

Unveiling singlet oxygen spin trapping in catalytic oxidation processes using in situ kinetic EPR analysis

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Singlet oxygen $({}^{1}O_{2})$ plays a pivotal role in numerous catalytic oxidation processes utilized in water purification and chemical synthesis. The spin-trapping method based on electron paramagnetic resonance (EPR) analysis is commonly employed for ¹O₂ detection. However, it is often limited to time-independent acquisition. Recent studies have raised questions about the reliability of the ${}^{1}O_{2}$ trapper, 2,2,6,6-tetramethylpiperidine (TEMP), in various systems. In this study, we introduce a comprehensive, kinetic examination to monitor the spin-trapping process in EPR analysis. The EPR intensity of the trapping product was used as a quantitative measurement to evaluate the concentration of ${}^{1}O_{2}$ in aqueous systems. This in situ kinetic study was successfully applied to a classical photocatalytic system with exceptional accuracy. Furthermore, we demonstrated the feasibility of our approach in more intricate ${}^{1}O_{2}$ -driven catalytic oxidation processes for water decontamination and elucidated the molecular mechanism of direct TEMP oxidation. This method can avoid the false-positive results associated with the conventional 2D $^{1}O_{2}$ detection techniques, and provide insights into the reaction mechanisms in ¹O₂-dominated catalytic oxidation processes. This work underscores the necessity of kinetic studies for spin-trapping EPR analysis, presenting an avenue for a comprehensive exploration of the mechanisms governing catalytic oxidation processes.

catalytic oxidation processes | electron paramagnetic resonance | kinetic study | singlet oxygen | direct TEMP oxidation

Singlet oxygen (${}^{1}O_{2}$) is the first excited electronic state of dioxygen and is ubiquitously generated in both natural and engineered environments (1), playing a crucial role in various oxidation processes (2, 3). As a nonradical oxidant, ${}^{1}O_{2}$ has garnered significant interest in numerous catalytic oxidation processes for water purification (4) and selective chemical synthesis (5). Notably, in the treatment of organic wastewater under high salinity conditions, such a nonradical may act as the primary reactive species for pollutant removal (6). Unlike radicals present in advanced oxidation processes (AOPs), ${}^{1}O_{2}$ exhibits a longer lifetime and a larger diffusion distance, rendering it suitable for durable oxidation and robust stability in complex environmental matrices (7). Although ${}^{1}O_{2}$ -dominated reactions have been extensively developed to improve the resistance of decontamination systems (7–9), current methods for directly monitoring ${}^{1}O_{2}$ production in catalytic oxidation processes remain inadequate.

A well-established process-oriented approach for identifying ${}^{1}O_{2}$ involves i) quenching experiments, ii) solvent exchange, and iii) spin trapping (10). However, the conventional method of measuring model pollutants and targeted products using chromatographic techniques results in limited data due to ex situ quantification. Also, typical ${}^{1}O_{2}$ quenchers may directly react with the oxidants, leading to false-positive results in ${}^{1}O_{2}$ identification. For instance, furfuryl alcohol (FFA) and azide are commonly used as quenchers for ${}^{1}O_{2}$, but they have been demonstrated to be nonselective for ${}^{1}O_{2}$ quenching (11). Reportedly, peracetic acid (PAA), a recently developed AOP oxidant, is reported to oxidize FFA without a catalyst (12). Likewise, previous studies have documented direct reactions between persulfate and azide (13). Consequently, the feasibility and reliability of conventional methods for detecting ${}^{1}O_{2}$ in catalytic oxidation processes should be reevaluated, and alternative appropriate methods should be developed to investigate ${}^{1}O_{2}$ generation kinetics.

The formation of ${}^{1}O_{2}$ in organic synthesis and biosystems has been extensively studied (14, 15). Nevertheless, direct detection methods such as two-photon microscopy and timeresolved phosphorescence have significant limitations, including poor anti-interference capacity and low sensitivity in aqueous solutions (16, 17). In situ detection of ${}^{1}O_{2}$ using specific dyes as spectroscopic probes is feasible but hampered by poor selectivity in complex catalytic oxidation processes (18, 19). Electron paramagnetic resonance (EPR) spectroscopy can identify active species using different spin trappers (20). Typically, 2,2,6,6-tetramethylpiperidine (TEMP) is a commonly used ${}^{1}O_{2}$ trapper, which forms a stable aminoxyl radical in the presence

Significance

 ${}^{1}O_{2}$ is a vital species for the selective oxidations of chemicals. However, detecting its production and understanding the underlying mechanisms in complex systems remains challenging. The spin-trapping method based on EPR (electron paramagnetic resonance) analysis has emerged as an indispensable tool for identifying the generation of ${}^{1}O_{2}$. Here, we applied EPR analysis to track the fates of ¹O₂ in catalytic oxidation processes, offering timedependent profiles of trapping products. These detailed examinations can unveil the molecular mechanism of direct 2,2,6,6-tetramethylpiperidine oxidation and mitigate the risk of false positives. This study paves the way for exploring ${}^{1}O_{2}$ generation in aqueous solutions and catalytic oxidations governed by other oxidative species and also offers thorough clarification from the mechanism of spintrapping to its application scenarios.

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of ${}^{1}O_{2}$ with a characteristic trilinear EPR signal (i.e., TEMPO) (21). Consequently, the EPR intensity of TEMPO can indicate the yield of ${}^{1}O_{2}$, but this method is still hindered by some interferences. Reportedly, TEMPO generation could result from the direct oxidation of TEMP by peroxymonosulfate (PMS), rather than from the ${}^{1}O_{2}$ -induced process, which raised concerns about the direct mutual validation between the EPR analysis and quenching experiments (10, 11). Therefore, a kinetic study of TEMPO generation is necessary to distinguish false-positive results and reliably evaluate ${}^{1}O_{2}$ production.

Recently, in situ EPR spectroscopy has emerged as a useful and reliable tool for monitoring ${}^{1}O_{2}$ in nonaqueous systems (22, 23) and has also been extended to kinetic studies in photocatalytic systems (24). Despite its potential, the application of kinetic EPR analysis in complex catalytic oxidation processes involving peroxides as oxidants has not been fully explored. Therefore, this work aims to conduct a kinetic investigation of ¹O₂ production in aqueous systems as a representative model. Initially, the feasibility of quantifying ¹O₂ using EPR intensity was explored. Subsequently, its applicability was verified by monitoring the $^{1}O_{2}$ production in well-established catalytic oxidation systems (8, 9). Furthermore, we examined the complex behaviors of catalytic oxidation systems that generate ${}^{1}O_{2}$ to revisit the ${}^{1}O_{2}$ -dominated catalytic reactions and correct the misleading results reported in previous studies. Our findings provide insights into the mechanisms underlying the complex catalytic oxidation processes.

