Response to Reviewer #1

Overview: *This manuscript describes a novel approach to SERS analysis of aerosol particles, where the nanoparticles are deposited onto the aerosol surface, as opposed to aerosol particles being deposited onto a more conventional SERS substrate. The manuscript thoroughly considers the prior Raman and SERS literature and makes a significant step forward in the spectroscopic analysis of aerosol particles. There are some significant shortcomings that need to be addressed, but overall this is manuscript has many positive features.*

Response: The authors like to thank the reviewer for the valuable comments. We have added more information in the revised manuscript based on the reviewer's comments. Revised and added text in the main manuscript and supporting information was highlighted in red.

Major comments

Comment #1: SERS is often most enhanced when two metal nanoparticles are at specified distance from each other with a predetermined geometry. How ordered are these nanoparticles? What methods have been used to image the silver nanoparticles are the aerosol particle surface? Is the assumption that the enhancement is coming entirely from individual silver nanoparticles?

Response: (1) We expect that most Ag nanoparticles are individually deposited on the particle surface without much aggregation. Ag nanoparticles used in the current study were synthesized by the citrate-reduction method. If the nanoparticles were aggregated, SERS spectrum would show enhanced peaks of citrate adsorbed on Ag nanoparticle surface as stabilizer (Munro et al., 1995). In our measurements of AS particles, we observed strong citrate peaks only for one analyte particle (Fig. S1(e), see comment #5), but absent for all other SERS spectra. This gives us confidence that the enhancement is mainly coming from individual Ag nanoparticles. To address the above consideration, we have added the following text:

"Ag nanoparticles used in the current study were synthesized by the citrate-reduction method. If the nanoparticles were aggregated, SERS spectrum would show enhanced peaks of citrate adsorbed on Ag nanoparticle surface as stabilizer (Munro et al., 1995). In our measurements of AS particles, we observed strong citrate peaks only for one particle (Figure S1(e)), but absent for all other SERS spectra. This gives us confidence that the enhancement is mainly coming from individual Ag nanoparticles."

(2) We have attempted to use SEM to visualize the presence of Ag nanoparticles on AS particles. However, the electron beam of SEM caused sample damage, leading to morphological changes to AS particle surface (see SEM images of a and b in Fig. A), in the absence of Ag nanoparticles. Moreover, the non-conductive AS particles were significantly charged so that the SEM image was distorted. The magnified image of AS particle (Fig. A (c)) shows protrusions that resemble Ag nanoparticles, but it is difficult to distinguish the nanoparticles from protrusions due to the morphological changes of AS. We have also attempted EDX analysis (JSM-6390, JEOL) but no signal of Ag element was observed probably because of the low concentration of Ag nanoparticles (Fig. B).

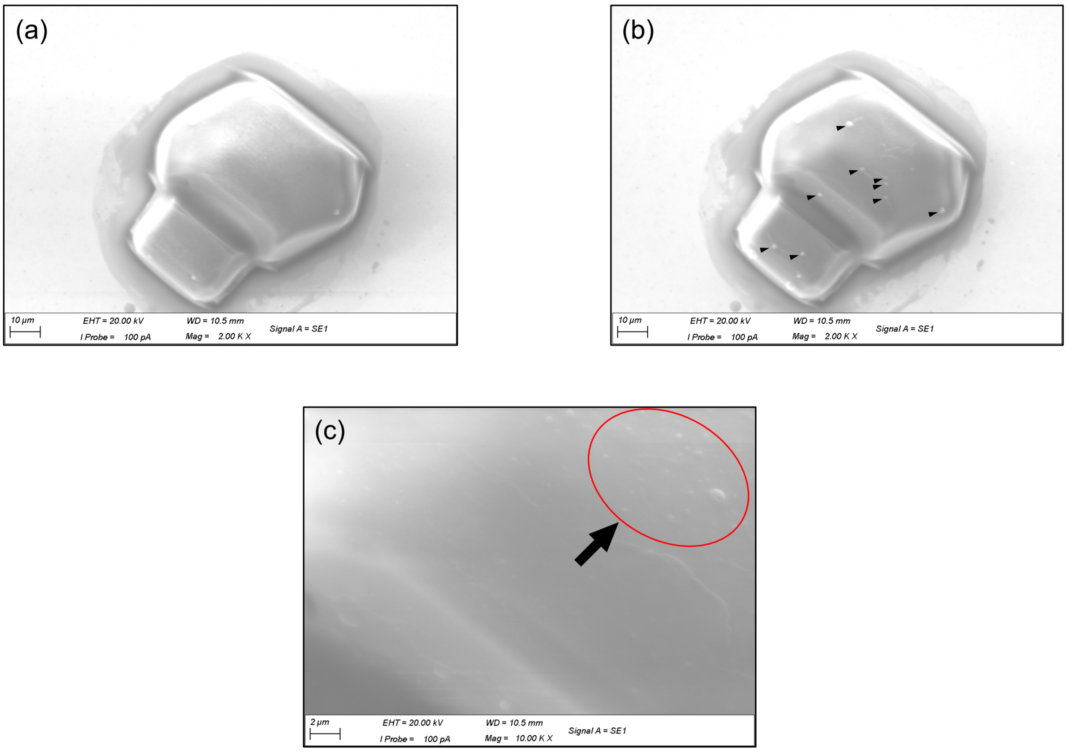

Figure A. SEM images of AS particle before (a) and after (b) an electron beam damage during observation. (c) an enlarged view of the surface of AS particle.

