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Received: 22 April 2025

Accepted: 26 January 2026

Cite this article as: Gao, J., Zhou, K., Guo, X. *et al.* Constructing scalable hydrophobe–water micro-interfaces for catalyst-free generation of H<sub>2</sub>O<sub>2</sub> via macroporous resins. *Nat Commun* (2026). <https://doi.org/10.1038/s41467-026-69085-w>

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## Constructing scalable hydrophobe–water micro-interfaces for catalyst-free generation of H<sub>2</sub>O<sub>2</sub> via macroporous resins

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### Abstract

Catalyst-free production of H<sub>2</sub>O<sub>2</sub> at hydrophobe–water micro-interfaces provides a sustainable synthesis route, yet its scalability remains challenging. We demonstrate that hydrophobic macroporous resins (MPRs) can serve as robust, metal-free platforms to construct scalable hydrophobic solid–water interfaces for continuous H<sub>2</sub>O<sub>2</sub> generation, achieving a mass-normalized production rate of H<sub>2</sub>O<sub>2</sub> as  $\sim 0.51 \mu\text{mol g}_{\text{MPR}}^{-1} \text{h}^{-1}$  and eventually  $\sim 1 \text{ mM}$ -level accumulation of H<sub>2</sub>O<sub>2</sub> after one week's stirring of the resin suspension under ambient atmosphere. Both macroporosity and hydrophobicity of MPRs are essential for the activity, and scale-up 1000 mL confirms practical feasibility. Mechanistic studies indicate that H<sub>2</sub>O<sub>2</sub> forms predominantly via the oxygen reduction reaction (ORR), optimally at pH 9. This process requires no external light or electrical energy input, exhibits high salt tolerance, and is potentially compatible with renewable power sources. This work exemplifies how porous materials can enable sustainable, scalable chemical synthesis and updates the fundamental understanding of the microinterface reactivity.

### Introduction

In the past decade, there has been a growing interest in a variety of aqueous interfaces, particularly hydrophobe–water interfaces such as gas–water, oil–water, and solid–water interfaces.<sup>1–13</sup> Intensive research has revealed that these interfaces possess unique chemical structures and exhibit distinct chemical reactivities from those observed in bulk solution chemistry.<sup>14–19</sup> For instance, studies have shown that in certain cases, microdroplets can significantly accelerate traditional chemical reactions by two to six orders of magnitude,<sup>20–22</sup> and even promote thermodynamically unfavorable reactions.<sup>7,21,23–26</sup> Very recently, particular attention has been paid to redox aqueous reactions at hydrophobe–water micrometer scale interfaces, specifically the spontaneous production of H<sub>2</sub>O<sub>2</sub> in water microdroplets without the use of any conventional catalysts or external energy sources such as light or electricity.<sup>8–10,27</sup> This cutting-edge topic was first reported by Zare's group in 2019 and has since sparked wide active investigation into water microdroplets. Although the underlying mechanism has not been fully understood, this phenomenon offers new insights into the unique properties of aqueous interfaces and presents a new method for producing H<sub>2</sub>O<sub>2</sub> under mild conditions.<sup>28</sup> As an indispensable chemical in various fields such as chemical synthesis, energy, environment, and human health, current industrial production of H<sub>2</sub>O<sub>2</sub> heavily relies on the energy-intensive anthraquinone oxidation method, which generates large amounts of organic waste and frequently necessitates the use of expensive noble metal catalysts.<sup>29</sup> In comparison, the microdroplet-driven H<sub>2</sub>O<sub>2</sub> generation from earth-abundant water is environmentally friendly and sustainable.

As experimental and theoretical studies continue to suggest that the generation of  $\text{H}_2\text{O}_2$  in water microdroplets occurs at the hydrophobe–water interface, a consensus has emerged that expanding such interfaces could greatly enhance overall interfacial reactivity.<sup>30</sup> One promising strategy involves dispersing hydrophobic micro- or nanoparticles in bulk water to create extensive reactive sites. However, the high interfacial energy between water and hydrophobic materials presents a significant challenge in achieving stable and scalable interfaces. This is often accompanied with spontaneous agglomeration of the hydrophobic entities in aqueous environments, resulting in a decrease in the overall contact area with water and a drastic reduction in the chemical reactivity at the hydrophobe–water interface.<sup>31,32</sup> As a result, air-water microdroplets prepared by pneumatic spraying or condensation typically have a limited lifetime of only a few milliseconds due to evaporation or coalescence, resulting in a relatively low equilibrium concentration of  $\text{H}_2\text{O}_2$  in the presence of  $\text{O}_2$  ( $\sim 1 \mu\text{M}$  after a complete removal of  $\text{O}_3$ ) and a limited yield of  $\text{H}_2\text{O}_2$ .<sup>8-10</sup> As an alternative, dynamic water-in-oil microdroplets (prepared by ultrasonic irradiation of a mixture of oil and water) have been reported to produce a higher concentration of  $\text{H}_2\text{O}_2$  (10 mM after one hour of reaction).<sup>33</sup> However, there are concerns about whether the detected  $\text{H}_2\text{O}_2$  was entirely produced at the oil–water interface,<sup>28</sup> as vigorous ultrasonic irradiation can also produce  $\text{H}_2\text{O}_2$  through mechanisms such as cavitation effects or ozone reaction.<sup>34-36</sup> Additionally, Wang's group has recently reported an interesting solid–liquid contact electrification method at the fluorine polymer–water interface, which can also lead to the formation of  $\text{H}_2\text{O}_2$  with a rate of hundreds of  $\mu\text{M}$  per hour.<sup>37,38</sup> Recently, Choi, Zare, and coworkers further extended this concept and developed a continuous flow column reactor packed with poly(tetrafluoroethylene) (PTFE) microparticles. Under continuous ultrasonic operation, a high  $\text{H}_2\text{O}_2$  production rate up to  $10.7 \text{ mM h}^{-1}$  was achieved by circulating the effluent.<sup>39</sup> However, this method is limited in its sustainability for green synthesis of  $\text{H}_2\text{O}_2$  from  $\text{H}_2\text{O}$ , as it is mainly restricted to fluorine-containing polymers (a kind of forever chemicals that are lowly dispersible in water) and relies on vigorous energy input such as ultrasonic irradiation or ball milling.<sup>40-42</sup> Therefore, achieving scalable hydrophobe–water micro-interfaces for sustainable synthesis of  $\text{H}_2\text{O}_2$  remains a challenge.

In our previous study,<sup>30</sup> by confining water microdroplets into an array of glass microwells on a chip, which were fabricated by photolithography, we observed a continuous production of  $\text{H}_2\text{O}_2$  until reaching an equilibrium concentration in one hour's lifetime of droplets. Our findings also showed that the rate of spontaneous generation of  $\text{H}_2\text{O}_2$  was directly proportional to the surface-to-volume ratio ( $S/V$ ) of the water microdroplets. This led us to the idea of constructing similar structures that could capture a large number of water microdroplets with high  $S/V$  values, using easily accessible and inexpensive materials.

Macroporous resins (MPRs), a kind of off-the-shelf and metal-free porous solid adsorbent, are commonly used in industrial water treatment for the removal of inorganic and organic pollutants.<sup>43-45</sup> They are typically created by polymerizing monomers in the presence of pore-forming agents. One of the key features of MPRs is their hierarchical porous structure, ranging from several nanometers to tens of microns, which provides a large surface area for adsorption. Our attention was drawn to the potential of MPRs to “grasp” water through porous structures and create a large number of long-lasting water microdroplets within their porous structures. This could be particularly beneficial if the walls of the pores in MPRs are intrinsically hydrophobic, as it would allow for the creation of stable and thus scalable hydrophobe–water micro-interfaces for the generation of  $\text{H}_2\text{O}_2$ . These water microdroplets also have the advantage of intimate communication with the bulk water, which differs from our previous separated water microdroplets confined in an array of glass microwells. We expect that the continuous diffusion of  $\text{H}_2\text{O}_2$  produced at these hydrophobe–water micro-interfaces into the bulk water could ultimately provide a sustainable manner to produce and accumulate  $\text{H}_2\text{O}_2$  under mild conditions.

Hence, in this study, we screened a range of commercially available MPRs with polystyrene/divinylbenzene (PS-DVB) backbones. Our findings revealed that it is possible to create scalable hydrophobe–water micro-interfaces using hydrophobic MPRs with facilitated production of  $\text{H}_2\text{O}_2$  from  $\text{H}_2\text{O}$  and  $\text{O}_2$ . It was found that, without the use of ultrasonic irradiation and surfactants, a production rate of  $\text{H}_2\text{O}_2$  of  $\sim 0.51 \mu\text{mol g}_{\text{MPR}}^{-1} \text{h}^{-1}$  and an eventual  $\sim 1 \text{ mM}$ -level accumulation of  $\text{H}_2\text{O}_2$  after one week's stirring under ambient atmosphere could be achieved in hydrophobic MPRs. This exceeds the previously reported  $\text{H}_2\text{O}_2$  concentration of  $\sim 1 \mu\text{M}$  formed in air–water microdroplets without ultrasonication.<sup>8–10,30</sup> As a proof of concept, scaling the system to a 1000 mL reaction volume was also conducted, demonstrating its practical scalability. Further investigations have elucidated that both the porous structure and the hydrophobic nature of the pore walls in MPRs are crucial for the generation of  $\text{H}_2\text{O}_2$ . Mechanistic study verified that the formed  $\text{H}_2\text{O}_2$  originates from oxygen reduction reaction (ORR), with optimal performance at pH 9. The existence of multiple reactive species (e.g.,  $\cdot\text{OH}$ ,  $\text{e}^-$ ,  $\cdot\text{O}_2^-$ ) indicated that interfacial charge separation and electron transfer drive the underlying  $\text{H}_2\text{O}_2$  formation.

## Results

### Screening and characterization of macroporous resins (MPRs) for $\text{H}_2\text{O}_2$ production

Prior to measurements, we conducted a general pre-treatment procedure on the obtained MPRs with different sizes, rigidities, and chemical compositions (Supplementary Table 1 and Supplementary Fig. 1) to remove the impurities from the industrial synthesis of MPRs (more details can be found in the Methods Section). To evaluate the potential of commercially available MPRs for the construction of scalable hydrophobe–water micro-interfaces, we mixed 20 mg of the treated MPRs (Supplementary Fig. 2) with 0.6 mL of deionized water in a 4 mL polypropylene (PP) tube. To ensure proper dispersion of the MPRs in the water, we added a polytetrafluoroethylene (PTFE) or glass-capped magnetic stir bar to the tube and used a magnetic stirring apparatus (Fig. 1). After a period of time, the resulting mixture was centrifuged and filtered through a filter membrane. For the most extensively studied XAD-1180N MPRs in this work, scanning electron microscopy (SEM) revealed that they had a wide range of sizes (1–10  $\mu\text{m}$ ) and highly heterogeneous porous structures after experiments (Supplementary Fig. 2b). The liquid supernatant was then analyzed using a widely used fluorescence method to determine the concentration of  $\text{H}_2\text{O}_2$ , based on the horseradish peroxidase (HRP)-catalyzed oxidation of Amplex Red (AR) by  $\text{H}_2\text{O}_2$  (Supplementary Fig. 3).<sup>46</sup> In addition, we also performed a UV–vis absorbance method using potassium titanium (IV) oxalate (PTO method, Supplementary Fig. 4 & Supplementary Fig. 5)<sup>8,9</sup> to verify the results.

According to the proposed procedures, we conducted a screening of both macroporous and microporous resins and monitored their rate of  $\text{H}_2\text{O}_2$  generation under identical conditions. In order to provide a comparison, we also tested several non-porous materials, including polystyrene (PS), PTFE,  $\text{SiO}_2$ , and agarose gel. Our results indicate that porous materials generally exhibit a higher rate of  $\text{H}_2\text{O}_2$  generation compared to non-porous materials with the same mass, as shown in Fig. 2A. Additionally, it was observed that hydrophobic MPRs displayed higher rates of  $\text{H}_2\text{O}_2$  generation compared to their hydrophilic counterparts (Fig. 2A). It is noteworthy that three MPRs with crosslinked PS-DVB structures, *i.e.*, XAD-1180N, XAD-2 and XAD-4, exhibited the highest initial production rate of  $\text{H}_2\text{O}_2$  ( $\sim 17 \mu\text{M h}^{-1}$  or  $\sim 0.51 \mu\text{mol g}^{-1} \text{h}^{-1}$ ) among all the materials that were tested. These three materials had broad size distributions in the range of 1–10  $\mu\text{m}$ , with main porous sizes of 30 nm, 9 nm, and 10 nm, respectively (Supplementary Table 1). Furthermore, we continuously monitored the generation of  $\text{H}_2\text{O}_2$  in several materials, including XAD-1180N, D101, XAD-7, and non-porous PS (Supplementary Fig. 6). For instance, during a kinetics test of XAD-1180N, we observed a steady increase in  $\text{H}_2\text{O}_2$  concentration, eventually reaching an accumulated concentration of 1 mM over the course of a week

(Fig. 2B). In view of the specificity of PTO method and HPR-based fluorescence method, which may respond to other reactive oxygen species (ROS), we also performed another  $^1\text{H}$  NMR measurements of the reaction solution using the method proposed by Bax and colleagues.<sup>47</sup> As shown in Supplementary Fig. 7, the  $^1\text{H}$  NMR spectrum of both the 100  $\mu\text{M}$   $\text{H}_2\text{O}_2$  standard and the reaction solution exhibits a singlet peak at a chemical shift of 10.97 ppm, which is characteristic of  $\text{H}_2\text{O}_2$ . Further quantitative integration of these singlet peaks revealed the same concentration of  $\text{H}_2\text{O}_2$  as that measured by the PTO method and the fluorescence method. Therefore, the reported values of 1 mM indeed reflect the concentration of  $\text{H}_2\text{O}_2$  rather than other ROS species. Importantly, this value exceeds those previously reported in sprayed or condensed water microdroplets by two to three orders of magnitude (1 mM versus  $\sim 1 \mu\text{M}$ ).<sup>8-10</sup> It should also be noted that although generation rate of  $\text{H}_2\text{O}_2$  for these MPRs is much lower than that of PTFE–water interface under vigorous ultrasonic irradiation ( $\sim 17 \mu\text{M h}^{-1}$  for MPRs vs.  $\sim 300 \mu\text{M h}^{-1}$  for PTFE),<sup>37,39</sup> the advantages of less intensive energy input for long-term accumulation of  $\text{H}_2\text{O}_2$  at ambient conditions and high tolerance to various salts (please see the following Fig. 5A) for these MPRs endows it more easily to be scaled up for a wide range of applications.

