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Photochemical Aging of Atmospheric Fine Particles as a Potential Source for Gas-Phase Hydrogen Peroxide

Pengfei Liu, Can Ye, Chenglong Zhang, Guangzhi He, Chaoyang Xue, Junfeng Liu, Chengtang Liu, Yuanyuan Zhang, Yifei Song, Xuran Li, Xinming Wang, Jianmin Chen, Hong He, Hartmut Herrmann, and Yujing Mu*



ABSTRACT: Atmospheric hydrogen peroxide (H_2O_2) , as an important oxidant, plays a key role in atmospheric sulfate formation, affecting the global radiation budget and causing acid rain deposition. The disproportionation reactions of hydroperoxyl radicals (HO_2) in both gas and aqueous phases have long been considered as dominant sources for atmospheric H₂O₂. However, these known sources cannot explain the significant formation of H_2O_2 in polluted areas under the conditions of high NO levels and low ambient relative humidity (RH). Here, we show that under relatively dry conditions during daytime, atmospheric fine particles directly produce abundant gas-phase H_2O_2 . The formation of H_2O_2 is verified to be by a reaction between the particle surface -OH group and HO₂ radicals formed by photooxidation of chromo-



phoric dissolved organic matters (CDOMs), which is slightly influenced by the presence of high NO levels but remarkably accelerated by water vapor and O_2 . In contrast to aqueous-phase chemistry, transition metal ions (TMIs) are found to significantly suppress H_2O_2 formation from the atmospheric fine particles. The H_2O_2 formed from relatively dry particles can be directly involved in in situ SO₂ oxidation, leading to sulfate formation. As CDOMs are ubiquitous in atmospheric fine particles, their daytime photochemistry is expected to play important roles in formation of H_2O_2 and sulfate worldwide.

KEYWORDS: air pollution, H_2O_2 , flow tube, CDOMs, photooxidation, DFT

INTRODUCTION

Sulfate is a major component of fine particulate matter $(PM_{2,5})$, which shows a significant impact on earth's albedo, air quality, and human health.¹ High sulfate concentrations occurring frequently during severe haze episodes in China,² however, cannot be adequately reproduced by models with traditional gas-phase (OH radicals) and aqueous-phase (H_2O_2) O_{3} , and O_{2} catalyzed by transition metal ions (TMIs)) oxidation pathways.³ Recent studies tried to explain the missing sulfate source by NO₂ oxidation in the aqueous phase, Mn-catalyzed oxidation on aerosol surfaces, H2O2 oxidation in aerosols with high solute strength and photosensitizing oxidation, and so on, but controversy still exists.^{1,4-9}

During severe haze episodes, the amounts of photochemical oxidants such as OH and H2O2 are usually considered to be insufficient due to greatly decreased solar radiation intensity.¹⁰ The H_2O_2 oxidation pathway was believed to make a minor contribution to sulfate production based on the extremely low H_2O_2 concentrations (0.01 ppbv) predicted by chemical transport models, which only accounted for gas-phase recombination of hydroperoxyl radicals (HO₂).⁴ Generally, atmospheric HO₂ formed by photochemical reactions of volatile organic compounds (VOCs) and carbon monoxide (CO) mainly experience two competition pathways: reaction with NO (R1) and recombination (R2).^{11–1}

$$HO_{2} + NO \rightarrow NO_{2} + OH$$

$$(k_{1} = 8.9 \times 10^{-12} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}, T = 298 \text{ K}) \quad (R1)$$

$$HO_{2} + HO_{2} \rightarrow H_{2}O_{2} + O_{2}$$

$$(k_2 = 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, T = 298 \text{ K})$$
 (R2)

 H_2O_2 formation through R2 becomes negligible when the NO mixing ratio is greater than 1 ppbv.^{14,15} However, remarkable elevation of the H₂O₂ level in ambient air with a NO concentration of several tens ppbv was observed frequently in

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the winter of the North China Plain¹⁶ (NCP, Figure S1A,B). Photochemical production of H₂O₂ in the aqueous phase (including cloud, fog water, atmospheric aerosol particle water, natural surface, and ground water) has also been reported before.¹⁷⁻²¹ Our recent study also proved that the interaction of humic-like substances (HULIS) and TMIs in deliquescent aerosols (relative humidity (RH) >50%) could produce gasphase H₂O₂.¹⁶ However, the pronounced H₂O₂ elevation in the NCP could also be observed under relatively dry conditions with atmospheric RH less than 50% that is usually below the deliquescence RH point of atmospheric particles²² (Figure S1A,B). Considering that relatively high daytime H_2O_2 levels were usually accompanied by the high concentrations of PM_{25} (Figure S1A,C), photochemical H_2O_2 production of "dry" PM_{2.5} was also suspected to be an important source for atmospheric H_2O_2 in the winter of the NCP.

