasound power of 1.28W (c) Depiction of acoustic cavitation and ultrasonic atomization when focused ultrasound encounters the water surface in sample A. Sample B has cavitation, but not protuberances nor droplets.

First, the effect of ultrasound on H_2O_2 formation in our setup was investigated. In both samples shown in Figure 1a, propagation of ultrasonic waves from the transducers through the water baths and the polypropylene tubes created acoustic cavities in the tubes. H_2O_2 was detected in both sample A and B (Figure 1b). The explanation for this result is sonolysis of water and thermolysis of dissolved O_2 create active radicals such as $^\bullet H$, $^\bullet OH$ and $^\bullet OOH$, which in turn react to form H_2O_2 and H_2.[7-9] These processes are driven by very high temperatures and pressures of the localized hot spots which are formed when these cavities collapse. Although sonochemistry is usually carried out at frequencies of 10 – 100 kHz,[8] and the fact that 1.7 MHz frequency used in this and the two previous studies[4, 5] should create less energetic cavities than those commonly used frequencies, [8, 10] the 1.7 MHz source is still sufficient to drive sonochemistry in water and create H_2O_2. We herein provide a precautionary alert that ultrasonic humidifiers used as household products can generate traces of H_2O_2. Sample A with an open water surface and

sample B with an isolated surface were utilized to compare the effect of protuberances and droplets on H_2O_2 formation. As shown for sample A, the acoustic radiation force creates a protuberance at the water surface and the coherent interaction between the waves incident on and reflected from the water surface results in the formation of numerous cavitation bubbles within the protuberance (see illustration in Figure 1c).[11] According to cavitation-wave theory[11], acoustic emissions from the cavitation bubbles along with capillary waves on the water surface enhance the breaking of capillary wave crests and facilitate the pinch-off of droplets. For sample B, the water surface is isolated by the stopper, which prevents the formation of protuberances and droplets. The amount of H_2O_2 generated in samples A and B is quite different and the difference results from the fact that sample A has both protuberance and droplets. Since the formations of the protuberance and water droplets are inseparable, it is impossible to evaluate the relative significance of the cavities in the protuberance and the air-water interface of the water droplets in the H_2O_2 formation. If the air-water interface of the water droplets produced H_2O_2, the droplets would finish their lifecycle (in the order of seconds before falling back to the bulk solution) in the tube, and therefore would also increase the amount of H_2O_2 in the bulk solution. As mentioned above, Mishra and coworkers confirmed that cavitation generated by the ultrasonic humidifier contributes to H_2O_2 production and that the air-water interface of the condensed water droplets does not produce H_2O_2.[5] Thus, at this point the explanation for our results in sample A, as well as their results, is that the protuberance creates a high concentration of cavities, which crucially contribute to the observed H_2O_2 production. Sample B has cavitation, but there is no protuberance for concentrating cavities, resulting in low H_2O_2 production. Besides, sample A has a better gas mixing due to the open surface and protuberance's dynamic, hence more O_2 is dissolved for more H_2O_2 formation. Note that Mishra and coworkers' conclusions were drawn

from analyzing condensed droplets from the water vapor source evolved ultrasonic irradiation; therefore, the current work focusing on the ultrasonically atomized droplets should follow the same principle. To reconfirm and gain more insights into this phenomenon, we chemically modified the surface of water droplets to evaluate its effects on H_2O_2 production.

