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Roles of Sulfur Oxidation Pathways in the Variability in Stable Sulfur Isotopic Composition of Sulfate Aerosols at an Urban Site in Beijing, China

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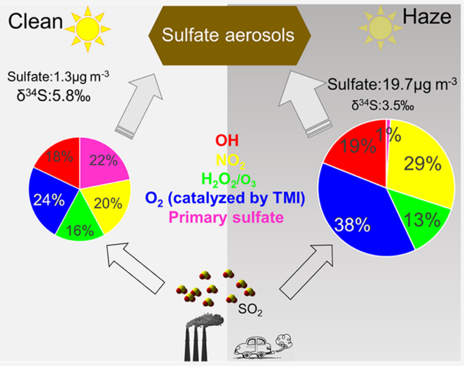

ABSTRACT: Sulfate (SO_4^{2-}) is an important chemical species in atmospheric aerosols, which strongly impacts atmospheric chemistry processes and climate change. Stable sulfur isotopes ($\delta^{34}S$) of sulfate aerosols in $PM_{2.5}$ were measured in Beijing from November 13 to December 2, 2018, to investigate the pathways of formation of sulfate aerosols. The results showed that SO_4^{2-} constituted a major fraction (18%) of water-soluble ions and significant enhancement of sulfate was observed during the haze period. The $\delta^{34}S$-SO_4^{2-} values averaged at 4.4 ± 1.4‰ during the full period, exhibiting a downward trend with an increase in sulfate concentration. The change in sulfur isotope values could not be explained by the changes in emission sources. Significant correlations were found between observed $\delta^{34}S$-SO_4^{2-} values and SO_2 oxidation ratios ($R = -0.88$; $p < 0.01$), indicating the changes in sulfur isotopes were attributed to the SO_2 oxidation processes. On the basis of Rayleigh distillation, the average fractionation factor between SO_2 and SO_4^{2-} was 4.0 ± 1.2‰. Combining sulfur isotopes and the Bayesian model, we quantified the contributions of primary sulfate, OH, H_2O_2/O_3, NO_2, and O_2 [catalyzed by transition metal ions (TMIs)] oxidation pathways to sulfate formation were 7%, 20%, 16%, 27%, and 30%, respectively. The contributions of TMI and NO_2 pathways increased from 24% and 20% during the clean period to 38% and 29% during the haze period, respectively. Our results highlighted that sulfur dioxide oxidized by TMI-catalyzed O_2 and NO_2 were the dominant pathways of sulfate formation in Beijing under haze pollution during the heating seasons.

■ INTRODUCTION

Sulfate (SO_4^{2-}) is unambiguously an important species in atmospheric aerosols, having an impact on atmospheric chemistry and climate change.[1−3] In the atmosphere, sulfate aerosols can be directly emitted from anthropogenic and natural sources (primary sulfate, e.g., sea salt, fly ash, or mineral dusts) or formed by gas-to-particle conversion (secondary sulfate).[4,5]

Sulfate aerosols are predominately produced by the oxidation of SO_2. Previous studies have shown that the known oxidation pathways of SO_4^{2-} formation mainly included aqueous-phase and gas-phase reactions. For gas-phase reactions, the reaction of SO_2 with hydroxyl radicals (OH) is a major pathway for the formation of sulfuric acid (H_2SO_4).[6] Immediately thereafter, the produced $H_2SO_{4(g)}$ may adhere to the surface of existing aerosol particles or nucleate to form new particles under favorable conditions (e.g., high relative humidity), increasing aerosol number concentrations and the number of cloud condensation nuclei (CCN), which has effects on direct and indirect radiation. On the contrary, sulfuric acid immediately reacts with NH_3 to produce ammonium sulfate aerosols. In the mineral dust particles, some semiconducting metal oxides (e.g., α-Al_2O_3, α-Fe_2O_3, and TiO_2) act as a photocatalyst that can yield electron (e^-_{cb})−hole (h^+_{vb}) pairs. The e^-_{cb}−h^+_{vb} pairs accelerate the production of OH radicals and drive the subsequent photooxidation of SO_2 to produce $H_2SO_{4(g)}$.[7−9] Recent studies have revealed that stable Criegee intermediates (sCIs, generated during the gas-phase ozonolysis of unsaturated hydrocarbons) could play a role in the gas-phase oxidation of SO_2, which produced $SO_{3(g)}$ and subsequently $H_2SO_{4(aq)}$ by reacting with $H_2O_{(aq)}$ in the atmosphere.[10,11] However, sCIs [e.g., $(CH_3)_2COO$, CH_2OO, etc.] can also directly react with water vapor, which limits atmospheric H_2SO_4 formation.[10] If sCIs react slowly with water vapor but quickly with SO_2, these sCIs may accumulate to higher concentrations and be more likely to oxidize atmospheric SO_2.[10]

