Water–solid contact electrification causes hydrogen peroxide production from hydroxyl radical recombination in sprayed microdroplets

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Contact electrification between water and a solid surface is crucial for physicochemical processes at water–solid interfaces. However, the nature of the involved processes remains poorly understood, especially in the initial stage of the interface formation. Here we report that H₂O₂ is spontaneously produced from the hydroxyl groups on the solid surface when contact occurred. The density of hydroxyl groups affects the H₂O₂ yield. The participation of hydroxyl groups in H₂O₂ generation is confirmed by mass spectrometric detection of ¹⁸O in the product of the reaction between 4-carboxyphenylboronic acid and ¹⁸O-labeled H₂O, resulting from H₂O plasma treatment of the surface. We propose a model for H₂O₂ generation based on recombination of the hydroxyl radicals produced from the surface hydroxyl groups in the water–solid contact process. Our observations show that the spontaneous generation of H₂O₂ is universal on the surfaces of soil and atmospheric fine particles in a humid environment.

contact electrification | water droplets | hydroxyl radical | hydrogen peroxide | solid–water interface

When two materials of different chemical composition are brought into intimate contact, it is common for the two materials to become oppositely charged. Early work suggested that this charging was caused by ion transfer, but more recent work, as reviewed by Lin, Chen, and Wang (1), indicates that electron transfer plays a dominant role in liquid–solid contact electrification (CE). Of special interest is CE involving water droplets and insulators, which began in the 1990s with studies by Matsui et al.; Yatsuzuka, Mizuno, et al.; and Yatsuzuka, Higashiyama, et al. (2–4). They found that the water droplet is always positively charged when it slides over an insulator surface. They conjectured that the adsorption of negative ions from water to the insulator surface was responsible for the contact charging between the water and the insulator. More recent work (1, 5) suggests that both electron and ion transfer occur at the liquid–solid interface but that electron transfer may often predominate. In water, if an electron is to be transferred, then it may seem likely that it would originate from the hydroxide anion (OH⁻) causing the formation of the hydroxyl radical (•OH), which may go on to recombine with other hydroxyl radicals to generate hydrogen peroxide (H₂O₂). A recent publication by Ben-Amotz predicted that hydrogen bond charge transfer in water may have far-reaching chemical implications (5), and it is proposed that even transfer from H₂O to form H₂O⁺ occurs in which the H₂O⁺ cation rapidly reacts with water to yield H₃O⁺ and •OH (6). While evidence of the formation of H₂O₂ in water droplets seems to have been well established (7–14), some have claimed that it arises solely from the adsorption of ozone (O₃) (10) or solely from cavitation (14). A recent study employing ultrapure nitrogen (N₂) as a nebulizing gas showed, however, that H₂O₂ in sprayed water droplets was formed without the adsorption of ozone (13), although there can be no denying that ozone adsorption promotes H₂O₂ production as does oxygen (O₂) adsorption (13), as is also the case for cavitation. The question has remained unsettled regarding where the electron that forms •OH goes. It has been speculated that the electron may jump onto positively charged droplets, be captured by water at the air–water interface, or go to the walls in some form of contact electrification (13). In what follows, evidence is presented that contact electrification plays a leading role, and that in the case of silica this involves hydroxyl groups on the solid surface in contact with water.

Electron transfer at a water–solid interface is induced by the overlap of electron clouds, which occurs when water molecules collide with atoms or molecules on the solid surface (15, 16). Notably, electron transfer at a water–solid interface can drive catalytic reactions and facilitate pollutant degradation (17). Liquid–solid triboelectric nanogenerators have also been designed based on this observation (1, 18). Despite advances in applications of electron transfer at water–solid interfaces, the exact nature of the physicochemical processes

Significance

Bulk water is a highly stable solvent, but water microdroplets possess strikingly different properties, such as the presence of hydroxyl radicals (•OH) at the microdroplet periphery. Previous studies demonstrated the recombination of •OH into H₂O₂ molecules and the capture of •OH by oxidizing other molecules, but the origin of the •OH has been a controversial topic with clear evidence that •OH can arise from external gases in contact with the microdroplet surface but also from the formation of the microdroplet itself. This study shows that the latter can primarily arise from contact electrification, which is shown to be a universal phenomenon for water–solid interfaces.


