

Response to Reviewers

Referee #1

This paper shows that, within the suite of measurements they present, the nighttime formation of SA is consistent with a simplified chemistry driven by alkene, ozone, and SO₂. Yet correlation does not constitute proof. Furthermore, the procedures and details of the methodology (which may be correct) are either only sketched-out or are hard to follow (thus this reader did not have full confidence in the material.) Furthermore, the authors supply caveats (more than one time and even in the abstract!) that their analysis could be subject to revision/flawed. Providing a detailed, time-dependent simulation (even a box model) would bring their conclusion into the firmly believable realm. Below are some details and other points. Note the revisions are too strongly suggested as 'major': they are by no means damning and they should not be difficult to include or address.

We thank the reviewer for the constructive comments and suggestions. As suggested, we have added more details of the methodology to make our analysis easier to follow. We did not quite follow the comment on “the authors supply caveats (more than one time and even in the abstract!) that their analysis could be subject to revision/flawed”, but we hope our point-to-point response to the comments as given below can address these concerns. The comments, our replies, and the corresponding changes in the manuscript and supplementary information are marked in black, blue, and green, respectively.

1) Somewhat careless with precision, quoting a four significant figure k_{app} from a slope that has at most two significant figures. A minor detail of course, but attention to detail should be demonstrated in all aspects. A welcome detail here would be to present the uncertainties in the values of the fitted slopes.

Response: Thanks a lot for your suggestions and we have revised the k_{app} values with two significant figures.

The fitted value, 95% confidence bounds, uncertainty of k_{app} and correlation coefficient R^2 for Clean-1 (Fig. 5(a)) and Clean-2 (Fig. 5(b)) condition are listed in Table S3. The uncertainties of k_{app} are 20.2% and 11.3% for Clean-1 and Clean-2 condition respectively.

For nighttime correlation between source term and sink term in Section 4.3 and Fig. 5, we mentioned in the manuscript that only under Clean-2 condition, there was a good correlation ($R^2=0.97$) for the mean values in all bins (Fig. 5 (b), Line 229-231, Page 9). For Clean-1 condition, there was only a subgroup of binned data with a source range from 1.0×10^{33} to 4.5×10^{33} (cm^{-3})³ that showed linear correlation (Line 223-224, Page 9). And for heavy polluted condition, no correlation was observed. (Line 253-254, Page 10).

We have also added one sentence in the manuscript to refer to this table. “The fitted value, 95% confidence bounds, uncertainty of k_{app} and correlation coefficient R^2 for Clean-1 and Clean-2 condition are listed in Table S3.” (Line 233-234, Page 9).

Table S3 Fitted value, 95% confidence bounds, uncertainty of k_{app} and R^2 for Clean-1 and Clean-2 condition.

Condition	k_{app} ($\text{cm}^6 \text{ s}^{-1}$)	95% Confidence Bounds ($\text{cm}^6 \text{ s}^{-1}$)	Uncertainty (%)	R^2
Clean-1	2.7×10^{-30}	$(2.1 \times 10^{-30} - 3.2 \times 10^{-30})$	20.2	0.97
Clean-2	2.6×10^{-30}	$(2.3 \times 10^{-30} - 2.9 \times 10^{-30})$	11.3	0.97

2) Overall sink was equated to the alkene O₃ SO₂ source but steady-state assumption was not fully discussed (not even sure what time period the data is averaged over?).

Response: The verification of the steady-state assumption is indeed necessary. We have added the following content in Section S2 to clarify why steady-state assumption can be assumed.

The net concentration change of gaseous SA is determined by both the source and loss terms, as shown in the following equation:

$$\frac{d[SA]}{dt} = k_{app} \cdot [Alkene] \cdot [O_3] \cdot [SO_2] - [SA] \cdot CS - \beta \cdot [SA]^2$$

We can compare the magnitude of the net concentration change to the overall loss rate. During nighttime (20:00-04:00) from 18th January to 16th March 2019, the median net concentration change of SA is about $181.60 \text{ cm}^{-3} \text{ s}^{-1}$ and the overall SA loss rate at the median SA concentration ($7.52 \times 10^5 \text{ cm}^{-3}$) is $1.61 \times 10^4 \text{ cm}^{-3} \text{ s}^{-1}$. As the loss rate (and source rate) is much faster than the net concentration change, the pseudo-steady state (PSS) assumption is valid for SA. Besides, the resolution of the SA data is 5 minutes, and the concentration, net concentration change, loss rate and production rate of SA are listed in Table S4 below.