To verify the above assumption, in this work, $PM_{2.5}$ filter samples collected from the NCP were investigated systematically using a flow tube reactor (Figure S2). We found that irradiation of $PM_{2.5}$ filter samples could lead to significant H_2O_2 formation for the first time. By a combination of a series of condition experiments and density functional theory (DFT) calculation, we proposed an interfacial reaction channel for H_2O_2 production. Furthermore, we also verified that the H_2O_2 released from fine particles plays an important role in the oxidation of SO₂ to sulfate.

MATERIALS AND METHODS

PM_{2.5} Filter Sampling. The PM_{2.5} filter samples were collected on prebaked micro-quartz fiber filters (Whatman, U.K.) by a series of programmed PM_{25} samplers at urban sites in Beijing (40.0° N, 116.3° E; Jectec Science and Technology, Beijing, China), Shanghai (31.1° N, 121.0° E; Thermo), and Guangzhou (22.7° N, 113.6° E; Thermo) and at rural sites in Wangdu, China (38.7° N, 115.3° E; Jectec Science and Technology, Beijing, China) and in Melpitz, Germany (51.5° N, 12.9° E; Digitel Elektronik AG, Hegnau, Switzerland). The PM25 filter samples in Beijing, Shanghai, Guangzhou, and Melpitz were obtained on 20 January 2016 (3 h), 16 December 2018 (24 h), 7 November 2018 (23 h), and 26 January 2020 (24 h), respectively. The PM_{2.5} filter samples in Wangdu were sampled parallelly on 13 December 2018 (WD-13-Dec-18, 4 h, 4 parallels), 18 January 2019 (WD-18-Jan-19, 8 h, 4 parallels), 25 December 2019 (WD-25-Dec-19, 12 h, 7 parallels), 2 January 2020 (WD-2-Jan-20, 24 h, 7 parallels), 10 January 2020 (WD-10-Jan-20, 12 h, 7 parallels), and 16 April 2020 (WD-16-Apr-20, 2/4/6/8 h). All of the filter samples were cut into the same surface area (d = 80 mm) and stored in a refrigerator until performing the photochemical experiments or other analysis. It should be noted that the loss of semi-volatile species (such as NH4+, NO3-, Cl-, and semi-volatile organic matters), filtration velocity (sampling flow rate), and aerosol mass loading were potential sampling artifacts for filter collections.²³ The evaporation loss, fast filtration velocity, and low aerosol mass loading could give rise to the underestimation of PM2.5 concentrations.²³ Additionally, there exist some visible differences between aerosols deposited on the filters and suspended in the atmosphere, probably resulting in a deviation for the H₂O₂ production in ambient air.