Considering that various radical initiators are typically used in the synthesis of macropolymers, we were concerned about whether their gradual release and subsequent reaction with water contributed to the high accumulated concentration of  $\text{H}_2\text{O}_2$ . In order to address this concern, we repeatedly determined the generation rate of  $\text{H}_2\text{O}_2$  by recycling the used XAD-1180N MPRs nine times. This process involved multiple cycles of washing, drying, redispersion, and reaction. Interestingly, as shown in Fig. 2C, the generation rate of  $\text{H}_2\text{O}_2$  remained nearly constant, indicating that the observed  $\text{H}_2\text{O}_2$  generation was an intrinsic behavior of XAD-1180N and not caused by the residual impurities in the MPRs.

Notably, during the dispersion of the tested materials into water, three distinct dispersion behaviors were observed. To facilitate observation, after a certain time of stirring, various mixtures were promptly transferred from the original PP tubes to glass vials and photographs were taken (Fig. 2D). A dynamic recording of the dispersed process of XAD-1180N MPRs, PTFE, and  $\text{SiO}_2$  over a four-hour stirring period is also shown in Supplementary Fig. 8. Hydrophilic  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{ZnO}$ , and other hydrophilic resins, which exhibited negligible production of  $\text{H}_2\text{O}_2$  (Fig. 2A), demonstrated uniform dispersion in water following several seconds to minutes of stirring (right bottle in the inset picture of Fig. 2D). In contrast, nonporous and hydrophobic materials like PTFE, PS, and polystyrene-divinylbenzene (PS-DVB) exhibited a reduced capacity for dispersion in water (middle bottle in the inset picture of Fig. 2D) and demonstrated a comparatively low production rate of  $\text{H}_2\text{O}_2$ . However, the dispersion process of porous resins, particularly hydrophobic MPRs, was found to be entirely different (Supplementary Fig. 8). Upon contact with water, these materials initially rose to the water surface, a behavior commonly observed in other hydrophobic materials devoid of porous structures. However, with continued stirring, they gradually transformed into a dispersed emulsion with the water. After four hours of stirring, it was observed that the dispersed state could be sustained for tens of minutes without significant bulk phase separation (left bottle in the inset picture of Fig. 2D). A more quantitative assessment of the dispersion process of these three types of materials was conducted by monitoring the time-evolved scattering intensity of mixture solutions at the bottom of the sample vials, further confirming the different dispersion behavior of XAD-1180 N MPRs (Fig. 2D). The effect of stirring speed on the dispersity of MPR over time and the generation rate of  $\text{H}_2\text{O}_2$  was also examined (Supplementary Fig. 9). It was observed that increasing the stirring speed resulted in a faster dispersion of MPR in water, leading to a higher average generation rate of  $\text{H}_2\text{O}_2$ . These observations highlight the distinctive characteristics of hydrophobic MPRs, indicating that MPRs can create a large number of long-lasting water microdroplets with high S/V values by “grasping” water into their porous structures. As stirring continues, the gradual extrusion of water into their pores may give rise to a substantial number of water microdroplets, which remain connected to the bulk water.

Therefore, considerable hydrophobe–water interfaces were established, which could support the impressive concentration of H<sub>2</sub>O<sub>2</sub> generation.

In our previous study, we demonstrated that the generation rate of H<sub>2</sub>O<sub>2</sub> in single water microdroplets at the oil–water interface is positively proportional to the S/V values of the water microdroplets—a finding that supports the hypothesis of H<sub>2</sub>O<sub>2</sub> formation occurring at the hydrophobe–water micro-interfaces.<sup>30</sup> This finding also motivated the present investigation into the correlation between the surface area of hydrophobic MPRs and their rate of H<sub>2</sub>O<sub>2</sub> generation. To this end, we adopted the widely used Brunauer-Emmett-Teller (BET) gas adsorption method to quantify the specific surface area of several hydrophobic MPRs (Supplementary Table 2). The BET analysis revealed a broad pore size distribution in these materials, ranging from several to tens of nanometers (as shown in the BET pore distribution of XAD-1180N shown in Supplementary Fig. 10). This is consistent with the heterogeneity of the porous structures of XAD-1180N, as observed in the SEM characterization (Supplementary Fig. 2b). This suggests that the water droplets confined within these pores may also exhibit a significant heterogeneity. Additionally, the BET results showed that among the materials tested, the most active MPRs (XAD-1180N, XAD-2, and XAD-4) exhibited slightly larger surface areas per unit mass, with values of 10.40, 13.80, and 14.24 m<sup>2</sup>, respectively (Supplementary Table 2). After normalizing the rate of H<sub>2</sub>O<sub>2</sub> generation by surface area, a linear correlation was observed with a constant of 1.3 μM m<sup>-2</sup> h<sup>-1</sup> (or 0.78 nmol m<sup>-2</sup> h<sup>-1</sup>, Fig. 1E), confirming that H<sub>2</sub>O<sub>2</sub> generation occurs at the hydrophobic surface of MPRs. Interestingly, it was found that several non-porous materials showed higher surface area-normalized activity of H<sub>2</sub>O<sub>2</sub> generation, that is, ~0.42 μmol m<sup>-2</sup> h<sup>-1</sup> for PS-DVB, ~0.02 μmol m<sup>-2</sup> h<sup>-1</sup> for PS, and ~0.004 μmol m<sup>-2</sup> h<sup>-1</sup> for PTFE (Supplementary Fig. 11). However, due to the high S/V values of MPRs per unit mass, MPRs exhibit significantly greater mass-normalized reactivity than these non-porous materials (~0.511 μmol g<sup>-1</sup> h<sup>-1</sup> for MPR, ~0.019 μmol g<sup>-1</sup> h<sup>-1</sup> for PS-DVB, ~0.015 μmol g<sup>-1</sup> h<sup>-1</sup> for PS, ~0.002 μmol g<sup>-1</sup> h<sup>-1</sup> for PTFE), making them more suitable as building blocks in the construction of scalable hydrophobe–water micro-interfaces for H<sub>2</sub>O<sub>2</sub> generation. Notably, the surface-normalized H<sub>2</sub>O<sub>2</sub> generation rate determined for MPRs was approximately 600 times lower than the value previously reported for microwell-confined water microdroplets (0.78 nmol m<sup>-2</sup> h<sup>-1</sup> vs. 0.462 μmol m<sup>-2</sup> h<sup>-1</sup>).<sup>30</sup> This discrepancy suggests that a substantial fraction of the hydrophobic surface area in the MPRs didn't contribute to the generation of H<sub>2</sub>O<sub>2</sub>, likely due to mass transfer limitations of water molecules into the hydrophobic inner pores of the MPR microspheres. This hypothesis is supported by subsequent atmospheric experiments (discussed in the following mechanism section) and consistent with a Cassie-Baxter wetting state of porous materials<sup>48-50</sup>, in which air or O<sub>2</sub> remains trapped within the porous structures of the MPRs (the cartoon of the top-right panel of Fig. 1). We propose that pre-saturation with water vapor—a method successfully applied to introduce water into the nanopores of activated carbon<sup>51</sup>—could enhance water penetration into hydrophobic MPR pores and mitigate this limitation in future applications.

### Influence of MPR hydrophobicity on the activity of H<sub>2</sub>O<sub>2</sub> generation

To further elucidate the critical role of hydrophobic surfaces in the generation of H<sub>2</sub>O<sub>2</sub>, two complementary *in situ* surface modification strategies were implemented. First, the hydrophobic resin XAD-1180N MPR was functionalized with hydrophilic dextran polymers (Fig. 3A & Supplementary Fig. 12a). As the amount of dextran precursors used during the surface functionalization process increased, a marked reduction in the hydrophobicity of XAD-1180N was observed, which correlated with a systematic decrease in the H<sub>2</sub>O<sub>2</sub> generation rate, as shown in Fig. 3B. For example, after treatment with 10% dextran precursors, the apparent water contact angle of XAD-1180N MPRs decreased from the original 148.5° to 133.0°, accompanied by a 60% reduction in the H<sub>2</sub>O<sub>2</sub> generation rate. This inverse relationship underscores the high sensitivity of interfacial reactivity to the wettability of the MPR–water interfaces. It is noteworthy that the apparent contact angles measured herein may exceed the intrinsic Young's contact angles due to air or O<sub>2</sub>

entrapment within the porous framework of MPRs (*i.e.*, Cassie-Baxter state<sup>48-50</sup>). Nevertheless, the consistent trend of enhanced H<sub>2</sub>O<sub>2</sub> generation with increasing surface hydrophobicity remains robust, as evidenced by the pronounced decline in activity upon hydrophilic modification. In the converse experiment, hydrophobic modification was applied to an inherently hydrophilic material. Sengarose, a highly porous and hydrophilic agarose gel, was grafted with hydrophobic butyl groups via its surface hydroxyl groups (Fig. 3C & Supplementary Fig. 12b). In contrast to the hydrophilic treatment of XAD-1180N, the introduction of butyl groups led to a gradual increase in H<sub>2</sub>O<sub>2</sub> production as the degree of grafting increased, as shown in Fig. 3D. Together, these two sets of experiment provide coherent and compelling evidence that surface hydrophobicity is a pivotal factor governing H<sub>2</sub>O<sub>2</sub> generation at the MPR–water micro-interfaces. Moreover, the consistent trends observed upon both hydrophilic and hydrophobic functionalization strongly suggest that the production of H<sub>2</sub>O<sub>2</sub> is not an artifact of residual impurities in the MPRs, but is intrinsically mediated by the properties of the solid–water micro-interfaces.

Recently, Zare and colleagues reported  $\sim 1 \mu\text{M}$  H<sub>2</sub>O<sub>2</sub> formation in air–water microdroplets after excluding contributions from ultrasonic effect and ozone reaction,<sup>10</sup> whereas we observed a much higher concentration of  $\sim 1 \text{ mM}$  H<sub>2</sub>O<sub>2</sub> at the MPR–water interfaces, though the latter is less hydrophobic than air. This discrepancy does not contradict the positive correlation between hydrophobicity and H<sub>2</sub>O<sub>2</sub> production. The low concentration of H<sub>2</sub>O<sub>2</sub> in air–water microdroplets arises from their transient lifetime (milliseconds to seconds), which limits sustained accumulation of H<sub>2</sub>O<sub>2</sub> despite potentially high interfacial reactivity. In contrast, the porous structure of MPRs stabilizes water microdroplets for extended periods (e.g., one week), facilitating continuous H<sub>2</sub>O<sub>2</sub> generation and accumulation. Regarding the influence of surface wettability on H<sub>2</sub>O<sub>2</sub> production, Mishra et al. recently demonstrated that hydrophilic surfaces (e.g., galvanic metals such as Mg, Al) can exhibit enhanced H<sub>2</sub>O<sub>2</sub> production via a single dissolved oxygen reduction mechanism at the metal–water interface.<sup>52</sup> This implies that distinct mechanisms may operate in different systems, each with specific interfacial requirements. We suggest that the critical underlying feature is the interface's capacity to facilitate charge separation and electron transfer—not hydrophobicity or hydrophilicity per se. In our case, hydrophobicity serves as an empirical and practical descriptor within comparable MPR systems, where it correlates reliably with H<sub>2</sub>O<sub>2</sub> production efficiency.

Previous results in water microdroplets also showed that the presence of oxygen gas can significantly promote the formation of H<sub>2</sub>O<sub>2</sub> by consuming the generated electrons.<sup>10</sup> We thus evaluated the influence of gas atmosphere on H<sub>2</sub>O<sub>2</sub> generation. Under argon or nitrogen saturation (achieved through rigorous degassing), H<sub>2</sub>O<sub>2</sub> production decreased tenfold compared to air or O<sub>2</sub> conditions (Supplementary Fig. 13a), aligning with earlier microdroplet reports. However, when only the aqueous phase was purged with N<sub>2</sub>—while leaving the MPR pores undegassed—H<sub>2</sub>O<sub>2</sub> generation remained comparable to that in air-saturated systems. This indicates that MPRs retain substantial trapped air/O<sub>2</sub> within their porous framework, maintaining the Cassie-Baxter wetting state<sup>48-50</sup> (inferred from the stabilized gas retention, though not directly visualized). Consequently, the hydrophobe–water micro-interfaces in our system comprise both MPR–water and air–water interfaces, possibly collectively enabling 1 mM-level H<sub>2</sub>O<sub>2</sub> accumulation.

