Diesel soot photooxidation enhances the heterogeneous formation of H$_2$SO$_4$

Both field observation and experimental simulation have implied that black carbon or soot plays a remarkable role in the catalytic oxidation of SO$_2$ for the formation of atmospheric sulfate. However, the catalytic mechanism remains ambiguous, especially that under light irradiation. Here we systematically investigate the heterogeneous conversion of SO$_2$ on diesel soot or black carbon (DBC) under light irradiation. The experimental results show that the presence of DBC under light irradiation can significantly promote the heterogeneous conversion of SO$_2$ to H$_2$SO$_4$, mainly through the heterogeneous reaction between SO$_2$ and photo-induced OH radicals. The detected photochemical behaviors on DBC suggest that OH radical formation is closely related to the abstraction and transfer of electrons in DBC and the formation of reactive superoxide radical ($\cdot$O$_2^-$) as an intermediate. Our results extend the known sources of atmospheric H$_2$SO$_4$ and provide insight into the internal photochemical oxidation mechanism of SO$_2$ on DBC.

The rapid increase in vehicle numbers has resulted in the emission of large quantities of black carbon (BC) into the lower atmosphere. BC particles in vehicle exhaust are mainly formed by incomplete combustion of hydrocarbon fuels. In particular, in northern China, BC mass concentrations of up to 20 $\mu$g m$^{-3}$ (nearly 10% of the total particulate matter) have been observed during haze episodes. High loading of BC can increase atmospheric stability through the formation of a temperature inversion, which will feed back to the development of extreme haze via suppressing air pollutant dispersion. Moreover, BC aerosol can influence climate by directly absorbing solar radiation and affecting cloud formation and surface albedo through deposition on snow and ice.

Recent works proved that the interactions between BC and other inorganic species can enhance the atmospheric oxidation capacity and contribute to the formation of complex air pollution. For instance, gaseous nitrous acid (HONO) is an important precursor of hydroxyl radical (OH) in the troposphere. Numerous studies have shown that the heterogeneous reduction of NO$_2$ on the BC surface is an important HONO source. Moreover, sulfate is the fastest-forming species and rapidly becomes the main component of secondary aerosols during the evolution of haze. Recent laboratory simulation and theoretical calculation works have indicated that soot can act as a catalyst to promote the heterogeneous oxidation of SO$_2$ to sulfate under dark conditions. Chamber experiments also proved that the catalytic role of soot in sulfate formation can be further amplified by reducing NO$_2$ to HONO in the presence of both NO$_2$ and NH$_3$ under dark conditions.

A recent field measurement in urban Beijing conducted by Yao et al. indicated that the catalytic oxidation of SO$_2$ on traffic-related soot can induce the formation of gas-phase SO$_3$ in the early morning. Therefore, the heterogeneous chemistry involving soot has recently attracted increasing attention in the field of atmospheric chemistry.

Relative to its role under dark conditions, some recent studies reported that both elemental carbon (EC) and organic carbon (OC) in BC exhibited conspicuous photo-reactivity due to their strong light absorption capability under illumination. The EC-initiated photo-oxidation of OC was found to proceed through radical reactions initiated by electron transfer, and the absorption of light by OC-induced direct photoaging by energy transfer. Recent observational evidence suggested that photochemical reactions on soot particles may contribute to the production of atmospheric sulfate during the daytime.

1State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 100085 Beijing, China. 2University of Chinese Academy of Sciences, 100049 Beijing, China. 3Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, 361021 Xiamen, China. e-mail: qxma@rcees.ac.cn; honghe@rcees.ac.cn
However, the intrinsic reaction mechanism of SO$_2$ on BC remains poorly resolved. Moreover, whether photoinduced radical chemistry can contribute to the heterogeneous conversion of SO$_2$ remains unclear.

In this work, a series of laboratory experiments are conducted to explore the underlying SO$_2$ oxidation mechanism on soot particles emitted from diesel vehicles (DBC) under light irradiation. In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements and thermogravimetric analysis mass (TGA–MS) analysis are applied to characterize the formation of surface H$_2$SO$_4$ on DBC under light irradiation. Combined with the reactive oxygen species (ROS) analysis from electron spin resonance (ESR), it is found that OH radical resulting from the conversion of superoxide radicals is the crucial oxidant during the heterogeneous conversion of SO$_2$ to H$_2$SO$_4$. These results help in understanding the sources of atmospheric oxidation capacity and particulate H$_2$SO$_4$.