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that accompany charge transfer is poorly understood. Recently, quantum theory calculations have been used to explain the interactions between water and atomically smooth solid surfaces by considering the coupling of water fluctuations to electronic excitations within the solid (19). In practice, atomically smooth solid surfaces do not exist in any material because of the presence of oxygen-containing chemical groups on the solid surface. Surface chemical groups may therefore play an important role in the physicochemical processes involved in electron transfer in the initial stage of water–solid contact, and in the corresponding interfacial redox chemical processes. However, the effects of surface chemical groups on the contact between water and a solid in the initial stage have usually been ignored. In research on water–solid interfaces, it is therefore crucial to understand the correlation between chemical groups and the physicochemical processes that occur in the initial stage of contact, as well as the interfacial redox chemical reaction. This study is hopefully an advance in this direction.

Results and Discussion

Spontaneous Generation of H$_2$O$_2$ in the Microfluidic Channel.

An ideal water–solid interface was set up by scaling a patterned polydimethylsiloxane (PDMS) slab on a flat glass substrate to produce a typical straight-channel microfluidic chip. The channel dimensions were 100 µm (width) × 20 µm (height). Deionized (DI) water was injected into the microfluidic channel to build a water–solid interface; this ruled out the effects of gas–phase species on the investigation of H$_2$O$_2$ spontaneous generation (Fig. 1A). An H$_2$O$_2$-sensitive water-soluble probe (10-acetyl-3,7-dihydroxyphenoxazine) was used to detect the production of H$_2$O$_2$ in the microfluidic chip (20). The resulting microfluidic chip was examined using fluorescence microscopy to establish a relationship between the water–solid interface and observed fluorescence intensity (Fig. 1B). A strong orange fluorescence emission was observed from microfluidics containing the probe under 530 nm laser excitation, as shown in Fig. 1C, but not in bulk water under the same conditions. A zoomed-in fluorescence microscopy image confirmed a fluorescence emission from the microfluidics in the straight channel (Fig. 1D). Fluorescence analysis indicated that H$_2$O$_2$ was generated spontaneously in the microfluidic channel. We confirmed that H$_2$O$_2$ was generated by collecting the water in the microfluidic channel and investigating its reaction with 4-carboxyphenylboronic acid (4-CPB) according to a reported method (6). Mass spectrometric analysis (SI Appendix, Figs. S1 and S2) showed that typical boronic acid cleavage occurred and confirmed the presence of H$_2$O$_2$, in good agreement with previous literature reports (6). Fig. 1E and SI Appendix, Fig. S3 show the fluorescence emission intensity as

![Fig. 1. Fluorescence imaging of spontaneous generation of H$_2$O$_2$ in a typical straight-channel microfluidic chip. (A) Schematic image of experimental setup of water–solid interface in the microfluidic chip. (B) Schematic image of fluorescence microscopy setup for imaging the microfluidic chip. (C) Digital image of fluorescence emission of the microfluidic chip. The sample in the chip contains 1 mM H$_2$O$_2$-sensitive probe as shown in (B). (D) The fluorescence microscopy image of the sample in the chip highlighted in the white dashed line frame in (C) (Scale bar, 300 µm). (E) The relationship between fluorescence intensity and reaction time of sample resting in microfluidic chip. (F) Calibration curve at 400 nm from the absorption spectrum of potassium titanyl oxalate (PTO) solution with added H$_2$O$_2$. Abs, absorption. The green star represents the concentration of H$_2$O$_2$ generated from the microfluidic chip. The excitation source is a green laser pointer (530 nm).](https://doi.org/10.1073/pnas.2209056119)
attributed to the effect of the water–solid interface. Notably, the concentration of \( \text{H}_2\text{O}_2 \) generated in the capillary device was of the same order of magnitude as that in the PDMS microfluidic channel. This result further rules out \( \text{H}_2\text{O}_2 \) production caused by radicals generated from newly prepared PDMS in the microfluidic device (22).

Ionic strength and pH have important effects on the water–solid interface, such as the formation of an electric double layer. We therefore investigated the spontaneous generation of \( \text{H}_2\text{O}_2 \) from NaOH, NaCl, and HCl solutions at various concentrations (Fig. 2C). The results show that \( \text{H}_2\text{O}_2 \) production decreased with increasing ionic strength. In addition, the concentration of \( \text{H}_2\text{O}_2 \) generated in DI water was higher than that generated in NaOH, NaCl, and HCl solutions. Among these, the NaOH solution had the least inhibitory effect on the spontaneous generation of \( \text{H}_2\text{O}_2 \). These data indicate that the water–solid interface may be the origin of the spontaneous generation of \( \text{H}_2\text{O}_2 \) under these conditions.