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For aqueous-phase reactions in cloud or smog,[12] SO_2 dissolves in droplets to produce S(IV) ($[SO_2 \cdot H_2O] + [HSO_3^-] + [SO_3^{2-}]$), and subsequently, S(IV) reacts with dissolved oxidants, such as hydrogen peroxide (H_2O_2), ozone (O_3), O_2 [catalyzed by transition metal ions (TMIs)], and nitrogen dioxide (NO_2), to yield sulfate aerosols. During the process, H_2O_2 is well-known as an important reactant to oxidize SO_2 to SO_4^{2-} aerosols due to its high solubility in cloud droplets. In contrast, the solubility of O_3 was 17 orders of magnitude lower than that of H_2O_2, and therefore, the concentrations of O_3 in droplets are much lower than H_2O_2 levels.[13] Oxidation of SO_2 to sulfate in the aqueous phase is significantly dependent on the pH values of droplets. As the pH value changes from 4.5 to 5.0, the reaction between S(IV) and H_2O_2 is a major mechanism for sulfate formation.[14] On the contrary, sulfate is mainly produced by the S(IV) + O_3 reaction under high-pH (>5−5.3) conditions.[12]

In addition, oxidation of S(IV) by O_2 and NO_2 also occurs during the aqueous-phase process of sulfate formation.[15] Numerous studies indicated that the reaction of S(IV) and O_2 can be neglected for sulfate formation because its reaction rate is much lower than that of S(IV) and H_2O_2 under atmospheric conditions.[16,17] However, in recent years, some studies suggested that this formation mechanism might be severely underestimated in haze and enriched dust-polluted atmospheres.[18,19] The solubility of NO_2 is much lower than that of H_2O_2, which results in slower S(IV) + NO_2 oxidation during the aqueous process.[16] Laboratory studies revealed that the reaction rate constant of the S(IV) + NO_2 oxidation increased with pH.[20] Some recent studies suggested that the S(IV) + NO_2 reaction conducted in aerosol liquid water might be an important pathway of sulfate formation during haze pollution in China, and it was called "haze chemistry".[16,21−25] During the haze chemical process, SO_2 is dissolved into aerosol liquid water and oxidized to form sulfate under high-NO_2 conditions. This pathway requires a considerable high aerosol liquid water content (ALWC) and NO_2 concentrations in the atmosphere, and its reaction rate also depends on the acidity in aerosols, which has a large uncertainty due to the possible existence of stable and metastable aerosols in the real atmosphere that cause the inhomogeneity of the atmospheric aerosol pH.[26] The relative contribution of different oxidation pathways to sulfate formation depends on multiple factors, such as the concentration of oxidants for photochemical and aqueous-phase oxidations, ALWC, and acidity of aerosols. Therefore, it is difficult to evaluate the contributions of these oxidation pathways by calculation through chemical kinetics due to the huge differences in these factors under different pollution conditions, influencing SO_2 reaction rates in various oxidation pathways.