**Results**

**Formation and characterization of sulfur-containing products on DBC surface**

The composition and structure of DBC were firstly analyzed and characterized using in-situ DRIFTS, XPS, and XRD methods. The detailed characterization results for DBC are shown in Fig. S1. In brief, DBC was found to be amorphous and highly graphitized. Various oxygen-containing groups (such as C=O, C–OH, and C–O–C) were detected in DBC through FTIR and XPS analysis.

Heterogeneous conversion of SO$_2$ on the DBC surface was systematically investigated using in-situ DRIFTS. The main peak at 1100 cm$^{-1}$ represents the characteristic vibrations of S=O bonds in sulfur-containing products (Fig. 1a). The significant increase in peak intensity with reaction time indicated that the heterogeneous reaction between SO$_2$ and DBC resulted in the production and gradual accumulation of sulfur-containing products. As shown in Fig. 1b–c, both the presence of DBC and light irradiation can remarkably promote the heterogeneous formation of sulfur-containing species compared to reaction under dark conditions and in blank experiments. This implies that the remarkable heterogeneous conversion of SO$_2$ to sulfur-containing species should be closely related to the photo-induced catalytic role of DBC. From Fig. S2, the observation of similar in-situ DRIFTS experimental results implies that DBC photooxidation would most likely promote the heterogeneous oxidation of SO$_2$ under low-level SO$_2$ conditions (~1 ppm).
According to the evolution of water and sulfur-containing fragments in previous studies, we have proved that the pyrolysis of H2SO4 intercalation compounds (H2SO4–GICs) could occur in the DBC/SiO2 or SiO2 particles. It was found that the uptake of SO2 (60 ppb) on DBC/SiO2 mixtures is much greater than that on SiO2. Moreover, the uptake of 10 ppb SO2 on DBC is also observed to last more than 10 h under light irradiation. These results indicate that the heterogeneous uptake of SO2 on DBC is significant even under conditions close to the real atmosphere. The comparison of extracted SO42− ions from different samples (Fig. 1d) further highlights the enhancing role of DBC on the heterogeneous oxidation of SO2 under both dark conditions and light irradiation. The formation of SO42− under dark conditions may be due to the catalytic oxidation of SO2 on the surface-active site of soot as reported in previous studies. The SO42− concentrations obtained under light irradiation are much higher than those under dark conditions. This is consistent with DRIFTS results and further proved the role of DBC in photocatalytic oxidation of SO2 under conditions close to the real atmosphere. To obtain the formation rates of sulfur-containing species on DBC, photooxidation experiments of SO2 (~60 ppb) on DBC of different masses were also carried out (Fig. S3). The measured formation rates of sulfur-containing species varied linearly with the mass concentration of DBC under light irradiation, and the mass normalization rate was determined to be ~1.0 × 10−3 μg m−2 s−1 according to the observed BC mass concentrations (10.4 ± 17.8 μg m−2). This is comparable with the reported formation rate of gaseous H2SO4 (~0.001–0.1 μg m−2 s−1) from the OH reaction pathway. These results suggest that the photooxidation of SO2 on BC could be an important source of sulfate in areas with high BC loading.

To further reveal the role of sulfur species on the DBC surface, several characterization techniques were employed. Given that trace amounts of metal elements that can act as catalysts may break off from the NOx selective catalytic reduction catalyst in diesel after-treatment systems and be emitted along with DBC, we investigated the elemental composition of DBC by XPS. From the survey XPS spectrum of DBC shown in Fig. S6, metallic elements were hardly detected in the DBC. This also implied that the sulfur-containing species detected were not metal sulfates, due to the lack of positive ions containing such metal elements. Thus, we speculated that the photooxidation of SO2 on DBC mainly produces H2SO4 or sulfur-containing organics rather than metal sulfate complexes.