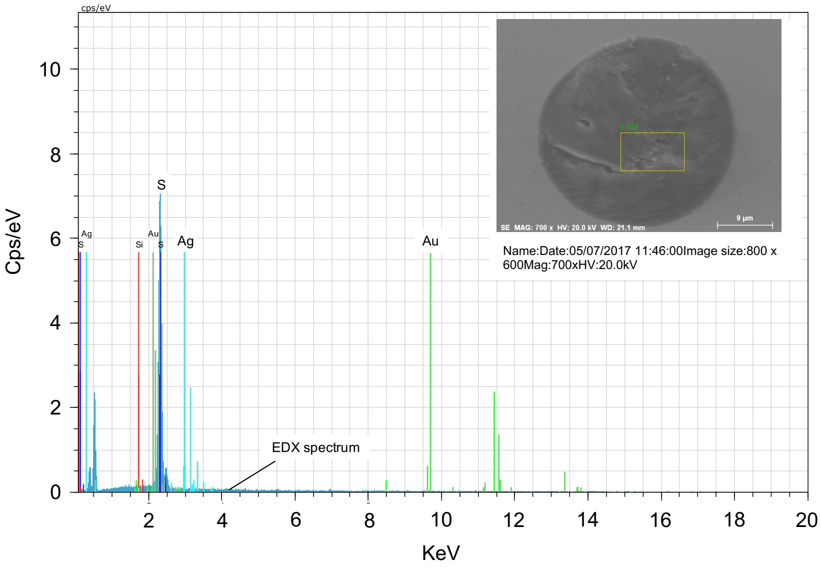

Figure B. EDX analysis of AS particle with Ag nanoparticle. The spectrum shows the peak of element of sulfur (i.e. SO_4) at ~2.3 KeV. No other elements were observed.

Comment #2: The size of the particles used calls some of the relevance of the findings into question. For example in Figure 3 the particles are 23 and 47 microns. It would be very helpful to have Raman of AS particles on top of silver nanoparticles for comparison. At these sizes it would not be surprising to see nanoparticles on top making a difference versus nanoparticles underneath, but no data on is given to support this claim. Also an optical image in the main text of AgNPs on top of the AS particles would be helpful are for particles 10s of microns in size, should be relatively easy to image.

Response: (1) The current manuscript is a proof-of-concept study for application of ES-SERS in chemical analysis of atmospherically relevant particles. As mentioned in the section 3.3, enhanced peaks at ~970 cm^{-1} did not drop as the size of analyte particle was down to 1.4 µm. This result demonstrates that the ES-SERS has the potential to characterize particles with atmospherically relevant size (below 1 µm). The above discussion has been described in the third paragraph in the conclusion.

(2) It is apparent that enhanced spectra from two cases (1) ES-SERS (Ag nanoparticles on the top of analyte particles) and (2) conventional SERS substrate (the nanoparticles underneath analyte particles) come from the different positions of analyte particles. SERS is a type of surface spectroscopy, which means that only the analyte molecules adsorbed to Ag nanoparticles contribute to the enhancement and its effect is the distance dependence (Dieringer et al., 2006). Therefore, ES-SERS is more sensitive to the surface of the analyte particles and is useful for surface characterization of atmospheric particles.

Although we do not have the data of direct comparison between the ES-SERS and conventional SERS substrates, we have compared our results with earlier works in the literature. We have added the following text and revised the corresponding text accordingly:

"Craig et al. (2015) reported an enhancement factor of 2.0 at $v(SO_4^{2-})$ mode of ~970 cm^{-1} using an SERS substrate with the AS particles on the top of Ag nanoparticles on the substrate. Furthermore, Fu et al. (2017) reported an enhancement factor of 6.1 for the same mode, using commercial SERS substrates with pre-determined gold-coated structure of inverted pyramids (Klarite, Renishaw Diagnostics Ltd.). Our results of AS/sucrose particles (Table 1) showed that the I_{SERS}/I_{NR}, which is the lower limit of enhancement factor, ranged from 12.4 to 163, much higher than the above studies. Note that I_{SERS}/I_{NR} is the lower limit of the enhancement factor ($I_{SERS}N_{vol}/I_{NR}N_{surf}$) conventionally used because N_{vol}/N_{Surf} is much greater than unity in the present case."

