



Direct, catalyst-free H₂O₂ synthesis via scalable plasma reactor

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ABSTRACT

Hydrogen peroxide is a cornerstone chemical, yet its industrial production via the energy-intensive anthraquinone process is confined to large, centralized facilities. This paradigm necessitates the hazardous transport and storage of highly concentrated H₂O₂, posing significant safety and logistical challenges. Decentralized, on-demand synthesis offers a compelling alternative, but current methods, including noble-metal catalysis, photocatalysis, and electrosynthesis, are hampered by limitations in product purity and concentration brought by catalysts and solvents/electrolytes. Here, using 3D printing technology, we designed and fabricated a novel, dual-cooling, plate-to-plate dielectric barrier discharge plasma reactor, which exhibits an excellent performance for H₂O₂ synthesis via H₂/O₂ plasma without catalysts or solvents. We identified the disproportionation reaction of hydroperoxyl radicals as the core reaction pathway for H₂O₂ synthesis based on combined zero-dimensional plasma kinetics modeling, in-situ cavity ring-down spectroscopy, and quantum chemistry calculations. Finally, through parallelization of 20 such reactors, we created a scale-up generator capable of stable, continuous operation, producing 1190 g H₂O₂ with 43 wt% concentration and Grade 1 purity in 120 h. This work presents a scalable, direct, and catalyst-free approach for H₂O₂ manufacturing, offering a promising alternative to large-scale, centralized production, and paving a pragmatic pathway toward safe, small-scale, and modular synthesis to facilitate the decentralized supply of essential chemicals.

1. Introduction

Hydrogen peroxide (H₂O₂) is one of the world's most important chemicals [1], with widespread applications in water treatment, medical disinfection, food processing, pulp and paper bleaching, and semiconductor manufacturing. Since the 1940s, the anthraquinone (AQ) process has dominated industrial H₂O₂ production, accounting for over 95% of global output [2] (approximately 6 million tons annually). This method involves a complex, multi-step cycle: hydrogenation of an

alkylanthraquinone solution, oxidation to produce H₂O₂, followed by extraction, purification, and regeneration of the working solution. However, the AQ process is inherently unsustainable, generating substantial waste and incurring significant capital and operational costs [2]. These economic constraints render it viable only in massive, centralized facilities [3]. Consequently, highly concentrated H₂O₂ must be transported over long distances and stored off-site. This practice introduces severe safety hazards, as concentrated H₂O₂ is unstable and can decompose violently, or even explode, during storage and transport

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[4–6].

To overcome the limitations of the centralized AQ process, significant research efforts have been devoted to developing decentralized and on-demand H_2O_2 synthesis methods. Noble metal catalysis has progressed on multiple fronts: macroscopic strategies, such as acid pretreatment of Au–Pd catalyst supports [7] or oxidation-reduction-oxidation cycling of Pd–Sn catalysts [8], effectively suppress side reactions; atomic-level insights, like Pd isolation within Au matrices, raise selectivity by tuning activation barriers [9]; and novel pathways, such as using SnSe nanosheets with tin vacancies, enable direct H_2O_2 synthesis from H_2O and O_2 under mild conditions [10]. Photocatalysis represents another promising route, with advances in covalent organic frameworks (COFs) through dynamic charge traps [11], robust linkage engineering [12], and heterocyclic isomer incorporation [13], even scaling to panel reactors for water treatment [14]. Porphyrin-based systems have realized photothermal synergy [15] and enhanced O_2 adsorption via imidazole functionalization [16], while other innovations include single-atom catalysts [17], metal-free polymers [18], and molecular nanopacking control [19]. Electrocatalysis offers a green alternative via the 2e^- ORR or WOR pathways [20], though standardized reporting of selectivity is needed [21]. Catalyst design has evolved from oxidized carbon surfaces [22] and defective graphene oxide [23] to atomic configuration tuning in Co–N–C single-atom catalysts [24] and supramolecularly adjusted cobalt phthalocyanines [25]. Theory-driven discovery has identified active Pt–Hg alloys [26], and hydrophobic layer construction shifts selectivity toward H_2O_2 [27]. Practical advances include solid-electrolyte reactors for the direct synthesis of pure 20 wt% H_2O_2 [28], stable NiPS_3 nanosheets in seawater [29] and tandem wastewater treatment systems [30]. Despite the significant progress, these methods are constrained by the required catalysts and solvent/electrolytes, which impose restrictions on the purity and concentration of the synthesized H_2O_2 . This inherent limitation makes the development of miniaturized production equipment challenging and unfavorable for truly decentralized and on-demand synthesis.

Non-thermal plasma provides a versatile platform for H_2O_2 synthesis through various reaction pathways. Recent state-of-the-art developments have predominantly focused on multiphase systems, including gas-liquid interfaces [31,32], sub-atmospheric plasma-water interactions [33], and solution plasma catalysis involving solid catalysts [34]. While innovative designs like biphasic microreactors [35] have improved throughput, these multiphase processes often encounter intense thermal degradation [36] and inherent mass transfer limitations across phase boundaries. In contrast, the direct synthesis of H_2O_2 from H_2 and O_2 via pure gas-phase plasma [37–41] offers distinct advantages. By operating entirely in the gas phase, this approach eliminates multiphase mass transfer resistance and avoids potential contamination from solvents or catalysts, thereby ensuring superior product purity and process simplicity. However, the practical development of plasma-based H_2O_2 synthesis technology has been hampered by the following obstacles. First, a fundamental understanding of the complex reaction network and radical kinetics in H_2/O_2 plasma remains elusive, hindering targeted process optimization. Second, the reported plasma reactors featuring a coaxial configuration suffer from critical limitations: they typically allow cooling only of the grounding electrode, leaving the high-voltage electrode prone to overheating, which risks thermal decomposition of H_2O_2 and compromises operational safety. Finally, conventional manual fabrication of glass plasma reactors struggles to ensure the uniformity and precision required for reliable parallelization and scale-up.

Here, we leverage 3D printing to design and fabricate a novel plate-to-plate, dual-cooling dielectric barrier discharge (DBD) plasma reactor, which shows excellent performance for H_2O_2 synthesis via H_2/O_2 plasma in the absence of catalysts and solvents. To unravel the reaction mechanism, we employed a multi-scale approach. First, zero-dimensional (0D) plasma kinetics modeling revealed that the disproportionation reaction of HO_2 radicals is the core pathway for H_2O_2

synthesis. We then employed in-situ cavity ring-down spectroscopy (CRDS) to measure HO_2 radical concentrations during the discharge to validate the reaction mechanism. Subsequently, we further clarified the energetically favorable pathway of key reactions through quantum chemistry calculations. Finally, by implementing a shared-electrode design, we successfully parallelized 20 individual reactors into a scaled-up device, producing 1190 g H_2O_2 with 43 wt% concentration in 120 h continuous operation. This technological advancement offers a compelling decentralization strategy to overcome the traditional “large-scale, centralized production, transportation, and storage” model, driving the transition toward “small-scale, on-demand, and modular synthesis” for H_2O_2 .