The pH measurement results in Fig. 2a show that the pH of SO2-aged DBC (~3.74) was lower than that of fresh DBC (~3.74), which suggested that H2SO4 was formed in the photooxidation reaction on DBC. To confirm the formation of particulate H2SO4, TGA–MS was employed to characterize H2SO4 on aged-DBC. From the TGA–MS of aged-DBC, a saddle-like change in SO2 (m/z 64 in Fig. 2b) and SO (m/z 48 in Fig. S7) fragments were observed in the temperature intervals of 200–400 °C and 400–600 °C, respectively. According to the evolution of water and sulfur-containing fragments in the TGA–MS of pure H2SO4 (Fig. S8), it could be found that the evaporation and pyrolysis of H2SO4 occur in the temperature range of 200–400 °C. Thus, the formation of SO2 fragments between 200 and 400 °C in the TGA–MS of SO2-aged DBC proved that H2SO4 exists in SO2-aged DBC. The SO2 fragments in the range 400–600 °C should be derived from other sulfur-containing species such as H2SO4 in graphite intercalation compounds (H2SO4–GICs) and C(2μmH2SO4)2H2SO4). Previous studies have shown that the pyrolysis of H2SO4–GIC could produce SO2 fragments in the range 400–600 °C. Furthermore, the similar formation and evolution of sulfur-containing fragments in TGA–MS of a H2SO4–DMS mixture (30 μL H2SO4 and 15 mg DBC) further support the supposition that the interaction between DBC and H2SO4 can produce some other sulfur-containing species (Fig. 2b).

Recent work reported that the soot surfaces upon irradiation can give rise to gaseous OH radicals. It can be speculated that these photoinduced OH radicals may react with SO2 to form gaseous H2SO4. Thus, to confirm the formation of gaseous H2SO4, the gaseous photochemical reaction of SO2 on DBC was measured in a quartz photoreaction flow tank (Fig. S9) using formaldehyde solution (4 ml, 11% v/v). As shown in Fig. 2c, the concentration of SO42− ions (1.0 ± 0.28 μg ml−1) after 24 h reaction under light irradiation was greater than that (0.7 ± 0.1 μg ml−1) under dark conditions. This further provided convincing evidence for the formation of gaseous H2SO4. The condensation of gaseous H2SO4 could be a source of surface H2SO4.
Heterogeneous formation pathway of H$_2$SO$_4$

A recent work by Li et al. proved that the EC-initiated photooxidation of soot mainly involves electron transfer and the formation of reactive oxygen species\(^1\). To shed light on the mechanism of DBC photodissociation in SO$_2$ oxidation, we also examined the generation of photoinduced electrons and reactive oxygen radicals during DBC photooxidation by using the spin-trapping EPR technique. TEMPO was used as the spin-trapping agent for photoinduced electrons. As shown in Fig. 3a, the ESR spectrum of a DBC suspension with TEMPO showed a characteristic signal of three peaks with an intensity pattern of 1:1:1, representing the radical spin-label of TEMPO. It is worth noting that the signal intensity of the TEMPO radical decreased once exposed to light irradiation, demonstrating that TEMPO was partially reduced to an ESR-silent molecule such as TEMPOH by photo-induced electrons\(^2\). Given that various oxygen functional groups and structural defects or disordered structures are ubiquitous on carbonaceous materials in DBC (Figs. S1a and S11), the formation of photo-generated holes (h+) on excited EC may abstract electrons from OC and subsequently donate electrons to other available acceptors such as adsorbed O$_2$ (Eq. (2))\(^5\). To further verify this, the photo-induced electron–hole pairs in residual EC were analyzed using TEMPO spin-trapping ESR spectra. As shown in Fig. S12, the remarkable decrease in the signal intensity of TEMPOH radicals after 120 min light irradiation further demonstrates that the residual EC from DBC can indeed induce the generation of holes or electrons (Eq. (2)). Thus, long-chain saturated alkanes in DBC can indirectly donate electrons to absorbed O$_2$ via excited EC (Eqs. (2) and (3)) and subsequently be oxidized to other organic oxygen-bearing compounds (Eq. (4))\(^3\).