**H\(_2\)O\(_2\) Generates from the Hydroxyl Groups on the Solid Surface.**

It is important to identify the O-atom source to further understand the effects of the water–solid interface on \( \text{H}_2\text{O}_2 \) production. We considered that possible O-atom sources at the water–solid interface include oxygen-containing groups on the solid substrate and dissolved \( \text{O}_2 \) in the water. Therefore, we examined the correlation between dissolved \( \text{O}_2 \) and \( \text{H}_2\text{O}_2 \) production (Fig. 2D). The amount of \( \text{H}_2\text{O}_2 \) produced remained at the same level regardless of how the amount of dissolved \( \text{O}_2 \) was changed. Our observations indicate that the \( \text{H}_2\text{O}_2 \) generated at the water–solid interface was not produced by oxidation with dissolved \( \text{O}_2 \); this finding was in good agreement with previously reported results for

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**Fig. 2.** Spontaneous generation of \( \text{H}_2\text{O}_2 \) at water–solid interface. (A) The fluorescent profiles of the spontaneous generation of \( \text{H}_2\text{O}_2 \) along the normal direction of the substrate (Top, the optical microscopy image of a typical straight channel; Middle, the corresponding fluorescence image; Bottom, the corresponding fluorescence intensity). (B) The correlation between generated \( \text{H}_2\text{O}_2 \) concentration and surface area/channel volume. Note that the measurements were carried out in capillary devices with various diameters. (C) \( \text{H}_2\text{O}_2 \) concentration as a function of different pH values and ionic strengths. (D) Dependence of \( \text{H}_2\text{O}_2 \) generation on dissolved gasses in water.
aqueous microdroplets (6, 23). Our results suggest that the O-atom source for H₂O₂ generation may come from oxygen-containing groups on the solid substrate.

We addressed the above issue by investigating the correlation between the density of hydroxyl groups on the substrate and H₂O₂ production. SiO₂ substrates were used to prevent interference from impurity elements in the substrates. The density of hydroxyl groups on the SiO₂ substrate was increased after typical O₂ plasma activation treatment; this was confirmed by using infrared spectroscopy and X-ray photoelectron spectroscopy (XPS) to examine the substrate (SI Appendix, Figs. S6 and S7) (24). Fig. 3 A shows that the fluorescence emission intensity of the H₂O₂-sensitive probe on the substrate treated with O₂ plasma (Fig. 3 A, Middle) was higher than that of the bare glass substrate (Fig. 3 A, Top). This result shows that H₂O₂ production at a water-solid interface can be enhanced by increasing the hydroxyl group density on the solid substrate. The density of hydroxyl groups on the SiO₂ substrate was decreased based on the modification of the substrate with 3-(methacryloyloxy) propyltrimethoxysilane (MPTMS) (SI Appendix, Fig. S8) (25). Fluorescence signals were hardly observed on the substrate, which was modified with MPTMS (Fig. 3 A and B, Bottom). This result can be attributed to the decrease of the density of hydroxyl groups on the substrate caused by the reaction between the mercapto groups of MPTMS and the hydroxyl groups. Therefore, surface hydroxyl groups on the solid substrate play a key role in H₂O₂ production at the water-solid interface. The disappearance of the fluorescence emission from the H₂O₂-sensitive probe offers solid evidence that the spontaneous generation of H₂O₂ is determined by the presence of surface hydroxyl groups on the solid substrate.

The Use of Isotopic Labeling. We designed an O-atom isotope experiment to further explore the origin of the oxygen atoms for the generation of H₂O₂ (Fig. 3 C). H₂O₂ plasma treatment was used to create sufficient ¹⁸O-labeled hydroxyl groups on the SiO₂ substrate. Spontaneous generation of H₂O₂ and corresponding boronic acid cleavage on the ¹⁸O-labeled SiO₂ substrate was performed to determine whether surface hydroxyl groups participate in the reaction at the water-solid interface. If the surface hydroxyl group is the origin of the O atom in the generation of H₂O₂, then the O-atom isotope signals would be observed in 4-hydroxybenzoic acid, as shown in Fig. 3 D. We therefore compared the 4-hydroxybenzoic acid productions on the SiO₂ substrates treated with O₂ and ¹⁸O plasmas. The intensity of the mass spectrometric peak at 139.04 m/z increased after isotope treatment (Fig. 3 E), which suggests that the O atom in the surface hydroxyl group plays an important role in the mass balance during the reaction. Additional isotope experiments were performed to further confirm the origin of the O atom during H₂O₂ generation. In these experiments, H₂¹⁸O was used to produce H₂O₂ on a typical SiO₂ substrate and on an ¹⁸O-labeled substrate. SI Appendix, Figs. S9 and S10 show that the intensity of the peak at 139.04 m/z obtained when H₂¹⁸O was used was slightly lower than that in Fig. 3 E, whereas the signal observed by using H₂¹⁸O on the ¹⁸O-treated substrate was slightly higher. However, all the peak intensities were of the same order of magnitude. We propose that the ¹⁸O signals observed in the H₂¹⁸O control experiments can be attributed to the rearrangement of O atoms between water molecules absorbed on the SiO₂ surface and the oxide substrate. These observations suggest that the O atoms