Sample Preparation. To investigate the impact of watersoluble components (WSCs) on the H_2O_2 production, the water-insoluble component (WISC) filter sample was obtained by extracting ultrasonically the origin PM_{2.5} filter sample (WD- 2-Jan-20) with ultrapure water for half an hour. Considering that imidazole-2-carboxaldehyde (IC) as a photosensitizer is commonly present in high pollution areas^{24,25} and citric acid (CA) is usually considered as one of the highly oxidized and functionalized secondary organic compounds in the atmosphere,²⁶ both IC and CA were selected as a proxy for chromophoric dissolved organic matters (CDOMs) in the experiments. To verify the contribution of CDOMs to the H_2O_2 production, the IC + CA filter sample was obtained by adding 5 mL of aqueous solutions of 0.04 M IC (Sigma-Aldrich, technical grade) and 0.08 M CA (Sigma-Aldrich, technical grade) to a blank quartz filter. We also try to assess the role of TMIs in the H_2O_2 production by preparing the IC + $CA + Cu^{2+}$ and $IC + CA + Fe^{3+}$ filter samples obtained by adding 5 mL of mixed aqueous solutions of IC + CA + CuSO₄ and IC + CA + $Fe_2(SO_4)_3$ to make sure 0.2 mol of IC + 0.4 mol of CA + 0.2 mol of Cu²⁺ and 0.2 mol of IC + 0.4 mol of CA + 0.2 mol of Fe³⁺ on blank quartz filters, respectively. For the purpose of investigating the influence of water-soluble ions (WSIs) on the H_2O_2 production, the K⁺ + NO₃⁻, Fe³⁺ + K⁺ + NO_3^- , $Fe^{3+} + K^+ + NO_3^- + Na^+ + Cl^-$, $Cu^{2+} + K^+ + NO_3^-$, and $Cu^{2+} + K^+ + NO_3^- + Na^+ + SO_4^{-2-}$ filter samples were obtained by adding 5 mL of aqueous solutions of KNO₃, KNO₃ + $Fe(NO_3)_3$, $KNO_3 + Fe(NO_3)_3 + NaCl$, $KNO_3 + Cu(NO_3)_2$, and $KNO_3 + Cu(NO_3)_2 + Na_2SO_4$, respectively, to make sure 2 mg of NO₃⁻, 2 mg of NO₃⁻ + 72 μ g of Fe³⁺, 2 mg of NO₃⁻ + 72 μ g of Fe³⁺ + 1 mg of Cl⁻, 2 mg of NO₃⁻ + 36 μ g of Cu²⁺ and 2 mg of NO₃⁻ + 36 μ g of Cu²⁺ + 2 mg of SO₄²⁻ on blank quartz filters, respectively. These soaked filter samples were dried at 105 °C for 4 h in a thermostat before photochemical experiments. In addition, to explore the effect of water vapor on the H_2O_2 production, the H_2O_2 -loaded filter sample was obtained by dropping 100 μ L of aqueous solutions of H₂O₂ (0.01 M) on the origin PM_{2.5} filter sample (WD-2-Jan-20) and placing at room temperature for 4 h until equilibrium was reached.

Flow Tube Experiments. As shown in Figure S2, a custom-made cylindrical quartz tube (9.8 cm inner diameter, 50 cm long) was used as a photochemical flow reactor, in which a quartz glass plate (40 cm \times 9.8 cm) was fitted snugly as a platform for placing sample filters. The flow tube was kept at 23 ± 2 °C during the experiments. Under ambient sunlight irradiation, the photolysis rate of NO_2 ($J(NO_2)$) in the atmosphere was simultaneously measured using a 4-pi- $J(NO_2)$ filter radiometer (MetCon, Germany), and the RH in the flow tube was kept at \sim 30%. Under UV lamp irradiation, the flow tube was surrounded by six fluorescent lamps (UVA range, Philips Cleo Effect 30 W = 300-420 nm, 41 cm, 2.6 cm o.d.) with a central wavelength of 350 nm (Figure S3), leading to a $J(NO_2)$ of 2.78 × 10⁻³ s⁻¹ in the flow tube. The RH in the flow tube was kept almost constant at \sim 15% during most UV lamp experiments and varied between 0 and 30% by regulating the flows of two mass flow controllers (MFC1 and MFC2, Figure S2) to investigate humidity effects on the H_2O_2 production. The gross flow of two channels of the carrier gases (air or pure N_2) was set at 5 L min⁻¹, and then the noontime production rate of H_2O_2 (P_{noon} , molecule cm⁻³ h⁻¹) under sunlight irradiation could be estimated based on the following equation

$$P_{\text{noon}} = \frac{10^{-9} \times C_{\text{noon}} \times \nu \times 60 \times 10^{-3}}{C_{\text{f}} \times V} \times C_{\text{A}} \times \frac{N_{\text{av}}}{10^{3} \times V_{\text{m}}}$$

where C_{noon} is the maximum concentration (~10 ppbv) of H_2O_2 at noontime in the flow tube; ν is the flow rate (5 L min⁻¹) of carrier gas in the flow tube; C_f is the PM_{2.5} concentration (μ g m⁻³) on the filter sample, which is listed in Table S1; V is the sampling volume (m³) for the PM_{2.5} sample; C_A is the estimated PM_{2.5} concentration (~150 μ g m⁻³) in the atmosphere during the polluted periods; N_{av} is the Avogadro constant (6.02 × 10²³ molecule mol⁻¹); and V_m is the molar volume (24.5 L mol⁻¹) of gas at 25 °C and 1 atm of pressure.