To verify whether the observed photogenerated electrons can further result in the formation of reactive oxygen radicals (•O$_2$ and OH radical), we chose two spin traps, DMPO and BMPO, to capture •O$_2$ and OH radical, respectively. As shown in Fig. 3c, four characteristic peaks of DMPO–•O$_2$ adducts were observed in a DBC suspension in methanol under light irradiation, while no signal was observed under dark conditions\(^5\). This demonstrated that electrons were transferred to the dissolved O$_2$ in the DBC suspension, resulting in the formation of •O$_2$ radical (Eq. (3)). Previous studies reported that O$_2^-$ radicals can interact with SO$_2$ or sulftie ion (SO$_5^{2-}$) to form a series of sulfur-containing radicals (SO$_{3^-}$, SO$_4^{2-}$, and SO$_4^{2-}$)\(^6\). The free radical chain reaction dominated by sulfur-containing radicals would eventually result in sulfate formation. However, it should be noted that these sulfur-containing radicals are scarcely detected in the BMPO spin-trapping ESR spectra of SO$_2$-aged DBC (Fig. 4a) according to the reported measurement methods\(^7\). Thus, the contribution of the
heterogeneous reaction between \( \text{SO}_2 \) and \( \cdot \text{O}_2 \) to \( \text{H}_2\text{SO}_4 \) should be limited despite the fact that this reaction may occur in this system. In addition to its direct oxidation capability, \( \cdot \text{O}_2 \) radical is also the key intermediate species in OH radical production during photo-induced interfacial reactions; thus, OH radicals in DBC suspension were further measured via the spin trapping EPR technique\(^6\). As shown in Fig. 4a, a significant signal of BMPO–OH adducts with a typical 1:2:2:1 quartet signal was observed, indicating that light irradiation could indeed cause the formation of OH radicals in the suspension of fresh DBC and DBC aged by \( \text{SO}_2 \). Almost no BMPO–OH adduct signals were observed in DBC under dark conditions or in ultrapure water under light (Fig. 4b). This further indicated that OH radical formation was closely related to the presence of DBC and light irradiation. These results proved that the photooxidation process of DBC indeed involves a complex electron transfer pathway and results in the generation of reactive oxygen radicals such as OH radicals (Eqs. (3), (5), and (6)). Moreover, the BMPO–OH adduct detected in aged-DBC treated with \( \text{SO}_2 \) apparently decreased relative to that in fresh DBC (Fig. 4a). This implied that the heterogeneous conversion of \( \text{SO}_2 \) to \( \text{H}_2\text{SO}_4 \) (Eqs. (7) and (8)) should be related to the consumption of OH radical from DBC. To further confirm this, the heterogeneous conversion of \( \text{SO}_2 \) on DBC under light irradiation was also investigated in the presence of high-level NO (radical scavenger). From the results of in-situ DRIFTS experiments shown in Fig. 3c, the presence of high-level NO (10 ppm) could significantly suppress the heterogeneous formation of \( \text{H}_2\text{SO}_4 \) on DBC. Moreover, the results of experiments in a coated-wall quartz flow tube reactor also showed that the presence of DBC indeed can promote the conversion of NO to HONO under light irradiation relative to the control experiment. Furthermore, the addition of \( \text{SO}_2 \) can also in turn hamper the heterogeneous conversion of NO to HONO (Fig. 4d). These results supported the hypothesis that the competing reactions of \( \text{SO}_2 + \cdot \text{O}_2 \) and \( \cdot \text{O}_2 + \cdot \text{OH} \) must exist during DBC photooxidation. This also proves that the heterogeneous oxidation of \( \text{SO}_2 \) by OH radicals should be an important formation pathway of particulate \( \text{H}_2\text{SO}_4 \) on DBC under light irradiation.