Effect of the electric field at the air-water interface on H_2O_2 formation

To be independent from Mishra and coworkers' conclusions[5], we initially hypothesize that both cavitation and droplet surfaces contribute to H_2O_2 formation. As we confirmed above, the former clearly creates H_2O_2, and the latter is discussed below. In a set of experiments similar to that on sample A, surfactant solutions with concentrations well below the critical micelle concentrations, were added into the tubes; we expected that the surfactants would alter the pristine air-water interface of the droplets but not the cavitation dynamics in the solution.[12, 13] Cationic, anionic and non-ionic surfactants as cetyltrimethylammonium chloride (CTAC), sodium dodecyl sulfate (SDS), and triton X-100 respectively, were used to modify the surface of water droplets. As ionic surfactants adsorb at water droplet surfaces, they create electric double layers and eventually strong electrostatic fields at these surfaces. Nonionic surfactants are not our focus as they adsorb at the surfaces but do not create electrostatic fields. A control experiment with triton X-100 solution was conducted to validate whether its adsorption to water droplet surface could alter the H_2O_2 formation. This control experiment yielded a similar amount of H_2O_2 to the pure water sample (see Figure S8). We then focus on experiments with ionic surfactants. It was reported that at the concentration of above 50 µM for both dodecyltrimethylammonium bromide (similar structure to CTAC) and SDS, these surfactants effectively adsorb at surfaces of cavitation bubbles and partially quench $^\bullet$OH radical production, thereby reducing H_2O_2 production.[8, 12] As the concentration of surfactants was set in the range of 5 nM to 50 µM in our experiment, we can

ensure that H_2O_2 formation from cavitation is the same for all samples presented in Figure 2. This condition allows us to evaluate only the influence of air-water interface on H_2O_2 production.
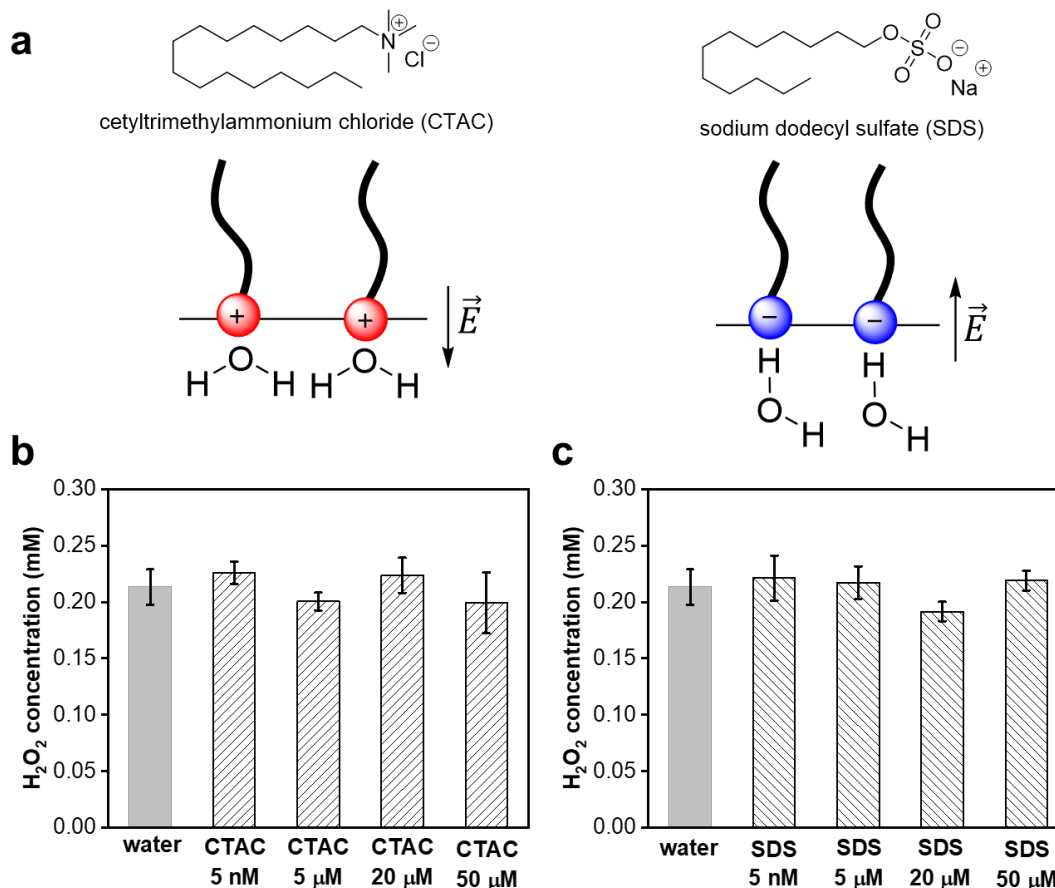