2. Results and discussion

2.1. 3D-printing reactor design and performance

The dual-cooling plate-to-plate reactor comprises an outer frame, a flow distributor, dielectric glasses, 316 stainless steel meshes, grids, electrode chamber supports, outer shell glasses, and clamping frames (Fig. 1a). All components, except for the dielectric glasses, outer shell glasses, and 316 stainless steel meshes, are fabricated via 3D printing. The outer frame, flow distributor, and two dielectric glasses form the discharge chamber, designed for H_2/O_2 plasma reactions. A seal gap between the inner side of the reactor outer frame and the outer side of the electrode chamber support allows for silicone injection to ensure airtightness (Fig. 1b). The detailed assembly process of the reactor is shown in Fig. S1–S2. To rapidly dissipate the heat generated during the discharge—thereby preventing H_2O_2 decomposition and reactor deformation—the high-voltage and grounded electrode chambers circulate low-temperature transformer oil and water, respectively. Transformer oil is used in the high-voltage electrode chamber to ensure effective cooling while providing electrical insulation. The experimental setup is illustrated in Fig. S3, and a photograph of the reactor is shown in Fig. S4.

We first investigated the effect of electrode chamber coolant temperature on reaction performance while maintaining a constant frequency of 7 kHz and a discharge power of 31 W, at a total H_2/O_2 flow rate of 500 mL/min (4% O_2). Upon increasing the coolant temperature from 5 to 30 °C (in increments of 5 °C), the O_2 conversion rises, but the selectivity, yield, and energy yield for H_2O_2 all drop (Fig. 1c, d). This decline in selectivity is driven by the synergistic effect of thermal decomposition and a plasma-induced reaction pathway shift. First, elevated temperatures inherently accelerate the thermal decomposition of H_2O_2 . Second, as experimentally illustrated in Figs. S6 and S7, a higher coolant temperature results in a brighter discharge accompanied by an increased number of discharge pulses, indicating a transition into an intense, localized filamentary mode. According to previous kinetic studies on H_2/O_2 plasma [41], such an intense, high-electron-density discharge leads to the over-activation of O_2 into atomic O and excited O_2 . These highly energetic species trigger destructive chain-branching reactions, shifting the reaction pathway toward H_2O formation and inducing severe secondary destruction of the synthesized H_2O_2 . Conversely, maintaining a lower temperature helps sustain a milder, more uniform discharge environment. This controlled regime restricts the over-activation of O_2 , fundamentally favoring the chain-termination pathway for continuous H_2O_2 synthesis while simultaneously suppressing its thermal decomposition. Thus, we fixed the electrode chamber coolant temperature at 5 °C to subsequently investigate the influence of discharge power. With increasing discharge power, the O_2 conversion consistently rises, while H_2O_2 selectivity initially increases and then declines (Fig. 1e), peaking at 48.1% at a power level of 16 W, where O_2 conversion reaches 23.6%. At 70 W, the space-time yield of H_2O_2 peaks at 36.4 g/L·h, while the energy yield reaches its maximum of 15.1 g/kWh at 21 W (Fig. 1f). Thermal imaging confirms that regardless of power variations, the temperature of the high-voltage and grounded

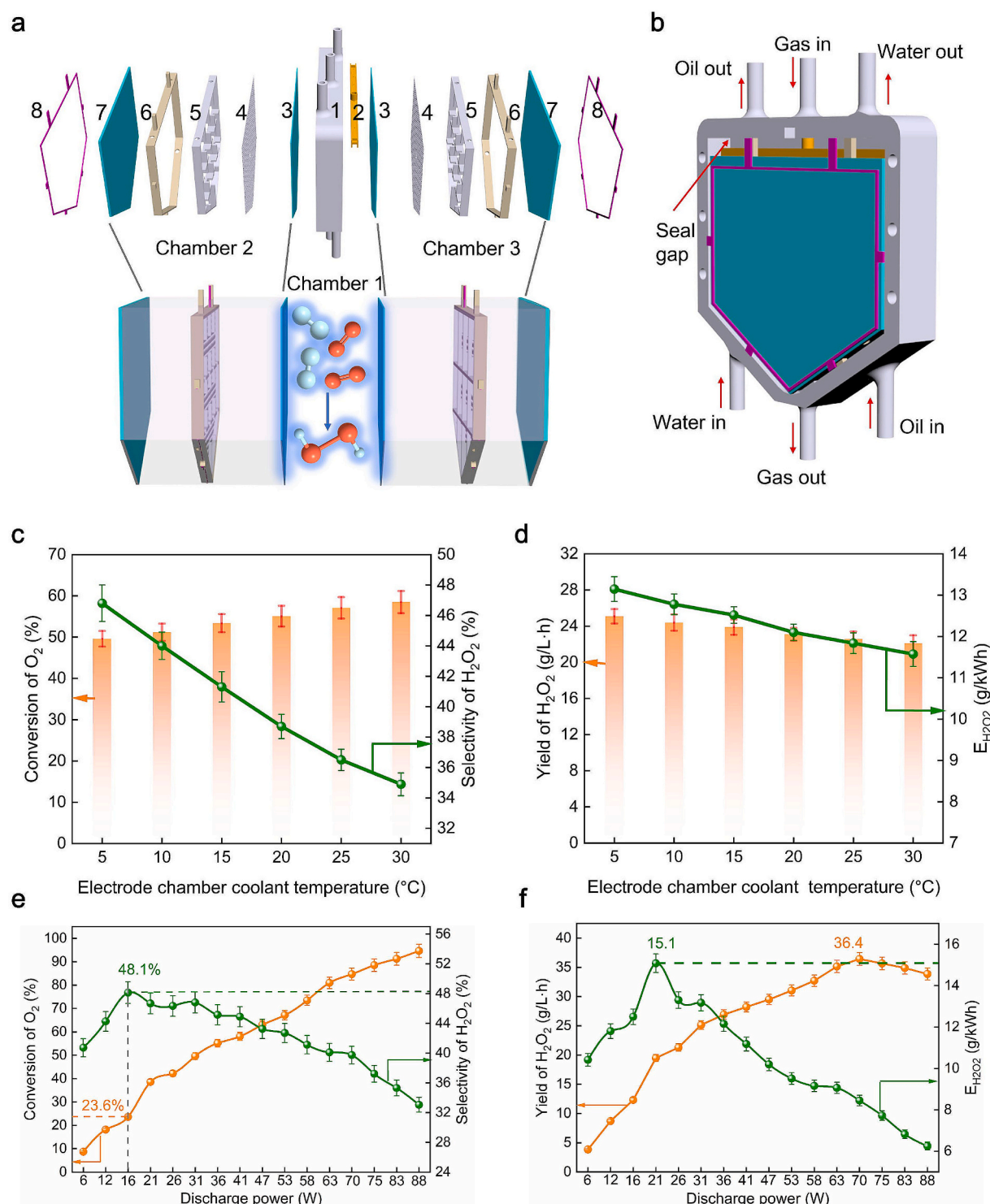


Fig. 1. 3D printing design and performance evaluation of the dual-cooling plate-to-plate plasma reactor. (a) Schematic of the reactor components. 1 outer frame, 2 flow distributor, 3 glass dielectric barrier, 4 316 stainless steel mesh, 5 grid, 6 electrode chamber support, 7 outer shell glass, 8 clamping frame. Chamber 1 is the plasma discharge chamber, Chamber 2 is the high-voltage electrode chamber with circulating transformer oil inside, and Chamber 3 is the grounded electrode chamber with circulating water inside. (b) Schematic of the whole reactor. Effect of electrode chamber coolant temperature on O_2 conversion and H_2O_2 selectivity (c), and on H_2O_2 space-time yield and energy yield (d), at 31 W and 7 kHz. Effect of discharge power on O_2 conversion and H_2O_2 selectivity (e), and on H_2O_2 space-time yield and energy yield (f), at a coolant temperature of 5 $^{\circ}C$.

electrode chambers remain stable at around 10 $^{\circ}C$ (Fig. S8, S9), indicating that the transformer oil and water provide highly effective heat removal. The Lissajous figures, discharge current waveforms and discharge images (Figs. S10-S12) show that both the number of discharge pulses and the discharge area increase with discharge power.