**Fig. 3.** Dependence of H₂O₂ generation on the surface OH groups on the SiO₂ substrate. (A) Fluorescent microscopy images of H₂O₂ generation on SiO₂ substrate with different surface treatments. (B) The corresponding fluorescence intensity profiles of H₂O₂ generation in (A). (C) Schematic of the O-atom isotope experiment setup. (D) Reaction scheme of H₂O₂-promoted/¹⁸O₂-promoted deborylation of 4-CPB. (E) Mass spectrum analysis of 4-hydroxybenzoic acid on SiO₂ substrates treated by O₂ and ¹⁸O₂ plasmas.
in H$_2$O$_2$ generation originate from surface hydroxyl groups on the substrate.

Several previous reports have indicated that hydroxyl radicals can combine to form H$_2$O$_2$ in the presence of water (6, 26). We therefore speculated that some of the hydroxyl groups on the solid surface generate hydroxyl radicals during contact between water and the solid surface and then combine to form H$_2$O$_2$. To support our speculation, water containing DMSO, which is a typical hydroxyl radical scavenger (27), was injected into the microfluidic channel, followed by a measurement of the H$_2$O$_2$ generation. As shown in SI Appendix, Fig. S11, it is difficult to detect the fluorescence signal from H$_2$O$_2$ in the presence of DMSO. This indicates that the spontaneous generation of H$_2$O$_2$ can be predominantly, if not completely, attributed to the recombination of hydroxyl radicals generated from the hydroxyl groups on the solid surface when the solid substrate contacts water.

The generation of hydroxyl radicals from hydroxyl groups is accompanied by electron transfer (28). On the basis of previous investigations of electron transfer in water–solid contact electrification, we assumed that electrons can play a fundamental role in driving the spontaneous generation of H$_2$O$_2$. We therefore measured the current flowing from the substrate to the ground when water contacted the substrate and simultaneously observed the fluorescence signal from H$_2$O$_2$ generation. SI Appendix, Fig. S12 shows that current changes occur in synchronization with the generation of H$_2$O$_2$. We also used Kelvin probe force microscopy (KPFM) to determine the surface charge density of the substrate before and after contact with water (SI Appendix, Fig. S13). The surface charge density of the substrate changed from 113.5 to −179.7 pC m$^{-2}$, which suggests that the substrate gained electrons on contact with water. Notably, it was estimated that the H$_2$O$_2$ generation reaction in the microfluidic channel would require a maximum of 2 $\times$ 10$^{-15}$ mol electrons, which is one order of magnitude lower than the amount of charge measured during contact. This finding also suggests that the change of the surface charge density when water contacted the substrate may have multiple origins, such as ion transfer, overlap of electron clouds, and surface hydroxyl groups on the substrate (5). We do not know the fate of all the charges detected on the solid surface, but we consider that the charge transfer at the water–solid interface is sufficient to produce H$_2$O$_2$.