Figure 2. Modifying droplet surfaces with surfactants does not change H_2O_2 production. (a) CTAC and SDS surfactants used in this study and the simplified presentations of their enhancement of the electrostatic field and water orientation near the interface as compared to clean air-water interface. Note that the hydrogen bonds between the water molecules and surfactant head groups may interfere the well alignment of water with the electric field. (b, c) H_2O_2 production when using CTAC and SDS at different bulk concentrations. Reaction conditions: 3 mL of surfactant solution, 6 h irradiation of 1.7 MHz ultrasound at room temperature. Error bars represent one standard deviation of the mean.

For a surfactant solution with a bulk concentration of 50 μM, the surface coverage is less than 10% of maximum surface coverage.[14] Since the ultrasonically atomized droplets are pinched off from the bulk, they have a comparable surfactant concentration to the bulk concentration. As the droplets in our experiment are quite large, about 7.2 ± 3.3 μm in diameter (see SI, section 1.4 and Figure S1), their surface coverage is expected to be close to the surface coverage of a flat surface of a bulk surfactant solution. Also, previous studies showed that despite of this low surface coverage, surfactants are still capable of altering the pristine air-water interface.[14, 15] In those studies, vibrational sum frequency generation spectroscopy on the air-water interfaces of similar surfactant solutions with a comparable concentration and surface coverage showed that interfacial water molecules experience a large electrostatic field, resulting in a strong alignment, as compared to those at a clean air-water interface.[14, 15] The presence of ionic surfactants and their counterions at the interfaces creates ionic double layers that induce a much stronger electric field than the neat air-water interface does.[14, 16] Therefore, it is expected that the interfacial water in the surfactant-added water droplets should experience a larger electric field. According to Zare and coworkers[4], the electric field at air-water interface is the driving force for ionizing OH^- anions and forming $^\bullet OH$ radicals. Eventually, the radicals recombine to form H_2O_2. In our work, as we increased the surfactant concentration, we expected a rise in the strength of electric field at the interface; however, we did not see any noticeable changes in H_2O_2 production (Figure 2). Note that our control experiments confirmed that the presence of surfactants does not interfere the H_2O_2 characterization by the PTO method. The oxygen of the interfacial water molecules points towards the air for the cationic surfactant or towards the bulk for the anionic version (see Figure 2a).[17] Note that this description is already simplified as the local water molecules near the interface may form hydrogen bonds with the SDS head groups and not have well alignments

with the electric field. When moving from one surfactant to another, the electric field flips and interfacial water molecules change their orientation; however, we did not see any influence on the H_2O_2 production. These results indicated that modifications of the air-water interface of water droplets have no effect on H_2O_2 production, which leads to the conclusion that H_2O_2 formation does not depend on the electric field at the air-water interface.

Effect of solutes in the bulk liquid on formation of H_2O_2

In contrast, the bulk concentration of dissolved oxygen and inorganic compounds in water liquid has large effects on H_2O_2 production. With regard to inorganic solutions used in this study, it is known that KCl and NaOH solutions have depletion of their ions at the air-water interface while HCl and NaSCN solutions have the opposite effect for H^+, Cl^- and SCN^-.[18, 19] These ion adsorption and desorption at air-water interfaces are insignificant when their bulk concentrations are well below 1 M. Their adsorption at the water surface is much weaker than the adsorption of surfactants. Thus, we expect that these inorganic compounds do not cause surface modification of the water droplets, and their behavior in the bulk is more important as they interfere the sonochemistry of water. These solutes can react with $^•H$ and $^•OH$ radicals initially generated from water sonolysis and influence the combination path of $^•OH$, therefore, form more or less H_2O_2 (Figure 3a).[8] Figure 3b shows that the H_2O_2 formation increases with the amount of dissolved oxygen in bulk water (see experimental section and Table S1 for concentrations of dissolved oxygen). The O_2 is expected to diffuse into the cavitation bubbles where it can undergo thermolysis to form oxygen atoms, which can then react with water to form $^•OH$ radical. The O_2 could also react with hydrogen atoms to form hydroperoxyl radical, which can combine with $^•OH$ radical to form H_2O_2 (see Figure 3a).[7, 20] The nonvolatile solutes react with hydrogen atoms and $^•OH$ radicals at the boundary of the cavities or in the bulk after the cavities collapse.[21] As