Based on the Lissajous figures and electrical parameters, we calculated the equivalent capacitance, average electric field strength, reduced electric field strength, electron energy distribution function (EEDF), and mean electron energy at various discharge powers (Fig. S13, S14). The dielectric capacitance increases, whereas the gas gap and total

equivalent capacitances decrease with increasing discharge power. Concurrently, both the overall average electric field and reduced electric field strengths rise, and thus the mean electron energy gradually increases. The combination of reaction performance and plasma diagnostics suggests that weaker discharges lead to a relatively lower mean electron energy, which favors H_2O_2 synthesis.

3. Reaction pathways from plasma diagnostics and chemical kinetics 0D modeling

To elucidate the underlying chemistry, we employed a zero-dimensional (0D) kinetic model using ZDPlasKin [42] to simulate the temporal evolution of species densities in the H_2/O_2 plasma. The model considers 38 species and 410 reactions (Tables S1–S7). The simulated O_2 conversion and H_2O_2 selectivity exhibit excellent agreement with the experimental results (Fig. S15), with relative errors largely confined to within 5%, which validates the reliability of our 0D model.

The temporal evolution of species densities during the discharge is plotted in Fig. 2a. The reactants, H_2 and O_2 , obviously exhibit the highest number densities. Highly energetic electrons collide with H_2 and O_2 molecules, generating substantial amounts of H and O atoms via electron impact dissociation, consistent with the lines of H (656.3 nm) and O (777.4 nm and 844.7 nm) observed by optical emission spectra (Fig. S16). Notably, the density of H atoms exceeds that of O atoms by several orders of magnitude, attributed to the higher initial concentration and lower dissociation energy of H_2 . Both OH and HO_2 radicals are also observed; however, the density of HO_2 radicals surpasses that of OH radicals by five orders of magnitude. This is consistent with the reaction pathways shown in Fig. 2f, where OH radicals are primarily formed through the reactions of HO_2 with H atoms and O atoms. Furthermore, the temporal profiles of HO_2 and H_2O_2 exhibit similar trends, indicating a strong correlation between HO_2 accumulation and H_2O_2 formation.

The time evolution of reaction rates for the key generation and consumption pathways of H_2O_2 , HO_2 , H_2O , and OH are plotted in

Fig. 2b–e. H_2O_2 is predominantly formed via $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$, with its rate being significantly higher than $\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$, due to the five-orders-of-magnitude-higher HO_2 radical density (Fig. 2a and b). This is further supported by path flux analysis (Fig. 2f). H_2O_2 consumption primarily occurs via $\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{H}_2\text{O} + \text{OH}$ and $\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O}$, driven by the high concentrations of reactive H atoms and OH radicals (Fig. 2a and b). As the primary intermediate in H_2O_2 synthesis, HO_2 is mainly formed via the three-body reaction $\text{O}_2 + \text{H} + \text{M} \rightarrow \text{HO}_2 + \text{M}$ (Fig. 2c). This is facilitated by the high concentrations of H_2 and O_2 , as well as the abundant H atoms generated from H_2 dissociation (Fig. 2a). Beyond H_2O_2 formation, HO_2 also reacts with H, O, and OH to produce OH and H_2O . For H_2O byproduct formation (Fig. 2d), OH radicals are crucial. They readily react with H, H_2 , HO_2 , and H_2O_2 to yield H_2O . The reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ shows the highest rate, largely due to excess H_2 in the system. Finally, the analysis of OH radical formation and depletion (Fig. 2e) shows that the reaction $\text{HO}_2 + \text{H} \rightarrow \text{OH} + \text{H}_2\text{O}$ exhibits the highest formation rate due to the high H atom density.

By integrating these analyses, we constructed a comprehensive reaction network for H_2O_2 synthesis in H_2/O_2 plasma (Fig. 2f and S17). The model unequivocally shows that H_2O_2 is predominantly formed through the disproportionation reaction $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$, while the critical intermediate, HO_2 , primarily originates from collisions between O_2 and H atoms.

3.1. Reaction pathways validation via in-situ spectroscopy diagnostics

While the HO_2 disproportionation pathway has been extensively proposed in conventional models [43–45], direct experimental validation in a pure H_2/O_2 discharge has remained highly elusive. This difficulty fundamentally arises from the transient nature, extremely low steady-state concentration, and severe background spectral interference of HO_2 , which render it virtually invisible to traditional diagnostic tools. To bridge this gap and experimentally validate the reaction