Investigation of formation mechanisms in atmospheric sulfate aerosols gives us a hint to better understand the sulfate budget, linked to climate changes on regional and/or global scales. Oxygen isotopic compositions, such as $\delta^{18}O$ and $\Delta^{17}O$, are frequently used to identify the mechanisms of formation of sulfate aerosols,[27−29] whereas $\delta^{34}S$ was considered to be attributed to the different SO_2 emission sources.[27,30] For example, the $\delta^{34}S$ value of DMS was in the range of +15−19‰,[31−33] while most anthropogenic sulfate displayed much lower $\delta^{34}S$ values such as that from coal combustion (+6.6 ± 3‰)[34] and traffic emissions (+5.8 ± 3.0‰).[35−37] Obviously, the different emission sources result in the different $\delta^{34}S$ values in sulfate aerosols.[31−38] Nevertheless, several recent studies used $\delta^{34}S$ values to quantify the relative contributions of the different oxidation pathways from SO_2 to sulfate.[15,19,39] In the conversion of SO_2 and SO_4^{2-}, the isotope fractionation effects would be produced through different oxidation pathways such as OH, NO_2, H_2O_2, O_3, and O_2 catalyzed by TMIs, resulting in different signatures of $\delta^{34}S$ in sulfate aerosols ($\delta^{34}S$-SO_4^{2-}).[19,40] Oxidation by H_2O_2 and O_3 produced sulfate with enriched ^{34}S (+15.1−19.9‰) relative to the reactant SO_2, whereas sulfate formed by TMI catalysis depleted ^{34}S values (−9.5 ± 3.1‰) relative to SO_2.[15] In general, $\delta^{34}S$ in atmospheric sulfate aerosols is definitely influenced by both the oxidation pathways and the emission sources, and the influence exhibits seasonal and geographic variability. Many previous studies have measured $\delta^{34}S$-SO_4^{2-} in Beijing and used $\delta^{34}S$-SO_4^{2-} to investigate the sources in Beijing.[27,33,41] Although some studies explored the pathways of formation of sulfate by model simulation[16] and chamber experiments,[23] these studies might not provide the direct evidence to support their conclusions in the real aerosol samples. In this work, $PM_{2.5}$ samples were collected during a short-term sampling period with high pollution in Beijing from November 13 to December 2, 2018. In addition to water-soluble ions, $\delta^{34}S$-SO_4^{2-} values were also determined to investigate the driving factors of the isotope compositions. Furthermore, we used a new approach to estimate the relative contributions of various oxidation pathways to sulfate aerosol formation by combining $\delta^{34}S$ techniques with a Bayesian model.

■ MATERIALS AND METHODS

The details of aerosol sampling, observations of tracer gases and meteorological parameters, and chemical analysis of ions are described in Text S1 of the Supporting Information. The $\delta^{34}S$-SO_4^{2-} was determined by a continuous flow isotope ratio monitoring mass spectrometry system (EA/GC/TG-IsoPrime, GV Instruments). Prior to sulfur isotope analysis, the pretreatment of aerosol samples had to be done; the detailed pretreatment of aerosol samples for $\delta^{34}S$-SO_4^{2-} analysis can be seen in Text S2. Subsequently, two different sulfur isotopes, ^{32}S and ^{34}S, were determined, and the $\delta^{34}S$ value of the aerosol sample can be calculated as

$$\delta^{34}S(‰) = [(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{standard} - 1] \times 1000‰ \quad (1)$$

where $(^{34}S/^{32}S)_{sample}$ and $(^{34}S/^{32}S)_{standard}$ are the $^{34}S/^{32}S$ ratios in the aerosol samples and the internal standard of NBS 127 ($\delta^{34}S$ = 21.1‰), respectively. One Alfa standard was inserted into every 10 samples to calibrate the deviation of $\delta^{34}S$ during the measurement. During the pretreatment process, sulfur isotope fractionation from SO_4^{2-} to $BaSO_4$ was not found because the $\delta^{34}S$ value in pure Na_2SO_4 (−6.54 ± 0.21‰) was close to that in the precipitated $BaSO_4$ (−6.54 ± 0.35‰) (Table S1).

■ RESULTS AND DISCUSSION

Sulfur Isotope of Sulfate Aerosols. The characteristics of water-soluble ions in aerosols, tracer gases, and meteorological parameters are discussed in Text S3 (Figures S1−S3). During the sampling period, the $\delta^{34}S$-SO_4^{2-} values ranged from 1.9‰ to 6.4‰ with a mean value of 4.4 ± 1.4‰ (Table S2), which was in agreement with that (4.6 ± 0.5‰) observed during the 2015 autumn in Beijing.[30] On the contrary, we also found the apparent differences in $\delta^{34}S$-SO_4^{2-} values under the