Additionally, NO (or SO_2) was added with a third flow of 5 mL min⁻¹ of 50 ppmv NO (or SO₂) in N₂ for NO (or SO₂) concentration influence studies. NO and SO₂ were measured using a chemiluminescence detector and a pulsed UV fluorescence analyzer, respectively (Model 42i and Model 43i, Thermo). H_2O_2 was measured using an Aero-Laser 2021 analyzer equipped with a fluorescence detector.^{16,27-29} After gaseous peroxides were stripped from air to buffered solution (pH = 5.8-6.0), total water-soluble peroxides including H_2O_2 reacted with p-hydroxyphenyl acetic acid (POPHA) and horseradish peroxidase, yielding a fluorescent dye that can be detected using a fluorescence detector. To separate H₂O₂ from organic peroxides, the stripping solution was divided into two channels. In one channel, catalase was added to selectively destroy H_2O_2 prior to the reaction with POPHA. Thus, the H_2O_2 concentration can be obtained from the signal difference between the two channels. The detection limit of the instrument was about 50 pptv with noise lower than 2% at a full scale. $^{28-30}$ Calibrations with liquid H_2O_2 standards (33.3 μ g L⁻¹) were performed before each experiment.

Smog Chamber Experiments. Three parallel fresh PM_{2.5} samples (WD-25-Dec-19) were put in an indoor 400 L Teflon bag (Figure S4), which was irradiated by six fluorescent lamps (UVA range, Philips Cleo Effect 30 W = 300-420 nm, 41 cm, 2.6 cm o.d.) with a central wavelength of 350 nm (Figure S3), providing a $J(NO_2)$ of 1.83×10^{-3} s⁻¹ in the chamber. The RH in the chamber was kept at ~30% by injecting 2.5 mL of ultrapure water based on the relation between atmospheric RH and saturated vapor pressure of water (2810 Pa at 23 °C). Four hundred milliliters of 50 ppmv SO2 or NO in N2 was also injected to guarantee 50 ppbv SO₂ or NO in the chamber. After air inflation, the bag was stabilized at room temperature for 1 h to make gas-phase species and water vapors mix sufficiently before photochemical experiments. As mentioned above, SO_{2} , NO_{x} and H_2O_2 were measured using a pulsed UV fluorescence analyzer, a chemiluminescence detector, and an Aero-Laser 2021 analyzer, respectively.

RESULTS AND DISCUSSION

As shown in Figure 1, under a constant flushing rate of 5 L min⁻¹ synthetic air $(O_2/N_2 = 20/80)$ with ~30% RH at 296 K, H_2O_2 concentration in the flow tube containing the PM_{2.5} filter sample increased quickly after exposing to sunlight in the early morning, reached a peak value in noontime, and then decreased with decreasing sunlight intensity in the afternoon. The nearly identical diurnal variations of H_2O_2 concentration and sunlight intensity indicated that solar irradiation plays a key role in trigging H_2O_2 formation from atmospheric PM_{2.5}. The slight decrease of the noontime peak H_2O_2 concentration for the PM_{2.5} filter sample on the second day (~8 ppbv) in comparison with the first day (~10 ppbv) implied that abundant H_2O_2 precursors exist in the PM_{2.5} sample. Based on a noontime peak H_2O_2 concentration of 10 ppbv in the flow



Figure 1. Diurnal variations of H_2O_2 and total peroxide concentrations in the flow tube containing a fresh $PM_{2.5}$ filter sample (WD-13-Dec-18) under sunlight irradiation. $J(NO_2)$ is the photolysis rate constant of NO_2 to represent the sunlight intensity, and humidified synthesis air of ~30% RH at 296 ± 2 K was used for flushing the flow tube with a flow rate of 5 L min⁻¹. The experiments were conducted on December 16–17, 2018.

tube, the amount of $PM_{2.5}$ on the filter sample (Table S1), and the assumed PM_{2.5} concentration (~150 μ g m⁻³) in the atmosphere during the polluted periods, the noontime H_2O_2 production rate from irradiating atmospheric PM25 could be estimated to be 1.3×10^9 molecules cm⁻³ h⁻¹. Considering the maximum concentrations of HO₂ radicals $(1.5 \times 10^8 \text{ molecules})$ cm⁻³) observed in the winter of the NCP, $^{31-33}$ the H₂O₂ production rate from gas-phase HO₂ recombination was estimated to be 1.2×10^8 molecules cm⁻³ h⁻¹. Moreover, ozonolysis of alkenes can also contribute to H₂O₂ production, the rate of which could be estimated to be 6.2×10^7 molecules $cm^{-3}h^{-1}$ with a H₂O₂ yield of 9% in moist air¹⁴ on the basis of the average concentrations of alkenes (~20 ppbv) and O_3 (~10 ppbv) during the winter campaign.³⁴ In comparison, the H_2O_2 production rate (1.3 × 10⁹ molecules cm⁻³ h⁻¹) from the photochemical aging of particles was 1-2 orders of magnitude higher than those of gas-phase formation pathways, suggesting that the unique pathway dominated H_2O_2 formation during polluted periods in winter. It should be mentioned that the actual H_2O_2 formation rate from irradiating the same amounts of PM_{2.5} suspended in the atmosphere may be significantly faster than the estimated value (1.3×10^9) molecules $cm^{-3} h^{-1}$) because only a thin surface layer of the $PM_{2.5}$ filter sample can receive solar irradiation,³⁵ e.g., H_2O_2 formation rates in the flow tube were approximately identical for the filter samples with different amounts of PM2.5 loading (Figure S5) under irradiation by fixed light intensity (six fluorescent lamps with a central wavelength of 350 nm, Figure **S**3).