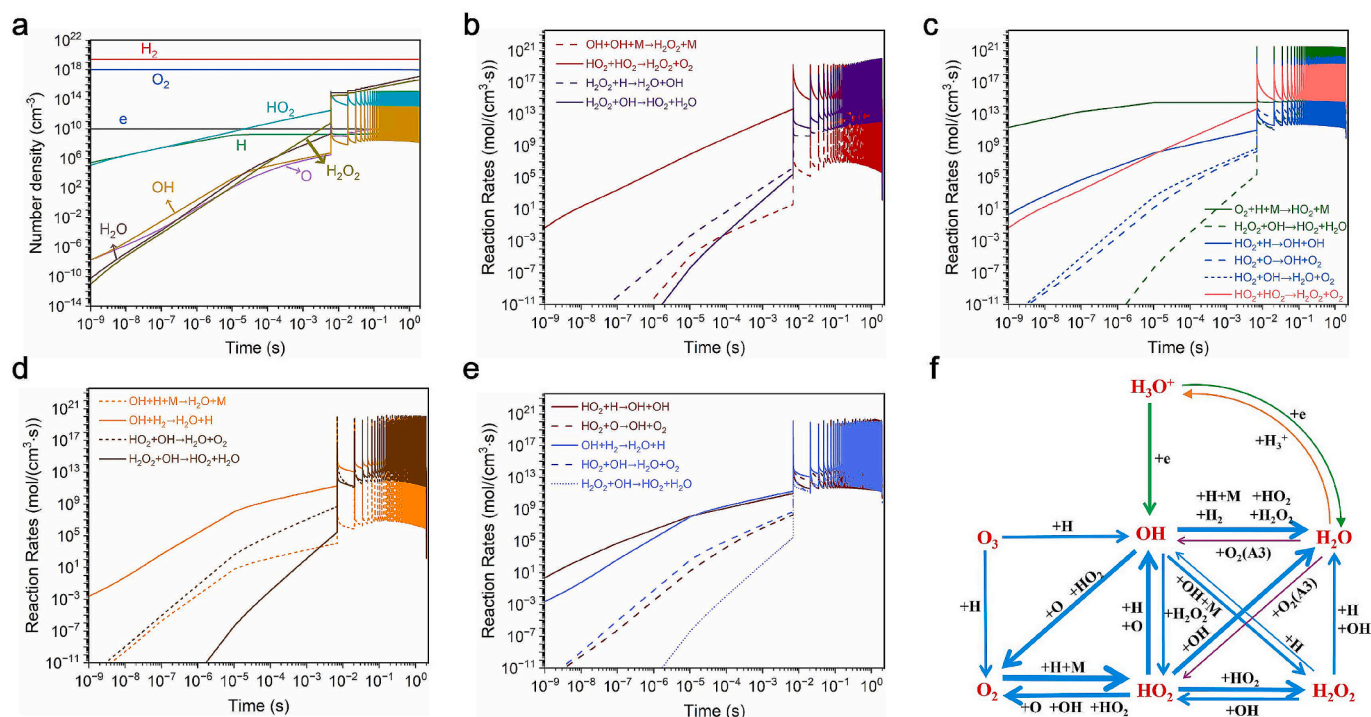


Fig. 2. Zero-dimensional plasma kinetic simulation. (a) Time evolution of the number densities of various species (including e, H_2 , O_2 , H, O, OH, HO_2 , H_2O , and H_2O_2) in H_2/O_2 plasma (16 W discharge power); Reaction rates of key generation and consumption pathways for H_2O_2 , HO_2 , H_2O and OH (b: H_2O_2 ; c: HO_2 ; d: H_2O ; e: OH); (f) Path flux analysis for H_2O_2 synthesis in H_2/O_2 plasma. Green arrows denote electron-ion recombination reactions, purple arrows represent reactions involving excited states, orange arrows indicate ionic reactions, and light blue arrows correspond to neutral-neutral reactions.

pathways, we directly measured the concentration of this key intermediate using high-sensitivity Cavity Ring-Down Spectroscopy (CRDS), a non-destructive diagnostic method [46,47]. A schematic diagram of the in-situ CRDS setup is shown in Fig. 3a, and the experimental system is illustrated in Fig. S18. The reactor was installed between the two cavity mirrors. This reactor still utilizes a dual-cooling structure, with the only difference being that the distance between the two dielectric glass barriers is 4.5 mm. Note that apertures with 3 mm diameter were reserved on both sides of the reactor to allow laser transmission with negligible loss. The entire discharge assembly was electromagnetically shielded to eliminate interference from the high-voltage power supply during DBD operation.

Fig. 3b shows a representative absorption spectrum recorded over the range of 6637.3–6639.2 cm^{-1} , with an averaging of 240 ring-down events for each data point. A series of HO_2 absorption peaks is clearly observed around 6638.2 cm^{-1} [48]. This specific absorption line, located in the near-infrared O–H first overtone $2\nu_1$ band, was strategically selected because it has been systematically established by extensive spectroscopic literature as an unambiguous “fingerprint” for the HO_2 radical, exhibiting the strongest absorption cross-section in this region [46–50]. However, in practical DBD plasma, the process also generated stable H_2O and H_2O_2 , which interfere with the target signal. To strictly eliminate this background absorption, we isolated the signal of the highly reactive HO_2 radical by leveraging its rapid decay after switching off the discharge [47]. A discharge-on spectrum was first recorded, after which power and gas flow were terminated. Following a three-minute delay for HO_2 to deplete, a background spectrum (containing only H_2O and H_2O_2) was acquired and subtracted from the active spectrum to yield the pure HO_2 signal (Fig. 3b). Because the observed HO_2 spectra contain multiple peaks, the resulting background-subtracted spectrum was fitted using a global Voigt profile to determine the absolute HO_2 concentration (Fig. 3c).

The HO_2 concentrations were measured at different oxygen fractions and discharge powers (Fig. 3d), and corresponding performance evaluation is shown in Table S8. Details of the raw measurement data are provided in Fig. S19, while the fitting results are shown in Fig. S20. As observed in Fig. 3e, the HO_2 concentration measured by in-situ CRDS is on the order of 10^{12} molecules· cm^{-3} , which is an order of magnitude lower than the value predicted by our OD plasma kinetics model (Fig. 2a). This discrepancy is attributed to the lower plasma density in the CRDS experimental reactor compared to the one simulated, caused by the broadened electrode gap and threefold larger volume. Crucially, as shown in Fig. 3e, the experimentally measured HO_2 concentrations exhibit a strong positive correlation with the H_2O_2 yield under various operating conditions. Furthermore, we observe a clear quadratic dependence between the H_2O_2 synthesis rate and the HO_2 number density measured by in-situ CRDS (Fig. S21), indicating that the reaction $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ is second-order, consistent with literature [51]. These results provide direct, compelling evidence for the dominant pathway of H_2O_2 generation, i.e., $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$.

Furthermore, our OD simulations indicate that the OH radical is the primary intermediate in the formation of the H_2O byproduct. To verify this, we used in-situ optical emission spectroscopy (OES) and observed that the intensity of the OH ($A^2\Sigma^+ \rightarrow X^2\Pi$) transition at 309 nm [52] shows a strong positive correlation with the H_2O production rate (Fig. S22), providing evidence for the role of OH in H_2O generation.

3.2. Kinetic insights from quantum chemistry calculation

To further investigate the competition among key elementary reactions, we performed kinetic calculations based on full-dimensional ab initio potential energy surfaces (PES). Spin-orbit couplings were not considered here; so the singlet (low-spin) and triplet (high-spin) state channels were treated separately. As shown in Fig. 4a, the singlet state oxygen $\text{O}_2(a^1\Delta_g)$ is difficult to generate at room temperature under the

current experimental condition. Therefore, the $\text{H} + \text{O}_2$ collision reaction predominantly proceeds through the endothermic triplet state $\text{O}_2(X^3\Sigma_g^-)$ channel, allowing the intermediate $\text{HO}_2(^2A'')$ to remain relatively stable for subsequent reactions, most likely in a rotationally excited state and either the ground or a low-lying vibrational state. Figs. 4b–e illustrate the energetically favorable pathways of four subsequent key reactions, all of which are highly exothermic and proceed either without a barrier or via a submerged one, indicating they can occur readily at room temperature.

The full-dimensional lowest triplet PES we used for the crucial HO_2 disproportionation-reaction was constructed by Li et al. [53] using a permutation-invariant-polynomial neural-network (PIP-NN)-based Δ -machine learning approach, incorporating 10,700 UCCSD(T)-F12a/AVTZ energy points and 64,600 corrected points. A relatively stable doubly hydrogen-bonded intermediate—the HO_2 radical dimer—is formed prior to the submerged hydrogen abstraction transition state (TS), as shown in Fig. 4b. Li et al. also constructed a full-dimensional triplet PES for the $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ reaction, based on 108,000 CCSD(T)-F12a/aug-cc-pVTZ points using the PIP-NN method [54]. The hydrogen-bonded complex well lies 3.3 kcal/mol below the reactant asymptote, and the submerged barrier is at -1.5 kcal/mol, as shown in Fig. 4c. In 2020, Xie, Hu and co-workers developed a multichannel full-dimensional PES for the HO_3 system, fitted to over 21,000 ab initio points at the MRCI-F12/VDZF12 level using the PIP-NN method [55]. As shown in Fig. 4d, the dominant low-spin channel for the $\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$ reaction features global minima at the planar cis- HO_3 and trans- HO_3 conformers, connected by an isomerization saddle point with a barrier height of 1.10 kcal/mol. For the $\text{H} + \text{HO}_2 \rightarrow \text{OH} + \text{OH}$ reaction, the low-spin channel is also energetically more feasible, featuring a deep potential well that supports the HOOH^* intermediate, as shown in Fig. 4e. Because the MRCI calculations do not describe the energies in the reaction interaction region with sufficient accuracy, we constructed a full-dimensional singlet-state PES for the $\text{H} + \text{HO}_2$ reaction based on the CCSD(T)-F12a/aug-cc-pVTZ level of theory. A total of 58,240 energy points, sampled using ab initio molecular dynamics (AIMD), were employed in the fitting procedure based on the fundamental invariants neural networks (FI-NN) approach. In the $\text{H} + \text{HO}_2$ reactant region and the $\text{OH} + \text{OH}$ product region, the energies of the triplet state were calculated and smoothly connected to the singlet-state PES of the interaction region using a sigmoid function. The PES also includes energy points for the $\text{O}(^1D) + \text{H}_2\text{O}$ and $\text{O}_2(^1\Delta) + \text{H}_2$ channels. Quasi-classical trajectory (QCT) calculations confirm that the PES is converged with respect to the number of ab initio points and the fitting process. Details of the PES are provided in Supporting Information (Figs. S23–S24, Tables S9–S10).