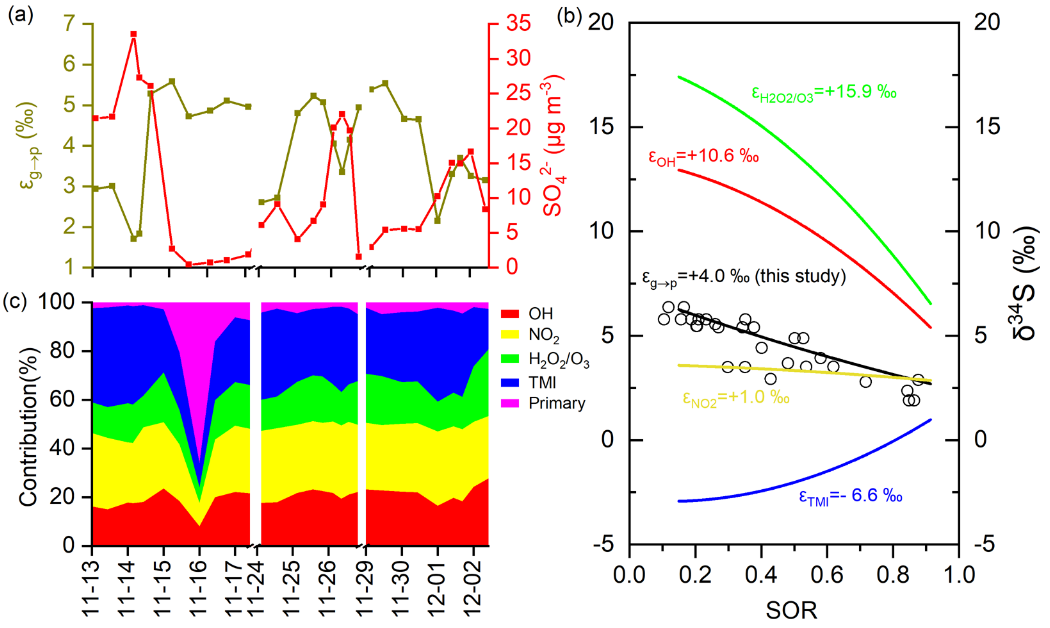

Figure 1. (a) Estimated fractionation factors ($\varepsilon_{g\rightarrow p}$) (earth yellow) and observed sulfate concentrations (SO_4^{2-}, red) throughout the sampling period. (b) Rayleigh distillation model of sulfate production. Black circles are the measured $\delta^{34}S$-SO_4^{2-} values from this study. The green line indicates the $\delta^{34}S$-SO_4^{2-} when SO_2 is oxidized solely by O_3 and H_2O_2.[19] The red line indicates the $\delta^{34}S$-SO_4^{2-} when SO_2 is oxidized solely by OH.[19] The yellow line indicates the $\delta^{34}S$-SO_4^{2-} when SO_2 is oxidized solely by NO_2.[40] The blue line indicates the $\delta^{34}S$-SO_4^{2-} when SO_2 is oxidized solely by TMI oxidation.[19] The black line is the best fit of measured $\delta^{34}S$-SO_4^{2-}, showing an average $\varepsilon_{g\rightarrow p}$ value of +4.0 ± 1.2‰. (c) Contribution of each formation pathway based on the Bayesian model calculation.

different $PM_{2.5}$-level conditions. During the clean ($PM_{2.5} \leq 35$ $\mu g\ m^{-3}$), moderate ($35\ \mu g\ m^{-3} < PM_{2.5} \leq 75\ \mu g\ m^{-3}$), polluted ($75\ \mu g\ m^{-3} < PM_{2.5} \leq 150\ \mu g\ m^{-3}$), and haze ($PM_{2.5} > 150\ \mu g\ m^{-3}$) periods, the mean values of $\delta^{34}S$-SO_4^{2-} were 5.8 ± 0.0‰, 5.5 ± 1.2‰, 4.7 ± 1.2‰, and 3.5 ± 1.1‰, respectively. Obviously, the average $\delta^{34}S$ values during the haze period were significantly lower than those during other three periods [$p < 0.05$ (Table S3)]. Such a decreasing trend of $\delta^{34}S$ from the clean period to the haze period might be interpreted by the changes in the contributions of various sources and formation pathways to sulfate under different pollution conditions.[15,19,30,39] In this work, six major emission sources (including coal burning, industrial processing, traffic emission, biomass burning, terrigenous origin, and biogenic sulfur) were considered in the quantification of source apportionment of sulfate aerosols, which might be important emission sources of atmospheric SO_2 in northern China.[27,42] However, our result showed that the relative contribution of each emission source did not significantly change ($p > 0.05$) under the different $PM_{2.5}$-level conditions based on the Bayesian calculation (uncertainties of 4−10%) (details in Text S4, Figure S4, and Tables S4 and S5). Therefore, the differences in $\delta^{34}S$ during the different PM-level conditions were likely attributed to the distinctive mechanisms of formation of sulfate aerosols.

