Superhydrophobic Surfaces as a Source of Airborne Singlet Oxygen through Free Space for Photodynamic Therapy

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ABSTRACT: A superhydrophobic (SH) sandwich system has been developed to enable “contact-free” airborne singlet oxygen (\(^{1}\text{O}_2\)) delivery to a water droplet. The contact-free feature means that the sensitizer is physically separated from the droplet, which presents opportunities for photodynamic therapy (PDT). Trapping of airborne \(^{1}\text{O}_2\) in a H\(_2\text{O}\) droplet residing on a lower SH surface was monitored with 9,10-anthracene dipropionate dianion by varying distances to an upper \(^{1}\text{O}_2\)-generating surface. Short distances of 20 \(\text{µm}\) efficiently delivered airborne \(^{1}\text{O}_2\) to the droplet in single-digit picomolar steady-state concentrations. Delivery decreases linearly with distance, but 50% of the \(^{1}\text{O}_2\) steady-state concentration is trapped at a distance of 300 \(\text{µm}\) from the generating surface. The 1270 nm luminescence intensity was measured within the SH sandwich system, confirming the presence of airborne \(^{1}\text{O}_2\). Physical quenching of \(^{1}\text{O}_2\) to ground-state \(^{3}\text{O}_2\) by the water droplet itself and both physical and chemical quenching of \(^{1}\text{O}_2\) by the water droplet containing the trap 9,10-anthracene dipropionate dianion are observed. Unlike a majority of work in the field of PDT with dissolved sensitizers, where \(^{1}\text{O}_2\) diffuses short (hundreds of nanometers) distances, we show the delivery of airborne \(^{1}\text{O}_2\) via a superhydrophobic surface is effective through air in tens of millimeters distances to oxidize an organic compound in water. Our results provide not only potential relevance to PDT but also surface bacterial inactivation processes.

KEYWORDS: singlet oxygen, physical quenching, superhydrophobic surface, liquid droplet, near IR detection, photodynamic therapy

INTRODUCTION

Several studies have focused on the generation of airborne singlet oxygen (\(^{1}\text{O}_2\)), including the formation of \(^{1}\text{O}_2\) at air/solid interfaces.\(^1\)–\(^6\) However, the literature is lacking with respect to airborne \(^{1}\text{O}_2\) delivery without the actual contact of the \(^{1}\text{O}_2\)-generating surface with a second (distal) surface receiving \(^{1}\text{O}_2\).

In this vein, we recently reported\(^7\) the formation of airborne \(^{1}\text{O}_2\) from the irradiation of sensitizer particles embedded in the plastron of a superhydrophobic surface (sensSH). In this earlier study, sensitizer coated poly(dimethylsiloxane) (PDMS) posts were capped with PDMS coated with hydrophobic fumed silica nanoparticles, thereby preventing direct contact between the suspended water droplet and the sensitizer particles in the plastron. Airborne \(^{1}\text{O}_2\) was shown to traverse the plastron and reach a water droplet containing a water-soluble anthracene trapping agent (1) suspended on the SH surface. Since some sensitizer particles could be located within micrometers of the water droplet in this configuration, we wondered whether sensSH surfaces would be suited to deliver airborne \(^{1}\text{O}_2\) over greater distances. However, no evidence yet exists for a “contact-free” delivery of \(^{1}\text{O}_2\) between a sensSH surface and a water sample.

Thus, we studied the possible transit of airborne \(^{1}\text{O}_2\) but with strictly no contact between the sensSH surface generating the \(^{1}\text{O}_2\) and the water droplet receiving the \(^{1}\text{O}_2\). We designed a sandwich structure that uses two separated superhydrophobic surfaces to enforce the delivery of airborne \(^{1}\text{O}_2\) from an upper generating layer (sensSH) to a water droplet perched on a lower native SH surface containing no sensitizer particles (Figure 1). The sensitizer-containing surface does not contact the droplet, and no sensitizer particles are transferred to the water. Reports exist on \(^{1}\text{O}_2\) gas bubbles\(^8\) and a SH surface with tips coated with silicone in contact with water,\(^7,9\) providing for minimal contact and sensitizer-free production of \(^{1}\text{O}_2\).

