Response to Reviewer #2

Authors present ES-SERS approach to characterize atmospheric aerosol particles. This is not a new approach, but new in terms of application as this is not been applied to atmospheric particles in the past. It seems such approach can be applied to atmospheric aerosols, and results are encouraging. Such approach was also recently published (El-Khoury, Johnson et al. 2015), therefore this is not a new approach and manuscript should be modified to reflect this. I have few major comments, and after these are addressed, I recommend the manuscript for publication.

Response: We thank you for useful comments. The earlier paper referred by reviewer #2 mentioned (El-Khoury, Johnson et al., 2015) utilized electrospray deposition of "analyte" solutions **onto 2-dimensional array of silver nanospheres on an SERS substrate**, which is a conventional approach of using a SERS substrate (Fig. 1a in the main text). In contrast, our approach (Fig. 1b in the main text) uses electrospray for generating and depositing Ag nanoparticles (SERS-active agent) onto the analyte atmospherically relevant particles. With our current approach, we will be able to characterize surface chemical composition of particles. Revised and added text in the main manuscript and supporting information was highlighted in red.

Comment #1: To simplify the reading, I suggest authors revise the particle definition terminology. It is confusing as aerosols are typically defined in the sense that these are the particles that are present in the atmosphere and affect Earth's radiative properties (optical and cloud). In this paper aerosol is defined as silver nanoparticles, and conventionally defined aerosol as 'analyte particles.' Please revise such that these analyte particles are now called aerosols and Ag nanoparticles as Ag nanoparticle only. Defining Ag nanoparticles as aerosol is confusing.

Response: We thank you for the comment. We agree that describing Ag nanoparticles as aerosol is confusing. To address the reviewer's comment, we have revised the terminology throughout the entire manuscript accordingly.

Comment #2: It is not clear why sucrose compound was used? Does this represent atmospheric organic aerosol composition? Please provide some references. Please clarify the necessary to coat the silicon wafer with gold. Are these wafers home grown or commercially available (part number? and vendor?).

Response: (1) Sucrose is widely used as a surrogate of viscous compound in the atmospheric aerosol community. We have accordingly provided the reference and added the following text in the section 2.1.

"In this study, atmospherically relevant particles of AS, AS mixed with SA, and AS mixed with sucrose were examined (Ling and Chan, 2008; Zobrist et al., 2008; Freedman et al., 2010; Chu and Chan, 2016)."

(2) The purpose of gold coating was to mask sharp and broad peaks derived from Si wafer at 520 and 900-1000 cm^{-1}, respectively. We have accordingly added the following text:

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

(3) The Si wafers used are commercially available (100, N type, Y Mart, Inc).

Comment #3: In section 2.2 it is mentioned that SEM images were obtained. Can they be inserted into the main paper? Why UV-vis was used? Describe typical CPC concentration values. What was the size of Ag nanoparticles (53 nm?) that was size-selected.

Response: (1) We prefer to keep the SEM images in the supporting information, because these are not our main results. Instead, we have inserted two figures of SERS results (Figs. S5 and S6) into the main manuscript to improve the readability in response to the reviewer's comment #7.

(2) UV-vis spectrometer was used for characterizing the selective absorption of Ag nanoparticles in liquid phase (colloidal suspension) as shown in Fig. S2. SERS relies on the excitation of localized surface plasmon resonance of metalic nanoparticles resulting in the selective absorption.

(3) CPC was used to obtain the size distribution of Ag nanoparticles suspended in gas phase. To address the reviewer's comment, the y axis of figure S3 was represented as particle number concentration (particles/cm^3). The typical CPC concentration was 40 to 50 particles/cm^3 at the mode size.

(4) We did not size-select the Ag nanoparticles. We have calculated the size (mode number) of 53 nm from the size distribution of Ag aerosols obtained with DMA and CPC (Fig. S3).

Comment #4: How spraying time of 1 hour was determined.