(3) The optical images of AS particles with and without Ag nanoparticles have been shown in Fig. S6.

Comment #3: Calculation of enhancement factors? Relative enhancement of specific modes?

Response: As mentioned in the section 2.4, we did not calculate enhancement factors because the estimation of the number of analyte molecules adsorbed onto Ag nanoparticles is rather difficult. Instead, we compared enhanced intensity with normal Raman intensity as defined as I_{SERS}/I_{NR} based on earlier works (Fu et al., 2017; Le Ru et al., 2007). The I_{SERS}/I_{NR} gives information on relative enhancement of each vibration mode as summarized in Table 1. The relative enhancement was clearly observed at $v(SO_4^{2-})$ mode for the AS/sucrose particles (Fig. 3). The I_{SERS}/I_{NR} at $v(SO_4^{2-})$ mode is approximately 7.6 times higher than that at v(C-H) mode (Table 1). This is likely due to the strong interaction between aqueous sulfate and Ag nanoparticles. To highlight this, we have added the following text:

"The I_{SERS}/I_{NR} at $v(SO_4^{2-})$ mode is approximately 7.6 times higher than that at v(C-H) mode (Table 1). This is likely due to the strong interaction between sulfate and Ag nanoparticles."

Comment #4: Optical and electron microscopy imaging of particles with and without nanoparticles on top would strongly improve the authors claims that the particles are sitting on top.

Response: Optical images of particles with and without Ag nanoparticles have been shown in Fig. 6 in the revised main manuscript. As mentioned in the response to comment #1, electron microscopy imaging was not useful to visualize Ag nanoparticles on AS particles. We believe that Ag nanoparticles are deposited on analyte particles because (i) enhanced peaks were observed only when the electrospraying was performed and (ii) the electrospray system enables deposition of Ag nanoparticles on any surface (from metallic to non-metallic substrate). In the comparison of the normal Raman and SERS spectra as shown in Fig 3, it is apparent that there is significant signal enhancement in SERS. Since the deposition of Ag particles was the only procedural difference in the two types of samples, we cannot think of any other possibilities that would lead to the enhancement. Hence we are confident that the ES-SERS can enhance the Raman signals. The latter point has been discussed in earlier work in the electrospray system (Gen and Lenggoro, 2015) that electrostatic deposition is dominant, compared to other mechanisms such as Brownian diffusion and gravitation. Therefore, Ag nanoparticles under the given electric fields can be deposited on a substrate as well as on AS particles. To address the reviewer's comment, we have added the following text:

"The electrospray system has been proven to be effective in depositing nanoparticles onto any surface (Gen and Lenggoro, 2015). We believe that Ag nanoparticles are deposited onto the analyte particle surfaces because Raman enhancement was observed only when electrospraying Ag nanoparticles was performed."

Comment #5: Only a few particles are analyzed throughout the entire paper. Some details on the reproducibility, consistency of enhancements, and overall quantification are needed to truly show that this is a method that can be extrapolated to other aerosol studies. As of right now with so few spectra there could be concerns that only the best examples were chosen, which more statistics would help alleviate.

Response: We have investigated 22 laboratory particles in total (AS, AS/SA and AS/sucrose particles). We have showed the results of two AS (Fig. 4), two AS/SA (Fig. 4) and nine AS/sucrose particles (Figs. 3, 5 and 6) in the original main manuscript with and without Ag nanoparticles. Furthermore, more than 10 spectra were obtained for each particle by scanning the surface from one edge to another edge to quantify the intensity ratio of $I_{\mathrm{SERS}}/I_{\mathrm{NR}}$. Therefore, more than 220 spectra were taken into consideration for overall quantification of $I_{\mathrm{SERS}}/I_{\mathrm{NR}}$ in Table 1. To address the reviewer's comments, we have added all spectra used (except for AS/sucrose particles smaller than 20 μm) for overall quantification of $I_{\mathrm{SERS}}/I_{\mathrm{NR}}$ in the revised supporting information as Figs. S1, S2 and S3, and the following text in the revised manuscript to reflect this. As shown in Figs. S2 and S3 (d) and (e), Raman enhancements at $\nu(\mathrm{SO_4}^{2-})$ and $\delta(\mathrm{OH\cdots O})$ (only for AS/SA particles), and $\nu(\mathrm{C\text{-}H})$ modes are observed for most spectra.

"All spectra for quantification of $I_{\mathrm{SERS}}/I_{\mathrm{NR}}$ (except for AS /sucrose particles smaller than 20 μm) are shown in Figs. S1, S2 and S3."