However, the literature is devoid of measurements for the steady-state concentration and number of airborne \(^{1}\text{O}_2\) molecules that diffuse outward from a SH surface over micrometer or millimeter distances.

The objective of the SH sandwich system developed here (Figure 2) is to determine how efficiently airborne \(^{1}\text{O}_2\) migrates as a function of distance to a distal water droplet. Our hypothesis is that airborne \(^{1}\text{O}_2\) will be detected tenths of millimeters beyond the generating surface. The steady-state concentration of \(^{1}\text{O}_2\) and the number of \(^{1}\text{O}_2\) molecules to
reach the water surface were estimated. In this vein, the airborne $^1\text{O}_2$ luminescence intensity at 1270 nm was also examined to gauge the utility of $^1\text{O}_2$ delivery from a superhydrophobic surface. Information on such contact-free SH surfaces adds key results to impact device development on the transport of airborne $^1\text{O}_2$ and deeper understanding of exposure of natural water droplets to reactive oxygen. The results also point to future use in PDT and biofilm eradication.

### EXPERIMENTAL SECTION

#### Materials and Instrumentation.

Silicon phthalocyanine dichloride (SiPcCl$_2$), (3-aminopropyl)trimethoxysilane (ATPS), and (3-glycidyloxypropyl)trimethoxysilane (GPTMS) were purchased from Sigma-Aldrich (Allentown, PA, USA). Deionized water was purified using a U.S. Filter Corp. deionization system (Vineland, NJ, USA). UV-visible spectra of the 9,10-anthracene dipropionate dianion in H$_2$O were collected on an Agilent spectrophotometer. The concentration of O$_2$ in water was measured with a O$_2$ Sens-Ion6 oxygen electrode (Hach Co., Loveland, CO, USA), where calibrations were conducted in air-saturated water. Optical energy was delivered from a CW diode laser (669 nm output, 383 mW, Intense Ltd.).

#### Fabrication of Superhydrophobic Surfaces.

The process for printing superhydrophobic surfaces was reported previously.$^{6-11}$ Briefly, PDMS posts, $\sim$1 mm tall, were printed in 1 cm $\times$ 1 cm arrays on 0.5 mm pitch on a glass slide. The silicon phthalocyanine (Si-Pc) glass particles (40–150 $\mu$m) were prepared as described previously.$^7$ The method for embedding of the Si-Pc particles into the SH surfaces was also reported previously.$^7$ An amount of sensitizer (8.3 $\times$ 10$^{-2}$ mol) is contained within the 20 mg particles that are embedded into the sensSH surface. An average number of Si-Pc particles per SH post was found to be $\pm$ 10 particles/post. Native SH surfaces containing no Si-Pc particles were also printed and used.

#### Apparatus.

A 25 $\mu$L H$_2$O droplet was deposited onto a native lower SH surface using a calibrated pipet. The sensitizer-particle embedded superhydrophobic (sensSH) surface was placed face down above the droplet, at the fixed distances of 20, 100, 200, 400, and 600 $\mu$m. These distances were measured in two ways: (1) with a caliper with 0.02 mm accuracy and (2) with photographic images using ruler reference points and pixel size correlations.

#### Airborne $^1\text{O}_2$ Trapping.

The sensSH surface was illuminated from the top with 669 nm light (383 mW) passing through an FT-400-EMT optical fiber (Thorlabs, Newton, NJ, USA). The laserhead was positioned directly above a glass slide holding the sensSH surface face down. The formation of airborne $^1\text{O}_2$ was probed with anthracene 1 trapping in a 25 $\mu$L H$_2$O droplet sitting on the lower native SH surface. The concentration of $^1\text{O}_2$ was determined with UV–vis by monitoring the disappearance of the absorption of 1 at $\lambda = 378$ nm at 10 min intervals for a total of 60 min. The concentration of 1 (0.2 mM) and pH of water (10.4) were chosen to readily detect 1 by UV–vis and solvate 1, respectively. The anthracene 1 trap is not capable of photosensitizing O$_2$ with the longer wavelength (i.e., 669 nm) light that was used. The disappearance of 1 over the course of the reaction was first-order. The structure of anthracene endoperoxide 2 has been previously characterized on the basis of NMR and UV–vis spectroscopy.$^{7,12,13}$ Evidence for the stability of 2 for several days has been established, unlike naphthalene endoperoxides, and benzene endoperoxide, where the new C–O bonds are unstable and thereby prone to expulsion of O$_2$.$^{14,15}$ All experiments were carried out at ambient temperature (22 $\pm$ 1°C). We did not observe changes in droplet volume greater than 1 $\mu$L due to evaporation. The water temperature was increased minimally by only 0.5°C over the 1 h irradiation period.