To explore the H_2O_2 formation mechanism from irradiation of atmospheric $PM_{2.5}$, a series of indoor experiments were further conducted in the flow tube under flushing synthetic air (5 L min⁻¹) with 0–30% RH at 296 K. For the $PM_{2.5}$ filter sample with and without the presence of 50 ppbv NO, as shown in Figure 2A, H_2O_2 concentrations rapidly achieved the same value just after turning on the lamps and gradually increased at an approximately identical rate during the course of irradiation. The almost independent H_2O_2 production on

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Figure 2. Key influencing factors on H_2O_2 production from $PM_{2.5}$ filter samples under irradiation of the UV lamps in the flow tube. The blank areas and the yellow shadows represent the dark condition and UV irradiation, respectively. All experiments were conducted at room temperature (296 ± 2 K) with flushing synthesis air or nitrogen (N₂) at a flow rate of 5 L min⁻¹. The detailed information of each $PM_{2.5}$ filter sample is described in Materials and Methods. (A) The experiments were carried out for the same $PM_{2.5}$ filter sample (WD-25-Dec-19) by flushing humidified synthesis air of ~15% RH with and without the presence of 50 ppbv NO or 50 ppbv SO₂. (B) The experiments were carried out for the same $PM_{2.5}$ filter sample (WD-2-Jan-20) by flushing synthesis air and N₂ with ~15% RH. (C) The experiments were carried out for the same $PM_{2.5}$ filter sample (WD-10-Jan-20) by flushing synthesis air with 0, 6.9, 13.3, 18.6, and 23.2% RH. (D) The experiments were carried out for the same $PM_{2.5}$ filter sample (WD-2-Jan-20) before and after being baked at 105 °C for 4 h by flushing synthesis air with ~15% RH. (E) The experiments were carried out for the same $PM_{2.5}$ filter sample (WD-2-Jan-20) before and after removing water-soluble components (WSCs) by flushing synthesis air with ~15% RH. (F) The experiments were carried out for blank filters loaded with IC (imidazole-2-carboxaldehyde) + CA (citric acid), IC + CA + Cu²⁺, and IC + CA + Fe³⁺ by flushing synthesis air with ~15% RH.

the high NO level further confirmed that the unexpectedly high H_2O_2 concentrations observed in the winter of the NCP should be attributed to other sources rather than the gas-phase reactions (R1 and R2).

The remarkable elevation of H_2O_2 for the irradiated $PM_{2.5}$ sample under flushing the synthesis air in comparison with high purity nitrogen (Figure 2B) indicated that O_2 is involved in H_2O_2 formation. Analogous to the H_2O_2 formation mechanism proposed in the aqueous phase, ^{17,18,36} O_2 may act as an electron acceptor for the electrons or triplet excited organics originated from irradiation of transition metal species^{37,38} and CDOMs^{39,40} in atmospheric PM_{2.5} to produce highly reactive superoxide radicals (O_2^-), leading to H_2O_2 formation. However, previous studies revealed that O_2^- could only be detected on the surface of soot and PM_{2.5} filter samples under relatively high RH (54–60%) conditions,^{35,41} implying that the H_2O_2 formation through the pathway of O_2^- might be minor for irradiating atmospheric PM_{2.5} under relatively dry conditions.

H₂O₂ formation from irradiation of the PM_{2.5} sample evidently increased with increasing RH (Figure 2C), whereas it was slightly affected by the original water content in the PM_{2.5} sample, e.g., the nearly same H₂O₂ levels for irradiating a fresh PM_{2.5} sample before and after being baked at 105 °C for 4 h (Figure 2D). Water vapor may play dual roles in H_2O_2 formation and release. On the one hand, the reaction rate for the recombination of HO₂ radicals has been shown to increase significantly with the presence of water vapor in the gas phase,⁴² which is likely to accelerate H₂O₂ formation on the surface of particles. On the other hand, water vapor was found to accelerate H_2O_2 release from the particle surface due to the competition for surface absorption sites between H_2O_2 and H_2O . For example, under dark conditions, the H_2O_2 concentrations increased sharply after switching the dry flushing air to humidified flushing air for the PM_{2.5} samples pre-irradiated or preloaded with H_2O_2 (Figure S6).