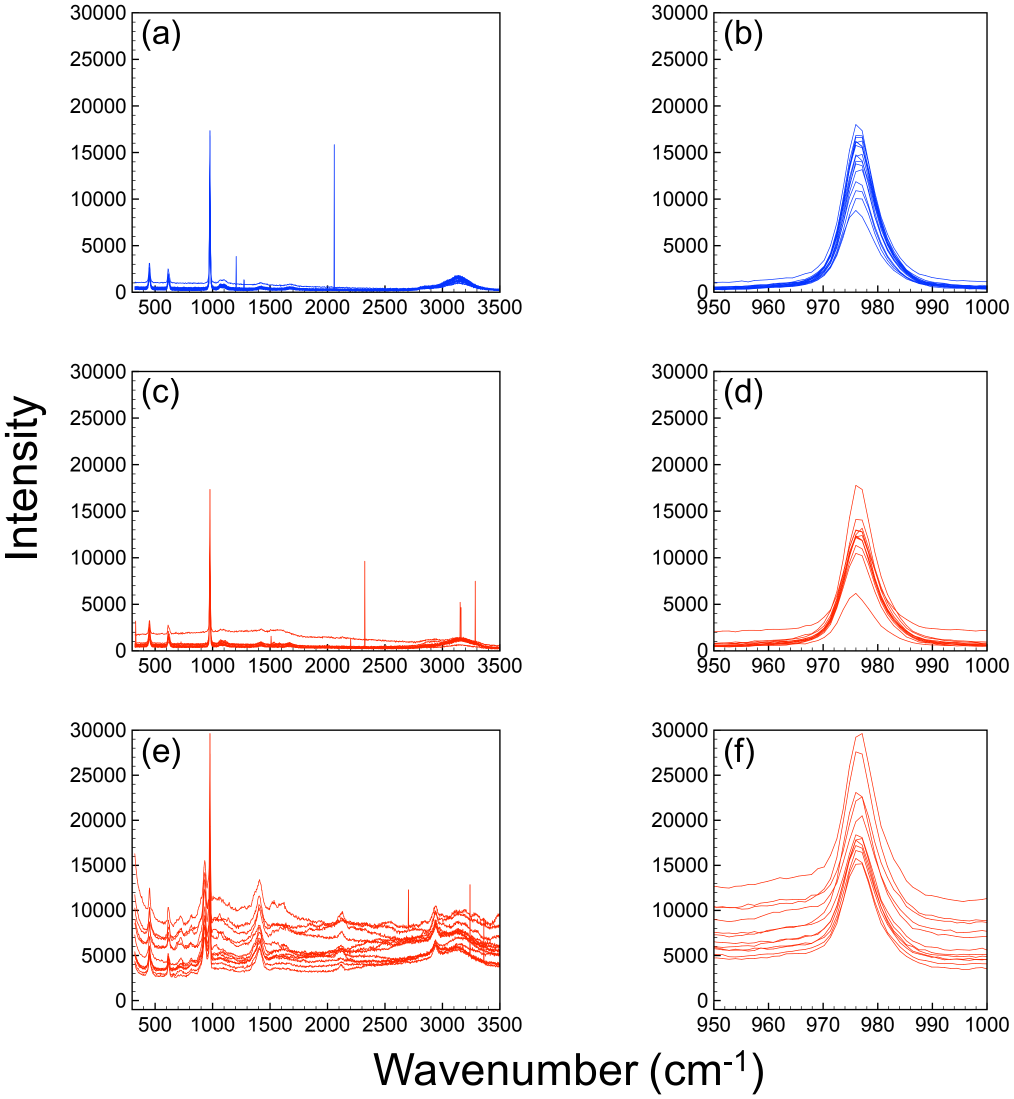

Figure S1. (a) Normal and (c, e) enhanced spectra of AS particles which were used for quantification of $I_{\mathrm{SERS}}/I_{\mathrm{NR}}$. (b, d, f) Magnified views of spectra at 950-1000 cm^{-1} corresponding to $v(SO_4^{2-})$. Note that in the presence of aggregated Ag nanoparticles, enhanced spectra (e) showed strong peaks of citrate at 2945, 1395, and 932 cm^{-1} corresponding to v(C-H), v(COO) and v(C-COO), respectively.