Table S4 Concentration, net concentration change, loss rate and production rate of SA during nighttime (20:00-04:00) from 18th January to 16th March 2019. Std means standard deviation.

	[SA] (cm ⁻³)	d[SA]/dt (cm ⁻³ s ⁻¹)	L _{SA} (cm ⁻³ s ⁻¹)	P _{SA} (cm ⁻³ s ⁻¹)
Median	7.52×10 ⁵	181.60	1.61×10 ⁴	1.60×10 ⁴
25 percentile	5.19×10 ⁵	78.37	4.83×10 ³	4.80×10 ³
75 percentile	1.05×10 ⁶	371.14	3.27×10 ⁴	3.26×10 ⁴

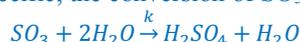
To clarify this consideration, we added the above explanation in the revised supplement as Section S2 (Line 16-25, Page 1) and the following sentence in the revised manuscript:

“Under pseudo steady-state (PSS) assumption (see Section S2 for detailed discussion about PSS assumption)” (Line 216-217, Page 8)

The time periods of the data in Fig. 5 and Fig. 6 are both from 18th January to 16th March 2019. Corresponding illustrations were added to the captions of Fig. 5 (Line 249, Page 10) and Fig. 6 (Line 285, Page 11).

3) Furthermore, SO₃ to SA was not discussed.

Response: Indeed, we did not discuss the conversion from SO₃ to SA, as the reaction is so fast that almost all SO₃ should be instantaneously converted to SA. To be more specific, the conversion of SO₃ to SA is based on the following reaction:



Then, the production rate of SA from SO₃ can be expressed as:

$$P_{[SA]} = k \cdot [SO_3] \cdot [H_2O]^2$$

where $k=3.9 \times 10^{-41} \exp(6830.6/T) \text{ cm}^{-6} \text{ s}^{-1}$ ((Jayne et al., 1997)). During the nights of the measurement period, the median concentration of H₂O was $4.97 \times 10^{16} \text{ cm}^3$, and the median temperature was 276.6 K, then the lifetime of SO₃ can be estimated as:

$$\tau_{SO_3} = \frac{1}{k \cdot [H_2O]^2} = \frac{1}{4.88 \times 10^3 \text{ s}^{-1}} = 2.05 \times 10^{-4} \text{ s}$$

As the lifetime of SO₃ is so short under typical atmospheric conditions, the oxidation of SO₂ is the rate-limiting step in the formation of SA.

To clarify this consideration, we added the above illustration in Section S1 (Line 2-14, Page 1) and the following explanation in the revised manuscript:

“The lifetime of SO₃ due to its fast reaction with H₂O to form SA is approximately $2 \times 10^{-4} \text{ s}$ (see detailed calculation in supplement Section S1), which indicates that this reaction is so fast that almost all SO₃ will be instantaneously converted to SA. In this case, the oxidation of SO₂ is the rate-limiting step in the formation of SA.” (Line 84-86, Page 3)

4) OH produced in alkene + O₃ reactions was not included: why not?

Response: This is a misunderstanding. We didn't mean to exclude the non-photochemical ·OH oxidation pathway. Actually, we do not attempt to separate the contributions of sCI and OH radical in this study, but instead, use the k_{app} as an empirical parameter to account for the overall effect of sCI and OH oxidation pathways.

We realized that the comparison between k_{app} and theoretical sCI oxidation rate is confusing that caused the misunderstanding. Besides, such comparison also suffers from large uncertainties. Therefore, we decide to remove such discussion in the revised manuscript so that the main message can be clearer. However, we need to point out that, this change in the manuscript will not change our conclusion that the ozonolysis of alkenes is responsible for the oxidation reactions (both sCI and non-photochemical OH radical) that drive the nighttime SA formation.