### Mechanistic insights into H<sub>2</sub>O<sub>2</sub> generation in the MPR system

Having confirmed the key role of macroporous features and hydrophobic surfaces in H<sub>2</sub>O<sub>2</sub> generation, we proceeded to investigate the underlying reaction mechanism, as mechanistic insight is essential for guiding future optimization and scalable implementation of MPR-based systems. Isotope experiments (H<sub>2</sub><sup>18</sup>O and <sup>18</sup>O<sub>2</sub>) were first conducted to trace the origin of oxygen atoms in the H<sub>2</sub>O<sub>2</sub> produced.<sup>37,53,54</sup> As illustrated in Fig. 4A, oxygen isotopes incorporated into H<sub>2</sub>O<sub>2</sub> can be detected via high-resolution mass spectrometry after cleavage of 4-

carboxyphenylboronic acid. While minimal  $^{18}\text{O}$  incorporation occurred under  $\text{O}_2/\text{H}_2\text{O}$  or  $\text{O}_2/\text{H}_2^{18}\text{O}$  conditions (mass spectrometric peak at  $m/z$  of 139.0286 is barely visible in Fig. 4B), strong labeling was observed with  $^{18}\text{O}_2/\text{H}_2\text{O}$ , confirming molecular oxygen as the predominant oxygen source. Moreover, the concentration of  $\text{H}_2\text{O}_2$  generated under the condition of  $^{18}\text{O}_2/\text{H}_2\text{O}$  nearly remained the same as that of normal  $\text{O}_2/\text{H}_2\text{O}$  conditions (Supplementary Fig. 14), which rules out significant  $\text{O}_3$  involvement in the MPR system. These results robustly support oxygen reduction reaction (ORR) as the primary pathway for  $\text{H}_2\text{O}_2$  formation in the presence of air or  $\text{O}_2$  atmosphere for the MPR system, rather than the recombination of hydroxyl radicals ( $\cdot\text{OH}$ ) from water oxidation reaction (WOR)<sup>8</sup> in the MPR system. To further examine the participation of reducing equivalents (e.g., electrons or hydrogen atoms) in the formation of  $\text{H}_2\text{O}_2$ —a phenomenon reported in air–water microdroplets—we employed a fluorogenic assay based on the reduction of resazurin (RZR) to fluorescent resorufin (RSF) (Supplementary Fig. 13b). Under an argon atmosphere, we stirred an aqueous solution of XAD-1180N MPRs and RZR for twelve hours and observed a higher formation of RSF compared to when the experiment was conducted under air conditions. Consistently, adding the electron scavenger p-benzoquinone (PBQ) to MPR–water mixtures markedly suppressed  $\text{H}_2\text{O}_2$  production (Fig. 4C). These findings confirm the presence of reductive species during  $\text{H}_2\text{O}_2$  generation, such as electrons or hydrogen atoms, which would have been scavenged by  $\text{O}_2$  in the presence of air (see Supplementary Fig. 13b). Additionally, superoxide anion radical ( $\cdot\text{O}_2^-$ ) scavenger experiments revealed that superoxide dismutase (SOD) can suppress the  $\text{H}_2\text{O}_2$  generation in the MPR system, while further introduction of SOD inhibitors, N, N-diethyldithiocarbamate (DDC) and  $\text{KN}_3$ , can restore the generation of  $\text{H}_2\text{O}_2$  (Fig. 4D and Supplementary Fig. 15a-b). The presence of  $\cdot\text{O}_2^-$  was also confirmed by a nitrotetrazolium blue chloride (NBT) reduction test, in which stirring the aqueous mixtures of MPR and NBT in the presence of  $\text{O}_2$  yielded a characteristic blue-purple formazan product (Supplementary Fig. 15c-d). Together, these data validate the dominant ORR pathway for  $\text{H}_2\text{O}_2$  formation in MPR systems under aerated conditions:  $\text{O}_2 \rightarrow \cdot\text{O}_2^- \rightarrow \text{H}_2\text{O}_2$  (Fig. 4I).

We next examined the influence of solution pH (ranging from 4 to 12, buffered by 0.1 M phosphate) on  $\text{H}_2\text{O}_2$  generation. The MPR system exhibited higher activity under alkaline conditions, with an optimum at pH 9 (Fig. 4E). This mild alkaline preference differs from the acidic optimum reported for ultrasound-mediated water-in-oil microdroplets (another hydrophobe–water interface) where ORR pathway dominated the  $\text{H}_2\text{O}_2$  formation under acidic settings,<sup>54</sup> but similar to Christian George’s recent observations of enhanced  $\text{H}_2\text{O}_2$  generation in alkaline hydrophobe–water droplets.<sup>55</sup>

Using electron paramagnetic resonance (EPR) spectroscopy with the spin trap 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trap, we detected the characteristic quadruplet signal of DMPO- $\cdot\text{OH}$  in MPR–water mixtures (Fig. 4F). We further quantified  $\cdot\text{OH}$  production using the fluorogenic probe terephthalic acid (TPA), which reacts with  $\cdot\text{OH}$  to form highly fluorescent 2-hydroxyterephthalic acid (hTPA, Supplementary Fig. 16a). The fluorescence intensity increased continuously over 12 hours, confirming the sustained generation of  $\cdot\text{OH}$  radicals. Quantitative analysis revealed that  $\cdot\text{OH}$  was produced concurrently with  $\text{H}_2\text{O}_2$ , but at a concentration approximately 200 times lower (Fig. 4G and Supplementary Fig. 16b-c). Adding the  $\cdot\text{OH}$  radical scavenger isopropanol (IPA) into the reaction mixture slightly increased  $\text{H}_2\text{O}_2$  production (Fig. 4H). A strong interfacial electric field (EF,  $10^9$  V/m), localized to a region of several angstroms at the hydrophobe–water interfaces, has been proposed to drive charge separation and potentially oxidize adsorbed hydroxide ions ( $\text{OH}^-$ ) or water to hydroxyl radicals ( $\cdot\text{OH}$ ), which could subsequently recombine to form  $\text{H}_2\text{O}_2$ .<sup>4,6-10,15-19</sup> Several recent studies by other groups have questioned the role of such strong interfacial EFs in the formation of  $\cdot\text{OH}$  from  $\text{OH}^-$ .<sup>11-13,52,56-59</sup> While our results confirm  $\cdot\text{OH}$  formation in the MPR–water system, we emphasize that detection of  $\cdot\text{OH}$  radicals alone does not prove water oxidation reaction (WOR), because  $\cdot\text{OH}$  may also originate from catalytic decomposition of  $\text{H}_2\text{O}_2$  via ORR pathway—a well-documented secondary reaction in redox systems.

Although the ORR pathway for  $\text{H}_2\text{O}_2$  formation in the MPR system is established and the hydrogen in  $\text{H}_2\text{O}_2$  unequivocally comes from  $\text{H}_2\text{O}$ , the source of electrons (or reducing equivalents) remains unresolved. In a recent study on sonicated emulsified water microdroplets, Rodriguez-Lopez and coworkers also identified ORR as the dominant route for  $\text{H}_2\text{O}_2$  formation, but noted that the origin of the reducing power remains unclear.<sup>60</sup> Current literature suggests two possible electron-donation pathways at aqueous microinterfaces: sole oxidation of solid surface (as proposed by Mishra and coworkers<sup>12,52</sup>) or oxidation of water (WOR, as suggested by Zare and George groups<sup>8-10,15,16</sup>), as shown in Fig. 4I. Both pathways would result in surface oxidation of the organic MPR framework, and X-ray photoelectron spectroscopy (XPS) analysis revealed slight oxidation of post-reaction MPRs (Supplementary Fig. 17). Directly distinguishing these mechanisms is challenging due to interfacial complexity and the lack of real-time electron-tracking tools.

To probe whether WOR contributes under our conditions, we designed an experiment in which  $\text{O}_2$  was replaced with the electron acceptor PBQ and  $\text{H}_2\text{O}$  was replaced by 100%  $\text{H}_2^{18}\text{O}$  (Supplementary Fig. 18). If WOR occurred,  $\text{H}_2^{18}\text{O}_2$  should form and be detectable via isotopic analysis. After two weeks of stirring under a nitrogen atmosphere, a low concentration of  $\text{H}_2\text{O}_2$  (i.e.,  $\sim 10\ \mu\text{M}$ ) was detected with the HRP-AR fluorometric method, but high-resolution mass spectrometry showed no detectable  $^{18}\text{O}$  incorporation into the peroxide product. Thus, under these experimental conditions, we cannot confirm a significant WOR contribution in our MPR system. Potential limitations—such as background interference from the resin matrix or adsorption of the probe—may have affected sensitivity. Further methodological refinements will be required to conclusively resolve the electron-transfer pathway. In summary, our mechanistic investigation establishes ORR as the dominant route for  $\text{H}_2\text{O}_2$  formation at MPR–water interfaces under aerated conditions, while the role of water oxidation remains unverified with the present data. These insights not only clarify the reaction pathway in our system but also contribute to the ongoing discussion on redox mechanisms at hydrophobic microinterfaces.

### Robustness and scalability of the MPR-based $\text{H}_2\text{O}_2$ production process

Further, the effects of various salts on the generation of the MPR system were examined. As shown in Fig. 5A, the introduction of 1 M  $\text{Na}_2\text{SO}_4$  and 1 M  $\text{NaCl}$  did not affect the generation of  $\text{H}_2\text{O}_2$  compared to pure water, while that of phosphate solution, tap water, and simulated seawater only slightly decreased the activity. This is significantly different from that of PTFE–water interface under vigorous ultrasonic irradiation, wherein addition of 1M  $\text{NaCl}$  leads to a  $>90\%$  decrease of  $\text{H}_2\text{O}_2$  generation.<sup>37</sup> This high tolerance of MPRs to various salts makes it a potential candidate for application in long-term oceangoing voyages, such as disinfection of ships, whilst the exact mechanism needs further study. Another interesting finding is that when XAD-1180N MPR was dispersed in a  $\text{CO}_2$ -saturated water and stirred for six hours, the average  $\text{H}_2\text{O}_2$  generation rate was similar to that of normal conditions, which may be due to the strong buffering capacity of the MPR (Fig. 5A). Furthermore, it was found that even after thermal treatment at  $300\ ^\circ\text{C}$  for four hours, the activity of MPR remained unaffected (Fig. 5B). These results demonstrate the robustness of the MPR system for constructing scalable hydrophobe–water micro-interfaces for catalyst-free synthesis of  $\text{H}_2\text{O}_2$ .

Subsequently, the potential for expanding these hydrophobe–water micro-interfaces, which are based on MPRs for  $\text{H}_2\text{O}_2$  generation, to a larger-scale reaction volume was considered, an essential step toward potential industrial application. As a proof of concept, the reaction volume was scaled from 0.6 mL to 1000 mL, representing an amplification factor of  $\sim 1800$ , and the generation of  $\text{H}_2\text{O}_2$  was monitored at ambient conditions. To facilitate the dispersion of MPRs, a mechanical mixer was utilized, as illustrated in Fig. 5C. Due to the well-defined particle size of

MPRs (1–10  $\mu\text{m}$ ), the generated  $\text{H}_2\text{O}_2$  could be easily extracted via low-cost and straightforward filtration. Over the course of one week, stirring of aqueous mixtures of MPRs, a continuous accumulation of  $\text{H}_2\text{O}_2$  was visually confirmed using a commercial  $\text{H}_2\text{O}_2$  test strip (Fig. 5D), reaching a final accumulated  $\text{H}_2\text{O}_2$  concentration exceeding 100  $\mu\text{M}$ . Quantified analysis further demonstrated a nearly linear increase in  $\text{H}_2\text{O}_2$  concentration during this period, with the resultant accumulated concentration reaching ca. 150  $\mu\text{M}$  (Fig. 5E). This outcome validates the operational viability of MPRs-based water micro-interfaces for the scalable synthesis of  $\text{H}_2\text{O}_2$ . Although the accumulated  $\text{H}_2\text{O}_2$  concentration decreased by approximately sevenfold compared to the small-scale (600  $\mu\text{L}$ ) system, this reduction is likely attributable to the lower stirring efficiency in the larger setup. As indicated in Supplementary Fig. 9, improved dispersion through optimized agitation enhances  $\text{H}_2\text{O}_2$  generation. However, for practical large-scale applications, milder stirring with a larger propeller could be employed, potentially coupled with sustainable energy sources such as wind, hydraulic, or tidal power, making the system particularly promising for remote or marine operations. Extending the reaction time is expected to enable accumulation up to  $\sim 1$  mM  $\text{H}_2\text{O}_2$  (Fig. 5E). Further enhancements in  $\text{H}_2\text{O}_2$  yield could be achieved through physical or chemical modification of MPRs (e.g., material process engineering) or via reactor optimization to improve the dispersion of MPRs and the mass transfer of  $\text{H}_2\text{O}/\text{O}_2$ . In this proof-of-concept scalable experiment, a resin loading of 100 g/L was used; higher loadings may be employed in future applications given the low cost, wide availability, and excellent recyclability of MPRs (e.g., over nine cycles without significant loss of activity; Fig. 2C). Notably, this process operates without energy-intensive inputs such as sonication or photo/electrochemical excitation and exhibits high tolerance to salts and elevated temperatures. Thus, the proposed MPR system represents a promising and sustainable strategy for scalable  $\text{H}_2\text{O}_2$  production.

## Discussion

In this work, we present a sustainable strategy for hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) production by employing the off-the-shelf, metal-free hydrophobic macroporous resins (MPRs) in water to provide scalable and tunable hydrophobe–water micro-interfaces. These interfaces enable the direct synthesis of  $\text{H}_2\text{O}_2$  generation from  $\text{H}_2\text{O}$  and  $\text{O}_2$  without conventional catalysts, external light or electrical energy input, or chemical additives. Simply stirring an aqueous suspension of MPRs – specifically those containing polystyrene/divinylbenzene (PS-DVB) backbones, such as XAD-1180N, XAD-2, and XAD-4 – achieves a mass-normalized  $\text{H}_2\text{O}_2$  production rate of up to  $\sim 0.51 \mu\text{mol g}_{\text{MPR}}^{-1} \text{h}^{-1}$  under ambient atmosphere, leading to an eventual  $\sim 1$  mM-level accumulation of  $\text{H}_2\text{O}_2$  within one week. This process operates without ultrasonication, surfactants, or custom-synthesized new materials.

As a proof-of-concept of scalability, operation in a 1000 mL reactor yielded an accumulated  $\text{H}_2\text{O}_2$  concentration of  $\sim 150 \mu\text{M}$  after one week. Systematic investigations shows that both the macroporous architectures and hydrophobic surface characteristics of MPRs are essential for efficient  $\text{H}_2\text{O}_2$  generation. This system performs optimally under alkaline conditions (pH 9) and maintains high tolerance to various salts, highlighting its robustness for diverse aqueous environments. Mechanistically, isotope labeling experiments ( $\text{H}_2^{18}\text{O}$  and  $^{18}\text{O}_2$ ) confirm that molecular oxygen is the predominant oxygen source for  $\text{H}_2\text{O}_2$  formation, with negligible  $\text{O}_3$  involvement, supporting the oxygen reduction reaction (ORR) as the dominant pathway. The detection of reactive intermediates (e.g.,  $\cdot\text{OH}$ ,  $\text{e}^-$ ,  $\cdot\text{O}_2^-$ ) further indicates that interfacial charge separation and electron transfer drive continuous  $\text{H}_2\text{O}_2$  formation. These findings resemble those reported in air–water microdroplet systems, but are achieved here through readily scalable solid–water interfaces, bringing new insights into microdroplet and micro-interface chemistry. Nevertheless, further research is needed to provide clearer insights into the latter aspects. Owing to its operational simplicity, compatibility with renewable energy sources (e.g., wind, hydraulic, or tidal power), salt tolerance, and minimal infrastructure requirements, the MPR-based system offers a promising route toward decentralized, green  $\text{H}_2\text{O}_2$  production, especially in remote or marine settings.