Mechanism for Spontaneous Generation of H$_2$O$_2$ at the Water–Silica Interface. Our experimental results and analysis revealed that the production of H$_2$O$_2$ at the water–solid interface originated from the radicals generated from surface hydroxyl groups when water contacted with the solid substrate. We investigated a possible reaction pathway involved in the surface hydroxyl groups. It is well known that hydroxyl groups on the surface of oxides are amphoteric in character (29). Moreover, early research demonstrated that surface acidic hydroxyl groups (Si-OH$_{a}$) contribute most to the generation of hydroxyl radicals (30). Thus, we investigated the correlation between the density of acidic hydroxyl groups on the SiO$_2$ surface and the generation of H$_2$O$_2$ at the water–solid interface. Notably, the density of acidic hydroxyl groups was measured, based on the reaction between NaOH and the acidic hydroxyl groups reported previously (31). The density of acidic hydroxyl groups on SiO$_2$ substrates fabricated under the same conditions in Fig. 3B is shown in SI Appendix, Fig. S14. We observed that the density of the acidic surface hydroxyl groups on SiO$_2$ treated by O$_2$ plasma was higher than the other two substrates. Next, the concentration of H$_2$O$_2$ generated on those substrates was recorded (shown in Fig. 4A). The linear relationship between H$_2$O$_2$ concentration and the density of acidic surface hydroxyl groups was in good agreement with the results in Fig. 2B. More importantly, we compared the density of the acidic surface hydroxyl groups before and after H$_2$O$_2$ generation. As shown in Fig. 4B, the density of the acidic surface hydroxyl groups decreased after the production of H$_2$O$_2$, which offers solid evidence that acidic hydroxyl groups act as a starting reactant in the pathway of H$_2$O$_2$ generation. Notably, acidic surface hydroxyl groups (Si-OH$_{a}$) may be ionized in water to generate hydronium cations and silanolate anions (Si-O$^{-}$). Thus, Si-O$^{-}$ groups are thought to be the initial source of O atoms to form H$_2$O$_2$ during the contact electrification process:

$$\text{Si} - \text{OH}_a + \text{H}_2\text{O} \rightarrow \text{Si} - \text{O}^- + \text{H}_3\text{O}^+ \quad [1]$$

When contact occurs between the SiO$_2$ surface and water molecules, the electron may transfer from H$_2$O to the solid surface (32) and thus form H$_2$O during this process. We tested the amount of H$_2$O$_2$ generated on the surface of SiO$_2$ depending on different temperatures. In order to meet the detection limit requirements, we used SiO$_2$ powder in contact with humid air to create a solid–liquid interface with a sufficiently large area for further investigation. As shown in Fig. 4C, there was an increase in H$_2$O$_2$ production with increasing temperature. This result could be attributed to the kinetic energy increase caused by the rising temperature, which might enhance the probability of the contact between water molecules and the SiO$_2$ surface and thus increase the probability of electron transfer. Moreover, the signal of H$_2$O$_2$ cannot be detected when the temperature is below 5 $^\circ$C. This result might be ascribed to the kinetic energy of water molecules, which is too low to generate enough electrons during contact electrification for the generation of detectable amounts of H$_2$O$_2$. A possible reaction pathway can be written as follows:

$$\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + e^- \quad [2]$$

Typically, Si–$^{18}$O$^-$ ions can work as a base to accelerate some reactions by promoting the stoichiometric deprotonation step (33, 34).

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**Fig. 4.** Correlation between Si–$^{18}$O$^-$ groups and H$_2$O$_2$ generation. (A) Dependence of the H$_2$O$_2$ concentration on the density of Si–$^{18}$O$^-$ groups. (B) Comparison of Si–OH$_{a}$ density before and after H$_2$O$_2$ generation. (C) Temperature dependence of H$_2$O$_2$ generation. The pink line is fluorescence intensity per pixel of 5 ml aqueous PTO solution without added H$_2$O$_2$. The yellow line is fluorescence intensity per pixel of 5 ml aqueous PTO solution with added 0.1 g SiO$_2$ powder and 0.5 mg H$_2$O$_2$.
Si-^{18}O^-\text{ions could react with } H_2O^+ \text{ to form hydroxyl radicals during the contact electrification process:}

\[ \text{Si-}^{18}O^- + H_2O^+ \rightarrow \text{Si-}OH + ^{18}OH^- \]  \[ [3] \]

Then, a hydroxyl radical recombination could yield H_2^{18}O_2:

\[ ^{18}OH^- + ^{18}OH^- \rightarrow H_2^{18}O_2 \]  \[ [4] \]

In fact, our proposed mechanism is built around the hypothesis that the overlap between the electron clouds of the water molecule and the solid surface during the contact will lead to the generation of H_2O^+ and OH^- species. However, various intermediates present in the above reaction pathway are difficult to test, so we believe that the mechanism of the spontaneous generation of H_2O_2 at the water–solid interface is still an open issue that requires further in-depth research.

