Responses to reviewer

Reviewer comments are in **bold**. Our responses are labelled with [R] and authors' actions with [A]. Line numbers in the responses correspond to the revised manuscript with track-changes. Modifications to the manuscript are in blue.

Reviewer 2

Zhou et al. investigated the sulfate formation from aerosol SO_2 oxidation by model biomass burning photosensitizers. The authors show clear evidence that biomass burning-derived photosensitizer particles can induce photosensitized oxidation of SO_2. The results will advance our understanding of sulfate formation pathways and therefore meet the metric for publication in ACP. I have some minor comments for the authors' consideration.

> [R0] We thank the reviewer for the valuable feedback and constructive suggestions. Detailed responses are given below.

Line 25: S(IV) is often used to represent dissolved species of SO_2. Can the authors confirm that the aerosol particles in this study are in the liquid phase?

> [R1] [A1] We have discussed the phase state of photosensitizer particles at line 100, though we could not directly observe it. It is expected that there is always surface adsorbed water or bulk phase water in partially dissolved VL particles, in which SO_2 will form S(IV). We would like to keep this terminology.

Lines 85-86: Are the particles uniformly coated? It would be helpful to provide the size distribution information of the coated particles.

> [R2] We did not obtain a uniform population for the organic-coated particles. However, we indeed considered the effect of the particle size on the sulfate RPA. The coating thickness estimated by particle size increase spanned a wide range from 100 nm to 2.2 μm, and different particle sizes may have effects on the sulfate RPA. As we have discussed in line 258 that the reactive uptake comprises the diffusion of SO_2 molecules, followed by oxidation of SO_2 at/near the surface or in the bulk of the particles. The decreased sulfate RPA with increasing particle size suggested the photosensitized sulfate formation at/near the surface of VL-coated particles, probably due to the prevalence of surface reactions or diffusional limitations of SO_2 in larger particles, especially in the poorly hygroscopic and potentially viscous VL matrix. Even though the sulfate RPA was size dependent, it generally exhibited the same descending order of

DMB>VL>SyrAld>BA in each size bin (Figure S7). The RPA and number percentage for each specific experimental condition in the main text (e.g., Figure 2) were calculated by taking the average of those values in different size bins in Figure S7. Hence the potential uneven coating thickness has been incorporated in the averages, which show consistent trends in Figure 2.

[A2] For clarity, we had added after line 170 that "Although the coating thickness estimated by particle size increase spanned a wide range from 100 nm to 2.2 µm, the number percentage and RPA of sulfate generally exhibited the same trend for the studied photosensitizers in each size bin (Figures S7). Figure 2 shows the average RPA of sulfate (circles) and the number percentage of sulfate-containing particles (diamonds) in DMB-, VL-, SyrAld- and BA-coated particles at dark and different UV intensities in the presence of SO_2, and the corresponding SO_2 consumption normalized by the average total particle surface area concentration before and after UV irradiation in the OFR detected by SPAMS (crosses). The RPA and number percentage of sulfate for each experimental condition were calculated by taking the average of those values in different size bins in Figure S7. Hence the potential uneven coating thickness has been incorporated in the averages, which show consistent trends in Figure 2. The average number percentages of sulfate-containing particles in DMB- and VL- coated particles are considerably higher (> 84%) under both I_1 and I_4 UV irradiances than under dark (< 2%). SyrAld-coated particles gave a slightly lower percentage of sulfate-containing particles of 43% and 83% at I_1 and I_4 UV irradiances. Upon increase of photon flux densities (I_1 to I_4), the RPA of sulfate increases for DMB-, VL- and SyrAld-coated particles, which is in line with the enhanced normalized SO_2 consumptions. The number percentage and RPA of sulfate exhibited a similar descending order of DMB>VL>SyrAld>BA in each size bin (Figure S7). Our observed trend of sulfate formation potential is in line with the secondary organic aerosol mass yield for syringol oxidation by $^3C^*$ of DMB (114%), VL (111%) and SyrAld (78%) in the literature (Smith et al., 2016; Smith et al., 2014)."

Lines 131-137: The authors tend to attribute the sulfate formation to SO_2 oxidation at the aerosol surface. However, the increase of SO_2 consumption with the increase in surface area cannot rule out the possibility of bulk phase reactions. Can the authors provide more insights on whether the reaction occurs at the surface or in the bulk?

[R3] In Figure 4, we found an overall inverse relationship between the sulfate RPA and particle size for VL-coated particles, which indicated that the relative sulfate content increased with the particle surface to volume ratio. This points to the importance of reactions on/near the surface, though we cannot exclude the existence of reactions in the inner bulk.

[A3] We have clarified this in the text as follows (lines 257-262): "The reactive uptake comprises the diffusion of SO_2 molecules, followed by oxidation of SO_2 at/near the surface or in the bulk of the particles. The decreased sulfate RPA with increasing particle size suggested the photosensitized sulfate formation at/near the surface of VL-coated particles, probably due to the prevalence of surface reactions or diffusional limitations of SO_2 in larger particles, especially in the poorly hygroscopic and potentially viscous VL matrix. We cannot exclude the occurrence of bulk phase reaction in the organic moiety, though it was likely less efficient than the surface reaction."

Line 138: Can the authors explain why only slight SO_2 consumption was observed in the presence of SyrAld-coated particles? The aerosol pH is also important to SO_2 oxidation. Is the pH of these particles similar?