Results and Discussion

Kinetic Studies Using EPR Spectra. Despite its use in monitoring ${}^{1}O_{2}$ production in photocatalytic processes (25), the quantitative capabilities of EPR analysis and its potential contribution to mechanistic investigations have not been fully explored. As illustrated in the data analysis process schematic (Fig. 1*A*), the kinetic constant (*k*) of ${}^{1}O_{2}$ generation can be calculated by analyzing the changing profiles obtained from in situ EPR analysis. These *k* values facilitated the comparison of ${}^{1}O_{2}$ productions in different systems. Also, the elimination of false positives resulting from noncatalytic processes can be achieved by subtracting the rate of TEMPO generation. Distinct kinetic characteristics may also provide insights into the underlying mechanism of ${}^{1}O_{2}$ generation.

To demonstrate the reliability of EPR analysis for kinetic studies, we monitored ${}^{1}O_{2}$ generation in a typical photodynamic ${}^{1}O_{2}$ production system (Fig. 1B). In such a photo-induced methylene blue (MB) system, $^{1}O_{2}$ can be generated through the energy transfer process between the dissolved molecular oxygen $(^{3}O_{2})$ and the photo-induced $^{\circ}MB^{+}$ (triplet) (26). The $^{1}O_{2}$ production initially followed pseudo-zero-order kinetics (SI Appendix, Fig. S1), indicating a quasi-steady-state concentration of dissolved dioxygen. By calculating the slopes of the linear interval, we identified that the reaction rate was linearly correlated with MB concentration $(R^2 = 0.989)$ and light irradiation intensity $(R^2 = 0.996)$ (Fig. 1) C and D). The EPR intensity of TEMPO was used to quantify the formation of the ${}^{1}O_{2}$ captured product, suggesting that EPR intensity could provide a relatively quantitative analysis of $^{1}O_{2}$ yield. Consequently, the time-dependent changing profiles of EPR spectra could enable reliable kinetic analysis and be used to track ¹O₂ formation in complex systems, such as catalytic oxidation systems. However, the EPR intensity might be affected by the loading volume and tuning condition of the EPR instrument (27), and the efficiency of the $^{1}O_{2}$ trapping by TEMP may not reach 100%. To avoid further errors, the TEMPO concentration was not measured in this experiment for absolute quantitative analysis.

We examined the effects of EPR active Mn^{2+} , Cu^{2+} , and Fe^{3+} on the EPR-based quantitation, considering their wide use in catalytic oxidation processes (*SI Appendix*, Fig. S3). Although Mn^{2+} caused noticeable interference with the TEMPO signal, the three-line EPR signal of TEMPO remained distinguishable. Furthermore, the obtained EPR intensities exhibited excellent linear correlations with the TEMPO concentration in the presence of Mn^{2+} and Cu^{2+} . However, dosing Fe^{3+} resulted in a reduction of the EPR intensity of TEMPO, which might be ascribed to the acidic conditions induced by Fe^{3+} and its contribution to the decomposition of TEMPO (28). Therefore, when identifying ${}^{1}O_{2}$ in the Fe^{3+} -abundant systems, it is imperative to comprehensively consider the effect of pH on reaction the mechanism and ${}^{1}O_{2}$ trapping.

Tracking the ${}^{1}O_{2}$ **Generation in Catalytic Oxidation Systems.** Notably, conventional AOPs for pollutant degradation predominantly rely on free radicals or high-valent metal-oxo species, rather than ${}^{1}O_{2}$ (6, 10). To demonstrate the applicability of this method for kinetically tracking ${}^{1}O_{2}$ in catalytic oxidation processes, we monitored the variations in EPR intensities in a well-established system exhibiting high selectivity in generating ${}^{1}O_{2}$ (8). Specifically, Fe₂O₃ nanoparticles were loaded onto the inner surface of CNTs (Fe-CNTs-I) to efficiently activate H₂O₂ and selectively generate ${}^{1}O_{2}$. Conversely, when Fe₂O₃ nanoparticles were decorated onto the outer surface of CNTs (Fe-CNTs-O), ${}^{1}O_{2}$ generation was hindered.

The results of the kinetic EPR analysis showed continuous ${}^{1}O_{2}$ generation in the Fe-CNTs-I/H₂O₂ system ($k = 44.8 \pm 0.4 \times 10^{-3}$ min⁻¹, $R^{2} = 0.997$), while no steady TEMPO generation was observed in the Fe-CNTs-O/H₂O₂ system (Fig. 1*E*). Since the conversion from TEMP to TEMPO was not highly selective, the oxidation of TEMP and TEMPO in such an oxidative system could potentially cause variations in the EPR intensity of TEMPO. Therefore, the EPR intensities of TEMPO obtained in the Fe-CNTs-O/H₂O₂ system also varied slightly, which might impact the identification of ${}^{1}O_{2}$ and lead to ambiguous results. However, our EPR analysis clearly revealed the changing profiles of the TEMPO signal and convincingly distinguished the steady and continuous formation of spin-trapping products in complex systems.

Differing from H_2O_2 , the direct oxidation of TEMP into TEMPO by PMS has been explicitly recognized (10, 11), which highlighted the importance of eliminating false positives in EPR analysis. Benzoquinone (pBQ) was reported to efficiently activate the PMS system to generate ${}^{1}O_{2}$ (29, 30). In this pBQ/PMS system, we demonstrated the advantages of kinetic EPR analysis over conventional field sweep two dimensional (2D) EPR measurement. The kinetic studies reveal that the effect of [pBQ] on TEMPO generation was pH-dependent (Fig. 1F). At pH 3.35, the TEMPO generation was entirely inhibited, consistent with the previously reported OH⁻-assisted mechanism (29). At pH 10.26, TEMPO generation significantly accelerated after dosing pBQ, indicating the generation of ${}^{1}O_{2}$. Conversely, dosing pBQ did not significantly affect the generation of TEMPO at pH 11.25, indicating that the TEMPO was mainly generated from the direct oxidation by PMS. These results unveil the diverse oxidation pathways in the *p*BQ/PMS system, which were primarily governed by pH conditions. At high pHs, PMS is strongly activated, resulting in the generation of ROS through alkaline activation or direct oxidation of specific substances. Such an intricate mechanism can easily lead to false-positive results in the identification of ${}^{1}O_{2}$ using conventional EPR analysis, which has also engendered some controversy (31). However, the time course of EPR spectra enabled a detailed comparison of the kinetic characteristics of TEMPO