To clarify this consideration, the following illustration are added to the revised manuscript:

“The ozonolysis of alkenes under dark conditions is capable of generating sCI as well as OH radical, both of which are able to oxidize SO₂ to form gaseous SA. However, the yields of both sCI and recycled OH radical remain largely unquantified. Therefore, we do not attempt to distinguish the contribution of sCI and OH radical on SA formation in this study, but rather treat them as a “bulk oxidant” and use an empirical parameter k_{app} to account for both oxidation pathways.” (Line 205-209, Page 8)

And the following discussion are deleted from the revised manuscript:

“In order to have a general understanding of the apparent rate constant of sCI-SO₂ reaction obtained from our measurement, we can roughly get an upper limit value by considering all nighttime SA is produced from the sCI mechanism. From the above discussion, the slope k_{app} can be expressed as $k_1 \cdot k_2 \cdot \phi \cdot f$, where f is the fraction of sCI which undergo the reaction with SO₂. It should be pointed out that k_2 is also an apparent rate constant which results from the combination of different measurement efficiency of alkenes (including undetected ones), different yields of sCI, and different rate constants of sCI reacting with SO₂. The fitted k_{app} is $2.618 \times 10^{-30} \text{ cm}^6 \text{ s}^{-2}$. If considering k_1 to be $1.0 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ (an intermediate value in the range of previous

studies, which has been explained in Section 2), then $k_2 \cdot \phi \cdot f = 2.618 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. As the real atmospheric chemical composition is far more complex than experimental ones, the value of $\phi \cdot f$ should be smaller. Thus, if further considering $\phi \cdot f$ to be 0.05, then the rate constant k_2 in this real atmospheric condition is approximate $5.236 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, which is in the same order of magnitude as measured values in experiments (see Section 2).” (between Line 234 and Line 235, Page 9)

5) A simple box model could include these and others such as $\text{HO}_2 + \text{NO}$ for example. Then presenting box model simulations absent the alkene-ozone chemistry might really draw a distinct comparison.

Response: Performing a well-tuned box model is indeed a useful way of verifying our findings. However, after thinking it through, we found that many species and parameters needed for the box model remain unquantified or largely uncertain. For example, the concentration of OH radical in the nighttime is one key parameter in such a box model, but lacking of a complete VOC measurement by GCMS will greatly limit the precision of the box model. And recent study also showed that current MCM method significantly under-predicts the concentrations of OH, HO_2 and RO_2 radicals. (Slater et al., 2020) Besides, the yields of sCI and OH radical as well as the rate constants concerning R1 to R5 of alkenes are largely scattered (Line 90-94 Page 3). Therefore, we prefer not to include the box model simulation in this manuscript, but clearly state the need for a box model based on further lab studies to fully to verify our results.

To clarify this consideration, the following discussion has been added to the revised manuscript:

“It should be pointed out that we are not able to further deconvolute the contribution of OH radical and sCI based on the ambient observation. A well-tuned box model is a useful tool to resolve it and verify the role of the ozonolysis of alkenes on the nighttime SA formation. However, such a modeling work is not included in our study, as the lacking of a complete VOC datasets in our measurement and the largely uncertain yields of sCI from the ozonolysis of various alkenes have caused challenges in ensuring the precision of the box-model.” (Line 263-267, Page 10)

6) Is not sub-3 nm really sub-2.45 nm?

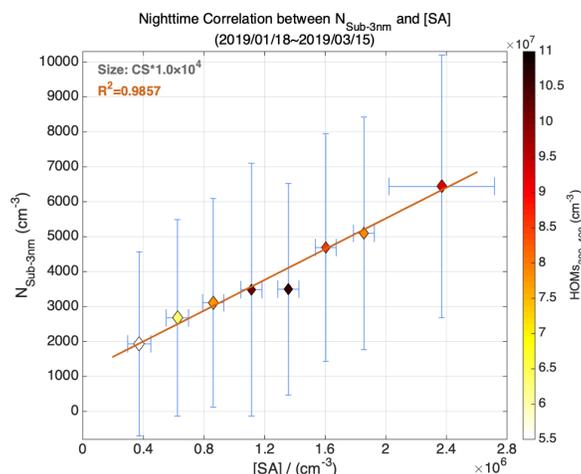
Response: Such a particle size range is determined by the instrument (PSM). According to the calibration of the instrument, the size bins of PSM are 1.3-1.44 nm, 1.44-1.5 nm, 1.5-1.61 nm, 1.61-1.81 nm and 1.81-2.45 nm, and the number concentration of sub-3nm particles is the sum of all those five size bins. Uncertainties in response of PSM to particles of different chemical composition (Kangasluoma et al., 2014) can shift the overall size-range where the PSM is sensitive, which is the reason why the total concentration measured between the lowest and highest size in PSM is generally referred as sub-3 nm particle concentration (see e.g. (Kontkanen et al., 2017)).