Response: The spraying time of 1 hour was determined based on earlier work (Gen and Lenggoro, 2015). The electrospray system used in the current study has a similar configuration with the system used in the earlier work. As mentioned in the introduction, we developed the ES-SERS method following the earlier work. To address the reviewer's comment, we have revised the corresponding text accordingly:

"Ag nanoparticles were deposited on the substrate at ambient pressure (1 atm) and the spraying time was 1 hour based on earlier work (Gen and Lenggoro, 2015)."

Comment #4: Model name and software version of the Renishaw Raman microscope should be mentioned. Please specify wavenumbers corresponding to compounds specified on line 198 (page 8).

Response: The software name and wavenumbers have been added in the section 2.4 as follows:

"Instrument control was performed with the Renishaw WiRE (Renishaw)."

"Raman enhancement was observed for vibration modes of $\nu(SO_4^{2-})$, $\nu(NO_3^-)$, ν(C-H), and ν(O-H) at ~970, ~1034, ~2930 and 3200 ~ 3500 cm^{-1}, respectively."

Comment #5: Section 2: Please mention here how submicron ambient aerosol were collected in this section. It is already mentioned in section 3.5. How particles between 0.05 and 0.15 um were collected. Using impactor? What stage and what was the 50% cut size. How samples were dried? And why it was necessary to dry the particles. Can drying process could alter the surface composition? Do you have Raman maps for ambient particles?

Response: (1) We used a cascade impactor (Model MPS-4G1, California Measurements Inc.) and selected the last stage where the 50% cut size is between 0.05 and 0.15 μm, which was described in the section 3.5. We have moved the description from the section 3.5 to section 2.1.

(2) The samples were kept in a desiccator filled with silica gels. This process dried the samples, which could vaporize some volatile organic compounds.

(3) We don't have Raman maps for ambient particles, because the particle size (< 0.15 μm) is below the spatial resolution of Raman analysis (~ 1 μm) and it also runs into the light diffraction limit.

Comment #6: Section 3.2: It is bit confusing to understand the comparison between Ag-coated SERS substrate and current SERS method. Why this comparison is carried out? In both cases the test aerosol are similar, so I expect the spectra from both methods should be similar. In terms of intensity, it can be just coincidence. It also raises important question, if both methods yield similar results, why one should use ES-SERS technique. One can use commercially available SERS substrates, which can save a lot of time in regards to sample preparation. Any thoughts? This result also contradicts the advantages of ES-SERS described in Introduction section.

Response: This comparison was carried out to examine the effect of Ag-sulfate interaction on Raman peaks, particularly the sulfate peaks (i.e. ~980 cm^{-1}). We observed a redshift at the sulfate peak for the ES-SERS experiments. The same redshift was also observed using the Ag-coated SERS substrate, suggesting that the results with the ES-SERS were not due to experimental error.

Unlike the conventional technique using an SERS substrate, our ES-SERS yields information on surface chemical compositions of analyte particles. If there are concentration gradients of species in radial direction in an analyte particle, the resulting spectra obtained from the two methods would be different. 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 the 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.

We have compared our results with earlier works. We have added the following text and revised the corresponding text accordingly:

"Craig et al (2015) reported an enhancement factor of 2.0 at $\nu(SO_4^{2-})$ 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."

Comment #7: Section 3 in general. One has to go back and forth between the main paper and supplementary information to understand the results. I suggest if some figures can be inserted into the main paper to improve the readability.

Response: We have moved Figs. S6 and S7 into the main text.

Comment #8: Section 3.3: Line 314-316. Is this observed in this study? and how such distance is determined? Are there any SEM images that shows such information.

Response: This distance dependence is a well-known result from Dieringer et al. (2006), also cited in the main text. We have discussed the size effect in this section based on the fact. Unfortunately, we don't have SEM images to show such information.

Comment #9: Line 332: To improve readability I suggest to add the values of wavelength and NA.

Response: We thank you for the comment. We have accordingly added the values.