In addition, we believe that the generation of H_2O_2 at the water–solid interface may provide a perspective on a physico-chemical process similar to that in the microdriput. We assume that the electron will transfer from one H_2O molecule to another H_2O molecule during their contact and that hydroxyl radicals may generate during the contact electrification. Thus, the generation of H_2O_2 at the water–solid interface is in good agreement with that at the surface of the microdriput.

Universality of H_2O_2 Generation from Water Contact Electrification. The universality of this phenomenon was investigated by observing the spontaneous generation of H_2O_2 on nine other types of substrates. As shown in SI Appendix, Fig. S15A, similar phenomena were observed on various substrates. In addition, we carried out a set of comparative experiments to investigate the changes of the surface charge before and after water–solid contact by using zeta potential measurements. SI Appendix, Fig. S16 shows the difference in zeta potential before and after the contact between water and these powder samples. It can be observed that the trend of the zeta potential difference depends on solids species in a manner consistent with the trend of the H_2O_2 generation on their surfaces. This result provides further proof of the importance of contact electrification in causing H_2O_2 production at the water–solid interface. More importantly, we tested the generation of H_2O_2 on the surfaces of standard soil (GBW07446) and atmospheric fine particles of 2.5 μm or smaller (PM_{2.5}) after they had been placed in an oven at room temperature (25 °C) at various relative humidities. SI Appendix, Fig. S15B shows that H_2O_2 generation increased with increasing relative humidity, which is in good agreement with a previous literature report (35). To rule out in situ catalytic processes in the soil, we also investigated H_2O_2 generation on O_3 plasma–activated and MTPMS-modified soil particles, respectively. The H_2O_2 generation yield was affected by changing the density of the hydroxyl groups on the surface of the soil. SI Appendix, Fig. S15C shows that H_2O_2 spontaneous generation also occurred at the surfaces of PM_{2.5} particles at various different values of the relative humidity. Note that the composition of atmospheric fine particles is very complex. Several publications have reported that the main components of China’s atmospheric fine particles include carbon black, nitrate, sulfate, and ammonium salt (36, 37). We carried out an energy dispersive X-ray spectroscopy measurement to analyze the main elements contained in our atmospheric fine particles sample. As shown in SI Appendix, Fig. S17, the main elements were C, N, S, and O. We believe that the composition of atmospheric fine particles is similar to that reported previously (37). The generation of H_2O_2 on the surface of PM_{2.5} particles could be attributed to their surface hydroxyl groups and contact between water and their surface. The results of this study may therefore help us understand the mechanism of H_2O_2 generation in the environment and explain how nature behaves, such as the seasonality of viral respiratory infections (38). In addition, we have considered a recent report (34) that glass surfaces can act as heterogeneous catalysts to accelerate various base-catalyzed reactions. The present study may help us further understand the heterogeneous catalytic reaction at the solid–water interface and design interfacial catalysts to replace homogeneous catalysts that need to be dispersed in the bulk phase.

Conclusions

In summary, our experimental and modeling results provide direct evidence for the spontaneous generation of H_2O_2 at water–solid interfaces from hydroxyl groups on the solid surface. These observations give a perspective on water–solid interactions and enhance our understanding of water–solid contact electrification. The identification of H_2O_2 generation from the surfaces of solid and atmospheric fine particle samples shows the possibilities of developing mechanisms for pollutant degradation and transformation in the environment. When combined with materials with high catalytic activities, these phenomena could have important applications in catalytic chemistry.

Materials and Methods

Materials. Unless otherwise stated, HCl (AR, Sinopharm Chemical Reagent Co., Ltd, China), NaOCl (AR, Sinopharm Chemical Reagent Co., Ltd, China), NaCl (AR, Sinopharm Chemical Reagent Co., Ltd, China), O_2 (99.999%, Wuhan Huahan Steel Group Gas Co., Ltd, China); heavy O_2 (99.99%, Wuhan Niuanduo Gas Co., Ltd, China), PITO hydrate (99.99%, Sigma–Aldrich, USA); 4-CPB (99.99%, Sigma–Aldrich, USA); anhydrous dimethyl sulfoxide (99.9%, Sigma–Aldrich, USA); 10-acyl-3,7-dihydroxyphenoxazine (KeyGEN Biotech Co., Ltd, China); H_2O standard solution (1,000 μg/mL, Beijing Northern Weiye Metrology Research Institute, China); PDMS prepolymer (TMV 615, Momentive, USA); graphite powder, CuO, ZnO, SiO_2, Al_2O_3, MnO_2, TiO_2, CuO; ZnO (Shanghai Aladdin Bio-Chem Technology Co., Ltd, China); and standard soil (GBW07446, China) were used in experiments. DI water (Merck Millipore, USA) was used in all experiments. SiO_2 substrates (optical grade, Sigma–Aldrich, USA), conductive glass substrates (NSG Pilkington FTO glass), and glass substrates (Jiangsu Fanhu Co., Ltd, China) were ultrasonically cleaned with acetone, ethanol, and DI water for 30 min before use.