More broadly, this work demonstrates how engineered porous materials can be used to create functional solid–liquid microscale interfaces for sustainable chemical synthesis, opening new avenues for applying interfacial phenomena in continuous-flow and industrially relevant systems.

## Methods

### Dispersing porous resins in water for H<sub>2</sub>O<sub>2</sub> generation

Commercially available macroporous and microporous resins microspheres of various sizes and compositions (Supplementary Fig. 1 and Supplementary Table 1) were ground into powders with a typical particle size of 1–10  $\mu\text{m}$ . The powders were washed by sonication in ethanol for 30 min, centrifuged, and this process was repeated three times. After vacuum-drying at 60 °C for 24 h, 20 mg of powder was dispersed in 0.6 mL of deionized water (DIW) in a 4 mL polypropylene (PP) tube containing a glass- or PTFE-coated magnetic stir bar (1500 rpm). Following stirring, the reaction mixture was centrifuged at 21,100  $\times g$  for 5 min (Legend Micro 21R, Thermo Fisher Scientific) and filtered through a <0.10  $\mu\text{m}$  membrane. The resulting particle-free filtrate was used for H<sub>2</sub>O<sub>2</sub> quantification by fluorescence (HRP-AR method) or absorbance (PTO method) assays, as detailed below. To provide a comparison, several other non-porous materials, including PS, PTFE, SiO<sub>2</sub>, and agarose gel, were also tested by the same method.

### Fluorescence-based H<sub>2</sub>O<sub>2</sub> quantification (HRP-AR method)

A working solution containing 10 nM HRP, 100  $\mu\text{M}$  AR, and 10 mM phosphate buffer (pH 7.4) was prepared. For the assay, 20  $\mu\text{L}$  of sample or H<sub>2</sub>O<sub>2</sub> standard (1–100  $\mu\text{M}$ ) solution was mixed with 180  $\mu\text{L}$  working solution in a 1.5 mL PP tube, vortexed for 15 s, and incubated for 3 min. A 100  $\mu\text{L}$  aliquot was transferred to a black 96-well plate, and fluorescence was measured ( $\lambda_{\text{ex}}$ =530 nm,  $\lambda_{\text{em}}$ =590 nm, gain=35) on a Biotek Synergy LX microplate reader. Kinetic measurements confirmed that the HRP-catalyzed conversion of AR to resorufin was complete within 3 min and remained stable (Supplementary Fig. 3a–b). The assay showed linear response for final H<sub>2</sub>O<sub>2</sub> concentrations of 0.1–10  $\mu\text{M}$  (Supplementary Fig. 3c). Samples exceeding this range were diluted with DIW prior to analysis.

### Absorbance-based H<sub>2</sub>O<sub>2</sub> quantification (PTO method)

An equal volume (200  $\mu\text{L}$ ) of 10 mM PTO solution and H<sub>2</sub>O<sub>2</sub> standard solution (1–200  $\mu\text{M}$ ) were mixed in a 1.5 mL PP tube, vortexed for 15 s, and incubated at room temperature for 2 min. Subsequently, a 200  $\mu\text{L}$  aliquot was transferred to a transparent 96-well microplate. Absorbance spectra were recorded from 350 to 650 nm using a microplate reader (Supplementary Fig. 4a). Calibration curves were generated by plotting the absorbance at 400 nm against H<sub>2</sub>O<sub>2</sub> concentration. A linear calibration curve ( $R^2 > 0.99$ ) was obtained in the range of 10–200  $\mu\text{M}$ , with a detection limit of  $\sim 5 \mu\text{M}$  (Supplementary Fig. 4b–c). Filtered samples were analyzed identically.

### <sup>1</sup>H NMR measurement of H<sub>2</sub>O<sub>2</sub>

H<sub>2</sub>O<sub>2</sub> was quantified via <sup>1</sup>H NMR spectroscopy following a reported protocol.<sup>47</sup> After 120 h's stirring of an aqueous dispersion of XAD-1180N MPRs, filtered reaction mixtures were spiked with 2-(N-morpholino)ethanesulfonic acid (MES) from a 50 mM in D<sub>2</sub>O stock to a final concentration of 1 mM, and the pH was adjusted to  $6.0 \pm 0.05$  using a calibrated pH meter. A commercial H<sub>2</sub>O<sub>2</sub> standard (100  $\mu\text{M}$ ) was processed identically as a reference. Spectra were acquired on a Bruker Avance III HD 600 MHz spectrometer equipped with a CPBBO cryoprobe. Results were cross-validated using the HRP-AR and PTO assays (Supplementary Fig. 7).

### Hydrophobic modification of agarose gel

Butyl groups were grafted onto the hydroxyl chains of agarose via a published procedure (Supplementary Fig. 12a).<sup>61</sup> Commercial agarose gel (containing 20% ethanol) was washed three times with deionized water, followed by solvent exchange with anhydrous dioxane. To ensure complete dehydration, the gel was suspended in anhydrous dioxane, agitated for 10 min, and centrifuged; this process was repeated five times. Subsequently, 1 mL of the dehydrated gel was mixed with 1 mL of anhydrous dioxane and 20  $\mu$ L of boron trifluoride etherate ( $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) catalyst, shaken at 100 rpm for 5 min, then treated with varying amounts of n-Butyl glycidyl ether at 45 °C for 45 min under shaking (100 rpm). Finally, the modified gel was washed alternately with dioxane and water (three cycles), followed by seven washes with DIW to remove residual reagents. This yielded butyl-agarose gels with tunable hydrophobicity.

### Hydrophilic modification of macroporous resins

Hydrophilic dextran chains were grafted onto MPR phenyl rings via a two-step Friedel–Crafts/nucleophilic substitution route (Supplementary Fig. 12b).<sup>62</sup> First, MPR beads were washed with ethanol, dried at 60 °C for 12 h, and swollen in carbon disulfide ( $\text{CS}_2$ ) for 12 h. Aluminum chloride ( $\text{AlCl}_3$ , 1.2 eq. based on styrene units) and 2-chloromethylacetyl chloride (1.0 eq., dissolved in  $\text{CS}_2$ ) were added. The reaction was stirred at 50 °C for 4 h. The intermediate MPR-Cl was washed, filtered, and dried. Second, MPR-Cl (1.0 g) was swollen in anhydrous DMSO (10 mL) for 12 h. Separately, dextran (MW 10,000, 0.4 g) was dissolved in anhydrous DMSO (40 mL) containing sodium hydride (0.236 g) to deprotonate hydroxyl groups. The activated dextran solution was mixed with the swollen MPR-Cl, and tetrabutylammonium bromide (TBAB, 0.5 eq.) was added as a phase-transfer catalyst, and the mixture was reacted at 65 °C for 24 h to yield the hydrophilic-modified resin.

### Contact angle measurement and BET analysis

Contact angles were measured on an optical contact angle meter.<sup>63, 64</sup> Powder samples were immobilized on double-sided adhesive tape, and excess powder was removed by repeated pressing to form a uniform thin layer. A 3  $\mu$ L droplet of deionized water was dispensed onto the sample surface using a computer-controlled needle. Images were captured immediately, and contact angles were calculated via the ellipse-fitting method in the instrument software. Specific surface areas and pore size distributions were determined via nitrogen adsorption-desorption isotherms using the BET method.<sup>65,66</sup>

### Atmosphere control experiment

Anaerobic experiments were conducted in a glovebox filled with high-purity nitrogen ( $\text{O}_2 < 0.1$  ppm). All components were rigorously degassed to eliminate atmospheric interference (Supplementary Fig. 13). Ultrapure water was deoxygenated following a modified protocol by Mishra et al.<sup>52</sup>: water was heated to boiling in a sealed beaker, followed by purging with nitrogen gas for 45 minutes. Dissolved oxygen in the resulting water was quantified using a Hach dissolved-oxygen meter and was consistently below 0.1 ppm. The water was then transferred and sealed in a vial within the glovebox. Dry MPR powder underwent five vacuum/nitrogen refill cycles in the glovebox antechamber, then continuous evacuation (>10 h) to remove the maximum amount of residual gas trapped within the pores. Sample assembly was performed entirely within the inert atmosphere.

For  $\text{O}_2$ -rich conditions, resin and a magnetic stir bar were loaded into a reaction tube fitted with a three-way valve. The system was purged to remove trapped gas, and oxygen-saturated deionized water was injected through the valve. An oxygen balloon was attached to the top of the tube to maintain a positive oxygen pressure during the reaction (Supplementary Fig. 13).

### Oxygen isotope labeling experiments and MS analysis

Oxygen-atom origins in  $\text{H}_2\text{O}_2$  were traced using  $\text{H}_2^{18}\text{O}$  and  $^{18}\text{O}_2$  via mass spectrometry (MS) after derivatization with 4-Carboxyphenylboronic acid (CPBA), which reacts stoichiometrically with  $\text{H}_2\text{O}_2$  to yield 4-hydroxybenzoic acid (4-HBA).<sup>54</sup> Incorporation of an  $^{18}\text{O}$  atom results in a characteristic +2 Da m/z shift in the 4-HBA spectrum. High-resolution MS analysis was performed on an Agilent 6540 Q-TOF. For  $\text{H}_2^{18}\text{O}$  experiments, MPR powders (20 mg) were stirred in 600  $\mu\text{L}$  of 30%  $\text{H}_2^{18}\text{O}$  for 100 h, filtered, and the supernatant was incubated with 2 mM CPBA for 1 h prior to MS analysis. For  $^{18}\text{O}_2$  experiments, reaction assembly was carried out in a nitrogen-filled glovebox. Degassed water and MPR powder were placed in a 4 mL PP tube. This tube and a 1 L gas bag filled with  $^{18}\text{O}_2$  were sealed together inside a transparent 2.5 L barrier pouch. To initiate the reaction, the gas bag was opened within the sealed pouch to create an  $^{18}\text{O}_2$  atmosphere, and the reaction tube was uncapped. The system was stirred for 100 h, followed by the same workup and analysis procedures used for the  $\text{H}_2^{18}\text{O}$  experiment.

### Quantitative determination of $\cdot\text{OH}$

Hydroxyl radicals ( $\cdot\text{OH}$ ) were quantified using terephthalic acid (TPA) as a fluorogenic probe.<sup>54</sup> Non-fluorescent TPA reacts specifically with  $\cdot\text{OH}$  to form the highly fluorescent 2-hydroxyterephthalic acid (hTPA). XAD-1180N MPRs were suspended in a 2 mM aqueous TPA solution and stirred. After the reaction, the supernatant was collected, and fluorescence intensity was recorded on a Hitachi F-7000 spectrophotometer ( $\lambda_{\text{ex}}=315\text{ nm}$ ,  $\lambda_{\text{em}}=425\text{ nm}$ ).  $\cdot\text{OH}$  concentrations were derived from a calibration curve constructed from authentic hTPA standards (<1000 nM) (Supplementary Fig. 16).

### Scalable experiment

A large-scale batch reaction was performed with 100 g of XAD-1180N MPRs dispersed in 1.1 L of DIW under ambient conditions. Mixing was achieved using a mechanical stirrer (Lichen, China) operated at 500 rpm with glass beads added to aid dispersion. Over one week, 2 mL aliquots were periodically collected, centrifuged, and analyzed using commercial  $\text{H}_2\text{O}_2$  test strips (Merck, Germany; Product No. 1.10011.0001), with results cross-verified by the HRP-AR assay described above.

### Data Availability Statement

All data that support the findings of this study are available from the corresponding author upon request. Source data are provided with this paper.

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## Acknowledgements

We acknowledge the financial support from the National Key Research and Development Program (No. 2024FYA1509600, W.W.) and the National Natural Science Foundation of China (Nos. 22474060, H.S.; 22327803, W.W.).

## Author Contributions Statement

All authors have given approved to the final version of the manuscript. H.S., Z.B.Z and W.W. designed the project. H.S., J.G., and W.W. wrote the paper. J.G., K.Z., and H.S. carried out most of the experiments and analyzed the data. X.L.G., K.R.Y., and S.Y.Y. participated in discussing the manuscript. W.W. conceived and supervised the project.

### Competing Interests Statement

The authors declare no competing interests.

### Figure Legends (for main text figures)

**Fig. 1 Illustrated experimental procedures for using macroporous resins (MPRs) to create scalable hydrophobe–water micro-interfaces for  $\text{H}_2\text{O}_2$  generation from  $\text{H}_2\text{O}$  and  $\text{O}_2$ .** Scale bar, 500  $\mu\text{m}$ . The top-right cartoon depicts the Cassie-Baxter state of MPRs during operation, in which a small amount of air or  $\text{O}_2$  is trapped within the porous structures of the MPRs.

**Fig. 2 Experimental demonstration of MPRs in the construction of scalable hydrophobe–water micro-interfaces for  $\text{H}_2\text{O}_2$  generation.** (A) The recorded initial generation rate of  $\text{H}_2\text{O}_2$  in different materials tested, including MPRs, non-porous materials, and hydrophilic materials. These values were obtained by dispersing the same mass (20 mg) of each material into 0.6 mL of deionized water. The detailed chemical information of these tested materials can be found in Supplementary Table 1. (B) The kinetic curves of  $\text{H}_2\text{O}_2$  generation monitored in XAD-1180N MPRs and the non-porous polystyrene (PS). (C) The recycled use of XAD-1180N MPRs for  $\text{H}_2\text{O}_2$  generation. (D) Time-dependent dispersion profiles of XAD-1180N MPRs, PTFE, and  $\text{SiO}_2$  in water over a four-hour stirring period, monitored via scattering intensity measurements. The inset picture shows the final dispersion state of each material after four hours. (E) The positive correlation of rates of  $\text{H}_2\text{O}_2$  generation with the surface area of hydrophobic MPRs is normalized to their mass. Data in (A) and (B) are presented as mean  $\pm$  standard deviation ( $n = 3$  independent experiments).

**Fig.3 Investigation of the role of the hydrophobic nature of the pore wall of MPRs in  $\text{H}_2\text{O}_2$  generation.** (A) Scheme of hydrophilic treatment of XAD-1180N MPRs by grafting dextran structures onto their phenyl rings. (B) The recorded rate of  $\text{H}_2\text{O}_2$  generation for XAD-1180N MPRs at different degrees of hydrophilic treatment and their contact angles. (C) Scheme of hydrophobic modification of sengarose, a typical porous and hydrophilic agarose gel, by grafting hydrophobic butyl groups onto its hydroxyl groups. (D) The generation rate of  $\text{H}_2\text{O}_2$  for sengarose at different levels of hydrophobic treatment and their contact angles. Data in (B) and (D) are presented as mean  $\pm$  standard deviation ( $n = 3$  independent experiments).

