Response to Reviewer 3:

This paper presents the hygroscopic behavior of BC particles generated from different types of fuel and aged with SO_2 for varying durations and explore the key factors that influence the hygroscopic of BC. They found that the presence of water-soluble substances in BC facilitates increase the number of water adsorption layers at high relative humidity. And the hygroscopicity of BC can be enhanced by the formation of sulfate ions due to heterogeneous oxidation of SO_2. I believe that the topic is interesting and it could be useful to the scientific community. However, some modifications are needed before they can be accepted.

Reply: We would like to thank you for the time and effort spent in reviewing the manuscript, which greatly improved the quality of our paper. The following is a point-by-point response to all the comments, and the manuscript has been revised substantially according to your comments.

Major Comments

Q1. The hygroscopicity of five different types of BC and the influencing factor was explored. However, only the aging of UBC was measured. The finding that low relative humidity has a limited effect on BC hygroscopicity is suitable for other black carbon (such as n-hexane flame BC, decane flame BC)? For example, will OC present in toluene flame BC lead to a decrease in the humidity turning point?

A1. We used UBC as a black carbon model for aging experiments because of sufficient sample amount for repeated experiments. Considering that the main product of SO_2 photooxidation on black carbon is sulfuric acid, we think that the weak effect of SO_2 ageing on the hygroscopicity of soot under low RH should be applicable to other black carbon. However, this need more experiments to verify, which is indeed our future plan to investigate how aging of OC affects the hygroscopicity of black carbon.

Q2. The key factor influencing the BC hygroscopicity was analyzed, including water-soluble ions, organic carbon content, and microstructure. However, BC size is very important for explore its hygroscopicity, but author seems to have neglected this. Please clarify.

A2. We agree that BC size is very important for explore its hygroscopicity. We added the results of TEM experiments on various soot samples. TEM images of soot samples are shown below. All soot samples consisted of typical spherical particles, which formed long chainlike agglomerates as reported in other studies (Han et al., 2012; Liu et al., 2010). The diameter distribution of soot particles based on TEM analysis are also shown below. Particles exhibit a relatively uniform particle size distribution.

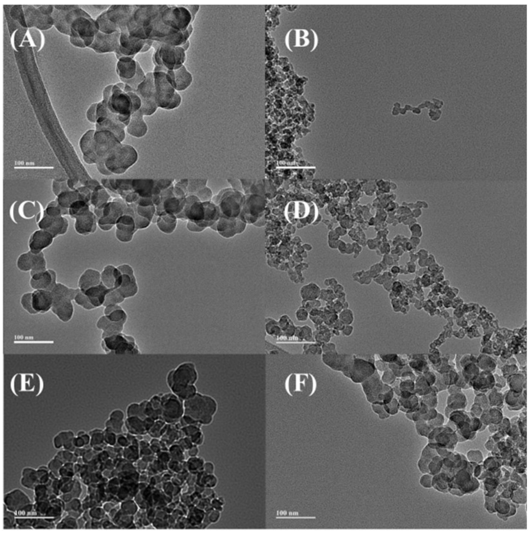

Figure 2. TEM images of n-hexane flame soot (A), decane flame soot (B), toluene flame soot (C), diesel soot (D), U-soot aggregates (E) before and (F) after aged with 5 ppm of SO_2 for 10 h.

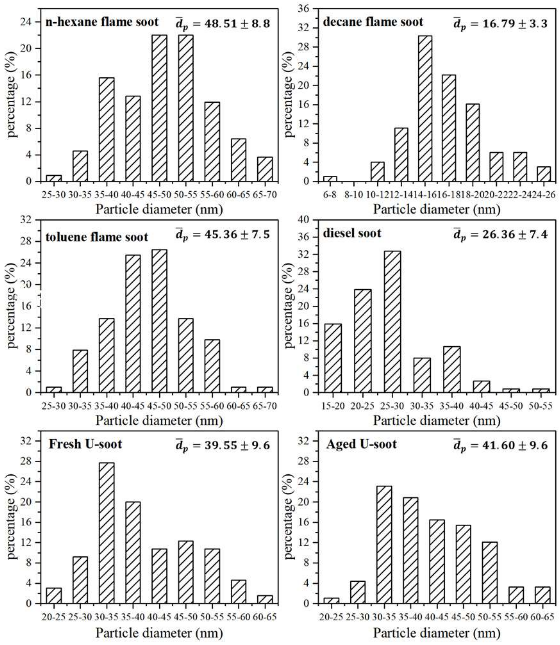

Figure 3. Diameter distribution of n-hexane flame soot, decane flame soot, toluene flame soot and diesel soot and U-soot particles before and after aged with 5 ppm of SO2 for 10 h.

Nevertheless, we used the vapor sorption analyzer (VSA) to study the hygroscopicity of BC, which can only show the hygroscopic behavior of the bulk black carbon powder. Thus, the effect of particle size on the hygroscopicity of soot are not analyzed.

These discussions have been added in the revised manuscript (Line 153-166).

Q3. Why the microstructure of DBC and UBC was not measured?

A3. In section 3.1, the inorganic ions present in five different black carbons were analyzed using IC. The findings revealed that DBC and UBC contained significant amounts of SO_4^{2-} and NO_3^- ions. On the other hand, the three prepared black carbons exhibited minimal levels of inorganic ions. Thus, the three prepared black carbons were chosen to investigate the impact of factors other than inorganic ions on the hygroscopic properties of black carbon. Because inorganic components affect the hygroscopicity more significantly than OC and microstructure, the information of OC and microstructure of DBC and UBC was not shown.