#### Direct Detection of Airborne $^1\text{O}_2$.

The formation of airborne $^1\text{O}_2$ was demonstrated by monitoring its 1270 nm luminescence with a photomultiplier tube (H10330A-45, Hamamatsu Corp.). Before reaching the photomultiplier, the light emitting from the system was
Scheme 1. SH Sandwich System in Which Irradiation of the sensSH Surface Forms Airborne $^1$O$_2$, Which Is Quenched Physically by the Water Droplet ($k_q$) and Anthracene 1 ($k_1$) or Where $^1$O$_2$ Is Trapped in a Chemical Reaction ($k_i$), Thereby Forming Endoperoxide 2

filtered through a 1250 nm long-pass and a 1270 nm band-pass filter (fwhm = 15 nm). The $^1$O$_2$ luminescence signals were registered on a 600 MHz oscilloscope. The samples were irradiated during 10 s to acquire 100 traces (10 Hz) that were averaged to obtain the luminescence intensity. A native SH surface with no sensitizer particles was used to measure the extent of intensity enhancement due to noise and light scattering, but not due to airborne $^1$O$_2$. Data points for intensity vs time for each experimental condition were corrected by subtracting the intensities corresponding to noise and light scattering. To evaluate the presence of oxygen or nitrogen gas, they were directed at the sensSH surface with a feed tube connected to a gas tank. The gas flow rate was 130 ± 10 mL/min in both cases. Experiments with the SH sandwich system included the presence of a 25 μL H$_2$O droplet alone or the presence of a 25 μL H$_2$O droplet containing anthracene 1.

RESULTS AND DISCUSSION

Figures 1 and 2 show the sandwich SH system studied here which releases airborne $^1$O$_2$. The release of airborne $^1$O$_2$ occurs from the upper layer by photosensitization of $^3$O$_2$ on the embedded sensitizer particles (sensSH) with the subsequent migration of $^1$O$_2$ through the air gap to the 25 μL H$_2$O droplet containing anthracene 1. The water droplet sits on a native SH surface which contains no sensitizer particles. As seen in Scheme 1 and described below, we find a distance dependence in the $^1$O$_2$ migration with this sandwich SH system, which led us to elucidate the process and is the topic of this work.

Kinetic Derivation. The SH sandwich is a threephase (solid–air–liquid) system. The first step in singlet oxygen formation is the activation of the solid sensitizer by visible light,

$$\text{sensSH} + h\nu(I_s) \rightarrow \text{sensSH}^*$$

(1)

where sensSH is the sensitizer particle embedded into the upper SH layer and $I_s$ is the rate of absorption of 669 nm light by the sensitizer molecules in the upper SH layer (eq 1). When ground-state molecular oxygen (i.e., $^3$O$_2$) encounters the excited sensitizer, singlet oxygen ($^1$O$_2$) is formed and the sensitizer reverts to the ground state,

$$^3\text{O}_2 + \text{sensSH}^* (\Phi_\Delta) \rightarrow ^1\text{O}_2 + \text{sensSH}$$

(2)

where $\Phi_\Delta$ is the quantum yield of $^1$O$_2$ production (eq 2). The $^1$O$_2$ formed is slowly quenched in air, but rapidly quenched in water to form ground-state $^3$O$_2$ (eq 3), where $k_d$ is the rate constant for quenching of $^1$O$_2$ by water and air. The fewer molecules available to quench $^1$O$_2$ in the gas phase enable it to diffuse much greater distances compared to the solution phase. In a water droplet, $^1$O$_2$ readily oxidizes 1 at the 9,10-position by a $[4 + 2]$ reaction. The $[4 + 2]$ reaction of $^1$O$_2$ is a common reaction in the field, although it is usually monitored in the solution phase with a solvated sensitizer, which is unlike our SH sandwich system with a physically separated sensitizer. The physical quenching ($k_q$) and chemical quenching ($k_i$) of $^1$O$_2$ by 1 are shown in eqs 4 and 5.