[R4] The pH of the DMB, VL and SyrAld particles were measured as 6.01±0.06, 6.15±0.12, 5.97±0.10, respectively. Although acidic environments would suppress SO_2 uptake, it was not applicable in the comparison of results of these photosensitizer particles, which are similarly neutral. SyrAld-coated particles show slight SO_2 consumption, which was consistent with its considerably lower average RPA and number percentage of sulfate-containing particles (Figure 2), than the DMB- and VL- coated particles. In general, we found that the sulfate formation potential (RPA and number percentage) exhibited the descending order of DMB>VL>SyrAld, which is in line with the secondary organic aerosol mass yield for syringol oxidation by $^3C^*$ of DMB (114%), VL (111%) and SyrAld (78%) in the literature (Smith et al., 2016; Smith et al., 2014).

[A4] We have added the potential reasons for the different sulfate formation efficiency after line 185: "Specifically, DMB has a higher quantum yield and longer lifetime of $^3C^*$ compared to VL (Felber et al., 2021), which can result in a higher sulfate formation efficiency. On the other hand, the direct photodegradation rate constant was higher for SyrAld than VL, likely suppressing the concentration of SyrAld in droplets/ particles and the photosensitized oxidation (Smith et al., 2016). However, photosensitization is still a research field for atmospheric chemistry with broad uncertainties (Felber et al., 2021). Further quantitative work on the quantum yield, lifetime, and the decay and quenching rate constants of the $^3C^*$ is needed."

We have added pH information after line 183: "The pHs of the DMB (6.01±0.06), VL (6.15±0.12) and SyrAld (5.97±0.10) particles were similar."

Lines 202-203: Are the size distribution of particles similar for VL-coated and KNO_3 particles?

[R5] [A5] As shown in Figure 4, both VL-coated particles and KNO_3 particles spanned a wide size range from around 400 to 2500 nm. However, it was clear that KNO_3 particles exhibited an RPA of 0 over the full-size range, while VL-coated particles exhibited an average sulfate RPA of 0.26.

Lines 221-223: What is the role of RH? If it is due to the fewer dissolved VL, then it means that the particle is in the liquid phase. Is it in contrast to the discussion in lines 195-199?

[R6] Firstly, the reaction between photoexcited SO_2 molecules and H_2O can produce secondary OH radicals (Kroll et al., 2018). However, this reaction played a negligible role in this study because we did not see effective sulfate formation in the control experiment using BA-coated particles as seeds in the presence of SO_2 (Figure 2). Furthermore, Corral Arroyo et al. (2018) also reported that the particle-phase photosensitized radical production was promoted at higher RH, due to the presence of more water as plasticizers and reduced particulate viscosity. In our system, the photosensitizers have low solubility and hygroscopicity, resulting in limited available dissolved VL to trigger photosensitization and possibly limited dissolved SO_2. In addition, lower RH could result in higher particulate viscosity, which hinders molecular diffusion and reaction (Kroll et al., 2018; González Palacios et al., 2016; Corral Arroyo et al., 2018). We have added this information to the text. In this study, the low RH experiments were conducted for the externally mixed VL and nitrate system to study whether the relative atmospheric importance of particulate photosensitization and nitrate photolysis are still the same as those under high RH conditions, given that nitrate concentration in droplets may be much higher under low RH. We found that sulfate formation was on VL-coated particles but not on externally mixed nitrate particles under both high and low RH conditions (Figure 4 and Figure S10). This analysis was not in contrast to the phase state discussion, as both aerosol liquid water in (partially) deliquescent particles and surface adsorbed water content on solid particles at 80% RH were expected to be higher than at 20% RH (Rubasinghege and Grassian, 2013).

We apologize that the location of the particle phase state discussion (originally in lines 195-199) led to confusion. We have moved it to 100, which better fits the method part.

[A6] We have added the potential RH effect on the photosensitized reaction after line 272: "When RH decreased to 20%, a significant reduction in the average RPAs from 0.26 to 0.002 was observed for VL-coated particles (Figure S10), attributable to the fewer dissolved VL for sulfate formation since VL has low solubility and hygroscopicity and the limited SO_2 dissolution (Liu et al., 2021). In addition, lower RH could result in higher particulate viscosity, which hinders molecular diffusion and reaction (Kroll et al., 2018;

González Palacios et al., 2016; Corral Arroyo et al., 2018). A systematic study of the effect of RH on the particle-phase photosensitized reaction is desirable. Overall, sulfate formation was found on VL-coated particles but not on externally mixed nitrate particles at both high and low RH in our study."

The original lines 195-199, which better fit the method part, have been moved to line 99 as follows. In addition, we have added discussions: "Depending on the experiment, the RH in the OFR was regulated at ~80% or 20% to achieve different content of aerosol water by passing HEPA-filtered and activated-carbon-denuded compressed air or pure N_2 through water bubblers. Note that the photosensitizers may be (polymorphic) solid or semi-solid due to their low solubility and hygroscopicity, even at 80% RH (Kavuru et al., 2016; Hussain et al., 2001). For example, Mochida and Kawamura (2004) reported that pyrolysis products of lignin with -COOH, including vanillic acid and syringic acid, showed no hygroscopic growth even at RH of more than 90%. They also proposed that other pyrolysis products with chemical structures such as –CHO may have even lower hygroscopicity than –COOH and would not show measurable particle growth. Though we could not observe the phase states of the particles, both aerosol liquid water in (partially) deliquescent particles and surface adsorbed water content on solid particles at 80% RH were expected to be higher than at 20% RH (Rubasinghege and Grassian, 2013)."

Lines 214-217: Are these results applicable to ambient conditions? Does this indicate that nitrate photolysis plays a negligible role in sulfate formation in ambient conditions?

[R7] [A7] Nitrate photolysis was found to be significant in triggering sulfate formation in the ambient (Gen et al., 2019; Zheng et al., 2020). Moreover, our study implies that photosensitization could be an even more effective pathway than nitrate photolysis contributing to sulfate formation. The residence time in the OFR may be too short (~ 2.5 min) to show effective sulfate formation via nitrate photolysis.

Reference

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