Furthermore, the measured $\delta^{34}S$-SO_4^{2-} displayed significant negative correlations with T ($R = -0.46$; $p < 0.05$), relative humidity (RH) ($R = -0.76$; $p < 0.01$), and SO_2 oxidation ratio (SOR = molar concentration of SO_4^{2-}/molar concentration of $[SO_4^{2-} + SO_2]$) ($R = -0.88$; $p < 0.01$) (Figure S5). Previously, the negative correlation between $\delta^{34}S$-SO_4^{2-} and SOR was also found in Nanjing, China, during a haze episode, indicating that SO_2 oxidation would change $\delta^{34}S$-SO_4^{2-} values.[43] Zhang et al.[44] suggested that a high RH enlarged the surfaces of droplets and wet aerosols in the atmosphere, which resulted in the aqueous-phase oxidation reactions of atmospheric SO_2 with oxidants. In addition, the significant correlation between $\delta^{34}S$ and RH might suggest that isotope fractionation occurred in aqueous-phase oxidation of SO_2 to sulfate formation. SOR is the formation ratio of SO_2 to sulfate, and ambient temperature and RH significantly influence sulfate formation during the different processes.[45,46] Consequently, significant correlation between $\delta^{34}S$-SO_4^{2-} and the aforementioned parameters might also suggest that the $\delta^{34}S$ values of sulfate were dependent on the different SO_2 oxidation processes.

Contributions of Oxidation Pathways to Sulfate Formation. Assuming the relative contribution of each source to sulfate aerosols was constant under the different air pollution conditions, the formation pathways of sulfate can be quantified using the $\delta^{34}S$ techniques (details in Text S5), and the results are shown Figure 1. On average, secondary sulfate produced through OH, H_2O_2/O_3, NO_2, and TMI oxidation pathways contributed 20%, 16%, 27%, and 30%, respectively, to the sulfate aerosols during the sampling period. In addition, the primary sulfate (calculated by $0.18 \times Ca^{2+} + 0.25 \times Na^{+}$)[30] contributed 7% to total sulfate mass. A high proportion of primary sulfate (low sulfate concentration) was observed on November 16. The backward trajectory (Figure S6) showed that dry air [RH ∼ 20% (see Figure S2)] was mainly from Inner Mongolia, passing the arid region and picking up enriched Ca^{2+} aerosols ($Ca^{2+} \sim 2.6\ \mu g\ m^{-3}$). On the contrary, the NO_2 concentration on November 16 was as low as 20 $\mu g\ m^{-3}$. The low-RH and -NO_2 conditions were unfavorable for the aqueous-phase reaction of secondary sulfate formation, leading to lower sulfate concentrations. This might be the reason for the large fraction of primary sulfate on this day, and the high level of primary sulfate was likely from the natural dust, such as $CaSO_4$. Our contribution of TMI (30%) to sulfate was in line with atmospheric chemistry modeling results in Beijing (19−36%)[47] and other cities over China (20−50%).[18] The contribution (20%) of the

OH pathway was also in agreement with values from the previous study (19−34%) in Beijing during the polluted season.[47] Figure S7a shows the relative contribution of the SO_2 + NO_2 pathway to sulfate formation under different NO_2 + ALWC conditions [ALWC was calculated by the ISORROPIA-II model (Text S6)]. The result showed that the relative contribution of the NO_2 pathway to sulfate production increased obviously with increasing NO_2 and ALWC concentrations. This suggested that the NO_2 pathway was more important in sulfate production under high-NO_2 and -ALWC conditions.[24] In addition, the contribution of the TMI pathway to sulfate formation also increased with increasing Fe and Mn concentrations as shown in Figure S7b. This was expected because Mn and Fe ions are important catalysts through the TMI oxidation process.