Fig. 1. (A) Schematic representation of the procedure used to convert time-dependent EPR spectra into kinetic data. (*B*) The mechanism for the photoconversion of dioxygen into ${}^{1}O_{2}$ using MB as a photosensitizer and the experimental setup for in situ EPR analysis of photodynamic ${}^{1}O_{2}$ generation. Linear correlation curves of the measured kinetic constants for ${}^{1}O_{2}$ generation (${}^{1}O_{2}$) vs. (*C*) MB concentrations and (*D*) light irradiation intensities. (*E*) Time-dependent changing profiles of EPR intensities for TEMPO in the previously reported Fe₂O₃/CNTs/H₂O₂ system with selective ${}^{1}O_{2}$ production. (*F*) Changing profiles of TEMPO generation in *p*BQ/PMS systems with different *p*BQ concentrations at different pH values.

generation, providing reliable evidence for the formation of ${}^{1}O_{2}$. Lower pH conditions promoted the protonation of PMS, thereby enhancing its stability and inhibiting the nucleophilic attack by *p*BQ. Consequently, the generation of ${}^{1}O_{2}$ occurred within a narrow pH range under weak alkaline conditions. Moreover, the reaction mechanism of *p*BQ/PMS system exhibited complexity, which showed the [*p*BQ]-dependence of the preference of ROS generation (*SI Appendix*, Fig. S4). Dosing a high concentration of *p*BQ (1mM) resulted in a clear signal of the DMPO–OH adduct. Conversely, when reducing the concentration of *p*BQ to 0.1mM, the generation of 'OH was found to be negligible.

Uncovering ${}^{1}O_{2}$ -Independent TEMP Oxidations. The previous results revealed that TEMPO could be generated through ${}^{1}O_{2}$ -independent pathways in catalytic oxidation systems, raising

concerns about the reliability of the conventional procedures based on EPR analysis. To further investigate the effects of direct TEMP oxidations on ${}^{1}O_{2}$ identification, we monitored the changes in TEMPO concentration under different operating conditions. The selectivity of direct oxidation was elucidated by using H₂O₂, peroxydisulfate (PDS), PMS, and PAA as oxidants. We observed that similar to the direct reaction of TEMP and PMS ($k = 91.1 \pm 4.2 \times 10^{-3}$ min⁻¹), PAA was also effective in oxidizing TEMP ($k = 33.0 \pm 1.1 \times 10^{-3}$ min⁻¹) (Fig. 2*B*). These results indicate that asymmetric oxidants, such as PAA, can effectively oxidize TEMP to produce TEMPO, which might be attributable to the high reactivity of the peroxide bond. Such misleading TEMPOgeneration reactions exhibit considerable rates in PMS- and PAA-based systems, and the rate constants are in the same order of magnitude as those of ${}^{1}O_{2}$ -induced TEMPO generation.



Fig. 2. (*A*) Direct oxidation of TEMP by asymmetric oxidants: structures of symmetric oxidants (i.e., H_2O_2 and PDS) and asymmetric oxidants (i.e., PAA and PMS). (*B*) The changing profiles of EPR intensities in the TEMP/oxidant systems, and the calculated kinetic constants of TEMPO generation (k_{TEMPO}); Conditions: [oxidants] = 800 μ M, [TEMP] = 10g L⁻¹. The effects of the (*C*) [PMS] and (*D*) [PAA] on the k_{TEMPO} values. (*E*) Comparison of the predicted k_{TEMPO} values and measured k_{TEMPO} values.

Overlooking the time dependence of chemical reactions, conventional EPR analysis may be severely interfered by direct TEMP oxidation.

The reaction rates of the PMS-TEMP and PAA-TEMP reactions also showed variation with different oxidant concentrations. As shown in Fig. 2D, the k value of the PAA-TEMP reaction was positively correlated with the PAA concentration, while the k value of the PMS-TEMP reaction initially increased linearly and then decreased with increasing PMS concentration. Considering that TEMPO could not react with PMS (*SI Appendix*, Fig. S5), we hypothesized that the intermediate products might be further attacked instead of being oxidized into TEMPO. By simulating the k value based on the k-[PMS] relationship at low PMS concentrations (<400 μ M), the reaction rate of the intermediate decay could be estimated (Fig. 2*E*).

Mechanism of Direct TEMP Oxidation. Kinetic EPR analysis provides an in-depth insight into the mechanism of direct TEMP oxidation. The inhibition of TEMPO generation in the PMS/ TEMP system by acid dosing revealed that the oxidation of TEMP in this system was attributed to alkaline conditions (Fig. 3 *A* and *B*). This alkaline environment is induced by TEMP itself, as it is a cyclic amine (32). However, the result of the solvent exchange experiment (H₂O to D₂O) suggests a distinction between the PMS-oxidation and the ${}^{1}O_{2}$ -trapping processes. Increasing the volume ratio of D₂O in the solvent significantly accelerated the production of ${}^{1}O_{2}$ in the photo-induced MB system (*SI Appendix*,

PMS (*SI Appendix*, Fig. S6*C*). The effect of D_2O on other direct oxidation pathway beyond the lifetime of 1O_2 might result in a different kinetic time course from the 1O_2 trapping process (33). Although the base activation of PMS has been reported to produce 1O_2 (34), further investigation is warranted to elucidate the specific oxidation mechanism in the presence of TEMP. To capture the possible radicals in the TEMP/PMS system, we dosed 5.5-dimethyl-1-pyrroline-*N*-oxide (DMPO) into the

Fig. S6A) while suppressing the direct oxidation of TEMP by

dosed 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) into the TEMP/PMS system as a radical trapper. The TEMP trapping of $^{1}O_{2}$ was reported to generate HO[•] as a by-product (35), which was also trapped in our experiment (Fig. 3B). The kinetic studies suggest that the generation of TEMPO was gradually accelerated, while the reaction underwent pseudo-zero-order kinetics after dosing DMPO (Fig. 3C). Moreover, the TEMPO generation was not affected at the initial stage $[k_{\text{blank}} = (130.0 \pm 4.7) \times 10^{-3} \text{min}^{-1}, k_{\text{DMPO}} = (127.3 \pm 2.6) \times 10^{-3} \text{min}^{-1}], \text{ implying a self-accelerating}$ mechanism that was quenched by DMPO. To better explain the formation of DMPO-OH, we dosed dimethyl sulfoxide (DMSO) and ethanol (EtOH) to quench the possibly generated $SO_4^{\bullet-}$ and HO' radicals (36). These two quenchers exhibited different effects on the EPR signal of the TEMP/PMS/DMPO system. EtOH completely suppressed the DMPO-OH generation, but even slightly promoted the production of TEMPO $[k_{\text{DMPO+EtOH}} =$ $(140.4 \pm 1.6) \times 10^{-3}$ min⁻¹]. However, DMSO entirely suppressed the TEMPO generation $[k_{\text{DMPO+DMSO}} = (19.7 \pm 0.7) \times 10^{-3} \text{min}^{-1}],$ but remarkably promoted the production of DMPO-OH. These



Fig. 3. (*A*) Changing profiles of EPR intensities showing the direct oxidation of TEMP by PMS and (*B*) the corresponding cyclic voltammogram at different pH values. (*C*) EPR signal obtained after TEMP and DMPO were dosed into PMS as a spin trapper. (*D*) The changing profiles of EPR intensities of TEMPO and DMPO-OH in the TEMP/DMPO/PMS system.

results indicate that DMPO–OH was created through a nonradical pathway in the TEMP/PMS/DMPO system, not by the trapping reaction between DMPO and $SO_4^{\bullet-}$ and HO[•] radicals.