Comment #10: Line 334: ..'gravity had affected..' is not clear. How gravity affects the shape. Shape (morphology) can be also altered during impaction.

Response: Gravity deforms the shape of droplets on a substrate and makes a contacting area between a droplet and a substrate larger, when the size of droplet is sufficiently large (e.g. > 10 μm). Therefore, substrate-deposited large droplets are not perfectly spherical; in other words, the contact angle is much smaller than 180 degree. Based on this, the height of droplet is always smaller than its diameter for large droplets. We have revised the text as follows:

"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 degree. Thus, the depth of substrate-deposited droplet is typically smaller than its diameter."

Comment #11: Line 347-348: Please mention what components were observed in minor and major category.

Response: Since Ag nanoparticles sit on the top of analyte particles, we define minor and major components as non-enhanced and enhanced ones, respectively. The non-enhanced and enhanced components reflect bulk chemical composition and surface chemical composition, respectively. To avoid confusion, we have deleted the descriptions of "minor" and "major" and revised the corresponding text as follows:

"Considering these facts, the constant enhanced intensity provides evidence that the enhanced spectrum contains information about the bulk chemical compositions (non-enhanced component) as well as the surface compositions (enhanced component), making the ES-SERS technique suitable for surface-sensitive detection."

Comment #12: Line 427:429: It is bit confusing. Does this imply that ES-SERS can only give surface composition but not bulk.

Response: The ES-SERS gives both bulk and surface information of chemical compositions, but only the surface compositions are enhanced due to the distance-dependence nature of SERS. Once we have a normal spectrum that contains only the bulk information, we will be able to extract the surface information by comparing a SERS spectrum with a normal spectrum. To clearly state those, we have added the following text:

"The spectrum obtained from ES-SERS contains both bulk and surface information of chemical compositions, but only the surface compositions are enhanced due to the distance-dependence effect (Dieringer et al., 2006). The complementary methods of Raman spectroscopy and ES-SERS (as surface-sensitive spectroscopy) can provide the bulk and surface chemical compositions, respectively by comparing normal and enhanced Raman spectra. They potentially help reveal the internal structure of individual particles such as their core/shell structure."

Comment #13: Line 428: 'comma' after word composition is missing. ....compositions, respectively,. . ..

Response: Thanks for the comment. We have accordingly added the comma.

Comment #14: Section 4: Please revise this section. Remove any new material that is not discussed in the main text. Remove any speculations or theories. Discuss them in the main text. Some editorial work is needed to understand the main message of the paper. Main conclusions are not clear after reading this section. Please see below some comments to improve this section further.

Response: Based on the reviewer's comment, we have revised and removed some text as below.

Comment #15: Line 433: This is not a new technique. Rephrase the sentence.

Response: We think that our method is a new technique as the publication referred by the reviewer is different from ours. Therefore, we prefer not to rephrase the sentence.

Comment #16: Line 436-439: Sentence is not clear. Cannot understand the phrase, please rewrite.

Response: To address the reviewer's comment, we have revised the sentence as follows:

"ES-SERS measurements showed that the I_{SERS}/I_{NR} ratios of the $\nu(SO_4^{2-})$ band at ~970 cm^{-1} for laboratory-generated AS, AS/SA and AS/sucrose particles followed the order: AS/sucrose (I_{SERS}/I_{NR} = 12.4) > AS/SA (I_{SERS}/I_{NR} = 3.3) > AS (I_{SERS}/I_{NR} = 1).".

Comment #17: Line 447-449: To improve readability, I would move this sentence to the main text. These past studies are not discussed either. Please discuss these. DMA is already defined for differential mobility analyzer (line 159).

Response: We thank you for the comment. We have removed the following text to improve the readability of this section:

"Adsorbed water has been investigated by limited techniques such as Fourier transform infrared spectroscopy (Al-Hosney and Grassian, 2005) and differential mobility analyzers (Romakkaniemi et al., 2001), which provide direct and indirect observations, respectively. ES-SERS can also contribute to elucidating the role of surface-adsorbed water in future studies."