Fabrication of Microchannel Structure Devices. The channel layout was drawn by L–edit software, and the mask was prepared by ultraviolet direct writing equipment. Subsequently, relief microchannels were built on the Si wafer by photolithography. The cylindrical channel (15.5 mm diameter) had a total length of 2 cm, a width of 100 μm, and a height of 20 μm. The PDMS prepolymer and the curing agent were mixed in a 9:1 mass ratio and then poured onto the silicon wafer with relief microchannel structure, decompressed and deformed, and heat-treated at 80 °C for 30 min, and finally PDMS with a microchannel structure was obtained. To fabricate microchannel-structured devices, holes were opened in the reserved position, and then PDMS monolith was attached to the clean glass substrate. A pressure of 0.1 MPa was applied externally and kept at 85 °C for 30 min to ensure stable bonding between PDMS and the glass substrate.

Qualitative Characterization of H_2O_2. 10-acyl-3,7-dihydroxyphenoxazine was used in the experiments as a fluorescent indicator of H_2O_2. 1 mM 10-acyl-3,7-dihydroxyphenoxazine aqueous solution was pumped into the microchannel at a flow rate of 20 μL h^{-1}, and the monolithic device was placed under an inverted fluorescence microscope for observation. A 350 nm laser was applied as an excitation light source, the exposure time was fixed, and the change of the overall fluorescence intensity in the channel was recorded. The device was placed under a microscope on its side to observe the diffusion of H_2O_2 from the glass surface. All fluorescence images were calculated using Image J software to obtain the average fluorescence intensity under different conditions.
To observe the effect of ionic strength on the formation of H$_2$O$_2$, 1 mM 10-acetyl-3,7-dihydroxyphenazine was added to DI water and different concentrations (10$^{-10}$, 10$^{-9}$, 10$^{-8}$, and 10$^{-7}$ M) of HCl, NaCl, and Na$_2$SO$_4$ solution, respectively. Different solutions were pumped into the microchannel at a flow rate of 20 μL h$^{-1}$, and the maximum fluorescence intensity was recorded. The fluorescence intensity of DI water was used as the standard to qualitatively explore the relationship between ionic intensity and H$_2$O$_2$ generation.

To investigate the effect of dissolved O$_2$ in the solution on the formation of H$_2$O$_2$, deoxygenated water was degassed and aerated. Deoxygenated water was continuously boiled for 30 m to achieve degassing, and another set of deoxygenated water was continuously bubbled with O$_2$ for 1 h to ensure higher dissolved O$_2$ content. Untreated DI water was used as a control group, and 1 mM 10-acetyl-3,7-dihydroxyphenazine was added to the three groups of DI water, which were pumped into the microchannel, and the maximum fluorescence intensity was recorded.

**Quantitative Characterization of H$_2$O$_2$.** The color reaction of PTO with H$_2$O$_2$ was considered as one of the methods to quantitatively characterize the concentration of H$_2$O$_2$. H$_2$O$_2$ solutions of 1, 2, 3, and 5 mg L$^{-1}$ were prepared using a 30% H$_2$O$_2$ standard solution and were mixed with 0.3 M PTO solution in a volume ratio of 1:1. The mixed solution was detected by a UV-vis spectrometer (UV-5500, Shimadzu, Japan), the absorbance at 400 nm was taken as the characteristic value, and the standard curve was drawn according to the concentration of corresponding H$_2$O$_2$.

The DI water was pumped through the microchannel at 20 μL h$^{-1}$, and then mixed with 0.3 M PTO solution by equal volume, and then its absorbance was measured by a UV-vis spectrometer. The absorbance at 400 nm was compared to the standard curve, and the concentration of H$_2$O$_2$ in deoxygenated water was finally calculated.