**Fig.4 Deciphering the mechanism of  $\text{H}_2\text{O}_2$  generation in the MPR–water system.** (A) Illustration of isotope labeling of  $\text{H}_2\text{O}_2$ -promoted deborylation of 4-carboxyphenylboronic acid into 4-hydroxybenzoic acid. (B) High-resolution mass spectrometric analysis of 4-hydroxybenzoic acid products produced under  $\text{O}_2/\text{H}_2\text{O}$ ,  $\text{O}_2/\text{H}_2^{18}\text{O}$ , and  $^{18}\text{O}_2/\text{H}_2\text{O}$  conditions. (C) Effects of electron scavenger p-benzoquinone (PBQ) on  $\text{H}_2\text{O}_2$  generation rate of XAD-1180N at normal (aerobic) conditions. (D) Confirmation of superoxide radical anions ( $\cdot\text{O}_2^-$ ) through the use of superoxide dismutase (SOD) and its inhibitor N, N-diethyldithiocarbamate (DDC). (E) Comparison of  $\text{H}_2\text{O}_2$  generation rates of XAD-1180N at different pH values in 100 mM phosphate buffer solution. DIW represents de-ionized water. (F) ESR trapping of hydroxyl radicals ( $\cdot\text{OH}$ ). (G) Quantification of time-evolved formation of  $\cdot\text{OH}$  radicals during the generation of  $\text{H}_2\text{O}_2$ , measured using terephthalic acid (TA) as a probe. (H)  $\text{H}_2\text{O}_2$  Evolution in the presence of  $\cdot\text{OH}$  radical scavenger isopropanol (IPA) at varying concentrations. (I) Proposed pathway of  $\text{H}_2\text{O}_2$  generation in the MPR–water system, involving interfacial charge separation, electron transfer, and formation of immediate species. ORR dominates  $\text{H}_2\text{O}_2$  formation, while the source of

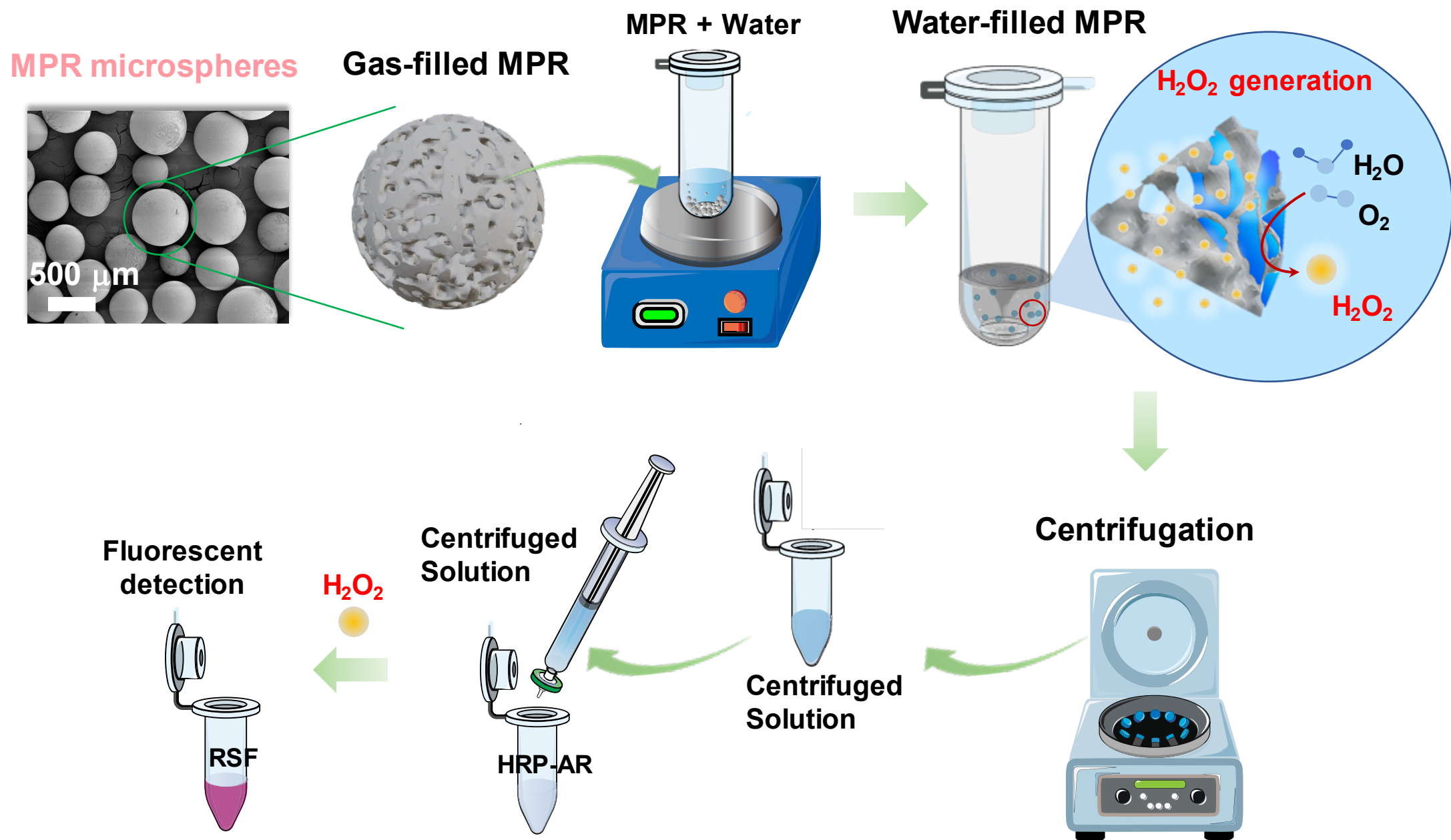
electrons remains unresolved. Two possible electron-donation pathways at aqueous microinterfaces are proposed: sole oxidation of the solid surface (path A) and oxidation of water (path B). Data in panels (D), (E), and (H) are presented as mean  $\pm$  standard deviation ( $n = 3$  independent experiments).

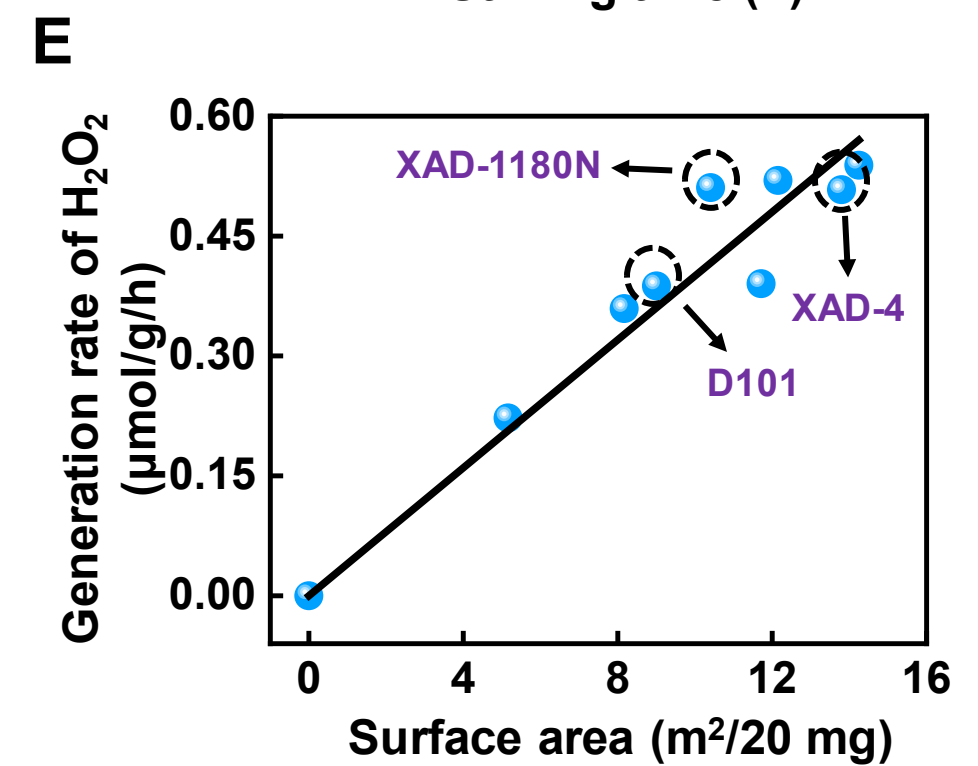
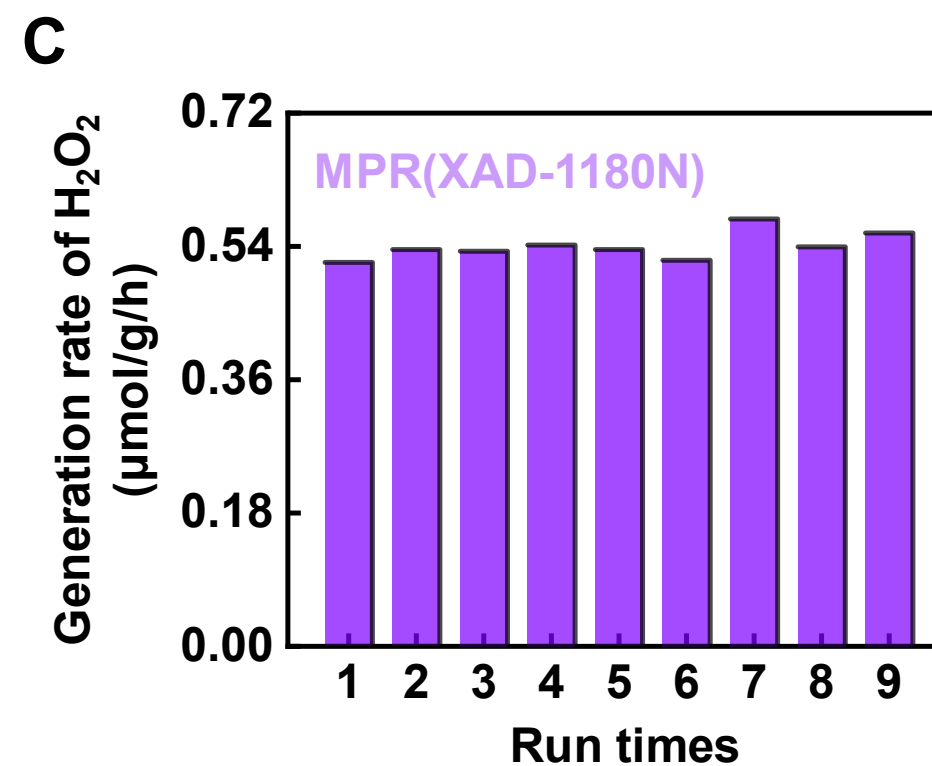
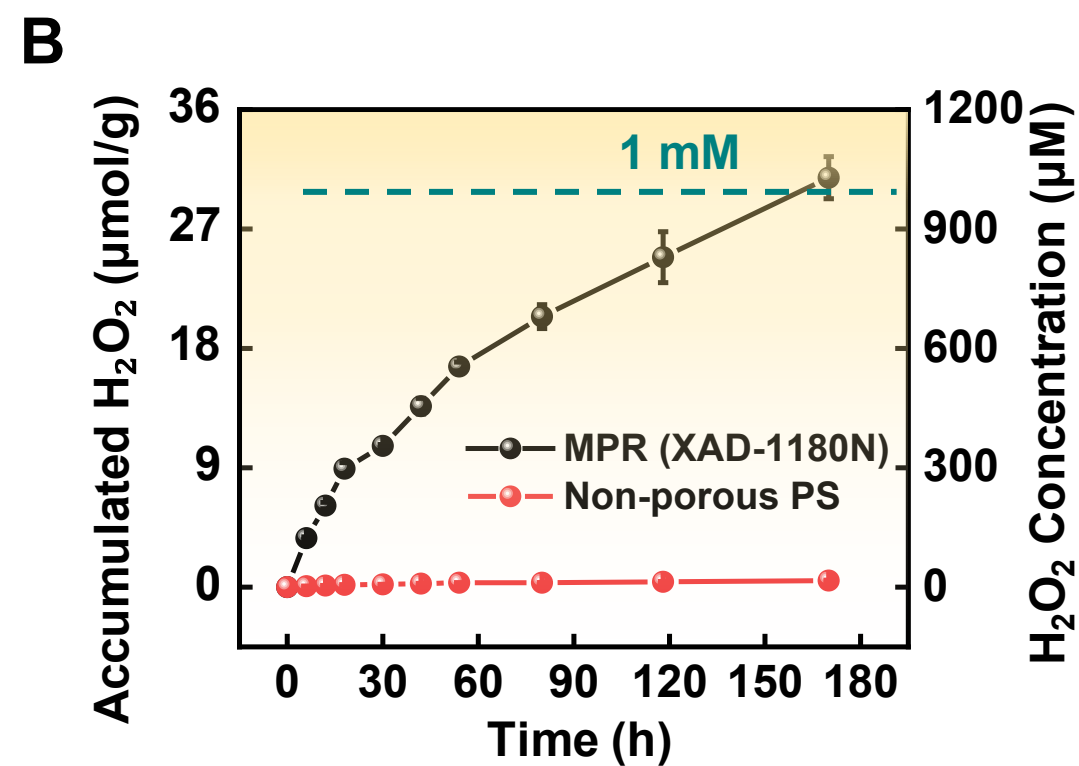
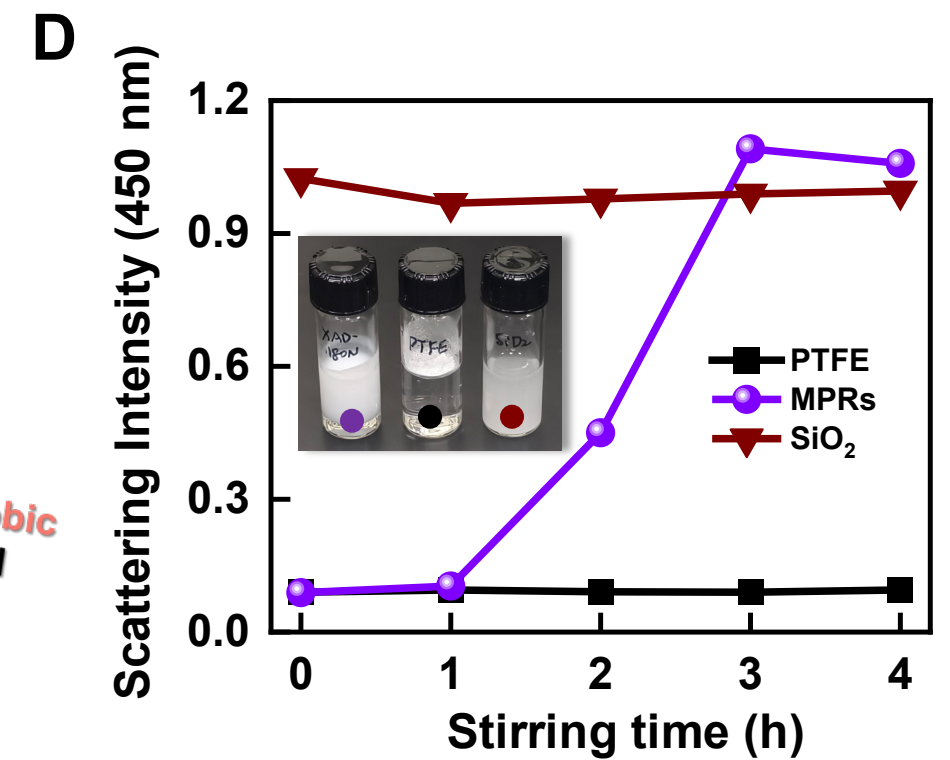
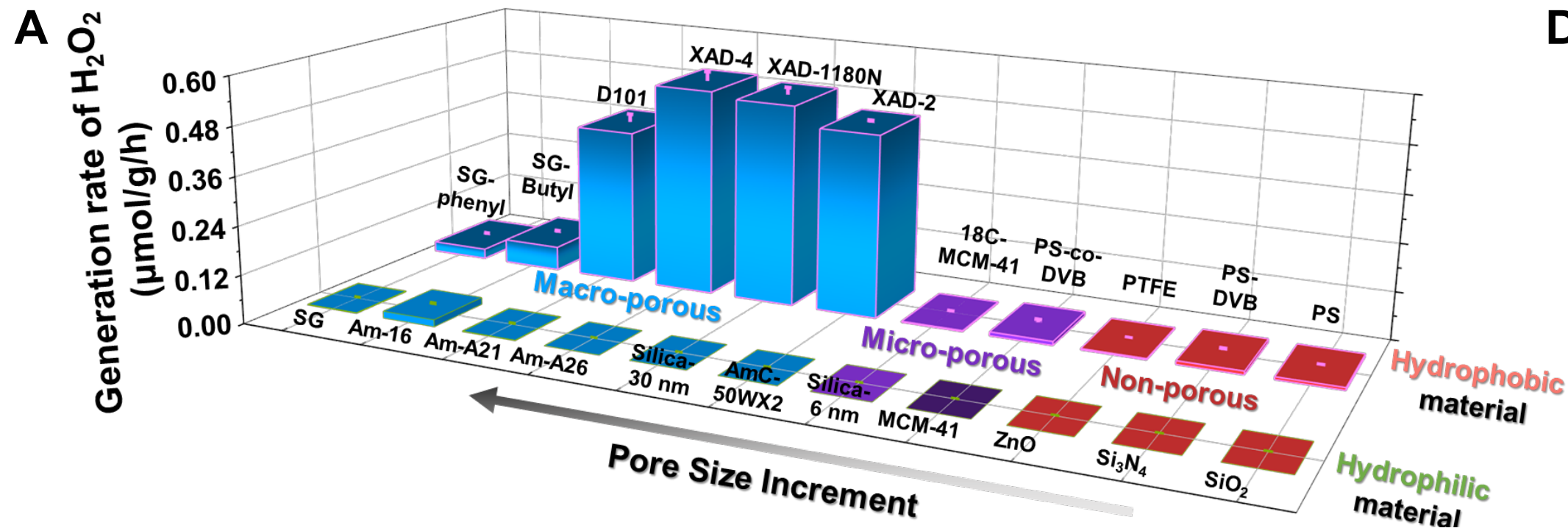
**Fig.5 Robustness of the MPR system for catalyst-free generation of  $\text{H}_2\text{O}_2$  from  $\text{H}_2\text{O}$  and  $\text{O}_2$  at ambient conditions.** (A) Effects of various salts (1 M  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{HPO}_4$ ), tap water, and simulated seawater (3.5 wt%  $\text{NaCl}$ ) on  $\text{H}_2\text{O}_2$  production in the MPR system. (B) Thermal treatment of XAD-1180N at 300 and 350 °C for four hours showed negligible effects on  $\text{H}_2\text{O}_2$  production activity, demonstrating the robustness of the MPR system for sustainable  $\text{H}_2\text{O}_2$  synthesis. (C) Experimental setup for a proof-of-concept demonstration of a one-liter reaction volume containing 1.1 L of deionized water and 100 g of XAD-1180N MPRs for the continuous generation of  $\text{H}_2\text{O}_2$ . A 500-rpm mechanical mixer with some glass beads was used to facilitate the dispersion of MPRs in the water. (D) A continuous generation of  $\text{H}_2\text{O}_2$  exceeding 100  $\mu\text{M}$  during one week of stirring of the aqueous dispersion solution of MPRs, as verified by a commercial  $\text{H}_2\text{O}_2$  test strip (Merck). For comparison, an aqueous solution containing 100  $\mu\text{M}$   $\text{H}_2\text{O}_2$  is used as a reference. (E) Quantification of continuous  $\text{H}_2\text{O}_2$  generation during one-week stirring of MPRs–water mixtures by HRP-AR assay. Data in (A) and (B) are presented as mean  $\pm$  standard deviation ( $n = 3$  independent experiments).