To clarify this consideration, the following sentence has been added to the revised manuscript:

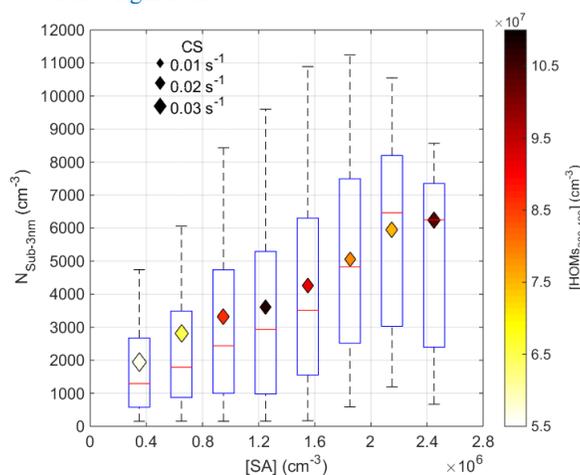
“(…) was measured with a Particle Sizer Magnifier (PSM) (Vanhanen et al., 2011), and the integrated number concentration of particles from PSM is referred as $N_{\text{Sub-3nm}}$ in the following” (Line 139-140, Page 5)

7) The last figure purports to correlate sub-3 nm to measured SA and there is a linear relationship provided. Two problems: large error bars (what do they mean?) and there is a source of particles at zero SA (or zero alkene+ozone). The correlation may be due to the fact that the ordinate and abscissa are both dependent on the alkene- O_3 chemistry yet sub-3 nm particles at 'zero' chemistry destroys the happiness of the association between ordinate and abscissa. Another issue is the lack of discussion regarding any proposed theoretical relationship between SA and number of particles.

Response: The large error bars indicate the scattering of those data points in each bin. For better illustration, we revised this plot with boxplots in SA bins (see below), which provide direct information on the data distribution. In the boxplot, the red line is the median value, the bottom and top blue lines are the 25 and 75 percentiles, and the whisker ranges cover the $\pm 2.7\sigma$ of those data in each bin. In addition, the mean values are added as diamonds.



Original Fig. 5 Nighttime correlation between $N_{\text{Sub-3nm}}$ and SA concentration during nighttime (20:00-04:00) from 18th January to 16th March 2019. The data points are colored by number concentration of HOM ($m/Q = 300 - 400$ Th) and the size is related to CS. Note that the data points are based on the binned data instead of the original one.



Updated Fig. 5 Correlation between $N_{\text{Sub-3nm}}$ and SA during nighttime (20:00-04:00) from 18th January to 16th March 2019. The binned diamonds are colored by number concentration of HOMs ($m/Q = 300 - 400$ Th) and the size is related to CS. The red line is the median value, the bottom and the top blue lines are the 25 and 75 percentiles, and the whisker ranges cover the $\pm 2.7\sigma$ of those data in each bin.

To clarify this consideration, we replaced the original Fig. 5 with the updated one in the manuscript. Please also note that Fig. 5 becomes Fig. 6 in the revised manuscript.

The particles at zero SA were most likely from other sources than SA. As we mentioned, our measurement site is close to two main urban traffic trunk roads, and these particles might come from directly emission of vehicles (Arnold et al., 2006; Barrios et al., 2012). In a recent study, it is shown that PSM is very sensitive to traffic-emitted sub-3nm particles (Ronkko et al., 2017).