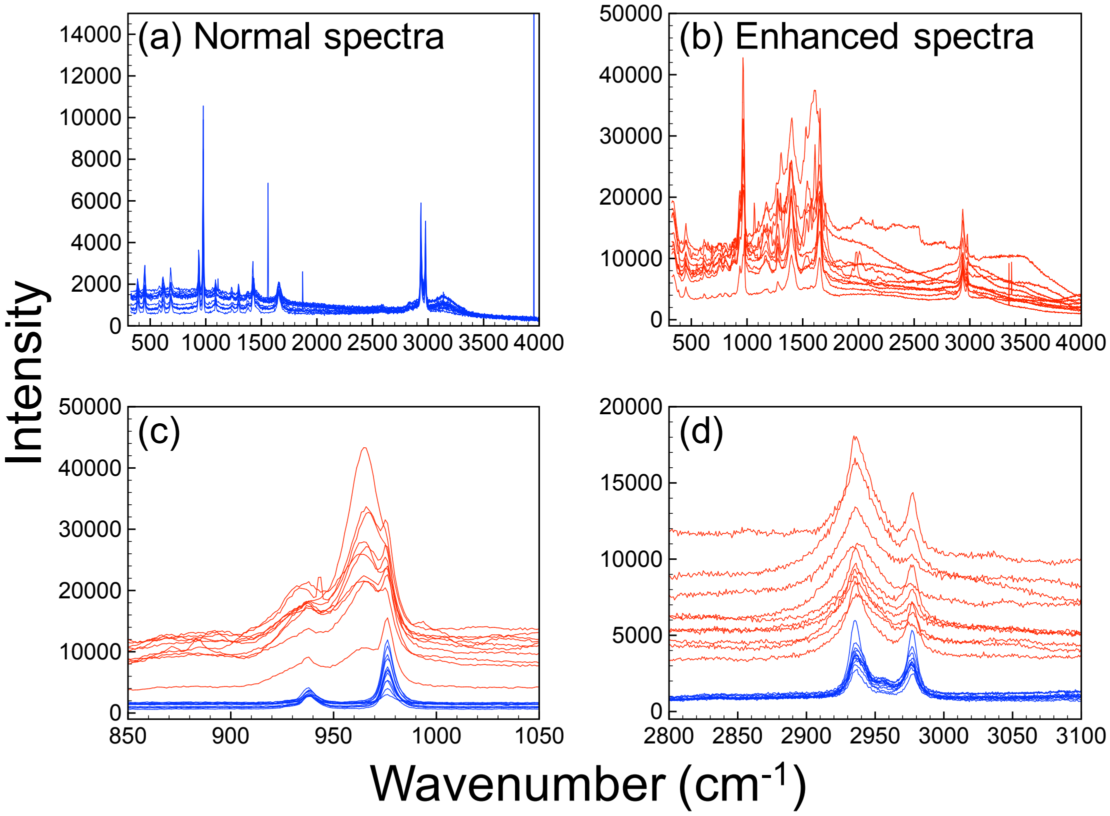

Figure S2. (a) Normal (blue) and (b) enhanced (red) spectra of AS/SA particles which were used for quantification of I_{SERS}/I_{NR}. (c, d) Magnified views of the corresponding spectra at 850-1050 and 2800-3100 cm^{-1} corresponding to $\nu(SO_4^{2-})$ and $\delta(OH\cdots O)$, and $\nu(C\text{-}H)$, respectively.