Two pathways of TEMPO generation were proposed and illustrated in Fig. 4*A*. Initially, TEMP undergoes hydroxylation, generating the EPR-silent TEMPO–H (37), which is then further oxidized by PMS to TEMPO–OH (38). TEMPO–OH can react with TEMPO–H, forming two molecules of TEMPO (**Pathway 1**). The self-catalyzed oxidation process began with the generation of TEMPO (**Pathway 2**). TEMPO could react with TEMPO–OH, generating an EPR-silent oxoammonium salt (TEMPOnium) and a new TEMPO molecule. Subsequently, TEMPOnium would react with TEMPO–H, ultimately producing a protonated TEMPO and another TEMPO (37, 39). When dosed in the TEMP/PMS system, DMPO could react with the TEMPOnium, quenching the self-catalyzed pathway and generating DMPO–OH.

An acidic solution would protonate amine (TEMP), forming ammonium salt (TEMPH⁺) and inhibiting its reaction with PMS. Also, a low pH inhibits the proton-leaving step in PMS oxidation. Therefore, the inhibition of TEMPO generation at low pH values could be explained. Moreover, it was observed that the overdosed PMS would inhibit the generation of TEMPO (Fig. 2 *C* and *E*), which was ascribed to the direct oxidation of TEMP to the TEMPOnium by PMS in the proposed mechanism. Thus, the pH- and [PMS]-dependences of direct TEMP oxidation can be explained. Moreover, the overdosed PMS might directly oxidize TEMP to TEMPOnium, thus decreasing the generation of EPR-active TEMPO.

Effect of Buffer on the TEMPO Generation. Buffers are widely used in catalytic oxidation processes to maintain a relatively constant pH value, which might significantly alter the reaction mechanisms (4, 9, 40). Therefore, we examined the effects of different buffers on the TEMPO generations from both ${}^{1}O_{2}$ -independent TEMP oxidation and ${}^{1}O_{2}$ -trapping. The difference between the effects of buffers on TEMPO generations in the TEMP/peroxides and TEMP/ ${}^{1}O_{2}$ systems confirms that PMS could direct oxidize TEMP into TEMPO without the production of ${}^{1}O_{2}$.

The effect of pH on direct oxidation has been elucidated (Fig. 3 A and B). We measured the k values in buffering agents at different pHs to gain further mechanism insight. The trends of pH effects in the TEMP/PMS and TEMP/PAA systems varied (Fig. 4B), suggesting divergent mechanisms in these two direct oxidations. A high pH value facilitated TEMP oxidation by PMS, whereas it inhibited the PAA-driven oxidation. In buffered PMS systems, almost all the k_{TEMPO} values were lower than those in pure PMS solution, indicating that the buffer ions and the pH values exerted a combined inhibitory effect. However, in the acetate-buffered TEMP/PAA system, acetate could not further suppress the TEMPO generation due to its intrinsic content. Thus, in such a system, the response of k_{TEMPO} to pH change clearly exhibited the effect of pH value on the direct TEMP oxidation by PAA, suggesting that high pH inhibits the direct TEMP oxidation. These findings imply that the commonly used buffers can affect the oxidation processes, which should be considered especially when investigating the effect of pH on catalytic oxidation processes.

We also proposed a different oxidation mechanism of the direct TEMP oxidation by PAA based on the aforementioned results (Fig. 4*C*). The acidic condition could accelerate the reaction between TEMP and PAA, suggesting that this reaction might not rely on a separate proton-leaving step. Unlike the SO_4^{2-} generated in PMS-based oxidation, the residual CH_3COO^- could accept H⁺ to form a weak acid (CH_3COOH , pKa = 4.8). These reactions might be assisted by the intramolecular hydrogen bond in the PAA molecule, which has been reported to enhance proton transfer efficiency (41). In addition, a high pH value would promote the ionization of PAA (CH_3COOH , pKa = 8.2), leading to increased spontaneous decomposition of PAA (42). This competitive consumption of PAA would inhibit the TEMPO generation via direct TEMP oxidation.

Next, we evaluated the effects of buffers on ${}^{1}O_{2}$ trapping in the photo-induced MB system. As shown in Fig. 5, borate buffer remarkably inhibited the TEMPO generation, and two carboxy-late buffers, including acetate and phthalate buffers, also decreased the generation rate of TEMPO. However, the probably generated CO₂ might interfere with the acquisition of EPR spectra in



Fig. 4. (*A*) Possible reactions of TEMP in the PMS solution. (*B*) Effects of various buffers on the direct TEMP oxidation by PMS and PAA. Conditions: [buffer] = 10mM, [oxidants] = 400μ M, [TEMP] = $10g L^{-1}$. Acetate buffers, \bigcirc -borate buffers, \diamondsuit -carbonate buffers, \bigstar -phosphate buffers. (*C*) The proposed mechanism for the direct TEMP oxidation by PAA, showing a hydrogen bond-assisted proton transfer without a separate proton-leaving step.

bicarbonate, thus showing a fluctuating effect on the TEMPO generation (*SI Appendix*, Fig. S10). Phosphate buffer, dosed at different concentrations, exerted a negligible influence on TEMPO generation. Notably, phosphite (HPO₃²⁻), which is known to possess considerable reductive ability (43), was unable to quench the generation of ${}^{1}O_{2}$, indicating a chemically selective reaction with ${}^{1}O_{2}$. Therefore, considering their limited reductive abilities, the ${}^{1}O_{2}$ induced by buffers is likely attributed to a physical quenching mechanism. This mechanism involves the suppression of ${}^{1}O_{2}$ through energy transfer, facilitated by the spin-orbit-induced intersystem crossing (44). This finding suggests that the use of buffers might commonly affect ${}^{1}O_{2}$ generation not only through pH control but also through physical quenching, potentially leading to a shift in the mechanism of catalytic oxidation processes.