demonstrated in Equation 3 and 4 in Figure 3a and experimental data for KCl and HCl solutions in Figure 3c, the Cl⁻ ion in low pH solution quenches •OH radicals, leaving fewer •OH radicals for producing H_2O_2. As expected, the SCN⁻ ion also quenches •OH radicals, resulting in lower production of H_2O_2 (see Equation 5 in Figure 3a). In contrast, the OH⁻ ions in NaOH solution quench hydrogen atoms, which favors H_2O_2 formation (see Equation 6 in Figure 3a). More experimental data and explanation are provided in Figure S5 and Table S2 in the SI. All these results confirm that cavitation in the bulk is the origin of H_2O_2 formation.
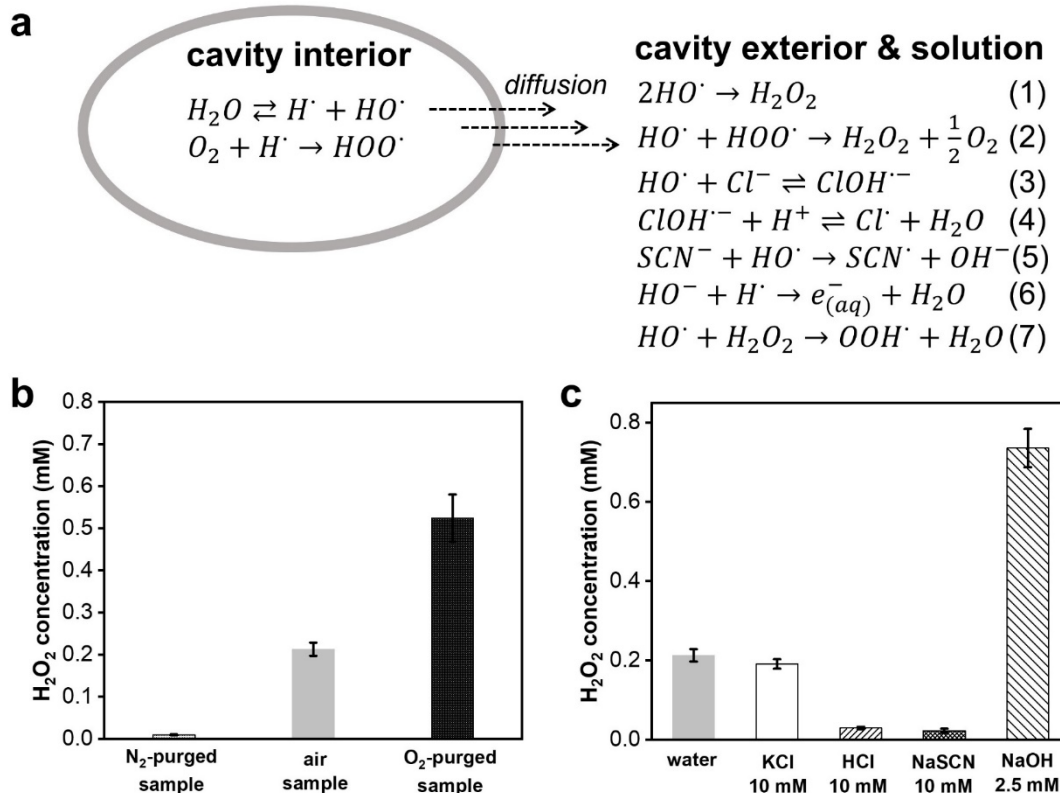

Figure 3. H_2O_2 production when using different solutes in the bulk liquid. (a) chemical processes during cavitation. (b, c) H_2O_2 production when using various gases and organic compounds. Reaction conditions: 3 mL of aqueous solution, 6 h irradiation of 1.7 MHz ultrasound at room temperature. Error bars represent one standard deviation of the mean.