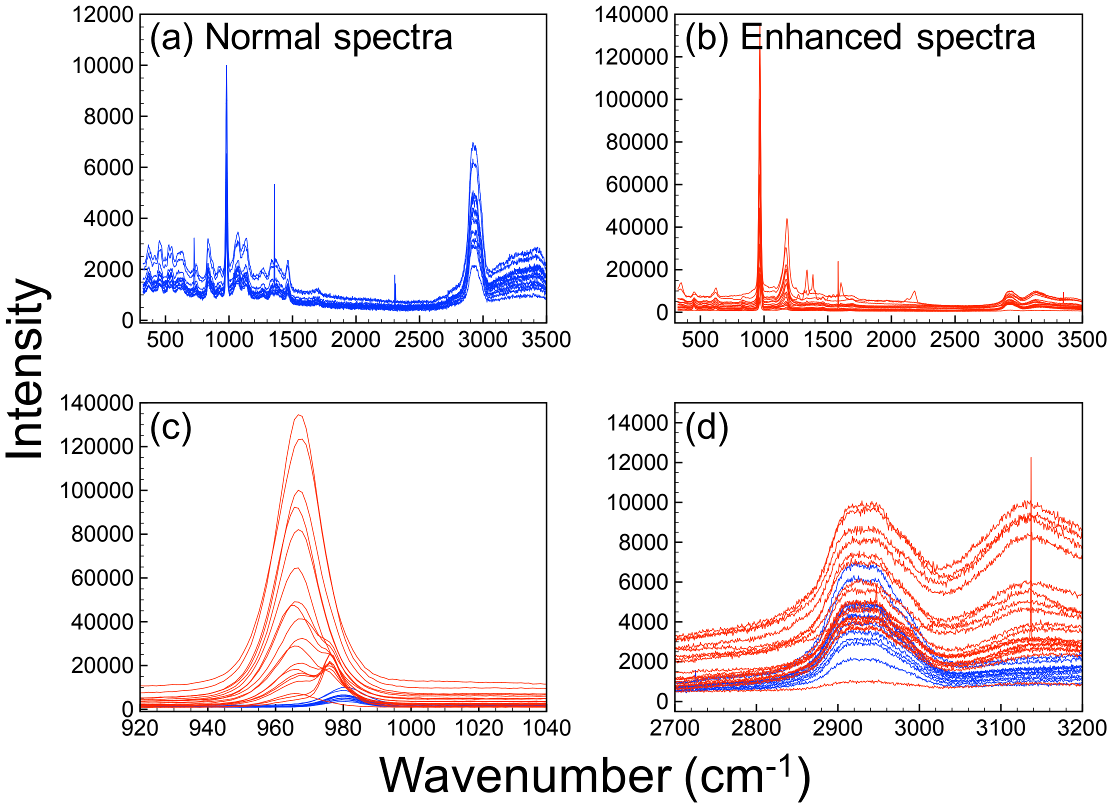

Figure S3. (a) Normal (blue) and (b) enhanced (red) spectra of AS/sucrose particles which were used for quantification of I_{SERS}/I_{NR}. (c, d) Magnified views of the corresponding spectra at 850-1050 and 2800-3100 cm^{-1} corresponding to $v(SO_4^{2-})$ and v(C-H), respectively.

Comment #6: The use of the gold coating on the Si wafer needs to be described in more detail. It is unclear the purpose of this and whether it plays a role in the enhancements. If the enhancements are from the gold or partially gold and partially silver, this is important for the overall findings. More information would be helpful to evaluate this possibility. Do AS particles on just Si with Gold sputtered coating give any enhancements? It seems like an expensive choice if there is no specific reason for doing it, so a more convincing description would be helpful.

Response: Sulfate has a major peak in the range of 900-1000 cm^{-1}. We used gold coating on the Si wafer for masking peaks from the Si wafer such as at 520 (sharp) and 900-1000 (broad) cm^{-1}. Since Raman enhancement mainly comes from roughened surfaces or nanostructures, we believe that the gold coating on Si wafer (flat surface) does not significantly contribute to Raman enhancement, although the high reflectivity of gold coating may increase the light collection efficiency. We have added the following text in the section 2.1 in the revised manuscript:

"The gold coating was used to mask peaks of Si wafer at 520 and 900-1000 cm^{-1}."

Comment #7: Lines 153-160: For the nanoparticles no information is given about the size distribution and physical characteristics. The methods used are listed, but not the values for the silver nanoparticle synthesized. Given the importance of the silver nanoparticle properties for generating an enhanced response, more details are needed about what is being deposited on the atmospheric or model system particles. The journal EnvSci:Nano has a nice list of suggested nanoparticle characterization criteria that all papers using nanoparticles should us, this might be a good guide as to the detail that should be included in the manuscript. Similarly since the size distribution after electrospraying with the DMA and CPC would be helpful to evaluate whether particles are individual particles or aggregates after ESI.

Response: We have discussed the size distribution and physical characteristics (visible absorbance due to localized surface plasmon resonance) of Ag nanoparticles in the section 3.1. The size distribution after electrospraying in the gas phase has been added in Fig. S3 in the original supporting information. The electrosprayed Ag nanoparticles were not aggregates, because the mode size (Fig. S3) was generally consistent with the primary particle size and the size of nanoparticles deposited on the substrate. To make this clearer, we performed additional experiments on SEM observation of naturally dried suspension of Ag nanoparticles before electrospraying. The SEM observation shows the primary particle size of 56 nm. To address the reviewer's comment, we have added the following figure as Fig. S7 as well as the following text in the revised supporting information and manuscript, respectively:

"The nanoparticles dried from the original suspension and those deposited (electrosprayed) on the gold-coated silicon substrate were observed with SEM as shown in Fig. S7 a and b, respectively. The size distribution of the deposited particles (Fig. S7b) shows a peak of ~67 nm which is close to the primary particle size (56 nm in Fig. S7a) and the particle size (53 nm in Fig. S6) of the aerosol from the electrospray."