$$^1\text{O}_2 + I(k_q) \rightarrow ^3\text{O}_2 + I$$

(4)

$$^1\text{O}_2 + I(k_i) \rightarrow 2$$

(5)

The use of 1 enables us to monitor the rate of $^1$O$_2$ capture in the water droplet to be estimated by the reduction of the concentration of 1.

The rate law can be expressed as

$$\text{rate} = (k_i + k_q)[^1\text{O}_2][1]$$

(6)

Instead of examining a second-order reaction with the rate proportional to the two reactant concentrations, $[^1\text{O}_2]$ and [1], we simplify the analysis with the steady-state (ss) approximation

$$-d[1]/dt = d[2]/dt = (k_i + k_q) [^1\text{O}_2]_{ss}[1]$$

(7)

$$-d[1]/dt = (k_i[1])/(k_d + (k_i + k_q)[1])$$

(8)

where $[^1\text{O}_2]_{ss} = (k_d - (k_i + k_q) [1])^{-1}$ (Supporting Information, equation f) and $k_q$ is taken to be zero since 9,10-disubstituted anthracene traps are known to be mainly chemical quenchers not physical quenchers of $^1$O$_2$. $^1$O$_2$ is a free radical and is rapidly quenched by $^3$O$_2$.

$$-d[1]/dt = (k_i[1])/(k_d + k_i[1])$$

(9)

Under the condition, $k_i[1] \gg k_d$ the reaction is zero order. However, under the condition $k_i \gg k_i[1]$; the reaction is first-order in the loss of 1, which is useful for a kinetic analysis

$$-d[1]/dt = k_i[^1\text{O}_2]_{ss}[1]$$

(10)

$$-d[1]/dt = k_{obs}[1]$$

(11)

$$k_i[^1\text{O}_2]_{ss}[1] = k_{obs}[1]$$

(12)

enabling us to obtain $k_{obs}$ from the slope of a plot of ln [1] vs time. $[^1\text{O}_2]_{ss}$ can also be obtained from $k_{obs}$ where the reported value for the rate of $^1$O$_2$ reacting with 1 ($k_i = 8.2 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$) is used to calculate the $^1$O$_2$ steady-state concentration at each distance. The solution to eq 12 gives
\[
\frac{k_{obs}}{k_i} = [^{1}O_2]_{ss}
\]  

(13)

The derivation of the equations for the steady-state approximation of \([^{1}O_2]_{ss}\) is shown in the Supporting Information.

**Trapping Results.** Table 1 shows how \(^1O_2\) trapping depends on the setup of the SH sandwich system. Setup 1

<p>| Table 1. Dependence of (k_{obs}) on the Distance between the Upper SH Surface and the Top of the 25 (\mu L) Water Droplet for Three Experimental Configurations |
|---------------------------------|-------------|-------------|-------------|</p>
<table>
<thead>
<tr>
<th>Distance ((\mu m)) (^a)</th>
<th>(k_{obs}) ((s^{-1}))</th>
<th>(k_{obs}) ((s^{-1}))</th>
<th>(k_{obs}) ((s^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.5 \times 10^{-5}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>1.2 \times 10^{-5}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>1.2 \times 10^{-5}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
<td>0.67 \times 10^{-5}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>600</td>
<td>0.33 \times 10^{-5}</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

“Refers to the shortest possible distance from the sensSH tips to the top of the water droplet. In reality the distance is a range since the reach is an additional 1 mm to the valley floor of the plasstron. \(^a\)Setup 1: Upper sensSH layer, lower native SH layer, irradiated with 669 nm light. \(^b\)Setup 2: Upper sensSH layer, lower native SH layer, no irradiation. \(^c\)Setup 3: Upper native layer, lower native SH layer, irradiated with 669 nm light.