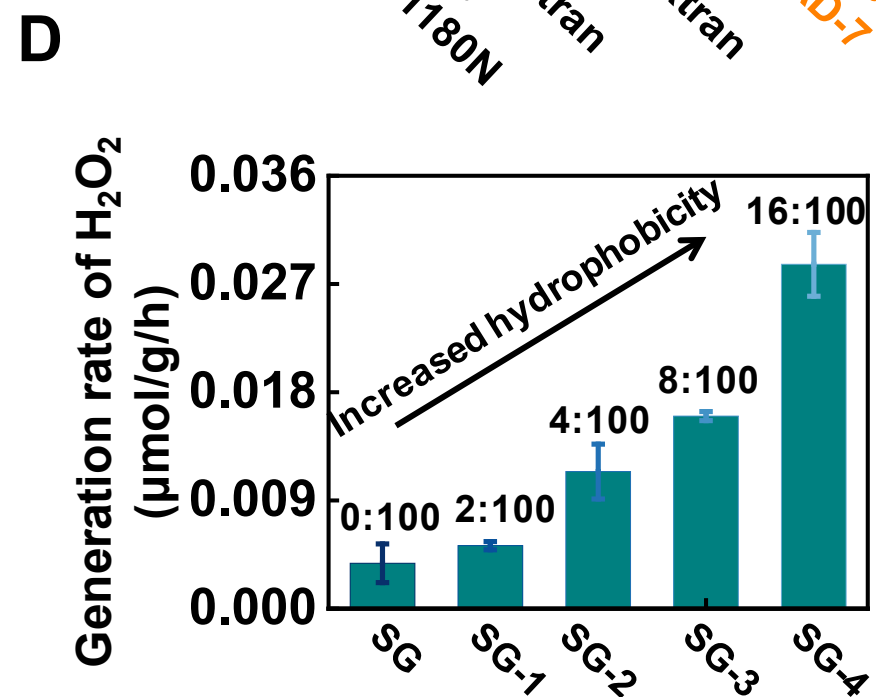
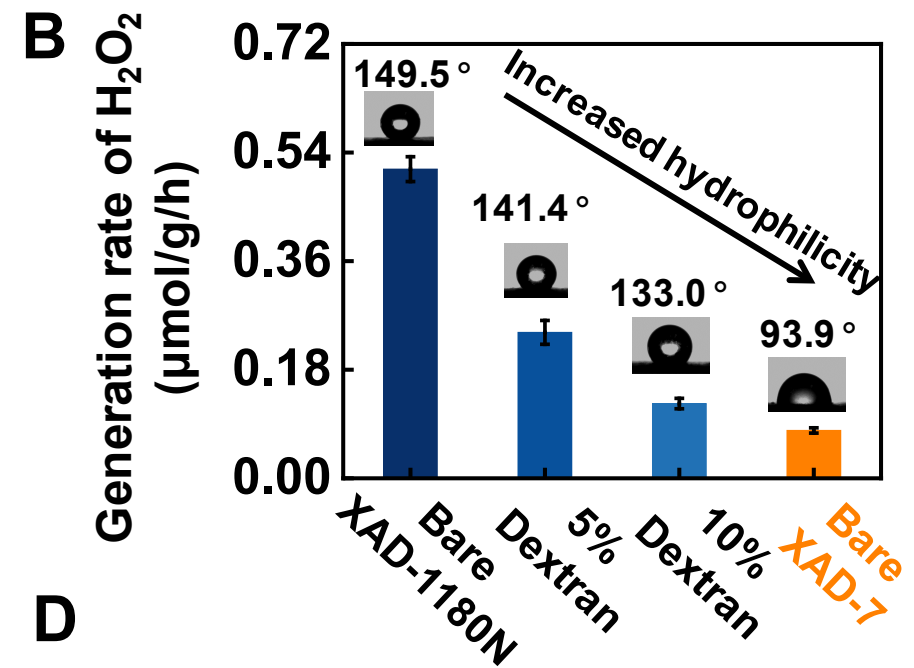
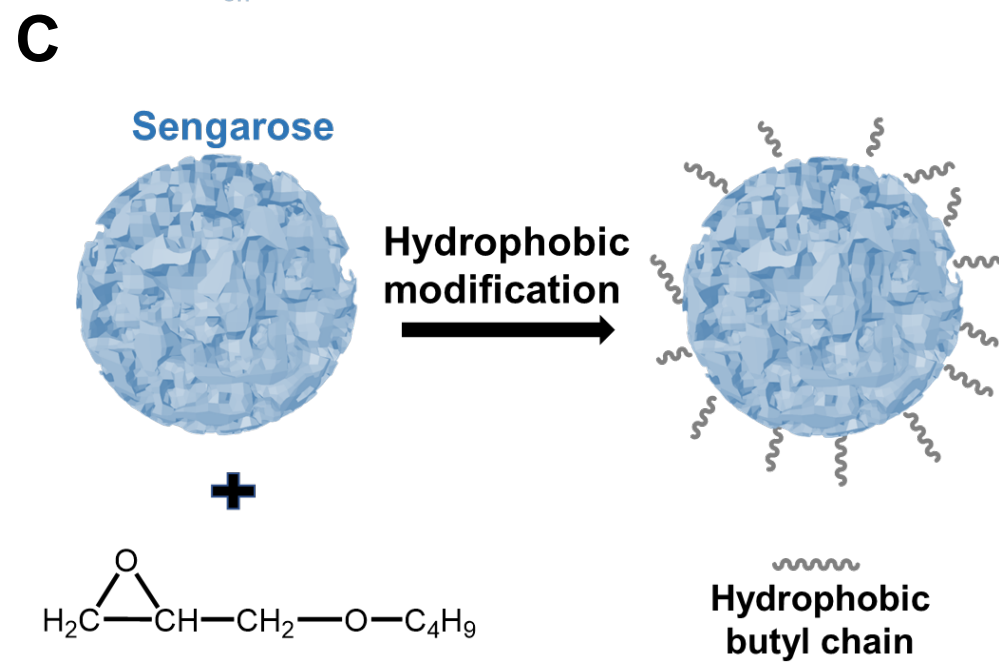
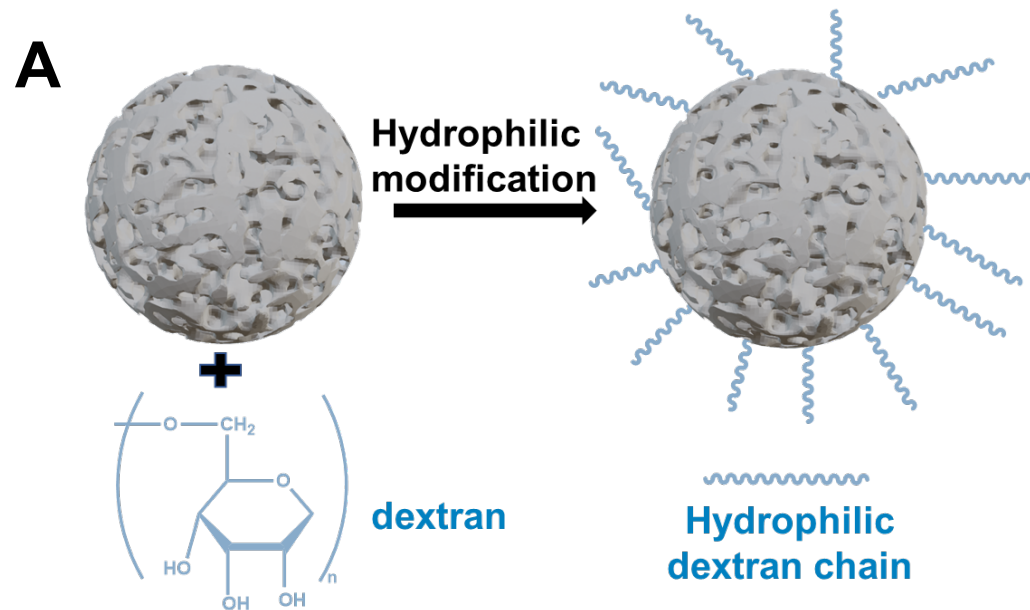
## Editorial Summary