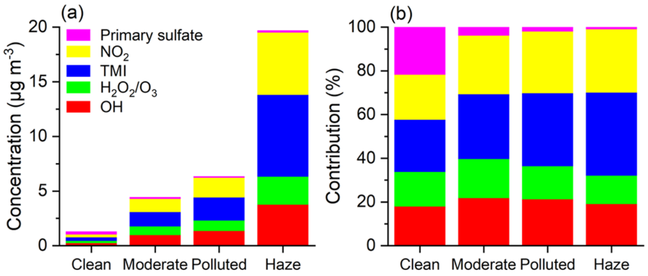

Figure 2. (a) Concentrations and (b) relative contributions of oxidation pathways (OH, H_2O_2/O_3, TMI, and NO_2) and primary sulfate of sulfate formation under different pollution levels.

The relative contributions of primary sources and secondary production by various oxidation pathways to particulate sulfate under the different $PM_{2.5}$ levels are shown in Figure 2 and Table S6. When the $PM_{2.5}$ concentration was <35 μg m^{-3}, primary sulfate accounted for 22% of total sulfate. In terms of secondary sulfate, the contributions of OH, H_2O_2/O_3, NO_2, and TMI oxidation pathways to sulfate formation were 18 ± 6%, 16 ± 5%, 20 ± 7%, and 24 ± 7%, respectively. When severe haze pollution occurred, the contributions of OH, H_2O_2/O_3, NO_2, and TMI oxidation pathways were 19 ± 3%, 13 ± 4%, 29 ± 2%, and 38 ± 7%, respectively. In Beijing, high sulfate concentrations via the NO_2 oxidation pathway through heterogeneous reaction have been reported in the recent studies.[16,23] The increased contribution of the TMI pathway likely resulted from high loadings of TMIs (e.g., Fe and Mn) in the atmosphere, which were emitted from local industrial sources in the haze events that enhanced the TMI oxidation rate. Our results highlighted that NO_2 and TMI oxidations were the major contributing pathways of particulate sulfate formation under severe pollution conditions in Beijing. The calculated contribution of the TMI pathway in the haze events was in agreement with the previous study, which suggested ∼36% of atmospheric sulfate in Beijing was produced via the TMI-catalyzed O_2 oxidation pathway.[47] In this work, the total fraction of TMI and NO_2 pathway to sulfate formation was 67% during the haze period, which was similar to the result (66−73%) that was investigated by oxygen isotopes during a Beijing haze event.[48] Previous studies have suggested that H_2O_2 oxidation was the dominant pathway of formation of atmospheric sulfate aerosols.[18,19,49] However, our results did highlight that the oxidations of SO_2 with NO_2 and TMI were the important formation pathways of sulfate aerosols in Beijing, especially during the haze event.

Using a sulfur isotope technique, we found a significant correlation between $\delta^{34}S\text{-}SO_4^{2-}$ values and SOR, indicating the changes in sulfur isotopes were strongly attributed to the chemical mechanisms of sulfate aerosols. On the basis of our results, we highlighted that a novel approach to quantifying the mechanisms of formation of sulfate aerosols was developed in this work, and the restriction and uncertainty of this new method are discussed in Text S7. The principle of the new approach was different from model simulations[16,47] and laboratory experiments.[23] Comparisons and validations for the results by the various approaches are needed. This will reduce the gap between real and estimated values of sulfate formation mechanisms, improving the precision and accuracy in the prediction of regional and global sulfate budgets.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.0c00623.

Detailed descriptions of analytical methods, additional data, figures, and tables (PDF)

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Author Contributions

Y.-L.Z. designed research. Y.Q., Y.S., and P.F. conducted the field work. M.-Y.F., H.C., and N.A. performed the laboratory experiments. F.C. and J.L. performed the model experiments. M.-Y.F. analyzed the data. M.-Y.F., Y.-C.L., and Y.-L.Z. wrote the paper. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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