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\begin{align*}
\text{EC} & \xrightarrow{\text{hv}} h^+ + e^- \\
\text{OC} + h^+ & \rightarrow \text{OC}^+ \\
\text{O}_2 + e^- & \rightarrow \cdot \text{O}_2 + \text{H}^+ \rightarrow \text{HO}_2^+ \\
\text{OC}^+ + \cdot \text{O}_2 + \cdot \text{OH} & \rightarrow \text{Carbonyl or others} \\
2\text{HO}_2^+ & \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 & \xrightarrow{\text{hv}} 2^*\text{OH} \\
\cdot \text{OH} + \text{SO}_2 + \cdot \text{O}_2 & \rightarrow \text{SO}_3 + \text{HO}_2^+ \\
\text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4
\end{align*}
\]

**Discussion**

The conventional view recognizes BC particles as a reducing agent in the atmosphere. For example, BC was found to initiate the heterogeneous reduction of \( \text{NO}_2 \) to HONO and hence elevate the atmospheric oxidation capacity in the atmosphere\(^9,10,22\). In this work, our experimental results indicated that DBC under light irradiation can act as an oxidation medium to directly promote the heterogeneous oxidation of \( \text{SO}_2 \) to \( \text{H}_2\text{SO}_4 \). Moreover, it was also proven that the promoting role of DBC photochemistry on the rapid conversion of \( \text{SO}_2 \) is linked to the photo-induced formation of OH radicals. As for the
proposed that these OH radicals mainly derive from the reaction of photoinduced singlet oxygen (O) and H$_2$O on soot based on the density functional theory (DFT) results. In this study, we found that the formation of OH radical is also closely related to the formation and conversion of the intermediate reactive superoxide radical (O$_2^-$) triggered by the abstraction and transfer of photoinduced electrons. Thus, our work further complements or improves the production mechanism of OH radicals on DBC under light irradiation, which provides insight into the photochemical reaction process on DBC.

H$_2$SO$_4$ in the atmosphere mainly comes from the reaction of SO$_2$ and H$_2$O, which is the critical precursor causing the rapid nucleation and growth of ultra-fine particle$^{16-32}$. Thus, exploring the unknown sources of SO$_2$ and H$_2$SO$_4$ is crucial for understanding the formation and growth of new particles. Recently, both DFT calculation and field observation indicated that the formation of gaseous SO$_2$ during the early morning is closely related to the catalytic oxidation of SO$_2$ on the surface of soot$^{30,33}$. Another field observation by Zhang et al. found that the photooxidation of BC-containing particles can further enhance the formation of sulfate$^{34}$. Here, our experimental results provide reliable experimental evidence for these recent observations and DFT calculation results, especially under light irradiation. Hence, the heterogeneous reaction of NO to H$_2$SO$_4$ driven by the photochemical process on DBC may very directly contribute to the rapid formation and growth of new particles in the atmosphere via inducing the formation of gaseous and particulate H$_2$SO$_4$. Our study highlights the photooxidation role of DBC in the heterogeneous formation of H$_2$SO$_4$, which has important atmospheric implications for understanding new particle formation and the source of atmospheric sulfate. It was worth noting that further model simulation and field observation in future studies should be effectively combined to quantitatively evaluate the contribution of this new pathway to H$_2$SO$_4$ formation in the atmosphere.

Additionally, black carbon has strong effects on regional and global climate due to the remarkable positive (warming) radiative forcing in the atmosphere$^{35-39}$. In particular, the internal mixing between BC and other aerosol components through processes such as gas condensation and coagulation can remarkably affect light absorption by BC$^{40-42}$. This work proved that the photooxidation of DBC could directly promote the heterogeneous conversion of SO$_2$ to H$_2$SO$_4$. Thus, an in-depth study of the optical properties of BC aerosol internally mixed with sulfuric acid in the future will help to evaluate the effect of variation of the mixing state on direct radiative forcing and climate.