Regarding the theoretical relationship between number concentration of sub-3nm particles and SA concentration, it is usually done by depicting the particle nucleation rate (J , e.g., $J_{1.5}$, $J_{1.7}$) as a function of SA concentration, and comparing it with other chamber or ambient studies with known mechanisms. Calculation from number concentration (N) to J involves many corrections including the correction of particle growth out of the size range. However, in these nighttime SA events, the determination of particle growth rate is challenging as the “banana shape” is not clear (please also see the reply to comment #2) of the other reviewer). This is the main reason why we used the number concentration, as a more objective term, instead of the calculated particle nucleation rate in this study.

However, to address the reviewer’s concern, we estimated J by ignoring the growth rate correction term in the calculation. Fig. R1 shows the correlation between $J_{1.5}/J_{1.7}$ and SA for Beijing measurement, Shanghai measurement (Almeida et al., 2013) and CLOUD experiments (Almeida et al., 2013; Kirkby et al., 2011). As shown in Fig. R1, data points in the nighttime and the

daytime are roughly falling on the same line, which also agree well with the data measured in Shanghai CLOUD chamber SA-DMA-H₂O experiment. The similar J – SA relationship between the nighttime and the daytime suggests a similar nucleation mechanism as SA-base clustering. However, as the calculation of J has the aforementioned uncertainty, we prefer not to include Fig. R1 in the manuscript.

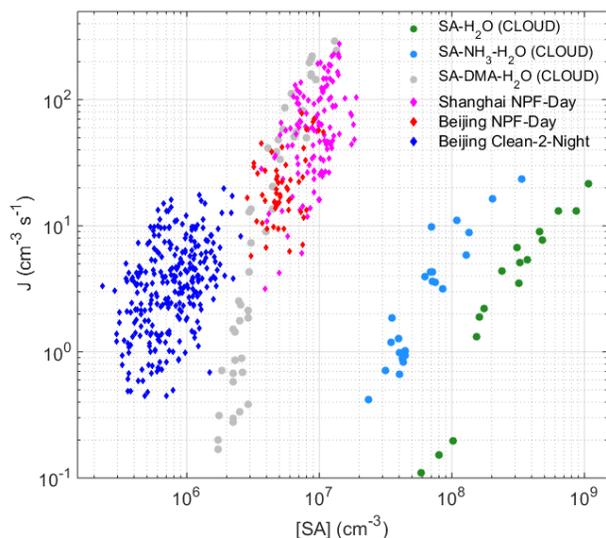


Fig. R1 Comparison of Beijing ambient, Shanghai ambient and CLOUD experimental cluster formation rates against SA concentration. Green, light blue and grey dots denote CLOUD J_{1.7} data for SA-H₂O, SA-NH₃-H₂O and SA-DMA-H₂O nucleation respectively (Almeida et al., 2013; Kirkby et al., 2011). Magenta diamonds represent Shanghai NPF J_{1.7} data (Yao et al., 2018). Red and blue diamonds are Beijing J_{1.5} data for NPF day (10:00-14:00) and Clean-2 night (20:00-04:00), respectively.

Furthermore, there was a negative correlation between N_{Sub-3nm} and highly oxygenated organic molecules (HOMs) (see Fig. S8 (a) below), which indicates that HOMs was not the main driver for the formation of nighttime sub-3nm particles. And to clarify this consideration, we added Fig. S8 (a) in the revised supplement.

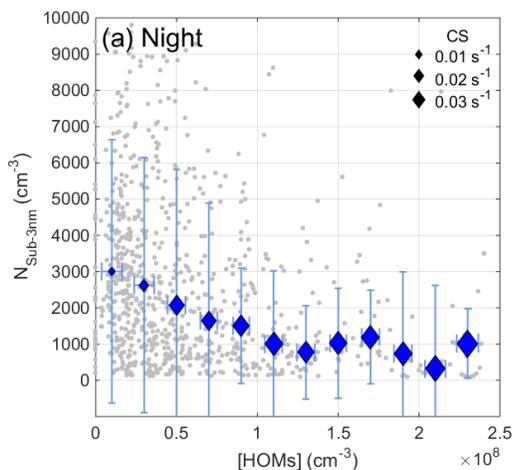


Fig. S8 (a) Correlation between N_{Sub-3nm} and [HOMs] during nighttime (20:00-04:00) from 18th January to 16th March 2019. The grey dots are original data points. The diamonds are binned data colored by number concentration of SA and the size is proportional to CS. The blue lines are standard deviation of data points in each bin.