Q4. The author has analyzed the influence of different factors on the hygroscopicity of BC, but in the ambient atmosphere, the main driving factor was difficult to identify. Could the author further discuss this through the results of this study?

A4. We agree that it is difficult to measure the hygroscopicity of black carbon in the atmosphere due to the complexity of its composition and atmospheric process. BC particles are emitted into the atmosphere from various sources, and their different origins lead to variations in their composition and microstructure, resulting in diverse hygroscopic properties. Moreover, the ambient atmosphere is highly intricate, comprising pollutants like nitrogen oxides, sulfur dioxide, volatile organic compounds, and others, which can alter the hygroscopic behavior of BC through heterogeneous reactions. Therefore, we intend to study the key properties that affect the hygroscopicity of black carbon through experimental simulation. In our previous investigation, we found that the reaction between SO_2 and BC leads to the formation of a sulfuric acid coating on BC surfaces (Zhang et al., 2022). In this study, we further revealed the promoting effect of inorganic ions (especially SO_4^{2-}) generated by aging on hygroscopicity of BC. On the other hand, in previous study, the presence of water was found to enhance the oxidation of SO_2 on BC (He et al., 2020). In this study, we studied the key physicochemical properties that affect the hygroscopicity of fresh black carbon, which could be helpful for understanding the aging process of black carbon from different sources. In summary, the interaction between water and SO_2 on BC surfaces reinforces each other, highlighting the importance of considering the hygroscopic properties of BC in the atmospheric processes.

Q5. For the prepared BC, the Raman spectra suggested that the ID/IG of n-hexane BC, toluene BC and decane BC increased in turn, and the hygroscopicity of BC showed the same tendency. But it is not very valid to conclude that the ID/IG was positively correlated with hygroscopicity. The discussion should be expanded to support your conclusion.

A5. We have added the relevant content after careful consideration of your suggestion. Previous study found that the ratio ID/IG is inversely proportional to the graphite crystallite size L_a (Knauer et al., 2009): $44/L_a = (I_D/I_G)$, where L_a is the graphite crystallite size as determined by X-ray. The intensities of D and G bands have been widely determined using the sum of D1 and D4 bands and the sum of D2 and G bands, respectively. The result of Raman spectra demonstrates that there is a positive correlation between the ID4/IG of the three prepared soot samples and their hygroscopicity, while the L_a of the three prepared soot samples exhibits a negative correlation with their hygroscopicity. These results imply that disordered graphitic lattice, polyenes, or ionic impurities (D4) could potentially serve as adsorption sites for water molecules. Moreover, smaller graphite crystallite size could enhance the adsorption capacity of water on soot.

These discussions have been added in the revised manuscript (Line 280-289)

Specific Comments:

Q1. Line 17: “were” should be revised as “was”.

A1. Grammatical error has been corrected in the revised manuscript: In this work, the hygroscopic behavior of soot particles generated from different types of fuel combustion and aged with SO_2 for varying durations ~~were~~ was measured by a vapor sorption analyzer. (Line 15-17)

Q2. Author found an increase in sulfate ions on UBC with longer aging times while the MRH of UBC remains relatively unchanged with SO_2 aging, does this mean the sulfate coating have no effect on the hygroscopicity of black carbon under low humidity?

A2. We think so. According to our previous study, the sulfate detected on UBC could also exist in the form of sulfuric acid (Zhang et al., 2022). Moreover, IC results demonstrated that the amount of newly generated sulfate on UBC after 10 hours of aging was only 0.706 % of its original mass. Such a minute quantity of sulfuric acid formation may not exert a significant influence on UBC's water absorption characteristics within the range of 10-30% RH.

Q3. Line 302: How do you define this “high” RH levels? Here the “noticeable augmentation” and “high RH” should be specified.

A3. Thanks for your suggestion. We have revised this sentence " Our results also demonstrated that a noticeable augmentation in the amount of water adsorbed on SO_2 aged BC at high relative humidity levels." to “Our results also demonstrated that a noticeable augmentation in the amount of water adsorbed on SO_2 aged soot at 90% RH, which is positively correlated with the amount of sulfate generated. (Line 316-318)”. At 90 % RH, the adsorbed water layers on UBC increases with increasing aging times. By analyzing the relationship between sulfate production during SO_2 aging of UBC and its water absorption mass at 90% RH, we found a linear relationship with a high correlation coefficient (R^2 = 0.9997). Our findings reveal that for every 1μg of SO_4^{2-} produced on the surface of each milligram of black carbon, there is a corresponding increase of 1.82μg in its water absorption mass at 90% RH. These discussions have been added in the revised manuscript. (Line 300-303)

Q4. Line 320: "And provides a basis for improving our understanding………..", means what provides….?

A4. Thanks for your reminding. We revised this sentence as "This study analyzed the key factors determining the hygroscopic property of soot, which can improve our understanding of the hygroscopic behavior of fresh soot and help to evaluate changes in hygroscopicity during the heterogeneous reactions of soot particles with pollutant gases in future studies." in the revised manuscript. (Line 333-336)

REFERENCE

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