(Figure 1B) used an irradiated sensitizer-embedded SH surface (sensSH) on the top and native SH surface on the bottom and irradiation from the top; setup 2 used the same surfaces (a sensSH surface on top and a native SH surface on the bottom) but with no irradiation; and setup 3 used native SH surfaces on both the top and bottom but with irradiation. Setups 2 and 3 did not lead to \(^1O_2\) trapping in the \(H_2O\) droplet when sensitizer-free SH surfaces were used or in the absence of light.

In an additional control experiment, no decrease in \(I\) was detected when the sensSH surface was placed above the water droplet for 1 h, and then the droplet itself irradiated in the presence of \(I\). Thus, sensitizer deposition into the water droplet was not observed, which we attribute to well-adhered silica Si-Pc particles to the SH surface and the covalent bonding of Si-Pc to the silica. Any loosely bound or unbound sensitizer particles were removed by forced air in the fabrication of the sensSH surface prior to use. Construction of calibration curves showed the UV–vis absorbance detection limit of the sensitizer is 1 \(\mu M\) and of anthracene \(I\) is 2–3 \(\mu M\). Very low concentrations of sensitizer deposited into the water droplet might be unobservable directly by UV–vis, but by \(^1O_2\) trapping using anthracene \(I\), it is observable to much lower concentrations. The reason is that one molecule of sensitizer can lead to an exponential amount of \(^1O_2\) as it is a photocatalyst attesting to the fine quantitation ability of anthracene \(I\). The capture of airborne \(^1O_2\) in water droplets in setup 1 enabled an analysis of the kinetics of the process, as we will see next.

**Observed Rate Constant \((k_{obs})\).** The data show there is a light and sensitizer-surface dependence that leads to airborne \(^1O_2\) trapping in the water droplet (Table 1, setup 1). Here, \(k_{obs}\) values were obtained as a function of distance between the sensSH surface and the top surface of the droplet from the slopes of plots of first-order data (ln \([I]\) vs time) for 10 min irradiation periods up to a total of 60 min. For illustration purposes, Figure S2 (Supporting Information) shows a plot of data for ln \([I]\) vs time at the distance of 600 \(\mu m\) between the upper sensSH surface and the top of the water droplet. For a distance of 20 \(\mu m\), \(k_{obs}\) was found to be 1.5 \(\times 10^{-5} s^{-1}\) with an \(R^2 = 0.999\). The magnitude of the slope is diminished when the distance between the sensSH surface and water droplet is increased. Upon increasing the distance between the sensSH and the water droplet by 30-fold from 20 to 600 \(\mu m\), \(k_{obs}\) decreased by 78%. Next, we sought information on whether the steady-state concentration of singlet oxygen was substantially changed at various distances between the sensSH and the water droplet.

**Steady-State Concentration of Singlet Oxygen \(([^1O_2]_{ss})\).** We calculated the steady-state concentration of \(^1O_2\) in the sandwich SH system as a function of distance between the sensSH surface and the water droplet (Table 2). As we noted above, the \([^{1}O_2]_{ss}\) calculation is not affected by the quenching of \(H_2O\) due to pseudo-first-order kinetic requirements being met for \(I\). Furthermore, the quenching of \(^1O_2\) by dissolved oxygen \((-^1O_2)\) is a physical process.21 The results show that the \(^1O_2\) steady-state concentrations within the surface layer of the droplet were calculated to be between hundreds of femtomolar (\(1.8 \times 10^{-13} M\)) at short distances (e.g., 20 \(\mu m\)) and tens of femtomolar \((4.0 \times 10^{-14} M)\) at long distances (e.g., 600 \(\mu m\)).

The results argue for low steady-state concentrations of \(^1O_2\). The \(^1O_2\) steady-state concentrations measured in the SH sandwich (three-phase) system are similar to our previous SH system, in which sensitizer particles were in contact with water (i.e., a two-phase system) with \((7.0–8.5) \times 10^{-12} M\).22 Other two-phase systems, such as a solid natural organic matter/water system \((1 \times 10^{-12} M)\),22,23 an aerosol/dissolved aromatic system \((1 \times 10^{-13} M)\), and a meso-tetra(N-methyl-4-pyridyl)porphine cation-exchanged (i.e., tightly adsorbed) onto porous Vycor glass in \(H_2O\) are also in the femtomolar region \((1 \times 10^{-14} M)\).23