In catalytic oxidation processes, the presence of other solutes, including inorganic ions and dissolved organic matter, also potentially affect the ${}^{1}O_{2}$ generation. In the MB system, Cl⁻, NO₃⁻, and SO₄²⁻ exhibited negligible effects on the generation and trapping of ${}^{1}O_{2}$ (*SI Appendix*, Fig. S12). However, K⁺, Ca²⁺ resulted in a slight reduction in the generation of ${}^{1}O_{2}$, which could be

attributed to their large ionic radius. Furthermore, Mg^{2+} effectively quenched the generation of ${}^{1}O_{2}$, likely due to its inherent acidity. While the previous studies primarily focused on the effects of anions, limited attention has been given to the ${}^{1}O_{2}$ decay and pH interference resulting from cations (6, 45). The complex effects exerted by chemically stable cations warrant in-depth investigations. Besides, humic acids (HAs) exhibited a slight inhibition on the ${}^{1}O_{2}$ generation (Fig. 5*F*), which might be attributed to factors such as light shading and slight ${}^{1}O_{2}$ decay. This result highlights the selectivity of ${}^{1}O_{2}$ in the presence of complex dissolved organic matters, offering a potential for effective pollutant degradation in practical wastewater treatment.

Effect of Solvent on ${}^{1}O_{2}$ **Trapping.** In typical AOP studies, solvent exchange (i.e., conducting the reaction in D₂O) and chemically quenching are commonly used to identify the generated reactive species (10). Thus, we examined the solvent effects of D₂O and aliphatic alcohols serving as radical quenchers on ${}^{1}O_{2}$ production in this study. When increasing the volume ratio of D₂O in the solvent, a remarkably accelerated ${}^{1}O_{2}$ production could be



Fig. 5. Effects of (*A*) borate buffer, (*B*) acetate buffer, (*C*) phthalate buffer, (*D*) phosphate buffer, (*E*) phosphite (HPO₃²⁻), and (*F*) HA under different concentrations on the kinetics of TEMPO generation when trapping photo-induced ${}^{1}O_{2}$ in MB solution. Conditions: [MB] = 100µM, [TEMP] = 10g L⁻¹.

observed in the changing profiles of EPR intensities, and the calculated kinetic constants at the initial zero-order stage linearly correlated with the ratio of D_2O (*SI Appendix*, Fig. S6A). The kinetic EPR studies can describe the generation processes of TEMPO in detail, further enabling more accurate quantitative analysis compared with conventional field sweep 2D EPR spectra (*SI Appendix*, Fig. S6 A and B).

The lifetime of ${}^{1}O_{2}$ could be lengthened in methanol (MeOH) ($k_{d}(H_{2}O) = 2.5 \times 10^{5} s^{-1}$, $k_{d}(D_{2}O) = 1.5 \times 10^{4} s^{-1}$, $k_{d}(MeOH) =$ $1.1 \times 10^{5} s^{-1}$) (11). However, an increase in MeOH concentration would not linearly increase the kinetic constant of TEMPO generation, differing from the effect of D₂O (Fig. 6*A*). In detail, low concentrations of MeOH remarkably inhibited the generation of TEMPO and even promoted the photo-reduction of the initially existing TEMPO (*SI Appendix*, Fig. S11). Increasing the volume ratios of MeOH conversely enhanced TEMPO formation. In addition, different aliphatic alcohols exhibited similar effects on the ${}^{1}O_{2}$ trapping process. These results reveal the complex effects of alcohols on the TEMPO formation in ${}^{1}O_{2}$ trapping. Aliphatic alcohols are widely used as quenchers for SO₄⁺⁻ and HO⁺ radicals (36), but their effects on the potentially generated ${}^{1}O_{2}$ have not been recognized before, which might mislead the identification of the dominated ROS.

The dosed alcohols at high concentration mainly exhibited solvent effects on the photocatalytic reaction. To show the chemical interaction between these alcohols and the ¹O₂-trapping process, the kinetic analysis was further conducted under low alcohol concentrations (Fig. 6B). EtOH and PrOH exhibited only a slight inhibition on TEMPO generation, with the pseudo-zero-order kinetics consistently maintained throughout the entire process. In contrast, MeOH substantially altered the kinetics of TEMPO generation, particularly affecting the reaction at the initial stage. At a concentration of MeOH of 40µM, a noticeable difference in the reaction rate at the initial stage was observed in comparison to the subsequent pseudo-zero-order process (after 4-min reaction). When [MeOH] reached 70µM, the generation of TEMPO was completely inhibited at the initial stage, and the existing TEMPO was photo-reduced. Subsequently, TEMPO accumulation gradually resumed and the reaction was transitioned into a pseudo-zero-order process. These findings suggest that MeOH could significantly affect the generation of ${}^{1}O_{2}$. Hence, to obtain reliable results, it is advisable to avoid the use of MeOH in quenching experiments. In addition, when employing other alcohols as quenchers, the results should be discussed in conjunction with a detailed kinetic EPR analysis.

Furthermore, we conducted an investigation into the kinetic profiles of ${}^{1}O_{2}$ generation in pure solvents (Fig. 6C), which revealed the crucial role of solvent polarity in governing the reaction rate (SI Appendix, Fig. S15). Solvents exhibiting moderate polarity, such as MeCN and BuOH, demonstrated an optimal condition for ¹O₂ generation in the photocatalytic MB system. Such a solvent preference could be attributed to the combined effects of facilitating electron transfer in the rate-limiting step and preventing the formation of unstable solvent-separated MB ions (46). Among the alcohols examined, we observed an increase in the k_{TEMPO} value from 91.1 to 5718.1 × 10⁻³min⁻¹ as the C numbers increased. The ¹O₂ generation in MeOH was found to be comparatively slower than that in aqueous solution (k_{TEMPO} = 212.3×10^{-3} min⁻¹). This result indicates a significant influence of the carbon chain length of alcohol solvents on ¹O₂ generation in the MB/h ν system, which potentially changed the distribution and mobility of photocatalysts through their aggregation (47). Moreover, it has already been reported that methanol disperses completely in water and cannot form a solvent cage to protect ${}^{1}O_{2}$ (48). Therefore, the collaborative interplay between solvent polarity and aggregation behavior plays a pivotal role in determining the rate of $^{1}O_{2}$ generation.

Quenching Effects in Kinetic EPR Analysis. We also evaluated the potential side effects of commonly used ${}^{1}O_{2}$ quenchers, similar to the radical quenchers. The effects of NaN₃, FFA, and tryptophan (TRP) on the ${}^{1}O_{2}$ trapping in the photo-induced MB system were examined, displaying distinct behaviors (Fig. 6D). These results provide clear insights into the different characteristics of the physical quencher (49) and chemical quenchers (50, 51).

NaN₃ efficiently inhibited the generation of TEMPO while leaving the initially present TEMPO in the commercial TEMP unaffected. This behavior confirms its role as a physical quencher, effectively suppressing ${}^{1}O_{2}$ through an energy transfer process without involving any redox reaction. In contrast, when dosing FFA and TRP into the photo-induced MB system, both TEMPO generation inhibition and reduction of TEMPO to EPR-silent products were observed. The presence of these chemical quenchers significantly changed the kinetic profiles, indicating the dual effects of chemical quenchers on the ${}^{1}O_{2}$ -trapping process.