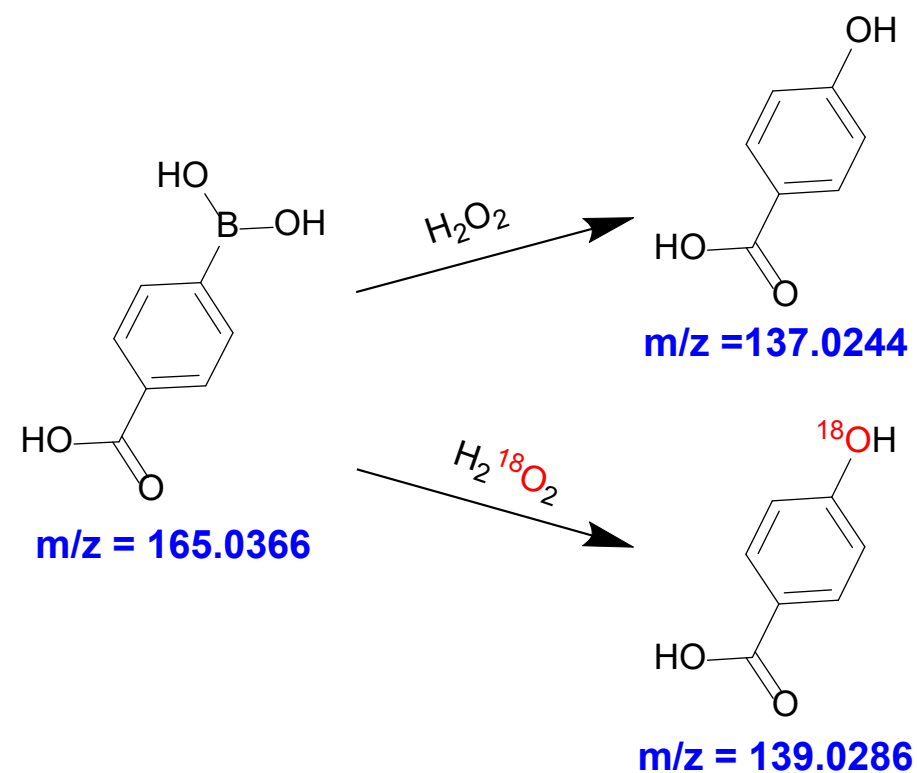
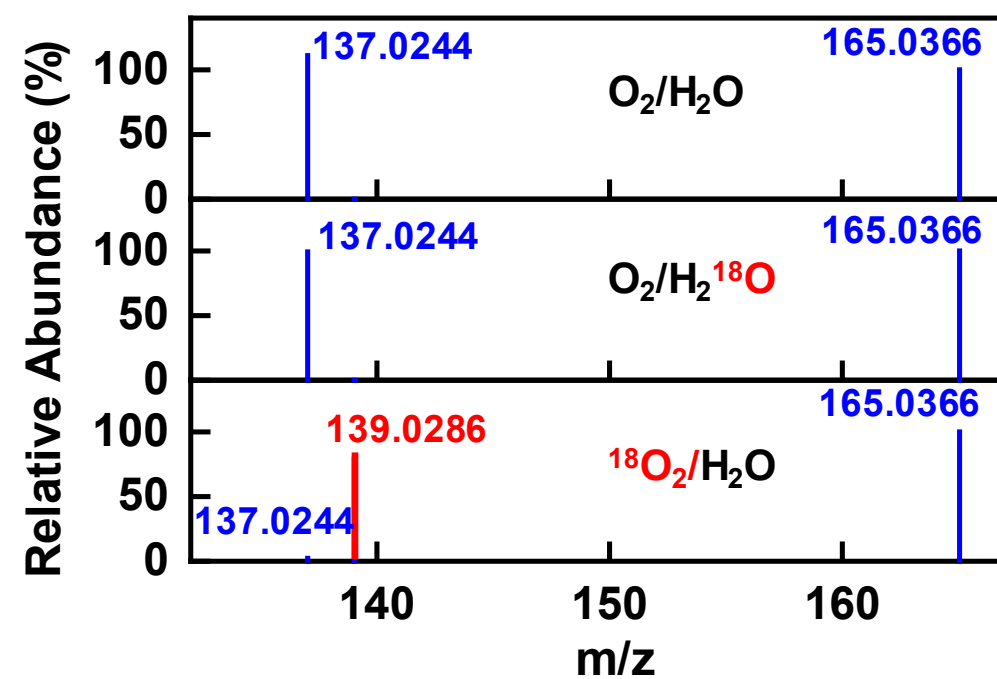
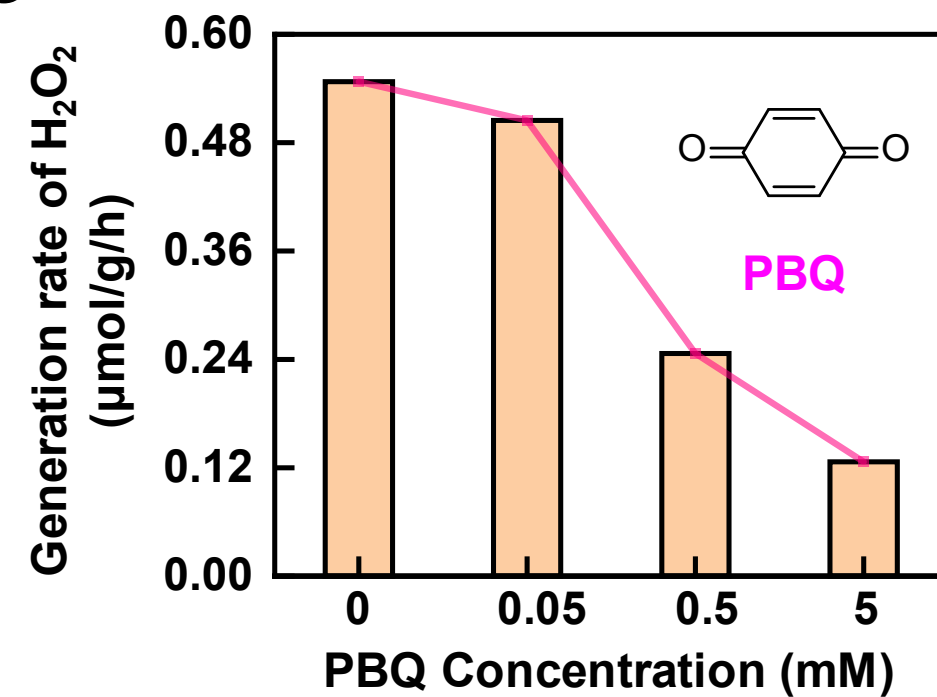
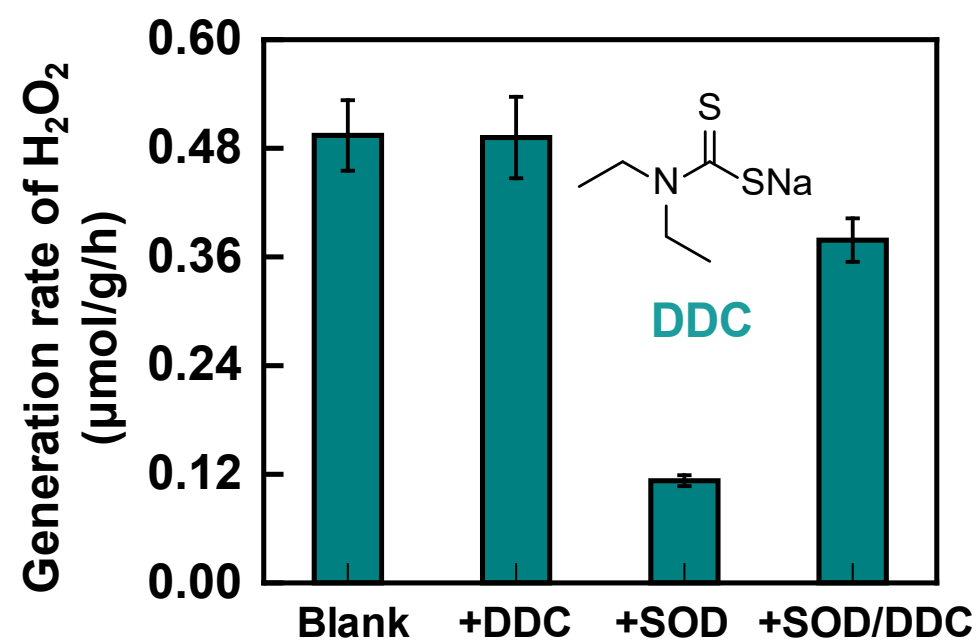
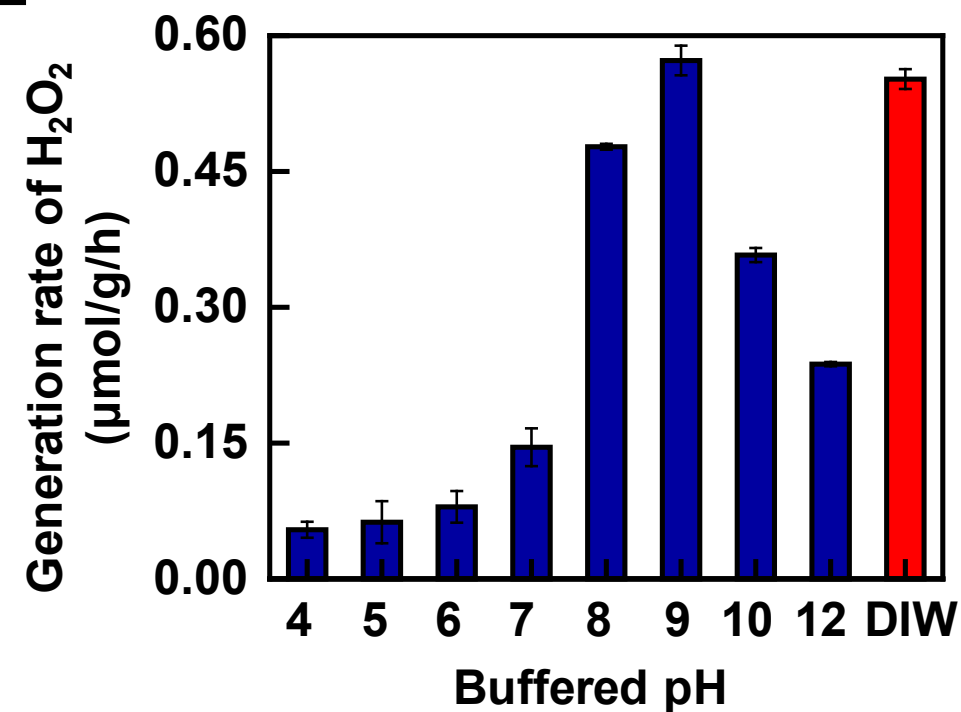
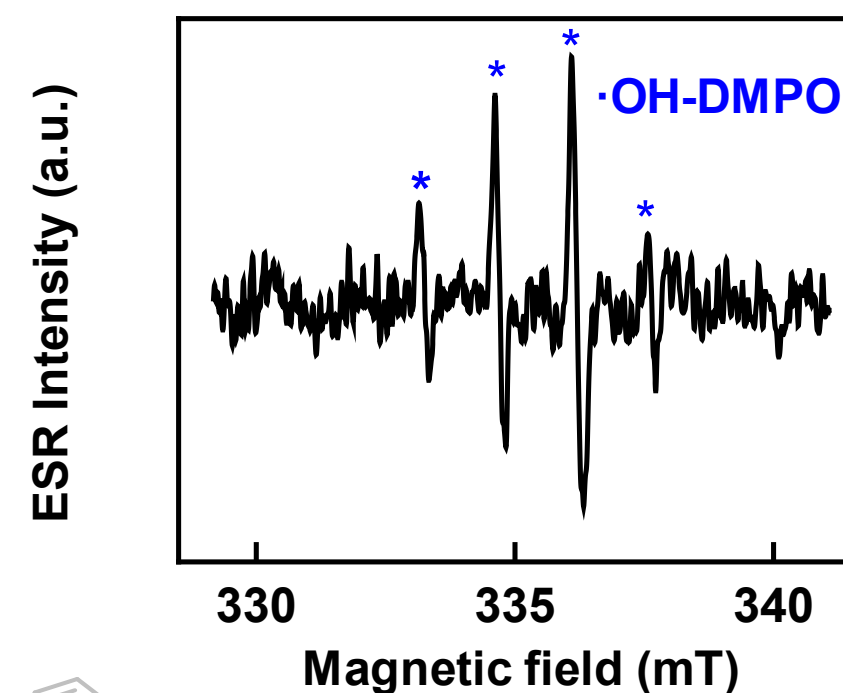
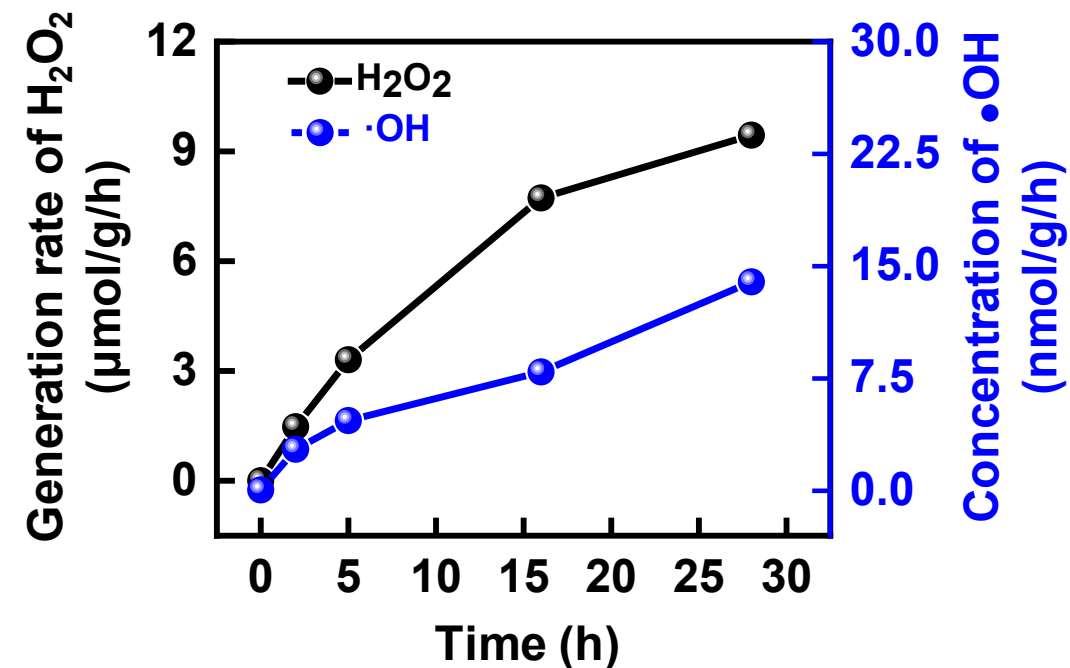
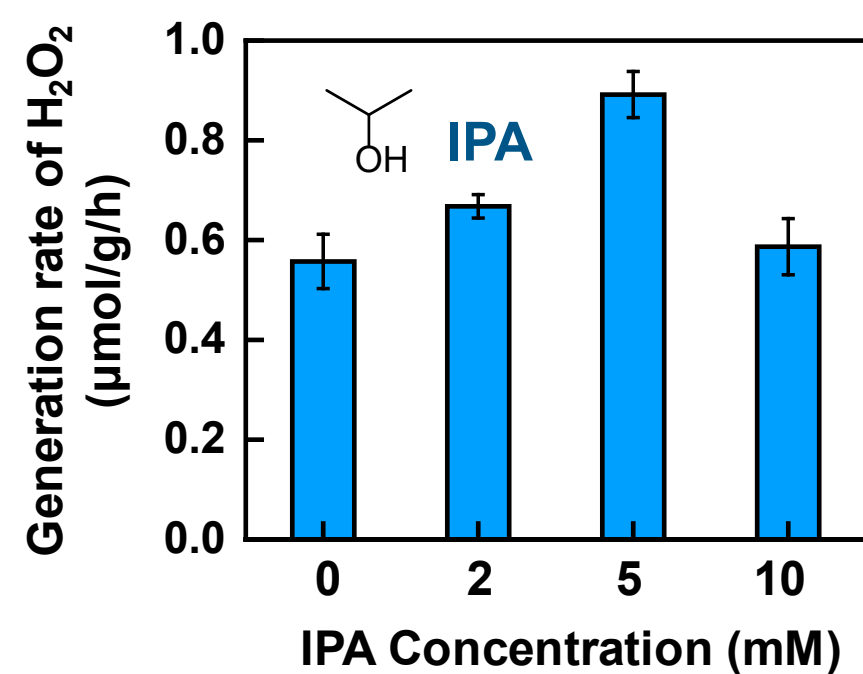
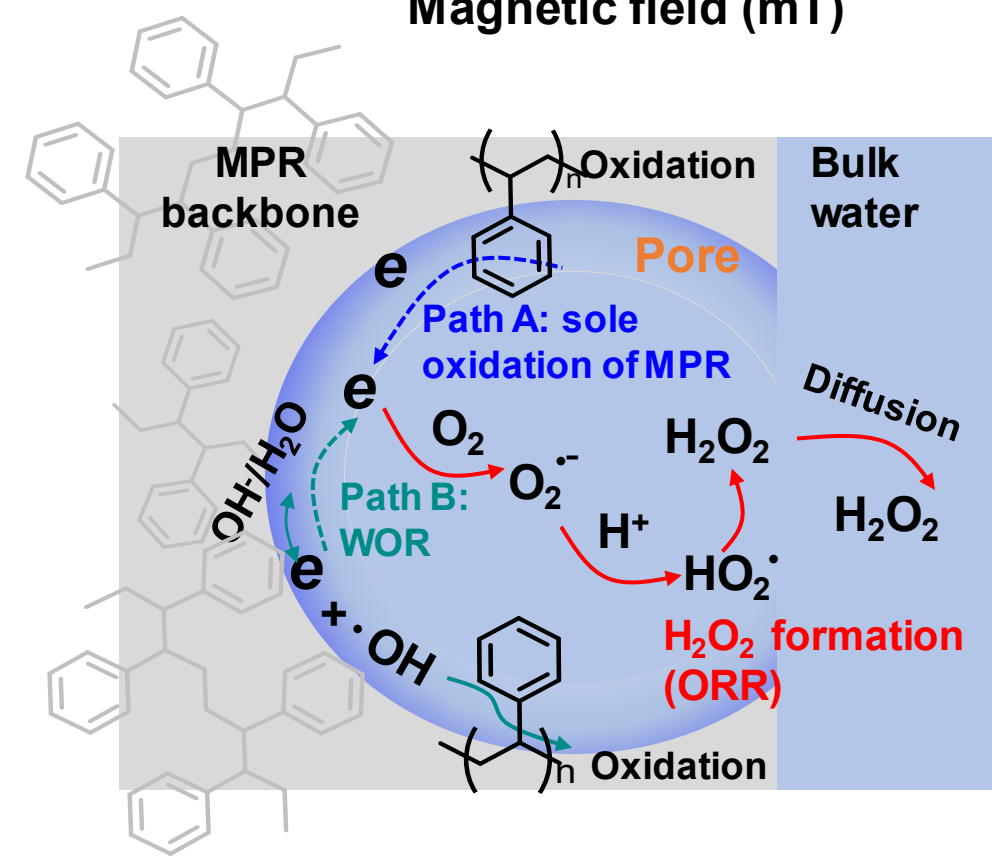
The catalyst-free production of  $\text{H}_2\text{O}_2$  at solid-water interfaces provides a sustainable synthesis route, yet scalability remains challenging. Here the authors demonstrate that hydrophobic macroporous resins can serve as robust, metal-free platform to construct scalable and robust hydrophobe-water interfaces for continuous  $\text{H}_2\text{O}_2$  generation.