Relating to the results observed in previous works

Combining all above experimental evidence, we conclude that the air-water interface does not produce H_2O_2, and that the detected H_2O_2 comes from sonolysis of water. The ultrasonic humidifier used in the Zare et al study[4] must generate H_2O_2, and this H_2O_2 evaporated from either the water reservoir (the part that experiences the ultrasound) of the humidifier or the atomized droplets. Eventually, the vapor H_2O_2 might co-condense with the water vapor to form water droplets on the substrates, resulting in detection of H_2O_2 in the condensed droplets. Unfortunately, the exact kinetics of H_2O_2 formation from the humidifier in that study is unknown to us, hence we cannot use our understanding to completely interpret experimental results in that work. We do, however, attempt to provide some insights that could generally explain the previous observation. Zare and coworkers observed a rise and fall in H_2O_2 production when the microdroplets grew. The rise could come from the increasing amount of H_2O_2 vapor being fed to the gas chamber in their experiment when the humidifier was turned on. Our kinetic study shows that the rate of producing H_2O_2 is high at the early operating time of the humidifier (see Figure S6); then the production reaches a plateau because H_2O_2 can quench the $^\bullet OH$ radical efficiently[22], and suppress any further formation of H_2O_2 (see Equation 7 in Figure 3c and Figure S7). The fall of H_2O_2 detection at later times of condensation (i.e., 2 – 10 min as reported) in that study could come from a slower rate of H_2O_2 condensation on the water droplets as the condensation progressed. Note that H_2O_2 has a boiling point of 150 $^\circ$C, thus it condenses faster than water at early times of the condensation. We suspect that the higher H_2O_2 detection observed for higher humidity in the Zare et al study[4] could come from the condition that the ultrasonic humidifier was allowed to run for a longer time, and it fed more H_2O_2 to the chamber storing water vapor. The variation in condensation conditions affects the H_2O_2 production observed in condensed water droplets. There is a discrepancy in H_2O_2 detection between the

Mishra (reported as ~ 1 μM)[5] and Zare (0.5-3.9 ppm or 15-115 μM)[4] groups, probably because the former used a much larger chamber (a glove box) that diluted H_2O_2 concentration in the air, resulting in less H_2O_2 condensing in water droplets. In our experiment, the amount of detected H_2O_2 is much larger (~ 220 μM after 6 h irradiation) because the ultrasonic irradiation is longer, and our simple experimental design avoids losses of H_2O_2 during condensation. In a related study[23], Zare and coworkers also reported that H_2O_2 was detected from water droplets produced via pneumatic spraying. However, Mishra and coworkers stated that air-borne ozone, pre-existing in the environment, is the source of H_2O_2 formation.[6] The sprayed water droplets have high surface areas for higher mass transfer of ozone into water, and the decomposition of ozone in water can form H_2O_2. In control experiments without air-borne ozone, Mishra and coworkers did not detect H_2O_2 in sprays (detection limit > 250 nM), and they concluded that the air–water interface did not spontaneously produce H_2O_2. Although we used a different approach of interface modification to study the phenomenon, our conclusion is well-aligned with their conclusion.

CONCLUSION

In conclusion, H_2O_2 detection described in the report by Zare and coworkers is expected to be dependent on the conditions of ultrasonic irradiation and properties of the bulk solution used in the ultrasonic humidifier. The conclusion that the droplet air-water interface generating H_2O_2 in that study may result from an experimental artifact. The physical insights from our work can explain experimental observations in both previous studies[4, 5].

ASSOCIATED CONTENT

Supporting information

Experimental details: chemicals and instruments, H_2O_2 characterization, acoustic power measurement, droplet size measurement, optical microscope image of water droplets, and UV-vis spectroscopic data.

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Notes

The authors declare no competing financial interest.

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