The number of \(^1O_2\) molecules that will transverse the air–water interface to react with the trap inside the droplet may be noted from the data (Table 2). The number of \(^1O_2\) molecules that are trapped by \(I\) in the droplet are 4.6 times higher at a distance of 20 \(\mu m\) compared to 600 \(\mu m\). The last column in Table 2 shows the yield of trapped \(^1O_2\) where we measured the decrease in \([I]\), which is assumed to result from reaction with singlet oxygen. The number of \(^1O_2\) molecules
reported in Table 2 reflect only those trapped by anthracene 1 in the droplet. A higher number of $^1\text{O}_2$ molecules would be expected to actually traverse the air gap of the device before reaching the droplet itself.

**H$_2$O vs D$_2$O Droplet.** In eq 9, the anthracene trapping agent 1 needs to be kept in low concentrations to calculate $[^{1}\text{O}_2]_{ss}$ and maintain first order in 1, while $k_d$ needs to exceed $k_f$ [1]. The singlet oxygen being quenched by H$_2$O in the reaction does not significantly affect the $[^{1}\text{O}_2]_{ss}$ measurements. The reason is that $k_d$ for $^1\text{O}_2$ in H$_2$O (2.86 $\times$ 10$^5$ s$^{-1}$) is 17-fold greater than $k_f[1]$ (1.64 $\times$ 10$^4$ s$^{-1}$) with an initial concentration for 1 of 200 $\mu$M. Thus, under our constant light intensity in H$_2$O, the disappearance of 1 fits first-order kinetics. Theoretically, it would have been favorable to reduce the concentration of $^1\text{O}_2$ by a factor of 10, from 200 to 20 $\mu$M, thereby increasing the $k_d/k_f[1]$ ratio from 1:17.4 to 1:174. This would slightly improve adherence of first-order kinetics, but make absorbance measurements less accurate.

If D$_2$O was used in place of H$_2$O, the solvent quenching rate of $^1\text{O}_2$ would decrease substantially ($k_d$($\text{D}_2\text{O}$) is 1.50 $\times$ 10$^5$ s$^{-1}$, whereas $k_d$($\text{H}_2\text{O}$) is 2.86 $\times$ 10$^5$ s$^{-1}$). In this case, the $[^{1}\text{O}_2]_{ss}$ at a distance of 20 $\mu$m can be calculated (eq 14).

$$[^{1}\text{O}_2]_{ss} = \frac{k_d(\text{H}_2\text{O})}{k_d(\text{D}_2\text{O})}[^{1}\text{O}_2]_{ss}$ = \frac{3.4 \times 10^{-12}}{(14)}$$

However, in D$_2$O, $k_d$ is $k_f[1]$ (when using 200 $\mu$M 1), which would result in a deviation from first-order kinetics, thereby providing an impetus for using H$_2$O instead of D$_2$O in the $[^{1}\text{O}_2]_{ss}$ measurements.

The lifetime of singlet oxygen is 20-fold greater in D$_2$O than H$_2$O, although pure D$_2$O is not better to use for these droplet experiments since estimation of the singlet oxygen concentration has the kinetic requirement for $k_d \gg k_f[1]$ for the loss of 1 to be first-order. Once $^1\text{O}_2$ reaches the H$_2$O droplet, it has a limited diffusion distance of $\sim$150 nm, so that it does not penetrate deep. Singlet oxygen has a longer diffusion distance in D$_2$O of 2.8 $\mu$m. In both cases this is a minute fraction of the width of the droplet ($\sim$4 mm). Furthermore, within this fraction the rate of diffusion of 2 out and in is thought to be sufficiently fast to maintain the concentration equilibrium throughout the droplet.