**Methods**

**Experimental procedure**

Diesel soot was collected from the diesel particle filter (DPF) of a China VI heavy-duty diesel engine (ISUZU from China). A diesel engine bench test was run under the conditions of the World Harmonized Transient Cycle (WHTC). China VI fuels were used in this study, meeting the GB T32859-2016 standard. The heterogeneous reactions of SO$_2$ or SO$_2$/NO on diesel soot particles were measured by in-situ DRIFTS (NEXUS 6700, Thermo Nicolet Instrument Corporation), equipped with a diffuse reflection chamber and a high-sensitivity mercury cadmium telluride (MCT) detector. The MCT was cooled by liquid N$_2$ prior to the measurement. The infrared spectra were collected by means of a computer using OMNIC 6.0 software (Nicolet Corporation, USA). All spectra reported here were recorded at a resolution of 4 cm$^{-1}$ for 100 scans in the spectral range 4000–650 cm$^{-1}$. The spectra are presented in the Kubelka–Munk (K–M) scale, which can provide a better linear relation with concentration via reducing or eliminating the mirror effect. To simulate solar irradiation, a high uniformity integrated xenon lamp (PLS-FX300HU, Beijing Perfectlight Technology Co., Ltd.) was used as the light source$^{43}$. Its visible spectrum ranges from 330 to 850 nm (Fig. S10a). The light in the near-infrared and infrared bands was filtered using a transmission-reflection filter (VISREF). DBC was placed into a cylindrical ceramic crucible in the diffuse reflection chamber before DRIFTS measurement. Before the reaction, the DBC was purged with 200 mL min$^{-1}$ air at 298 K and 55% RH until the infrared spectrum was unchanged. Then the samples were exposed to 10 ppm SO$_2$ balanced with 200 mL min$^{-1}$ synthetic air for at least 12 h.

The experiments on HONO detection were conducted in a coated-wall quartz flow tube reactor (34 cm length, 1.6 cm i.d.$^{44,45}$). The coated tube with the deposited DBC sample was horizontally placed in the main reactor. Synthetic air, as the carrier gas, introduced NO and SO$_2$ into the coated flow tube at a total flow rate of 21 min$^{-1}$. Inorganic gases (SO$_2$ and NO) were introduced into the flow tube through a movable injector with 0.3 cm radius. HONO was measured by a long-path absorption photometer (HONO-1000, Beijing Zhichen Technology Co. Ltd), while the reactant gas SO$_2$ in the coated flow tube was measured by a Thermo Scientific analyzer (43I SO$_2$ analyzer). To better simulate the heterogeneous conversion of SO$_2$ on DBC under close-to-atmosphere conditions, heterogeneous experimental tests with low SO$_2$ concentrations (~60 and 10 ppb) were further carried out in a quartz tube plug flow reactor (40 cm in length, 0.6 cm in diameter) at 37% RH. Before loading the sample into the plug flow reactor, ~2 mg of DBC was needed to be diluted using ~1 g silica sand (analytically pure, 1 mm in diameter) to ensure the reaction gas could flow fluently through the DBC. To further verify that DBC photooxidation in the presence of SO$_2$ could also promote the formation of gaseous H$_2$SO$_4$, the heterogeneous reaction of SO$_2$ (~60 ppb) on DBC (~0.25 g) powder alone was carried out in a quartz photoreaction tank at 50% RH. Prior to the reaction, the 0.25 g DBC powder was uniformly dispersed into a shallow quartz vessel (7 cm in diameter and 0.4 cm in depth) and then placed into the photoreaction tank. The outlet of the quartz photoreaction tank was connected with a quartz trap bottle (2 cm in diameter and 7 cm in depth) with 4 ml formaldehyde solution (20% v/v). Gaseous H$_2$SO$_4$ from the interaction between SO$_2$ and DBC was captured using ultrapure water in the quartz trap. The captured H$_2$SO$_4$ was analyzed using IC. The designed RH in the DRIFTS chamber or in the flow tube was obtained by varying the ratio of dry zero air to wet zero air. A flow of humid vapor was generated by bubbling zero air through ultrapure water. A Vaisala HMP110 probe was used to monitor the changes in RH online.