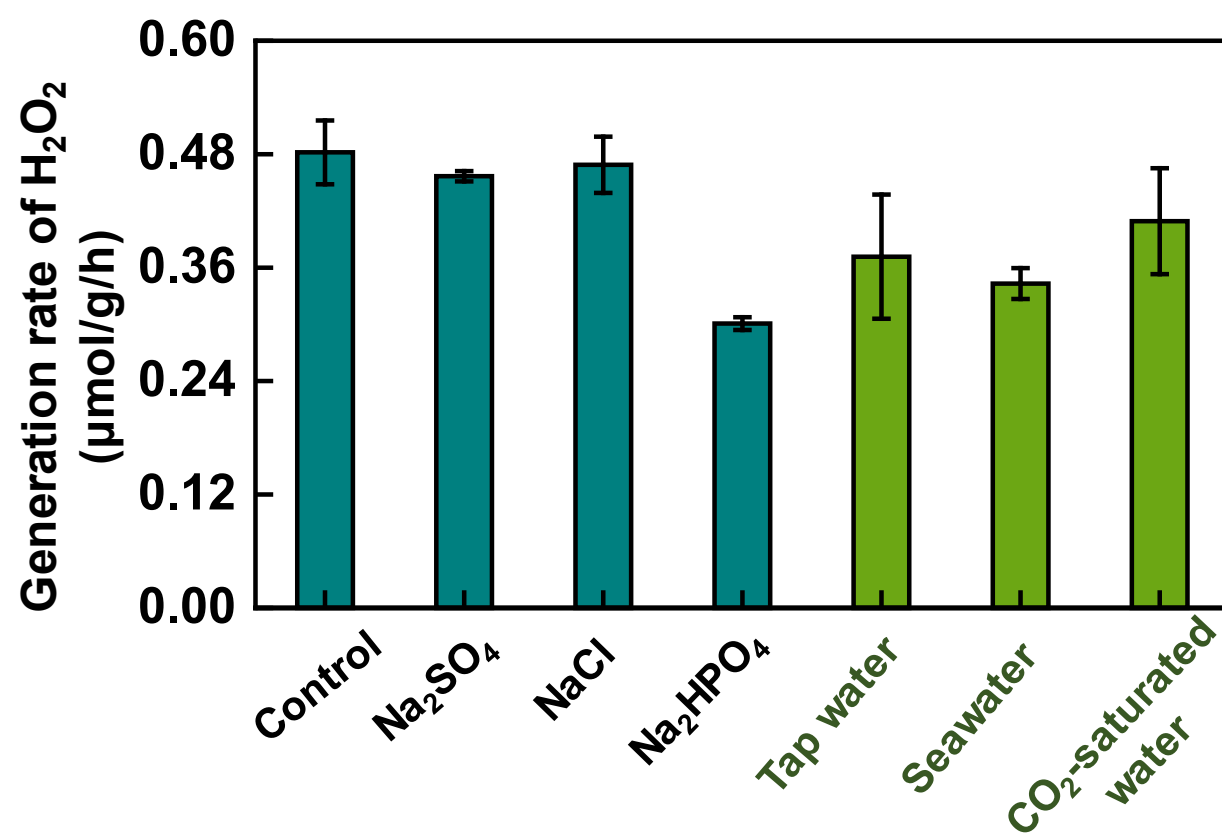
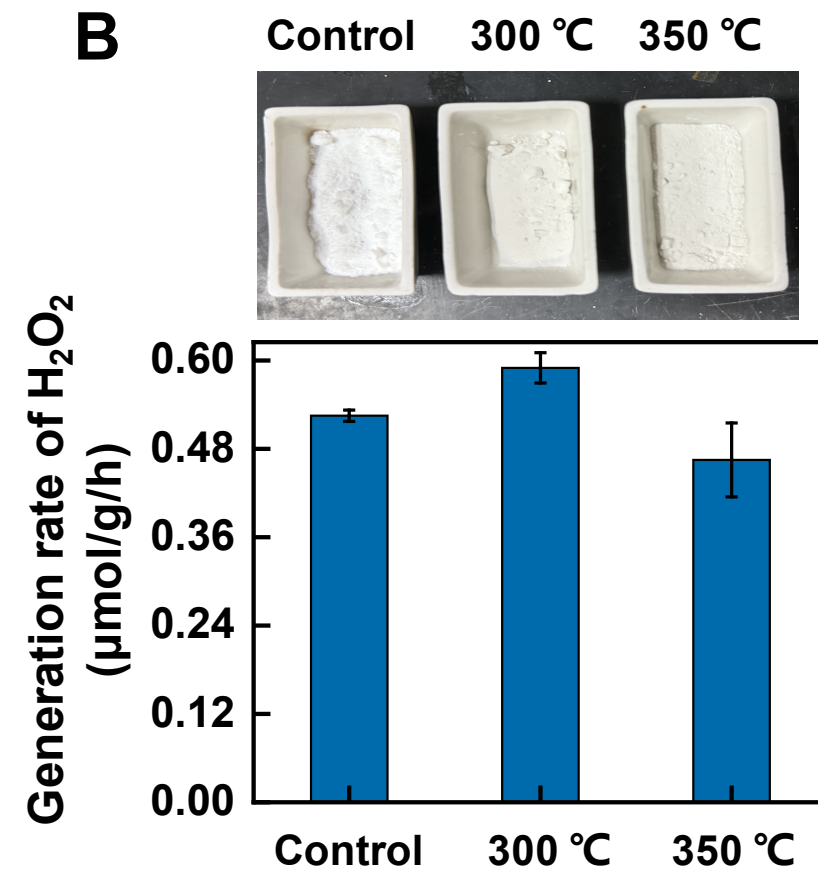
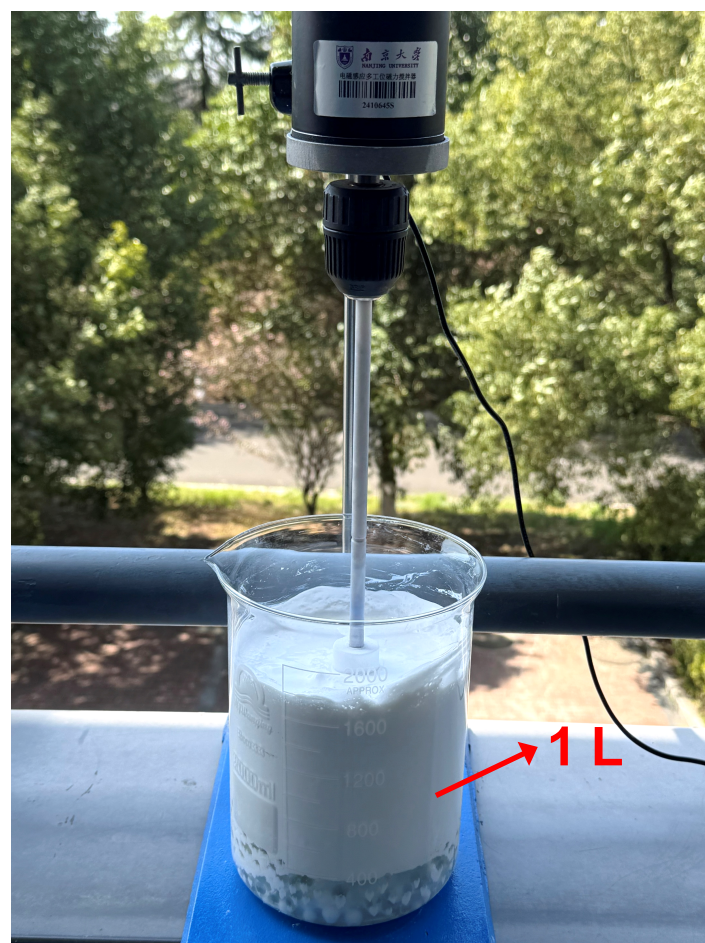
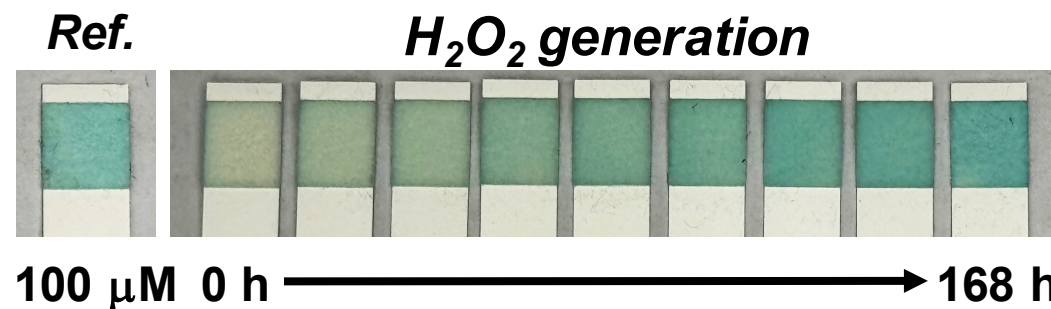
**Peer review information:** *Nature Communications* thanks Himanshu Mishra, who co-reviewed with Muzzamil Eatoo; Ryan Sullivan; and Richard Zare for their contribution to the peer review of this work. A peer review file is available.







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