Comment #18: Line 465-466: This is new and speculative. Please move to the main text and discuss. Do you have any maps that support this premise? Check (Baustian, Cziczo et al. 2012) for further information regarding maps and morphology.

Response: (1) This is not a new statement. We have already discussed this in line 421 in the original main text.

(2) We don't have Raman maps to support the premise. The earlier paper referred by the reviewer used Raman mappings for particles larger than 1 μm. The size of ambient particles discussed here (in the line 465) is below 1 μm (0.05 and 0.15 μm). Such maps may not give the detailed information on morphology in the current study.

Comment 19 #: Line 467-472: Paragraph text is confusing. How this is relevant to the present study. I suggest delete or modify and move to the main text.

Response: In this paragraph, we would like to describe (i) some limitations of ES-SERS that need further studies and (ii) a possible solution to overcome the limitations. We have revised this paragraph as follows:

"The direct contact of Ag nanoparticles to analyte molecules results in a peak shift, which could pose an obstacle to tracing the phase transition as well as identifying functional groups of the analytes. Recent studies have introduced the use of core-shell composite gold nanoparticles to eliminate the chemical enhancement (Li et al., 2010; Li et al., 2013). The outermost inert shell layer of the nanoparticle prevents its direct contact (i.e. coupling) with analyte molecules. Using such novel nanoparticles could further extend the application of the proposed ES-SERS technique in atmospheric studies."

Comment #20: Figure 8: In caption mention the wavenumber corresponding to sulfate and organics. How Organics peaks were identified?

Response: The enhanced Raman spectrum shows a peak at 1777 cm^{-1} that is likely assigned to carbonyl group, indicative of organic components. This explanation was described in the line 414 in the original main text. To make this clearer, we have revised the caption as follows:

"**Figure 10**. Normal (blue) and enhanced (red) Raman spectra of ambient PM. The particle size is between 0.05 and 0.15 µm. Sulfate peaks at 451, 615 and 977 cm^{-1}, and D and G bands at 1341 and 1598 cm^{-1}, respectively, were observed. Enhanced spectra further showed peaks at 1039 (nitrate) and 1777 (carbonyl group, indicative of organic components) cm^{-1}. The illustrations (not to scale) present experimental configurations for normal Raman and SERS measurements. The normal spectrum includes the bulk chemical compositions of BC and sulfate and the enhanced one includes the bulk compositions as well as the surface compositions (i.e. sulfate and organics)."

Reference:

Chu, Y., and Chan, C. K.: Reactive uptake of dimethylamine by ammonium sulfate and ammonium sulfate–sucrose mixed particles, J. Phys. Chem. A, 121, 206–215, doi: 10.1021/acs.jpca.6b10692, 2016.

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.

Freedman, M. A., Baustian, K. J., Wise, M. E., and Tolbert, M. A.: Characterizing the morphology of organic aerosols at ambient temperature and pressure. Anal. Chem., 82, 7965-7972, doi: 10.1021/ac101437w, 2010.

Gen, M., and Lenggoro, I. W.: Probing a dip-coated layer of organic molecules by an aerosol nanoparticle sensor with sub-100 nm resolution based on surface-enhanced Raman scattering, RSC Adv., 5, 5158-5163, doi: 10.1039/c4ra03850a, 2015.

Ling, T. Y., and Chan, C. K.: Partial crystallization and deliquescence of particles containing ammonium sulfate and dicarboxylic acids, J. Geophys. Res., 113, D14205, doi: 10.1029/2008jd009779, 2008.

Zobrist, B., Marcolli, C., Pedernera, D. A., and Koop, T.: Do atmospheric aerosols form glasses?, Atmos. Chem. Phys., 8, 5221-5244, doi: 10.5194/acp-8-5221-2008, 2008.