Using the above full-dimensional PES, we calculated the thermal rate constants at 298 K for the four reactions with the QCT method, which has been shown to yield reliable rate coefficients at room temperature for many bimolecular reactions, as compared to ring-polymer molecular dynamics (RPMD) and quantum dynamics calculations. The calculated thermal rate coefficients are summarized in Fig. 4f along with the corresponding values from the NIST database. Notably, the calculated rate coefficient for the HO_2 disproportionation reaction is of the same order of magnitude as the other three competing reactions, confirming its kinetic feasibility. Considering that molecules in the reactor may be in a non-equilibrium state, we also computed initial state-specific rate constants at 298 K for the four reactions to examine the influence of rovibrational excitation. Our calculations reveal that the rate coefficients for vibrationally excited HO_2 are negligible, and that lower initial rotational excitation favors the HO_2 disproportionation reaction over the other three competing reactions. This suggests that further cooling of the reactor could enhance the efficiency of H_2O_2 synthesis in future applications.

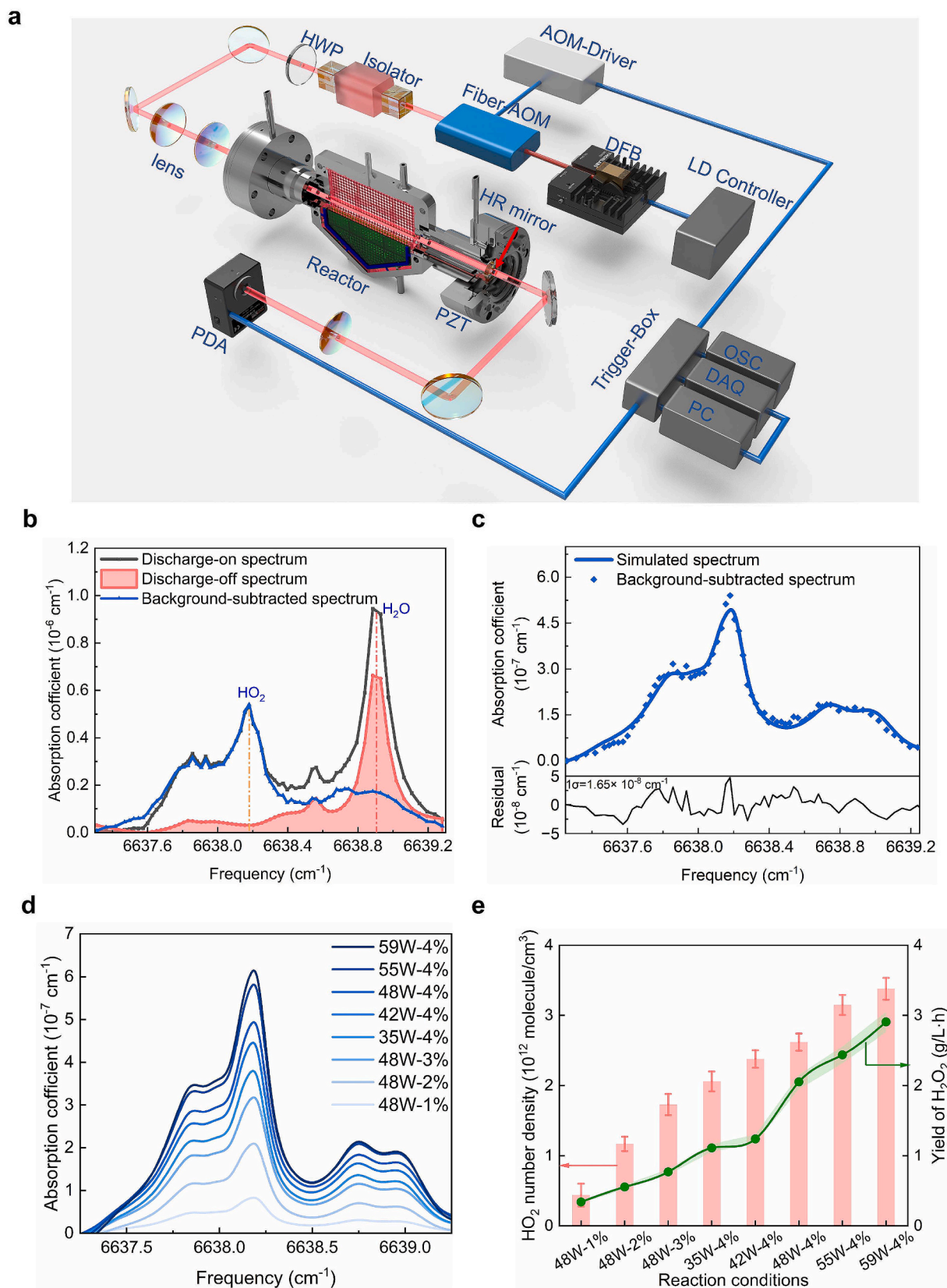


Fig. 3. Measurement of HO_2 radical by in-situ Cavity Ring-Down Spectroscopy (CRDS). (a) In-situ CRDS optical setup for HO_2 detection. The abbreviations: DFB, distributed feedback diode laser; LD Controller, Laser Diode Controller; Fiber-AOM, Fiber acousto-optical modulator; HWP, Half-Wave Plate; PZT, piezo actuator; PD, photodiode detector; DAQ, data acquisition system; OSC, Oscilloscope; PC, personal computer. (b) Absorption spectra during discharge on and off, with background-subtracted spectrum. (c) Background-subtracted spectrum with Voigt profile fitting and residuals. (d) Simulated HO_2 spectra under varying discharge powers and O_2 concentrations. (e) Positive correlation between HO_2 concentration and H_2O_2 yield.