 H_2O_2 formation decreased significantly for the PM_{2.5} sample after removing WSCs through ultrasonic extraction (Figure

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Figure 3. Pathways for the reactions of HO_2 radicals with surface hydroxyl to produce H_2O_2 over carbonaceous soot surfaces (modeled by graphene) with and without the presence of water vapors as well as the optimized geometries of the reactant complex (RC), transition states (TS), intermediate species (IM), and product complex (PC). Cyan, red, and white circles denote C, O, and H atoms, respectively. The imaginary frequency of the transition state is presented.



Figure 4. H_2O_2 production in the flow tube (A) and the values of MAE₃₅₀ and TMEs/PM_{2.5} proportions (B) for PM_{2.5} filter samples collected from different areas in China (Wangdu (WD-2-Jan-20), Beijing, Shanghai, and Guangzhou) and Germany (Melpitz). The experiments were carried out for the PM_{2.5} filter samples by flushing humidified synthesis air of ~15% RH (296 ± 2 K) at a flow rate of 5 L min⁻¹. The blank areas and the yellow shadows in (A) represent dark conditions and UV irradiation, respectively.

2E), indicating that the principal precursors for H_2O_2 in $PM_{2.5}$ may be a kind of WSCs. However, the contributions of WSIs including TMIs to H_2O_2 formation should be excluded because of very small H_2O_2 production for irradiating the blank filter loaded with K⁺, Na⁺, Fe³⁺, Cu²⁺, NO₃⁻⁻, SO₄²⁻, and Cl⁻ (Figure S7).

The most recent studies reported that organic mixtures of CDOMs and non-photoactive organics could produce evident gas-phase HO₂ radicals under ultraviolet (UV) irradiation, which was attributed to the reaction of O₂ with the ketyl radicals formed from the reactions of triplet excited CDOMs with non-photoactive organics.^{25,26} Because CDOMs are prevailingly present in atmospheric fine particles,^{19,25} H₂O₂ formation from the atmospheric PM_{2.5} was suspected to mostly link to the photochemical processes of CDOMs. As expected, evident H₂O₂ formation of a proxy for CDOMs (imidazole-2-carboxaldehyde (IC)) and citric acid (CA) under irradiation

(Figure 2F). Besides H_2O_2 formation, certain amounts (ppbv levels) of small carbonyls such as formaldehyde (HCHO), acetaldehyde, acetone, and propionaldehyde were also detected by irradiating the PM_{2.5} samples (Figure S8), indicating that organic compounds (i.e., CDOMs) in PM_{2.5} were evidently photodegraded during irradiation. Photo-degradation of organic compounds usually produces both carbonyls and HO₂ radicals.^{43,44} Thus, besides the proposed reaction of CDOMs in PM_{2.5} might be an important source of HO₂ radicals.

Although TMIs have been proposed to play a significant role in H_2O_2 formation through aqueous-phase photochemical reactions,⁴⁵ H_2O_2 formation from the filter treated by IC + CA was evidently suppressed with the presence of ferric ions (Fe³⁺) and cupric ions (Cu²⁺) under relatively dry conditions (Figure 2F), suggesting a different H_2O_2 formation mechanism for dry PM_{2.5} from those proposed for the aqueous phase. The more significant suppression of H_2O_2 formation by Fe³⁺ (Figure 2F) might be mainly attributed to H_2O_2 consumption through a Fenton-like reaction (e.g., heterogeneous photo-Fenton).⁴⁶

Taking all of the above experimental phenomena into account, a large fraction of HO_2 produced from R3 was suspected to react with the surface -OH group on atmospheric $PM_{2.5}$ to form H_2O_2 through R4.

CDOMs +
$$hv(\lambda \ge 290nm) \xrightarrow{O_2} HO_{2(ad)}$$
 + small carbonyls
(R3)

$$HO_{2(ad)} + surface - OH \xrightarrow{H_2O_{(g)}} H_2O_2 + O - surface$$
(R4)

To verify the speculation, DFT calculations were conducted using a graphene-based carbon surface as a model^{47,48} (see Section S3 in the Supporting Information) because graphenelike carbon (e.g., soot) is one of the essential components for atmospheric $PM_{2.5}$.^{49,50} As shown in Figure 3, R4 is easy to take place under ambient conditions with a very low energy barrier of 12.5 kJ mol⁻¹ and further become barrierless in the presence of one or more water molecules (Figure S9).