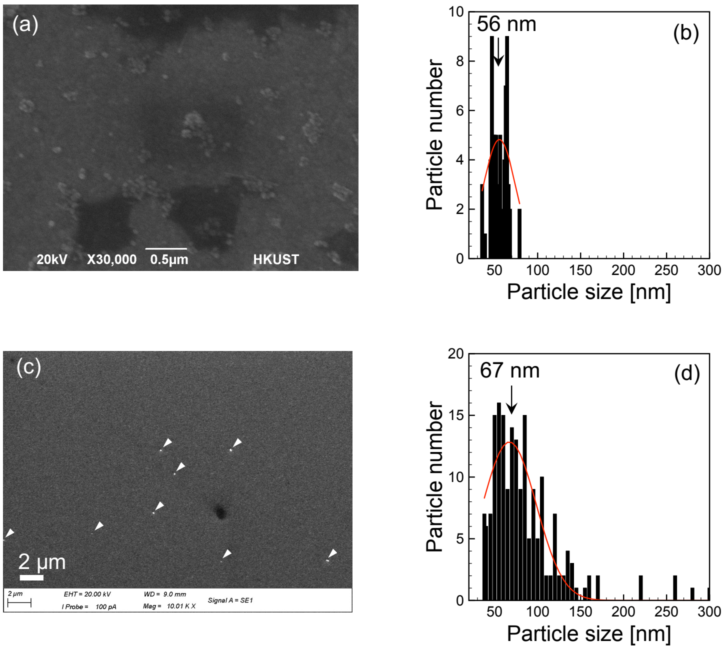

Figure S7. (a, c) SEM images of and (b, d) size distributions of Ag nanoparticles after naturally dried suspension and deposited (electrosprayed) on the substrate, respectively. Inset images shows typical SEM images. 71 and 208 particles were totally counted to obtain the size distributions for (b) and (d), respectively. The solid lines were fitted to normal distribution.

Comment #8: Lines 140-148: The aerosol size distribution also needs to be described in more detail. What was the size distribution of aeorsols. All of the information given is that the aerosols are generated and deposited (in the methods). Information like the mode, any size selection, etc would be very helpful in understanding the particle properties. Are the AS particles are assumed to be effloresced crystals since they are stored at < 10% RH and then analyzed at 60% (below the deliquescence RH of AS)? This could impact the enhancement of the SERS by determining nanoparticle/ammonium sulfate interacttions.

Response: (1) We assume that the Reviewer asked for the size distribution of analyte particles, because we have already shown the size distribution of Ag nanoparticle aerosols in the original supporting information (Fig. S3). In this study, we deposited analyte particles in the laboratory and collected ambient PM collected using a cascade impactor (Model MPS-4G1, California Measurements Inc.). We did not calculate the size distribution of the laboratory generated particles, but chose particles larger than 20 μm for most cases as mentioned in the section 2.4. For ambient PM, particles smaller 0.15 μm were selected to test the ES-SERS. To address the reviewer's comment, we have added the following text in the section 2.1 and changed the title accordingly:

"Ambient PM was collected on gold-coated Si substrates at the South Gate of the Hong Kong University of Science and Technology using a cascade impactor (Model MPS-4G1, California Measurements Inc.) on the morning of 9 May 2016. Collected particles between 0.05 and 0.15 μm in aerodynamic diameter were used as analyte particles."

(2) Since AS particles have effloresced before the RH was set at 60%, no enhancement was observed, likely because of the weak interaction between ammonium sulfate and Ag nanoparticles. In contrast, the aqueous AS/sucrose particles at 60% RH showed the significant enhancement at the sulfate vibration mode (Fig. 3), suggesting the strong interaction.

Comment #9: For the enhancement (162) reported on line 354, what size particles does this refer to? Is it possible that a larger particle versus a smaller particles is playing a role? This is part of why more details are needed for the aerosol sizing.

Response: The size of AS/sucrose particle is 1.4 μm for the $I_{\mathrm{SERS}}/I_{\mathrm{NR}}$ of 162. To make this clearer, we have revised the corresponding text accordingly:

Revised text:
Hence $I_{\mathrm{SERS}}/I_{\mathrm{NR}}$ increases with decreasing size, resulting in the largest $I_{\mathrm{SERS}}/I_{\mathrm{NR}}$ of 162.0 for the $\nu(\mathrm{SO_4}^{2-})$ mode at a particle size of 1.4 μm.

No clear role of analyte particle size in Raman enhancement was observed for laboratory-generated particles (Fig. 6). As discussed in the second paragraph in the section 3.3, this is because Ag nanoparticles are deposited on the surface of analyte particles and the surface area irradiated by a laser was constant over the size range studied (1.4 ~ 40 μm) due to the smaller laser spot diameter (1 μm). If the size of analyte particle is smaller than a laser sport diameter, enhanced intensity probably decreases with the size of analyte particles. However, the above discussion cannot be extended to the result of ambient PM (< 0.15 μm) collected by impactors, which were concentrated onto a submillimetre-sized spot area on the substrate during impaction.

Minor comments

Comment #1: Line 80: The Ofner paper referenced is of TERS, which while similar to SERS, should be specifically noted as such.

Response: We agree. We have accordingly revised the corresponding text as follows:

"Recently surface enhanced and Raman spectroscopy (SERS) and tip enhanced Raman spectroscopy (TERS) have been applied for characterizing atmospheric particles (Craug et al., 2015; Ofner et al., 2016)."

Comment #2: Line 329-331: The depth of focus section is not clear and should be discussed in more detail.