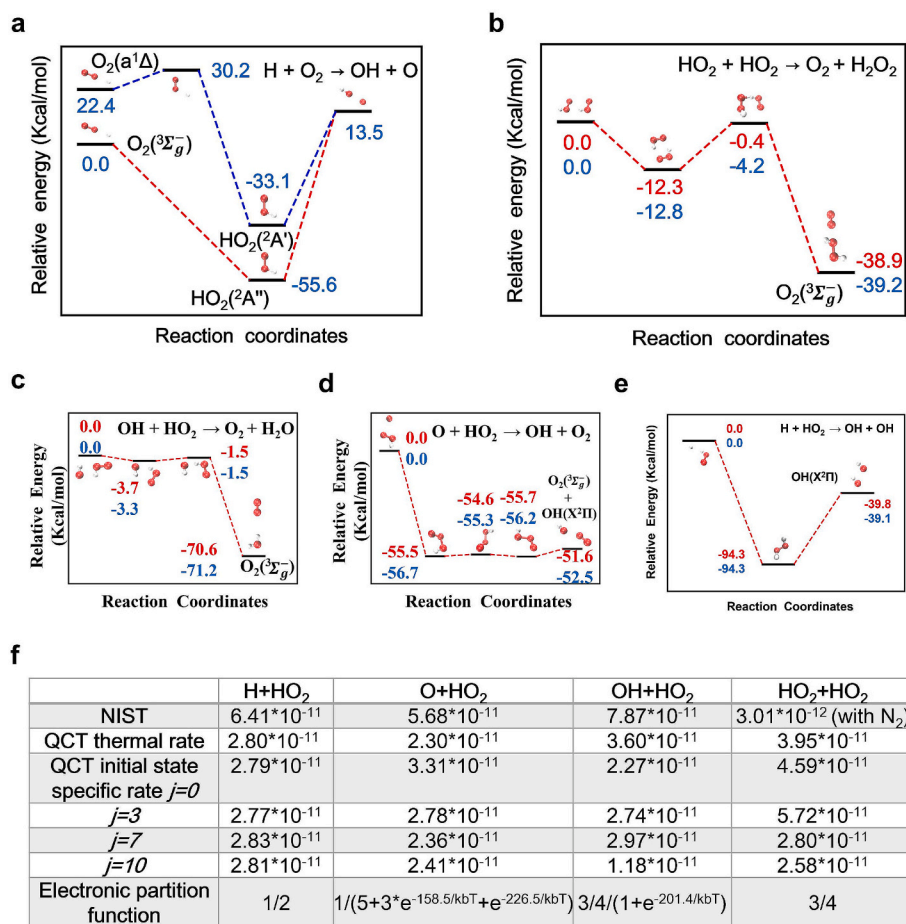


Fig. 4. Potential energy schematics of the energetically favorable pathway for the reactions. (a) $H + O_2 \rightarrow OH + O$, (b) $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, (c) $OH + HO_2 \rightarrow H_2O + O_2$, (d) $O + HO_2 \rightarrow OH + O_2$ and (e) $H + HO_2 \rightarrow OH + OH$. Energies of the stationary points obtained from the PES are shown in red, whereas those from AE-CCSD(T)/CBS calculations are shown in blue. (f) Thermal rate coefficients at 298 K for the four reactions (in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), obtained from the NIST database and QCT calculations based on the full dimensional PES, along with the initial rotational state-specific rate coefficients from the QCT calculations.

3.3. Scale-up hydrogen peroxide generator

To explore the conceptual feasibility of modular scaling, we constructed a multi-unit assembly by connecting multiple reactors in parallel (Fig. 5a, Fig. S25). In this parallel configuration, adjacent reactors are positioned to align electrodes of the same polarity. All electrodes of a like polarity are then electrically connected to a common power supply. The complete generator consists of four such systems, with each system comprising five parallel reactors powered by a single supply, for a total of 20 reactors. This modular integration was facilitated by an optimized cooling configuration in each reactor unit (Fig. 5b). In this improved design, the electrode cavities are filled with a saturated NaCl solution to maximize conductivity, and cooling plates circulating low-temperature transformer oil are attached to the external surfaces for efficient heat removal. The collector is a quartz gas-liquid separator equipped with a cooling jacket circulating cooling oil at 0 °C. Its specific structure is shown in Fig. S26.

We conducted a 120-h continuous synthesis experiment at a total power of 504 W and a total gas flow rate of 10 L/min, with the coolant inlet temperature maintained at 0 °C. As illustrated in Fig. 5b, the scale-up generator utilizes multiple cooling plates connected in series. The external coolant setpoint of 0 °C, rather than the 5 °C used for the single reactor, was purposefully chosen to minimize the massive cumulative heat load across the multi-unit system. However, thermal imaging revealed that the maximum operating temperature on the outer walls of the reactor electrode chambers in the scale-up system reached 16.8 °C (Fig. S27). This temperature is notably higher than that of a single

reactor (~10 °C), which is attributed to both the cumulative plasma heat dissipation and the heat intrusion into the coolant delivery lines and connecting tubes between adjacent cooling plates from the ambient air (~22 °C). Although this temperature rise is expected to cause a slight decrease in H_2O_2 selectivity based on our single-reactor evaluation, the overall scaled-up system nevertheless maintained highly stable operation throughout the 120-h extended run. Additionally, the current polyurethane (PU) connecting tubes provide limited thermal insulation. Future industrial deployments will address this by utilizing highly insulated pipelines and further decreasing the coolant temperature to minimize heat ingress and cumulative thermal loads, thereby ensuring an ideal low-temperature reaction environment. To ensure operational safety, the O_2 concentration was strictly maintained at 4% throughout the process. The discharge exhibits excellent stability throughout the extended operation. The O_2 conversion remains stable at approximately 64%, ultimately yielding 1190 g H_2O_2 with a concentration of 43 wt% (Fig. 5c). More importantly, inductively coupled plasma (ICP) elemental analysis of the synthesized H_2O_2 solution confirmed that the product purity meets the Grade 1 standard for high-purity H_2O_2 set by SEMI. The detailed impurity concentrations are presented in Table S11.

Furthermore, disassembly of the reactor revealed that the resin exhibited no signs of deformation, such as cracking or pulverization after the reaction (Fig. S28). Similarly, no significant change was observed for the 316 stainless steel mesh (Fig. S29). In future applications, highly inert materials such as titanium (Ti) wire or graphite electrodes could be employed to completely eliminate the risk of corrosion. This successful demonstration of stable, long-term, and high-