**Distance Dependence.** The relative $k_{sb}$ values (Table 1 data, red curve) and the yield of trapped $^1\text{O}_2$ (Table 2 data, blue curve) are plotted as a function of sensSH–droplet distance ($d$) in Figure 3. In both cases, plots of relative $k_{sb}$ and yield of 2 (yield of trapped $^1\text{O}_2$) vs time decreases rapidly with distance. Clearly, the plots show a steep decrease in the concentration of singlet oxygen delivered to the droplet as the distance between the sensSH surface to the droplet increased. This leads us to propose that the transit of airborne $^1\text{O}_2$ is favored at <300 $\mu$m distances in the SH sandwich system. This compares to the approximate distance of 200 $\mu$m for airborne $^1\text{O}_2$ previously reported in a shallow vessel system.$^6$

In the context of production of airborne $^1\text{O}_2$, there are caveats unique to the superhydrophobic surface. A relationship exists where the $^1\text{O}_2$ formed near the tip ends reaches the water droplet to a greater extent than the $^1\text{O}_2$ formed deep in the plastron. The sensitizer particles at the tip will yield the shortest $^1\text{O}_2$ diffusion distance and thus less $^1\text{O}_2$ is wasted (i.e., decays to the ground state before encountering the droplet) as a consequence compared to particles residing for example 1 mm deep at the valley floor of the plastron. The current SH sandwich consists of a three-phase system where $^1\text{O}_2$ is generated on the PDMS posts, where most is delivered from the tip rather than deep in the plastron, as illustrated in Figure 2.

**Luminescence from Airborne $^1\text{O}_2$.** For evidence of the appearance of airborne $^1\text{O}_2$ in our SH sandwich system, luminescence measurements at 1270 nm were carried out. These experiments were done using the same system configuration described above, where the sensSH surface was irradiated from the top down. One hundred luminescence intensity vs time data points for various experimental conditions were collected and averaged to generate the data in Figure 4 (representative data collected over 4.5 ms are shown in Figure S2). The signal intensity in ambient conditions due to irradiation of the native SH surface alone

![Image](https://dx.doi.org/10.1021/acsabm.0c00114)

**Figure 4.** Luminescence intensity at 1270 nm for the (first column) native SH surface containing no sensitizer particles; (second column) sensSH surface; (third column) sensSH surface with oxygen gas flowing at a rate of 130 mL/min; (fourth column) sensSH surface with nitrogen gas flowing at a rate of 130 mL/min; (fifth column) SH sandwich system with no water droplet; (sixth column) SH sandwich system with the water droplet as physical quencher; (seventh column) SH sandwich system using a water droplet with 0.2 mM 1 as chemical quencher. The distance between the sensSH surface and the water droplet was 150 $\mu$m, and the system is open. Errors represent the standard deviations from duplicate experiments.

![Figure 3](https://www.acsabm.org)

**Figure 3.** Dependence of the reaction rate of $^1\text{O}_2$ with 1 (0.2 mM) and yield of trapped $^1\text{O}_2$ with increasing distance of the sensSH surface to the 25 $\mu$L H$_2$O droplet.
is ∼0.015 mV, which is attributed to background (Figure 4, first column). A 5-fold intensity enhancement was observed upon replacement of the native SH surface by the sensSH surface alone with no native lower SH surface in the vicinity (Figure 4, second column). Next, experiments were performed by flowing O₂ and N₂ gas at a rate of 130 mL/min onto the sensSH surface. A ∼30% intensity increase (Figure 4, third column) was observed when going from static air to flowing O₂ gas. However, replacement of O₂ by N₂ gas resulted in a 50% signal drop (Figure 4, fourth column). The SH sandwich system is an open system so that a complete drop in the signal is not expected. However, these data are consistent with a signal mainly from ¹O₂ phosphorescence. No significant intensity decrease was detected when a native SH surface was placed 150 μm below the sensSH surface in the absence of a water droplet (Figure 4, fifth column). The sensitivity of the signal was tested by placing a 25 μL water droplet alone and a 200 μM solution of 1 on the lower native SH surface in the sandwich system (Figure 4, sixth and seventh columns). Here, the signal intensity reduced by 5% and 13% in comparison to the SH sandwich system alone. Carboxylic acid salts have been shown to reduce the surface tension of water.⁴⁻⁶ Due to the droplet adopting a slightly flatter shape in the presence of 1 and NaOH, airborne ¹O₂ arrives at a larger quenching area compared to a water droplet in their absence, which accounts for the 8% intensity increase in the former. Interestingly, no variation in the 1270 nm luminescence intensity was observed as a function of [1] concentrations at 0.2, 10, and 20 mM (Figure S3). This lack of sensitivity is attributed to two factors; the first one is the area of the sensSH surface that is approximately 10 times larger than the surface area of the water droplet. With the droplet located in the center of the sandwich, the signal was mainly due to airborne ¹O₂ produced on the SH surface above the droplet. Therefore, luminescence intensity is an average where ∼90% of the signal is ¹O₂ deactivated by air and only ∼10% by the water droplet. The second factor is that most of the ¹O₂ that contacts the water droplet is physically quenched by water; kₙ is 17-fold greater than the chemical quenching rate (kₙ).