8) The outliers are numerous in many of the plots in Fig. 2. How were they decided upon? In this vein it is not clear what data was included for each of the points in Fig. 4 for example. All data between 10 pm and 4 am?

Response: Please note that now Fig. 2 is Fig. 3, and Fig. 4 is Fig. 5.

The outliers in Fig. 3 are the ones out of the $\pm 2.7\sigma$ range of all selected data. If the data is normally distributed, this $\pm 2.7\sigma$ range will cover 0.7 - 99.3 percentiles of the data. Corresponding illustrations have been added to the captions of Fig. 3 (Line 186, Page 7) in the revised manuscript.

Data points in Fig. 5 are the ones during nighttime (20:00-04:00) from 18th January to 16th March 2019. Corresponding illustrations have been added to the captions of Fig. 5 (Line 249, Page 10). Fig. 5 (a), (b), (c) and (d) are for Clean-1, Clean-2, mildly polluted and heavy polluted conditions respectively. The definition of Clean-1, Clean-2, mildly polluted and heavy polluted conditions have been illustrated in the manuscript (Line 199-201, Page8 and Line 226-227, Page 9). For better understanding of Fig. 5, the legends in four subplots have been changed from ‘Vis ≥ 12 km’, ‘Vis ≥ 16 km, $[O_3] \geq 2 \times 10^{11}$ cm⁻³’, ‘Vis: 4-12 km’ and ‘Vis ≤ 4 km’ to ‘Clean-1’, ‘Clean-2’, ‘Mildly polluted’ and ‘Heavy polluted’ accordingly.

9) "SIZE = CS*xyz" was included in many of the plots but a reference size was not easy to find.

Response: Thanks a lot for your suggestions. We've added three CS references points (CS=0.01 s⁻¹, 0.02 s⁻¹ and 0.03 s⁻¹) in all relevant plots.

10) " calibration coefficient " has no meaning by itself. Needs some context (an equation) and perhaps some comparisons. It can be argued that this quantity should have units of Hz Hz⁻¹ attached to it also.

Response: Thanks for your suggestion. We have now added the following equation to clarify how SA concentration is calculated.

The quantification of sulfuric acid is derived from the ratio of bisulfate ions relative to primary ions as follows:

$$[H_2SO_4] = \frac{HSO_4^- + H_2SO_4NO_3^-}{NO_3^- + HNO_3NO_3^- + (HNO_3)_2NO_3^-} \times C$$

The calibration factor, C, is determined from direct calibration where gaseous sulfuric acid of known amounts is produced and injected into the instrument. A more detailed information about the calibration is discussed by Kürten et al. 2012 (Kurten et al., 2012). The units of bisulfate and primary ions are both counting rates in ions·s⁻¹ and cancel each other, and therefore, the unit of C is the same as that of sulfuric acid concentration in cm⁻³.

To clarify this consideration, we added the following illustration in the revised manuscript:

“The quantification of sulfuric acid is derived from the ratio of bisulfate ions (with counting rates unit in ions·s⁻¹) relative to primary ions as follows:

$$[H_2SO_4] = \frac{HSO_4^- + H_2SO_4NO_3^-}{NO_3^- + HNO_3NO_3^- + (HNO_3)_2NO_3^-} \times C$$

The calibration factor, C, is determined from direct calibration by injecting gaseous sulfuric acid of known amounts into the instrument (Kurten et al., 2012).” (Line 114-118, Page 4)

11) Why have PM2.5, visibility and CS all plotted in Fig. 2? Figure 2 would be cleaner if you pick one and plot the correlation between it and the others in the supplement...

Response: Thanks for your suggestion and please note that Fig. 2 now is Fig. 3. The correlation among these three parameters have been shown in Fig. S3.

From the perspective of cleanliness, picking one parameter among PM_{2.5}, visibility and CS, and moving the correlation figure to the supplement is reasonable. PM_{2.5} is the most commonly used parameter to describe pollution level, visibility is used to distinguish pollution level in Section 4.3, and nighttime SA events were highly associated with CS level (Table S2). As all these parameters are useful for the later discussion, we are prone to keep them in the current form.