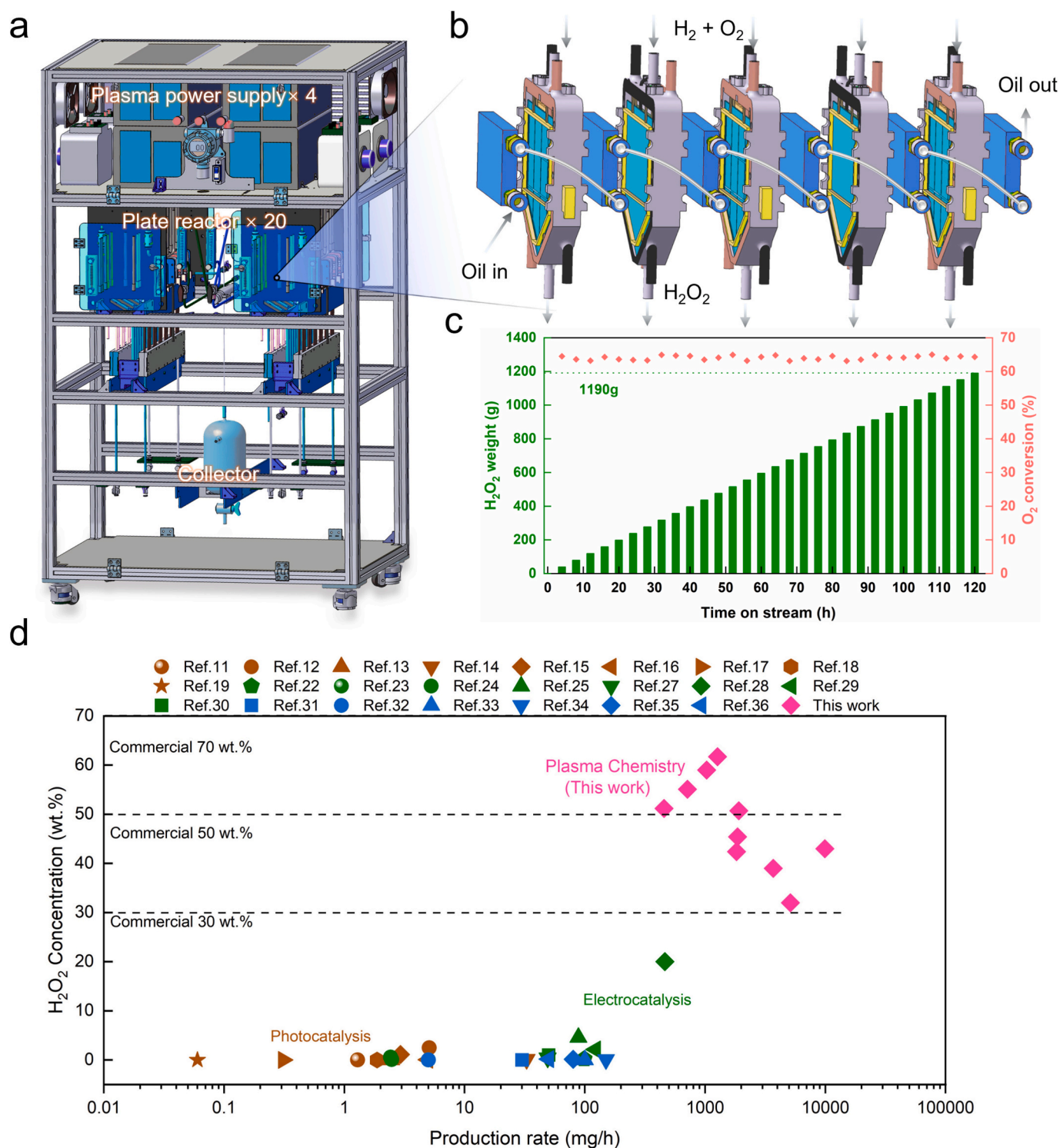


Fig. 5. Fabrication of scale-up H₂O₂ generator. (a) Schematic of the scaled-up apparatus. (b) Schematic diagram of the reactor cooling system and parallel connection. (c) O₂ conversion and weight of synthesized H₂O₂ during a 120-h plasma synthesis process in the scaled-up apparatus. (d) Comparison of H₂O₂ concentration and production rate between this work and other reported literature. Brown represents photocatalysis, green represents electrocatalysis, blue represents gas-liquid phase plasma, and rose red represents this work.

yield production validates the scalability and robustness of our design. It should be noted that due to the highly integrated and compact architecture of the current 20-unit prototype generator, individual isolation of each reactor cell for separate performance sampling is physically restricted. Consequently, the localized unit-to-unit performance variance and exact gas flow distribution profile across the entire parallel

array remain unquantified at this stage. Evaluating this inter-reactor variability is undoubtedly a crucial pre-requisite for optimizing large-scale plasma processing. To address this engineering limitation, future iterations of the scale-up device will incorporate a modular gas manifold design equipped with individual micro-flow meters and independent sampling ports, enabling precise tracking of fluid dynamics and

synthesis uniformity throughout the monolithic array. To bridge the gap between this foundational milestone and authentic industrial deployment, future engineering efforts will systematically address the remaining scale-up challenges. Specifically, further development will focus on optimizing fluidic and electrical uniformity across larger arrays and enhancing system-level energy efficiency. Furthermore, while the 3D-printed Polylactic Acid (PLA) components (i.e., the electrode chamber support and grid) successfully maintained their mechanical integrity without macroscopic deformation during the 120-h test—largely due to the low operating temperature significantly retarding the hydrolysis kinetics—PLA is inherently susceptible to chemical degradation in saturated brine over extended periods. Therefore, to ensure an extended reactor lifespan, future configurations will not only substitute these PLA prototypes with highly chemically inert polymers (e.g., Polypropylene) to resist brine hydrolysis, but also upgrade the current resin-based architectures to more advanced ozone- and UV-resistant 3D printing materials (such as PTFE or PEEK).

Our approach holds significant potential for further optimization and application-specific customization. By fine-tuning reactor dimensions and electrode spacing, we enhanced both the selectivity and concentration of H_2O_2 (Table S12), reaching 60 wt%. We also evaluated the optimized reactor using the parallel scale-up strategy. Notably, both the H_2O_2 concentration (30 wt% ~ 60 wt%) and production rate significantly outperform current state-of-the-art results in electrocatalysis, photocatalysis and multiphase plasma methods (Fig. 5d). Despite these superior production metrics, the current energy efficiency of 19.7 g/kWh remains relatively modest compared to established industrial benchmarks. However, our preliminary exploration of the scaled-up apparatus reveals that the optimization of energy efficiency is a multi-dimensional challenge; beyond conventional reactor geometry refinements, we identified that the precise impedance matching between the plasma power supply and the reactor load is a decisive factor in significantly enhancing the energy performance (Fig. S30). Concurrently, improvements in feedstock purity, quartz dielectric quality, and