Response: We have revised and added the following text:

"This estimated value is smaller than the nominal threshold of 10 µm observed in the size dependence of the normal Raman signals, because gravity had affected the shape of the analyte particles deposited on the substrate, reducing the particle height (<10 µm). Gravity deforms the shape of droplets on a substrate, when the size of droplet is sufficiently large (e.g. > 10 µm). A contact angle of large droplet to a substrate is much smaller than 180 degrees. Thus, the depth of substrate-deposited droplet is typically smaller than its diameter."

Comment #3: More details on Gen and Lenggoro method need to be added.

Response: We have added the following text in the introduction:

"They employed the electrospray deposition of positively charged Ag nanoparticles on a silicon wafer that had been dip-coated with an organic thin film. The concentration of the organics on the substrate ranged from ~1 to 30 nanograms/m^2. The Raman mapping allows direct measurement of a spatial distribution of organic molecules on a solid surface with the detection limit above 3.54 molecules/μm^2. Numerical electrodynamic simulations have revealed that singly charged Ag nanoparticles (50 nm) can be deposited on any surface, i.e., from metallic to non-metallic substrates, under an electric field of > 10^4 V/m."

Comment #4: Figure 4: It would be nice to see the rest of the Raman spectrum (perhaps as an inset) to evaluate any nanoparticle effects.

Response: We have added the entire Raman spectra in Figures S1, S2 and S3 in the revised supporting information.

Comment #5: Figure 6: Why does the peak shift to lower frequencies? More information on this would be helpful.

Response: This redshift is likely due to strong interaction between sulfate ion and Ag nanoparticles, as reported by earlier works (Campion and Kambhampati, 1998; Stockle et al., 2000) and described in the second paragraph in the section 3.2.

Comment #6: Figure 7: For the particles that is very weak signal for very large particles. What is the RH of the particles when analyzed? Is it really safe to assume they are aqueous? Many prior Raman aerosol paper show much sharper sulfate features for ambient particles, why does the SERS struggle here so much?

Response: The RH during Raman analysis was 60 %. More importantly, the particles were dried at RH = 10% before they were conditioned at 60%. Hence, the AS and AS/succinic acid particles were solid in the current study. Nonetheless, enhanced spectra showed water peaks at 3200-3500 cm^{-1}, which are attributed to surface adsorbed water. As shown in Figs. 3 and 4, we observed sharp sulfate peaks at ~980 cm^{-1}.

Comment #7: Figure 8: Why is the v(O-H) stretching region not shown? - This is a minor point, but the figures take a very long to load, which I would guess is related to the resolution used. Please check that the figures load easily for a future draft (hopefully this is not just my computer having issues).

Response: We have revised Fig. 8 (Fig. 10 in the revised manuscript) to show the entire Raman spectra. We have reduced the data size of the figure.

Reference:

Campion, A., and Kambhampati, P.: Surface-enhanced Raman scattering, Chem. Soc. Rev., 27, 241-250, doi: 10.1039/a827241z, 1998.

Dieringer, J. A, McFarland, A. D., Shah, N. C., Stuart, D. A., Whitney, A. V., Yonzon, C. R., Young, M. A., Zhang, X., and Van Duyne, R. P.: Surface enhanced Raman spectroscopy: new materials, concepts, characterization tools, and applications, Farad. Discuss., 132, 9-26, doi: 10.1039/B513431P, 2006.

Fu, Y., Kuppe, C., Valev, V. K., Fu, H., Zhang, L., and Chen, J.: Surface-enhanced Raman spectroscopy: A facile and rapid method for the chemical component study of individual atmospheric aerosol, Environ. Sci. Technol, 51, 6260-6267, doi: 10.1021/acs.est.6b05910, 2017.

Le Ru, E. C., Blackie, E., Meyer, M., and Etchegoin, P. G.: Surface enhanced Raman scattering enhancement factors: A comprehensive study, J. Phys. Chem. C, 111, 13794-13803, doi: 10.1021/jp0687908, 2007.

Munro, C. H., Smith, W. E., Garner, M., Clarkson, J. W. P. C., and White, P. C.: Characterization of the surface of a citrate-reduced colloid optimized for use as a substrate for surface-enhanced resonance Raman scattering, Langmuir, 11, 3712-3720, doi: 10.1021/la00010a021, 1995.

Schmidt, M. S., Hübner, J., and Boisen, A.: Large area fabrication of leaning silicon nanopillars for surface enhanced Raman spectroscopy, Adv. Mater., 24, OP11-OP18, doi: 10.1002/adma.201103496, 2012.

Stöckle, R. M., Suh, Y. D., Deckert, V., and Zenobi, R.: Nanoscale chemical analysis by tip-enhanced Raman spectroscopy, Chem. Phys. Lett., 318, 131-136, doi: 10.1016/s0009-2614(99)01451-7, 2000.