### SUMMARY

The data taken together provide evidence for the facile transit of airborne ¹O₂ over a 20 μm distance, but this transport decreases rapidly with increasing distance. The data are also consistent with previous reports of airborne ¹O₂ traveling tens of millimeter distances to reach a liquid⁵ or solid surface.⁶ An important finding in our study is the steep drop in the number of singlet oxygen molecules that reach the water droplet depending on the distance separated from the upper ¹O₂-generating SH surface. Furthermore, the luminescence data for ¹O₂ in the air gap of the SH sandwich is consistent with physical and chemical quenching of ¹O₂ with the droplet and with 1 within the droplet, respectively.

### CONCLUSION

The SH sandwich system demonstrates a facile method for the delivery of ¹O₂ in a contact-free manner. Because the sensitizer is isolated from the droplet, the sensitizer cannot participate in solution-phase photochemistry. In fact, some sensitizers are known to undergo electron-transfer reactions in the presence of O₂ in solution.⁷⁻⁸ This leads to the formation of reactive intermediates and byproducts, such as decomposed sensitizer molecules. Not only do our results show that ¹O₂ can be delivered to a water droplet that is fully free from contact with the sensSH surface, they show a strong distance dependence correlation. Using a native SH surface to support the droplet on the lower portion of the sandwich structure proved highly advantageous because it facilitated recovery of the entire droplet without leaving any significant residue on the surface. Essentially no liquid remained on the native SH surface after it was removed with a pipet and so the concentration of 1 could be analyzed accurately.

Our work reveals key virtues of using airborne ¹O₂ in a contact-free SH system. But an appreciation for airborne ¹O₂ is only slowly increasing as a means to oxidize compounds⁹ and inactive bacteria.¹⁰⁻¹³ As of yet, there is only sparse mention of airborne ¹O₂ in the organic chemistry and photobiology literature, which we feel can be greatly expanded on due to advantages the contact-free system provides. So far, Midden et al.⁶ developed a shallow vessel system where ¹O₂ gas reached a water layer to be quenched there. Majima et al.⁷ studied airborne ¹O₂ in a TiO₂ system where it reached a solid surface. A previous example of airborne ¹O₂ toxicity is in planktonic²⁴ and biofilm conditions,¹⁷ where facile inactivation took place and thus shows promise in the field of PDT. We propose that a contact-free SH surface may be an efficient means to inactivate bacteria. Importantly, ¹O₂ toxicity can be realized in which the sensitizer does not contact the organism. In the current SH sandwich study, only the ¹O₂ oxidation of anthracene 1 and luminescence of ³O₂ were examined.

Future work in the area would benefit from increased loading of the plastraon with triplet sensitizer sites that may be used to increase the output of airborne ¹O₂. Also, an assessment of singlet oxygen sensitizers (e.g., phthalocyanine, chlorin, and metal—organic ones)¹⁰⁻¹³ and particle types (e.g., porous, nonporous, and plasmonic nanoparticles),¹⁵⁻¹⁷ and contributions from convection would also help in the optimization of SH surfaces for ¹O₂ output. Such future studies are important for gaining an understanding of the delivery of airborne ¹O₂ to infected biological sites.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsabm.0c00114.

Kinetic derivation, photograph of the SH sandwich system, plot of ln [1] vs time, and plots of singlet oxygen luminescence intensities with various apparatus setups (PDF)

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Notes

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REFERENCES

(2) Choudhury, R.; Greer, A. Synergism Between Airborne Singlet Oxygen and a Trisubstituted Olefin Sulfonate for the Inactivation of Bacteria. Langmuir 2014, 30, 3599—3605.