To explore the relationship between the concentration of H$_2$O$_2$ and the solid-liquid interface, capillaries with different diameters were used as experimental objects. First, 1 mM of 10-acetyl-3,7-dihydroxyphenazine solution was pumped into different diameter (30, 150, 200, 250, and 500 μm) capillaries at different flow rates, respectively. The flow rates of DI water pumped into the different capillaries were 20, 120, 320, 500, and 2,000 μL h$^{-1}$, which ensured that the solution was advancing at the same rate in the capillaries. Then 0.5 mL DI water was collected at the exit of the capillary, mixed with 0.3 M PTO solution by equal volume, and its absorbance at 400 nm was measured by a UV-vis spectrometer and compared to the standard curve; finally, the concentration was calculated.

**Effects of Surface Hydroxyl Groups on H$_2$O$_2$ Generation.** XPS and a Fourier transform infrared spectrophotometer (Bruker) were used to characterize the surface group changes of glass substrates after O$_2$ plasma treatment. XPS was performed on a multifunctional imaging electron spectrometer (ESCALAB 250Xi, Thermo) using monochromated Al Kα radiation (1486.6 eV).

The potential changes of the glass substrate surface before and after the flow of DI water were obtained by XPS experiments. Experiments were performed on a commercial atomic force microscope (AFM) instrument (Multimode 8 Bruker, USA). AFM probe (NSC18, MikroMasch, USA); Au coated; tip radius: 25 nm; spring constant: 2.8 N m$^{-1}$) was used as the conductive tip. At the same time, we also used conductive glass as the substrate and cooperated with the electrochemical workstation to detect the drop of DI water on the O$_2$ plasma-treated substrate and to record the change of the current.

To investigate the effect of surface hydroxyl groups on the formation of H$_2$O$_2$, O$_2$ plasma was used to increase the surface hydroxyl groups and MPIMS was used to reduce the surface hydroxyl groups. An untreated glass substrate was used as the control. Next, 20 μL of 1 mM 10-acetyl-3,7-dihydroxyphenazine solution was added dropwise to different glass substrates, and the fluorescence images were recorded under an inverted fluorescence microscope; finally, the mean fluorescence intensity was calculated using Image J.

Next, 100 μL of 4-CPB solution was pumped through the microchannel at 20 μL h$^{-1}$ and a 0.5 mL sample was collected at the outlet. The samples were analyzed using liquid chromatography-mass spectrometry in negative mode, and 4-CPB, 4-carboxyphenyl, 4,4'-oxyz (benzoic acid), and boric acid were observed separately. The relative abundance of 4-hydroxybenzoic acid remained low, which may have been caused by low turnover resulting from poor ionization efficiency or short reaction times when no voltage was applied.

To explore the source of O atoms during H$_2$O$_2$ generation, a H$_2$O$_2$/O$_2$ mixture and H$_2$O$_2$ water were used in the experiments. The microchannels were treated with O$_2$ plasma and O$_2$ plasma, respectively, for 20 min before bonding. Then 100 μL of 4-CPB solution was pumped through the microchannel. In addition, 4-oxo-2-oxo-phenylboronic acid was dissolved in H$_2$O$_2$ to conduct experiments, and the samples at the outlet were analyzed using high-resolution liquid chromatography-mass spectrometry, and the intensity changes of 137 m/z and 139 m/z corresponding to 4-oxo-phenylboronic acid were compared.

The Boehm titration method was used to determine the hydroxyl density of the material surface. The silica glass was cut into a 0.5 × 0.5 cm square and a 2 g sample was dissolved in 25 mL anhydrous ethanol, followed by adding 75 mL of 20 wt% NaCl solution. The solution was stirred slowly and a pH meter (Metler, SevenExcellence) was used to detect the overall pH change of the solution in real time. The pH of the solution was adjusted to 4 with 0.1 M HCl. After the pH was stabilized, 0.1 M NaOH solution was slowly added dropwise to bring the pH of the solution back to 9 and the amount of NaOH was recorded. The number of hydroxyl groups per square nanometer (N) on the surface of the material was calculated according to the following equation:

$$N = \frac{CV_{Na} \times 10^{-3}}{S}$$

where C is the concentration of NaOH (mol/L), V (mL) is the volume of NaOH consumed as the pH rises from 4 to 9, N$_A$ is Avogadro’s constant, and S is the surface area of the sample.

**Additional Information.** The formation of H$_2$O$_2$ on the surface of natural materials is presented in the SI Appendix.

**Data Availability.** All study data are included in the article, the SI Appendix, and the publicly available link: https://github.com/RichardZare/Contact_Electro_Spectra_PNAS_Data_Repository.

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