**DBC characterization**

Surface chemical states were analyzed by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Scientific). An X-ray powder diffractometer (Bruker D8 ADVANCE 28 diffractometer) with Cu K$_\alpha$ radiation ($\lambda=0.15406$ nm) operated at 40 kV and 40 mA was used to characterize the crystalline form and interlayer spacings of the DBC power. The patterns were measured over the 2$\theta$ range from 10$^\circ$ to 80$^\circ$ with a scanning step size of 0.02$^\circ$. The OC in DBC was analyzed and identified via gas chromatography coupled with mass spectrometry (GC–MS, Agilent 6890–5973). DBC was first ultrasonically extracted for 10 min using 20 ml of dichloromethane (CH$_2$Cl$_2$), which was filtered through a quartz sand filter. The obtained supernatant liquid was subsequently concentrated with 200 mL min$^{-1}$ of dry zero air for at least 12 h. The UV–vis spectra of residual EC and OC were measured using the UV–vis spectrometer (Perkin Elmer LAMBDA 650).
Analysis and characterization of oxidizing agents and products
Thermal gravimetric analysis. The sulfur-containing species produced during diesel soot photooxidation were investigated using a combined method of thermogravimetry–mass spectrometry (TGA–MS). In brief, a Mettler-Toledo thermogravimetry system (TGA, DSC1-1600HT) was coupled with a quadrupole mass spectrometer (MS, ThermoStar-GSD-350, Pfeiffer Vacuum) by a silica capillary at a temperature of 250 °C. The MS system was equipped with an electron ionization source with the voltage at 70 eV and provided the mass spectra up to m/z 300. TGA–MS was carried out over the range 35–800 °C with a 30 K min⁻¹ gradient. The whole experiment was accomplished under an inert purge gas of N₂ with a constant flow rate of 70 ml min⁻¹. In a typical desorption run, a blank test of the empty sample crucible was performed at 25 °C in an N₂ stream (the carrier gas flow rate: 50 ml min⁻¹ and the shielding gas flow rate: 20 ml min⁻¹). Afterward, the sample was weighed and placed in the sample container. The pure DBC (15 mg), SO₂-aged DBC (15 mg), pure H₂SO₄ solution (60 µL), and an H₂SO₄–DBC mixture (30 µL H₂SO₄ (1.8 mol/L) and 15 mg DBC) were placed in sequence in an alumina crucible of the main fragment components of H₂SO₄ (H₂SO₄, SO₃, SO₂, SO, respectively), were chosen to further verify H₂SO₄ formation.

ESR measurements. An electron spin resonance spectrometer (ELEXSYS E500 ESR; Bruker) with a modulation frequency of 100 kHz and a microwave frequency of 9.5 GHz was used to capture reactive radical signals. 5-tert-butoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO) added to a freshly prepared 0.1 M aqueous solutions. 5,5-dimethylpyrroline-N-oxide (DMPO) was used for capturing OH radicals in the DBC suspension. DBC suspensions loaded in a quartz container. The pure DBC (15 mg), SO₂-aged DBC (15 mg), pure H₂SO₄ solution (60 µL) were placed in sequence in an alumina crucible of 70 µl. The mass spectra of m/z 98, 80, 64, and 48, which correspond to the main fragment components of H₂SO₄ (H₂SO₄, SO₃, SO₂, SO, respectively), were chosen to further verify H₂SO₄ formation.

IC analysis. To quantitively the H₂SO₄ concentration under different conditions, ion chromatography (IC, Model DIONEX ICS-2100, Thermo Scientific, Inc., USA) was employed to analyze the changes in the concentrations of water-soluble ions (such as SO₄²⁻ and NO₃⁻). A certain amount of SO₄²⁻ may be contained in the primordial DBC samples due to the combustion of sulfur-containing species in fuel. Thus, DBC samples were ultrasonically extracted using ultrapure water at least 10 times to exclude interference from these preexisting SO₄²⁻ ions in the measurement of newly produced SO₄²⁻ ions during IC analysis. After the reaction finished, DBC samples (25 mg) obtained under different experimental conditions were first dispersed in 20 mL of ultrapure water and sonicated for 10 min, and subsequently filtered using a syringe filter (13 mm diameter, 0.22 µm pore-size). The filtered liquid was split in half. Half of the samples were directly analyzed by IC.

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

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Author contributions
H.H. designed and supervised the research. P.Z. designed and performed the experiments. Q.M. gave guidance for the experimental research. T.C., Q.M., B.C., Y.W., Y.M, and Y.Y. provided suggestions for the manuscript. P.Z. and H.H. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to Qingxin Ma or Hong He.

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