As CDOMs are ubiquitous in atmospheric fine particles,^{19,25} the PM_{2.5} filter samples from different regions are expected to produce H_2O_2 under light irradiation. As shown in Figure 4A, evident H₂O₂ formation can be found for all irradiated PM_{2.5} filter samples collected from Chinese cities (Beijing, Shanghai, and Guangzhou) and rural areas in both Germany (Melpitz) and China (Wangdu). Due to the significant suppression of H_2O_2 formation by TMIs (Figure 2F), the large difference of H₂O₂ concentrations generated among the PM_{2.5} filter samples depends not only on the content of CDOMs but also on the proportion of transition metal elements (TMEs, Fe and Cu) in PM_{25} (TMEs/PM₂₅). Although the mass absorption efficiency at 350 nm (MAE₃₅₀, as a proxy for the content of CDOMs; see Section S2 in the Supporting Information) for the Beijing sample was the highest (Figure 4B), its H₂O₂ production was significantly lower than that for the Wangdu sample (Figure 4A), which might be ascribed to the significant suppression effect of TMEs on H₂O₂ production due to the highest TMEs/ $PM_{2.5}$ in the Beijing sample. The significantly lower H_2O_2 peak concentrations in Beijing than those in Wangdu from field observation²⁸ under similar conditions might be attributed to the relatively high TMEs/PM2.5 in Beijing. The suppression effect of TMEs on H₂O₂ production was also supported by the experimental results for the PM2.5 filter samples from Shanghai, Guangzhou, and Melpitz: the values of MAE₃₅₀ for the three samples were approximately at the same level, whereas H₂O₂ production for the Melpitz sample with relatively high TMEs/ PM_{2.5} was the lowest. The highest H₂O₂ production for the Wangdu sample was in accordance with the highest ratio of MAE_{350} to $TMEs/PM_{2.5}$ (Figure 4B).

The significant suppression of H_2O_2 formation in the presence of 50 ppbv SO_2 for irradiating the $PM_{2.5}$ sample (Figure 2A) indicated that in situ H_2O_2 formed might be directly involved in oxidation of SO_2 on the particle surface. The significant decay of SO_2 and evident sulfate formation were also observed in a chamber containing $PM_{2.5}$ samples under UV irradiation (Figure S10), which provided further evidence for the above speculation. The most recent study also proposed that the particle surface reactions of reactive species (such as OH radicals and H_2O_2) with SO_2 were responsible for

sulfate formation based on UV irradiation (300-420 nm) of Beijing urban PM_{2.5} samples under 0–90% RH conditions.³⁵ The barrier for SO₂ directly reacting with H₂O₂ to produce H_2SO_4 is predicted to be 85.9 kJ mol⁻¹ (Figure S11), implying that it does not easily occur under ambient conditions. However, the overall energy barrier for SO₂ oxidation with surface -OH assistance over carbonaceous soot surfaces is low enough to be surmountable (52.7 kJ mol⁻¹, Figure S12) at room temperature.⁵¹ As an acidic gas, SO₂ uptake by atmospheric PM25 in the NCP is usually considered to be very weak because PM2.5 is usually acidic with a pH range of ~4–5,^{4,9,52} which could be certified by the very stable SO_2 concentration in the chamber under dark conditions (Figure S10). The remarkable SO₂ uptake by the PM_{25} samples under irradiation, however, may challenge our current understanding of the heterogeneous or multiphase reactions that mainly emphasize on the acidity of atmospheric PM_{2.5} for the uptake of atmospheric SO₂. Additionally, H₂O₂ should be abundant in daytime PM2.5 with respect to gas-particle partitioning because of its remarkable in situ production, and thus, the actual SO₂ oxidation rate by H_2O_2 on atmospheric PM_{2.5} is expected to be largely underestimated by current models that assume H_2O_2 in $PM_{2,5}$ follows Henry's law.^{4,53}