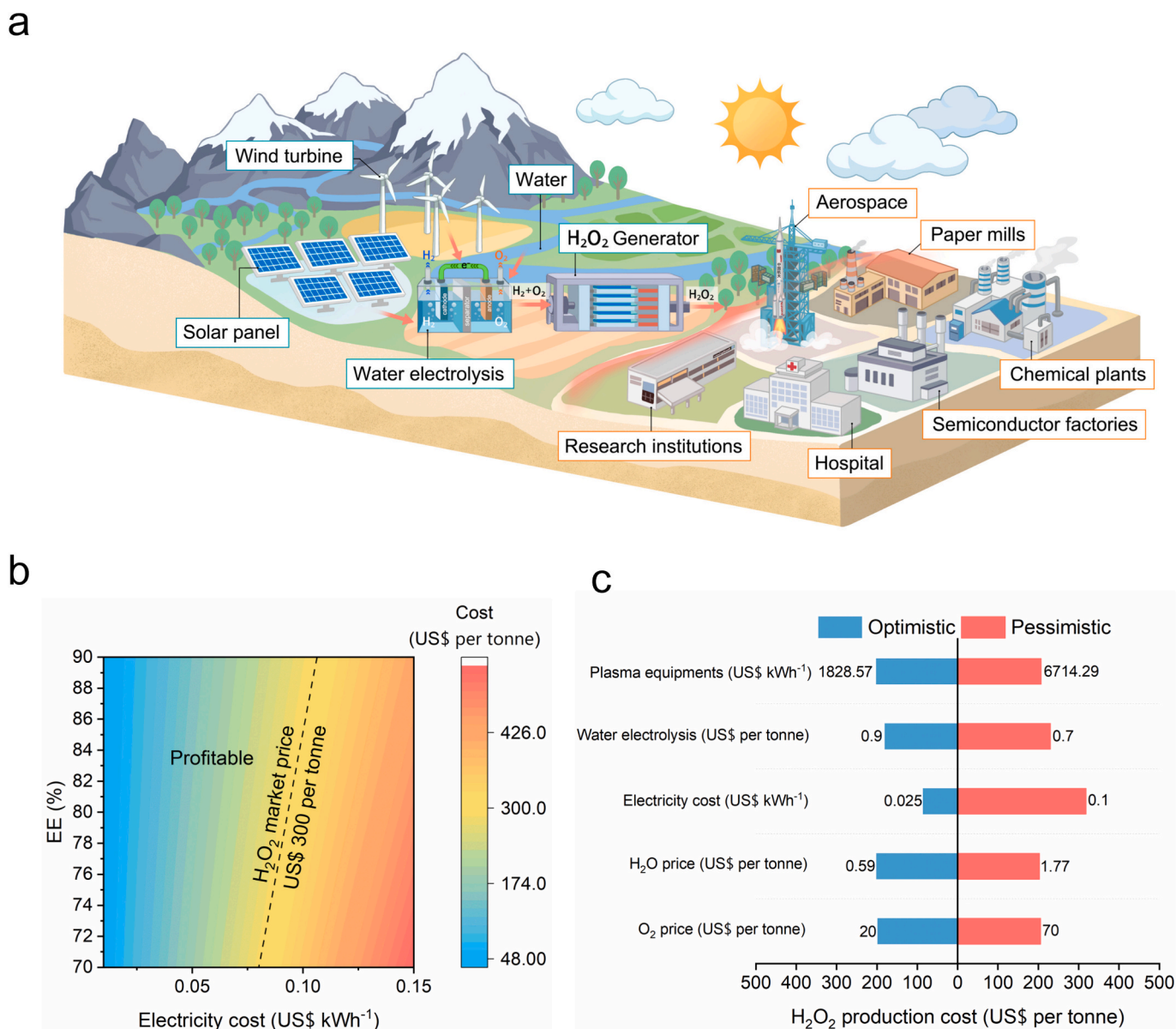


Fig. 6. Application scenarios and Techno-Economic Analysis of H_2O_2 generator. (a) Concept of sustainable production and applications of H_2O_2 . (b) Projected cost of H_2O_2 plasma synthesis as a function of energy efficiency (EE) and electricity cost. The region above the black dotted line represents the profitable zone. (c) Single-variable sensitivity analysis of the production cost of H_2O_2 . The values shown in the figure represent the optimistic and pessimistic parameters for each metric. The parameters listed in Table S13 were selected for this study.

operational cleanliness will be pursued to elevate the product purity beyond the current Grade 1 standard, with the potential to achieve even higher purity grades. Such advances would enable direct, catalyst-free production of H_2O_2 with tailored concentration and purity, meeting the stringent requirements of diverse end-use sectors, from microelectronics and pharmaceuticals to aerospace and beyond, without the need for further purification or handling.

Building upon the scaled-up H_2O_2 generator, we propose a novel, sustainable, and safe distributed production model for H_2O_2 (Fig. 6a). Renewable energy sources, such as solar or wind power, are utilized to electrolyze water, and the produced H_2 and O_2 are subsequently fed into our generator (i.e., plasma reactor, also powered by renewable energy) for high-purity H_2O_2 production without any other feedstock or chemicals. This point-of-use production strategy enables end-users—including chemical plants, paper mills, hospitals, research institutes, semiconductor factories, and the aerospace industry—to generate H_2O_2 on-site and on-demand. Consequently, this approach fundamentally circumvents the safety risks and logistical challenges associated with the conventional storage and transportation of bulk H_2O_2 . Crucially, because the H_2 feedstock is generated on-demand via upstream water electrolysis and immediately consumed by the plasma reactor, this integrated design also fundamentally eliminates the severe explosion hazards tied to H_2 transportation and bulk storage. A techno-economic analysis (TEA) was conducted to further validate the feasibility of this process (Fig. S31, Tables S13–S15). The analysis indicates that the apparatus maintains robust profitability, even in scenarios with fluctuating electricity prices and energy efficiencies (Fig. 6b). More importantly, the H_2O_2 production cost exhibits a moderate response to changes in various influencing factors, which endows the process with strong resilience against market fluctuations (Fig. 6c).

Beyond its impressive production metrics, this system offers compelling environmental advantages. First, its purely gas-phase, catalyst- and solvent-free operation fundamentally eliminates auxiliary chemical waste, circumventing the heavy metal leaching and solvent disposal issues inherent in conventional methods. Second, decentralized, on-site synthesis inherently enhances safety by eradicating the explosion risks and transportation-related carbon footprint associated with bulk H_2O_2 logistics. Finally, as an electrically driven module, it couples seamlessly with renewable energy sources (e.g., solar, wind), offering a practical route to zero-carbon chemical manufacturing.

4. Conclusions

We have designed and fabricated a novel dual-cooling plate-to-plate DBD reactor using 3D printing, achieving a new benchmark for the direct, catalyst-free synthesis of H_2O_2 from H_2/O_2 plasma. Through a combination of 0D plasma kinetics modeling, in-situ CRDS diagnostics, and quantum chemistry calculations, we provided definitive evidence that H_2O_2 is formed predominantly via the disproportionation reaction of HO_2 radicals ($\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$). Our experimental measurements confirm a strong positive correlation between the HO_2 concentration and the H_2O_2 yield, validating the reaction mechanism. By successfully parallelizing 20 reactors, we engineered a scalable generator that produces 1190 g of 43 wt% H_2O_2 with Grade 1 purity over 120 h of continuous operation, demonstrating a promising route for practical, on-demand H_2O_2 production. In addition, the concentration and purity of H_2O_2 have great potential to be further improved. This approach overcomes critical limitations of current methods. The catalyst- and solvent-free plasma process ensures high purity, while 3D printing enables the rapid, uniform fabrication of reactor units, which is crucial for predictable and scalable performance. Ultimately, this work pioneers a modular “chemical factory in a box” concept. By circumventing complex downstream purification and condensation operations, and mitigating the logistical risks of bulk transport and storage, it provides a highly pragmatic framework.

CRediT authorship contribution statement

Dongxing Li: Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation. **Shao-Pei Wang:** Writing – original draft, Visualization, Software, Methodology, Formal analysis, Data curation. **Qun Chen:** Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation. **Shengyan Meng:** Writing – original draft, Visualization, Formal analysis, Data curation. **Zhaojun Zhang:** Resources, Methodology, Formal analysis. **Jintao Sun:** Writing – review & editing, Visualization, Software, Resources, Methodology, Investigation, Formal analysis, Data curation. **Shu Liu:** Writing – review & editing, Resources, Methodology, Formal analysis, Data curation, Conceptualization. **Cun-Feng Cheng:** Writing – review & editing, Resources, Methodology, Formal analysis, Data curation. **Qi Chen:** Resources, Methodology. **Shui-Ming Hu:** Resources, Methodology. **Dong H. Zhang:** Resources, Methodology. **Annemie Bogaerts:** Resources, Methodology. **Hongchen Guo:** Resources, Methodology. **Yanhui Yi:** Writing – review & editing, Visualization, Resources, Methodology, Formal analysis, Data curation.

Declaration of competing interest

Authors H. Guo, Y. Yi, and D. Li are inventors on two pending patent applications (Application No. 202410904853.1, 202410904916.3) related to this work. Additionally, authors Y. Yi, D. Li and H. Guo are inventors on three other pending patent applications (Application No. 202410902689.0, 202410902670.6 and 202610132317.3), also related to this work. The remaining authors declare no competing interests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.180264>.

Data availability

Data will be made available on request.

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