Fig. 6. Effects of MeOH, EtOH, and PrOH (*A*) at high concentration levels and (*B*) at low concentration levels on the kinetics of TEMPO generation when trapping photo-induced ${}^{1}O_{2}$ in MB solution. (*C*) Kinetic constant of TEMPO generation in different pure solvents. (*D*) Quenching effects on ${}^{1}O_{2}$ generation of NaN₃, FFA, and TRP on the kinetics of TEMPO generation when trapping photo-induced ${}^{1}O_{2}$ in MB solution. Conditions: [MB] = 100µM, [TEMP] = 10g L⁻¹. Abbreviation: MeOH: methanol; EtOH: ethanol; PrOH: isopropanol; BuOH: tert butanol; MeCN: acetonitrile; DMK: acetone; THF: tetrahydrofuran; DMF: *N*,*N*-dimethylformamide; DMSO: dimethylsulfoxide; NaN₃sodium azide; FFA: furfural alcohol; TRP: tryptophan.

An ideal quencher should exclusively quench the generated ${}^{1}O_{2}$ while remaining inert toward other reactions. However, both FFA and TRP, as chemical quenchers, could react with the oxidative

[•]MB²⁺, enabling the photocatalytic cycle to continuously reduce TEMPO into EPR-silent products (*SI Appendix*, Fig. S17). Although these quenchers could efficiently quench ¹O₂ through a redox reaction, the reductive quenching of TEMPO would introduce the misinterpretation of ${}^{1}O_{2}$ identification. For instance, the substantial reduction in TEMPO signal observed upon the addition of these chemical quenchers can result in a higher TEMPO intensity in the unquenched system compared to the quenched system, potentially leading to a mistaken indication of ${}^{1}O_{2}$ generation. Also, the decline in substrate removal efficiency during the quenching experiments might be attributed to the competitive reactions between PMS and FFA or between PAA and TRP, which do not support the presence of a ${}^{1}O_{2}$ -dominated pathway (11, 52).

Role of ${}^{1}O_{2}$ in Pollutant Degradation. To obtain reliable ${}^{1}O_{2}$ identification results, a conventional kinetic experiment regarding pollutant degradation was in the previously studied pBQ/PMS system. PMS could efficiently react with pBQ to generate ${}^{1}O_{2}$ via the nucleophilic attack of PMS on the carbonyl carbons of pBQ (29, 30). The MB degradation and TEMPO generation exhibited different responses to pH change (SI Appendix, Fig. S18), suggesting that ¹O₂ was not the dominant ROS responsible for MB degradation. Moreover, the effect of [pBQ] on TEMPO generation was pH-dependent. At pH 3.35, both TEMPO generation and MB degradation were entirely inhibited, which is consistent to the previously reported OH⁻-assisted mechanism(29). At pH 10.26, TEMPO generation was remarkably accelerated after dosing pBQ, indicating the generation of ${}^{1}O_{2}$. However, MB was slowly removed, implying the poor reactivity of the generated ${}^{1}O_{2}$ with MB in the pBQ/PMS system. At pH 11.25, dosing pBQ did not remarkably affect the generation of TEMPO, suggesting that TEMPO was primarily generated from the direct oxidation by PMS under alkaline activation. Also, the absorbance kinetics suggest a negligible impact of *p*BQ on MB degradation. Therefore, the MB degradation might be dominated by another mechanism, such as oxygen-centric radicals or direct oxidation (30).

These results reveal the diversity of oxidation pathways in catalytic oxidation systems and the consequent complexity of pollutant degradation. Considering that the reactivity of a specific pollutant with ${}^{1}O_{2}$ was governed by its chemical structure and experiment parameters, a quenching experiment should be conducted to evaluate the contribution of ${}^{1}O_{2}$ to its degradation.

Conclusions

The time course of EPR spectra enabled continuous tracking of TEMPO generation, offering more in-depth kinetic information than conventionally used 2D EPR spectra. By varying the experimental parameters, the effects of the solvent or solutes on TEMPO generation could be directly monitored, facilitating reliable mechanistic investigations. With this approach, we distinguished the mechanism differences between direct TEMP oxidations and TEMPO generation after ¹O₂ trapping by revealing their distinct kinetic behaviors. Moreover, the time-dependence tracking of TEMPO enabled a detailed kinetic analysis of ¹O₂ generation under various conditions, providing more direct evidence for the presence of ¹O₂ and its role in pollutant degradation. Our work demonstrates that kinetic EPR analysis can serve as a promising strategy for investigating the generation of reactive species from a kinetic perspective and may offer valuable insights into the mechanisms of catalytic oxidation systems.

 F. Thorning, P. Henke, P. R. Ogilby, Perturbed and activated decay: The lifetime of singlet oxygen in liquid organic solvents. J. Am. Chem. Soc. 144, 10902–10911 (2022).

Z. Liang, Q. Zou, J. Xie, Y. C. Lu, Suppressing singlet oxygen generation in lithium-oxygen batteries with redox mediators. *Energy Environ. Sci.* 13, 2870–2877 (2020).

 R. Ossola, O. M. Jönsson, K. Moor, K. McNeill, Singlet oxygen quantum yields in environmental waters. *Chem. Rev.* 121, 4100–4146 (2021).

Materials and Methods

Chemicals. Unless otherwise stated, all reagents in this work were purchased from Macklin Biochemical Co., China. The spin trap reagent for singlet oxygen (${}^{1}O_{2}$), 2,2,6,6-tetramethylpiperidine (TEMP, >98%), and PAA solution (15%) were purchased from Aladdin Industrial Co., China.

Generation of ¹O₂ **in a Photodynamic System.** To explore the feasibility of quantifying the generated TEMPO by EPR intensity, we monitored the ¹O₂ generation in a typical photodynamic system. MB is widely used as a photosensitizer to stably generate ¹O₂ (Fig. 1*B*). In our experiment, an in situ photocatalytic experiment was conducted in the cavity of the EPR spectrometer. The MB solution was siphoned into a capillary tube and irradiated with a 300W Xenon lamp (PLS/SXE 300D/300DUV, Beijing Perfect light Co., China) equipped with a 420-nm cutoff filter. Time-resolved EPR spectra of TEMPO were obtained simultaneously after the start of the photoreaction. By adjusting the distance between the lamp and the capillary tube, we changed the irradiation intensity to the capillary and measured the corresponding intensities using an optical power meter (PD100D, Thorlabs Inc., Germany).