ATMOSPHERIC IMPLICATIONS

 $\rm HO_2$ formed by photochemical reactions of atmospheric $\rm PM_{2.5}$ not only contributes to $\rm H_2O_2$ but also acts as a source of atmospheric $\rm HO_2$ radicals, e.g., the chamber experiment for irradiating $\rm PM_{2.5}$ filter samples in the presence of NO showed evident conversion of NO to NO₂ despite less impact on $\rm H_2O_2$ formation (Figure S13). Therefore, the recent modeling study that considered atmospheric $\rm PM_{2.5}$ as a $\rm HO_2$ sink for explaining the increasing trend of O₃ with decreasing atmospheric $\rm PM_{2.5}$ in the NCP⁵⁴ probably needed to take potential $\rm HO_2$ production from photochemical aging of $\rm PM_{2.5}$ into account. Furthermore, the significant underestimation of atmospheric $\rm HO_2$ under high NO conditions over polluted regions by strictly constrained box models^{55–59} may be due to photochemical production of $\rm HO_2$ radicals from atmospheric $\rm PM_{2.5}$.

 $\rm H_2O_2$ production from daytime $\rm PM_{2.5}$ represents an additional source for atmospheric $\rm H_2O_2$ to initiate oxidation of atmospheric $\rm SO_2$, leading to sulfate formation. This source of $\rm H_2O_2$ is currently not considered in model estimations of the regional and global sulfate budget for rationally evaluating its impact on global radiative forcing and deterioration of regional air quality as well. Additionally, the health effects of atmospheric PM_{2.5} may be largely underestimated because the current estimations do not consider supersaturated $\rm H_2O_2$ in daytime PM_{2.5}, which can pass directly through the respiration system to cause DNA damage due to the strong oxidizing property of $\rm H_2O_2$.⁶⁰ Furthermore, as additional primary sources of atmospheric HO_x (OH and HO₂) radicals, both HO₂ radicals and HCHO produced from daytime PM_{2.5} may play an important role in atmospheric chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c04453.

Additional details about the field campaign, chemical and optical analysis, and DFT calculations; supplemen-

tary flow tube and smog chamber experimental results; sketch of reactor setups, optical spectra, diurnal variation of pollutants, and DFT calculations (Figures S1–S13); and average concentrations of chemical species in different $PM_{2.5}$ filter samples (Table S1) (PDF)

AUTHOR INFORMATION

Corresponding Author

Yujing Mu – Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; University of Chinese Academy of Sciences, Beijing 100049, China; orcid.org/0000-0002-7048-2856; Email: yjmu@ rcees.ac.cn

Authors

Pengfei Liu – Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; orcid.org/0000-0001-6237-3759

Can Ye – Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; Present Address: State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China; orcid.org/0000-0003-4350-0892

Chenglong Zhang – Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; University of Chinese Academy of Sciences, Beijing 100049, China

Guangzhi He – Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; University of Chinese Academy of Sciences, Beijing 100049, China; orcid.org/0000-0003-1770-3522

Chaoyang Xue – Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; Present Address: Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), CNRS-Université Orléans-CNES, 45071 Orléans, France; orcid.org/0000-0001-6673-7716

Junfeng Liu – Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; University of Chinese Academy of Sciences, Beijing 100049, China

Chengtang Liu – Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Yuanyuan Zhang – Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; University of Chinese Academy of Sciences, Beijing 100049, China

Yifei Song – Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; University of Chinese Academy of Sciences, Beijing 100049, China

Xuran Li – Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; University of Chinese Academy of Sciences, Beijing 100049, China

Xinming Wang – State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China; University of Chinese Academy of Sciences, Beijing 100049, China; orcid.org/0000-0002-1982-0928

Jianmin Chen – Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science and Engineering, Institute of Atmospheric Sciences, Fudan University, Shanghai 200438, China; © orcid.org/0000-0001-5859-3070

Hong He – Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; University of Chinese Academy of Sciences, Beijing 100049, China; orcid.org/0000-0001-8476-8217

Hartmut Herrmann – Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science and Engineering, Institute of Atmospheric Sciences, Fudan University, Shanghai 200438, China; Atmospheric Chemistry Department (ACD), Leibniz Institute for Tropospheric Research (TROPOS), 04318 Leipzig, Germany; Environmental Research Institute, Shandong University, Jinan 250100, China; orcid.org/ 0000-0001-7044-2101

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.1c04453

Author Contributions

P.L., C.Y., C.Z., and G.H. contributed equally to this work. Y.M. designed research; P.L., C.Y., C.Z., G.H., and C.X. performed research; J.L., C.L., Y.Z., Y.S., and X.L. were involved in part of the work; G.H., X.W., J.C., H. He, and H. Herrmann contributed new reagents/analytic tools; P.L., C.Y., C.Z., and Y.M. analyzed data; and P.L., C.Y., and Y.M. wrote the paper.

Notes

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