Kinetic EPR Spectra for Detecting ${}^{1}O_{2}$. TEMP was used as a trap for ${}^{1}O_{2}$ to produce TEMPO with a characteristic three-line EPR signal (53). Before EPR acquirement, the ${}^{1}O_{2}$ generation system and the spin trapper were mixed into a 2-mL vial and transferred into EPR capillary tube (1mm inner diameter). The capillary tube was immediately inserted into the cavity of the EPR spectrometer. The TEMPO signals were acquired by an EMX Plus EPR spectrometer (Bruker Co., Germany). The modulation amplitude, microwave power, and microwave frequency were set at 2.0 G, 2.0 mW, and 9.8422GHz, respectively. All scans were performed at ambient temperature with the following EPR instrument settings: sweep width, 120 G; power, 2.0 mW; modulation amplitude, 2.0 G; time constant, 10.24ms; conversion time, 6.94ms; and sweep time, 24.98s. The spectra were continuously acquired without delay.

Data Analysis. A typical procedure for converting time-resolved EPR spectra into kinetic data was shown in Fig. 1*A*. The procedure involves the extraction of the EPR signal intensities at different time intervals and the fitting of these data to determine the kinetic constant of ${}^{1}O_{2}$ generation. The EPR intensity (i.e., peak-to-peak amplitude) has been recently used as an indicator for quantifying EPR-active species (54–56). Herein, the amplitudes of the three peaks of the generated TEMPO were measured in each of the obtained time-resolved EPR spectra. The average intensities were used to estimate the relative concentration of TEMPO and then indicate the ${}^{1}O_{2}$ generation. Thus, by kinetically analyzing the accumulated TEMPO, the ${}^{1}O_{2}$ generation rate could be readily calculated.

Monitoring ¹**O**₂ **Generation in Catalytic Oxidation Systems.** To verify the proposed method, we monitored the ¹O₂ generation in a typical photodynamic system and two catalytic oxidation systems, namely Fe-CNTs (carbon nanotubes)-I/ H_2O_2 and BiOBr-OV/PMS systems. The corresponding procedures are described in detail in *SI Appendix*. After constructing the above catalytic oxidation systems, the reaction solution was mixed with TEMP solution (10g L⁻¹) at a volume ratio of 1:1. Such a mixture was drawn into a capillary tube and then placed into the EPR cavity, and kinetically monitored the reaction.

Data, Materials, and Software Availability. All data are included in the article and/or *SI Appendix*.

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- D. Zhang et al., Tailoring of electronic and surface structures boosts exciton-triggering photocatalysis for singlet oxygen generation. Proc. Natl. Acad. Sci. U.S.A. 118, e2114729118 (2021).
- T. Lei *et al.*, Lewis acid-relayed singlet oxygen reaction with enamines: Selective dimerization of enamines to pyrrolin-4-ones. *J. Am. Chem. Soc.* 144, 16667–16675 (2022).
- F. Chen et al., Efficient decontamination of organic pollutants under high salinity conditions by a nonradical peroxymonosulfate activation system. Water Res. 191, 116799 (2021).

- Y. Zhao et al., Janus electrocatalytic flow-through membrane enables highly selective singlet oxygen production. Nat. Commun. 11, 6228 (2020).
- Z. Yang, J. Qian, A. Yu, B. Pan, Singlet oxygen mediated iron-based Fenton-like catalysis under nanoconfinement. Proc. Natl. Acad. Sci. U.S.A. 116, 6659–6664 (2019).
- Y. Bu et al., Peroxydisulfate activation and singlet oxygen generation by oxygen vacancy for degradation of contaminants. Environ. Sci. Technol. 55, 2110–2120 (2021).
- W. Ren et al., Origins of electron-transfer regime in persulfate-based nonradical oxidation processes. Environ. Sci. Technol. 56, 78–97 (2022).
- J. Lee, U. von Gunten, J. H. Kim, Persulfate-based advanced oxidation: Critical assessment of opportunities and roadblocks. *Environ. Sci. Technol.* 54, 3064–3081 (2020).
- Y. Lefebvre, Oxidation of furans I. Synthesis of 6-hydroxy-2H-pyran-3(6H)-ones. Tetrahedron Lett. 13, 133–136 (1972).
- P. Shao et al., Revisiting the graphitized nanodiamond-mediated activation of peroxymonosulfate: Singlet oxygenation versus electron transfer. Environ. Sci. Technol. 55, 16078–16087 (2021).
- P. Di Mascio et al., Singlet molecular oxygen reactions with nucleic acids, lipids, and proteins. Chem. Rev. 119, 2043–2086 (2019).
- A. A. Ghogare, A. Greer, Using singlet oxygen to synthesize natural products and drugs. *Chem. Rev.* 116, 9994–10034 (2016).
- S. B. Partanen, P. R. Erickson, D. E. Latch, K. J. Moor, K. McNeill, Dissolved organic matter singlet oxygen quantum yields: Evaluation using time-resolved singlet oxygen phosphorescence. *Environ. Sci. Technol.* 54, 3316–3324 (2020).
- S. K. Han, T.-M. Hwang, Y. Yoon, J. W. Kang, Evidence of singlet oxygen and hydroxyl radical formation in aqueous goethite suspension using spin-trapping electron paramagnetic resonance (EPR). *Chemosphere* 84, 1095–1101 (2011).
- H. Gunduz, S. Kolemen, E. U. Akkaya, Singlet oxygen probes: Diversity in signal generation mechanisms yields a larger color palette. *Coord. Chem. Rev.* 429, 213641 (2021).
- R. Knoblauch, J. Moskowitz, E. Hawkins, C. D. Geddes, Fluorophore-induced plasmonic current: Generation-based detection of singlet oxygen. ACS Sens. 5, 1223–1229 (2020).
- S. Suzen, H. Gurer-Orhan, L. Saso, Detection of reactive oxygen and nitrogen species by electron paramagnetic resonance (EPR) technique. *Molecules* 22, 181 (2017).
- Y. Nosaka, A. Y. Nosaka, Generation and detection of reactive oxygen species in photocatalysis. Chem. Rev. 117, 11302–11336 (2017).
- A. C. Luntz, B. D. McCloskey, Li-air batteries: Importance of singlet oxygen. Nat. Energy 2, 17056 (2017).
- F. Gerg et al., Operando EPR and EPR imaging study on a NaCrO₂ cathode: Electronic property and structural degradation with Cr dissolution. J. Phys. Chem. Lett. 12, 781–786 (2021).
- H. F. V. Victoria et al., Detection of singlet oxygen by EPR: The instability of the nitroxyl radicals. Free Radical Biol. Med. 180, 143–152 (2022).
- C. Mendoza *et al.*, Heterogeneous singlet oxygen generation: In-operando visible light EPR spectroscopy. *Environ. Sci. Pollut. Res.* 28, 25124–25129 (2021).
- E. O. Bobylev, D. A. Poole III, B. de Bruin, J. N. H. Reek, M₆L₁₂ nanospheres with multiple C₇₀ binding sites for ¹O₂ formation in organic and aqueous media. *J. Am. Chem. Soc.* **144**, 15633–15642 (2022).
- Y. Yang, G. Banerjee, G. W. Brudvig, J. H. Kim, J. J. Pignatello, Oxidation of organic compounds in water by unactivated peroxymonosulfate. *Environ. Sci. Technol.* 52, 5911–5919 (2018).
- Y. Ma, C. Loyns, P. Price, V. Chechik, Thermal decay of TEMPO in acidic media via an N-oxoammonium salt intermediate. Org. Biomol. Chem. 9, 5573–5578 (2011).
- Y. Zhou et al., Activation of peroxymonosulfate by benzoquinone: A novel nonradical oxidation process. Environ. Sci. Technol. 49, 12941–12950 (2015).
- J. Gu, Y. Song, Y. Yang, C. Guan, J. Jiang, Mechanical insights into activation of peroxides by quinones: Formation of oxygen-centered radicals or singlet oxygen. *Environ. Sci. Technol.* 56, 8776–8783 (2022).
- S. Wacławek, H. V. Lutze, V. K. Sharma, R. Xiao, D. D. Dionysiou, Revisit the alkaline activation of peroxydisulfate and peroxymonosulfate. *Curr. Opin. Chem. Eng.* 37, 100854 (2022).
- H. K. Hall Jr., Steric effects on the base strengths of cyclic amines. J. Am. Chem. Soc. 79, 5444–5447 (1957).

- X. Zhou et al., Identification of Fenton-like active Cu sites by heteroatom modulation of electronic density. Proc. Natl. Acad. Sci. U.S.A. 119, e2119492119 (2022).
- I. Berruti et al., The reactivity of peroxymonosulfate towards sulfamethoxazole. Catal. Today 413-415, 113975 (2022).
- A. Schürmann, B. Luerßen, D. Mollenhauer, J. Janek, D. Schröder, Singlet oxygen in electrochemical cells: A critical review of literature and theory. *Chem. Rev.* **121**, 12445–12464 (2021).
- H.-Y. Gao *et al.*, First direct and unequivocal electron spin resonance spin-trapping evidence for pH-dependent production of hydroxyl radicals from sulfate radicals. *Environ. Sci. Technol.* 54, 14046–14056 (2020).
- R. Amorati, G. F. Pedulli, D. A. Pratt, L. Valgimigli, TEMPO reacts with oxygen-centered radicals under acidic conditions. *Chem. Commun.* 46, 5139–5141 (2010).
- W.-M. Zeng, Z.-L. Wang, Y.-H. He, Z. Guan, Electrochemical radical-radical cross-coupling: Direct access to β-amino nitriles from unactivated imines and alkyl nitriles. *Green Chem.* 24, 4928–4934 (2022).
- N. A. Romero, K. A. Margrey, N. E. Tay, D. A. Nicewicz, Site-selective arene C-H amination via photoredox catalysis. *Science* 349, 1326–1330 (2015).
- S. G. Patra, A. Mizrahi, D. Meyerstein, The role of carbonate in catalytic oxidations. Acc. Chem. Res. 53, 2189–2200 (2020).
- S. K. Thiyagarajan, R. Suresh, V. Ramanan, P. Ramamurthy, Deciphering the incognito role of water in a light driven proton coupled electron transfer process. *Chem. Sci.* 9, 910–921 (2018).
- W. P. da Silva, T. D. Carlos, G. S. Cavallini, D. H. Pereira, Peracetic acid: Structural elucidation for applications in wastewater treatment. *Water Res.* 168, 115143 (2020).
- K. Zhang, B. M. Shafer, M. D. Demars II, H. A. Stern, R. Fasan, Controlled oxidation of remote sp³ C-H bonds in artemisinin via P450 catalysts with fine-tuned regio- and stereoselectivity. J. Am. Chem. Soc. 134, 18695–18704 (2012).
- W. R. Haag, T. Mill, Rate constants for interaction of ¹O₂ (¹Δ_g) with azide ion in water. *Photochem. Photobiol.* 45, 317–321 (1987).
- R. Luo et al., Singlet oxygen-dominated non-radical oxidation process for efficient degradation of bisphenol A under high salinity condition. Water Res. 148, 416–424 (2019).
- M. Khalid et al., Solvent polarity influence on chemiexcitation efficiency of inter and intramolecular electron-transfer catalyzed chemiluminescence. J. Photochem. Photobiol. A: Chem. 433, 114161 (2022).
- Y. Wang, G. Wang, J. Yao, H. Li, Restricting effect of solvent aggregates on distribution and mobility of CuCl₂ in homogenous catalysis. ACS Catal. 9, 6588–6595 (2019).
- R. Li, H. Chen, Y. Li, C. Lu, J.-M. Lin, Enhancing effect of alcoholic solvent on hydrosulfite-hydrogen peroxide chemiluminescence system. J. Phys. Chem. A 116, 2192–2197 (2012).
- A. Žadlo et al., The role of hydrogen peroxide and singlet oxygen in the photodegradation of melanin. Photochem. Photobiol. Sci. 19, 654–667 (2020).
- M. J. Llansola Portolés et al., Silicon nanoparticle photophysics and singlet oxygen generation. Langmuir 26, 10953–10960 (2010).
- M. Marazzi et al., Induced night vision by singlet-oxygen-mediated activation of rhodopsin. J. Phys. Chem. Lett. 10, 7133–7140 (2019).
- D. M. Bednarski et al., Sterilization of epidermal growth factor with supercritical carbon dioxide and peracetic acid; analysis of changes at the amino acid and protein level. *Biochim. Biophys. Acta* 1868, 140334 (2020).
- Z. Barbieriková, D. Dvoranová, V. Brezová, "Application of EPR techniques in the study of photocatalytic systems" in *Materials Science in Photocatalysis*, E. I. García-López, L. Palmisano, Eds. (Elsevier, 2021), pp. 125–138, chap. 8.
- Kang et al., Adsorption and activation of molecular oxygen over atomic copper(I/II) site on ceria. Nat. Commun. 11, 4008 (2020).
- A. R. Meyer et al., Atomic structure of light-induced efficiency-degrading defects in boron-doped Czochralski silicon solar cells. Energy Environ. Sci. 14, 5416–5422 (2021).
- C. E. Dutoit *et al.*, Monitoring metallic sub-micrometric lithium structures in Li-ion batteries by *in situ* electron paramagnetic resonance correlated spectroscopy and imaging. *Nat. Commun.* 12, 1410 (2021).