



Physicochemical analysis of individual atmospheric fine particles based on effective surface-enhanced Raman spectroscopy

Zhenli Sun,¹ Fengkui Duan,^{1,*} Kebin He,^{1,2,*} Hui Li,¹ Shuo Yang,¹ Liu Yang and Tao Ma¹

¹State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, 5 Beijing 100084, China

²State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Tsinghua University, Beijing 100084, China

Correspondence to: Fengkui Duan (duanfk@tsinghua.edu.cn); Kebin He (hekb@tsinghua.edu.cn)

- Abstract. Fine particle associated with haze pollution threatens the health of more than 400 million people in China. It is 10 therefore of great importance to thoroughly investigate and understand its composition. To determine the physicochemical properties in atmospheric fine particles at the micrometer level, we described a sensitive and feasible surface-enhanced Raman scattering (SERS) method using Ag foil as a substrate. This novel method enhanced the Raman signal intensities up to 10,000 a.u. for v(NO₃⁻) in fine particles with an enhancement factor of at least 56. The SERS effect of Ag foil was further studied experimentally and theoretically and found to have an enhancement factor of the order of ~ 10^4 .
- 15 Size-fractionated real particle samples with aerodynamic diameters of 0.4–2.5 μm were successfully collected on a heavy haze day, allowing ready observation of morphology and identification of chemical components, such as soot, nitrates, and sulfates. These results suggest that the Ag foil based SERS technique can be effectively used to determine the microscopic characteristics of individual fine particles, which will help to understand haze formation mechanisms and formulate governance policies.

20 1 Introduction

Atmospheric particulate matter (PM), one of the most complex pollutants, can have negative effects on visibility, climate change, regional air quality, and human health (Adachi et al., 2010; Dockery and Pope, 1994). Therefore, obtaining detailed information of both morphology and chemical compositions of individual particles during air pollution episodes is of fundamental importance for explaining haze formation. Several analytical techniques have been used for single particle

25 analysis, including electron microscopy (Li et al., 2016), aerosol-time-of-flight mass spectrometry/single particle aerosol mass spectrometry (Zhang et al., 2015), atomic force microscopy (AFM) (Posfai et al., 1998), and scanning transmission X-ray microscopy with near-edge X-ray absorption fine-structure spectroscopy (Pöhlker et al., 2012). Raman spectroscopy offers obvious advantages in non-destructive, ultrasensitive, and rapid detection, making it a promising technology for single particles analyses (Batonneau et al., 2006; Nelson et al., 2001; Sobanska et al., 2012; Ault et al., 2013; Sobanska et al., 2014;





Zhou et al., 2014). However, Raman microscopy is not widely used in the field of atmospheric studies due to the poor detection limits and insufficient spatial resolution.

Raman signals can be strongly increased when molecules are attached to nanometer-sized gold and silver structures called Surface-enhanced Raman scattering (SERS) phenomena (Kneipp, 2002). SERS provides a rapid and efficient platform

- 5 for chemical analyses due to the explosive development of nanofabrication and improvements in instrumentation (Li et al., 2010; Halvorson and Vikesland, 2010). This technique has great potential in the field of atmospheric science and has been applied preliminarily (Craig et al., 2015; Ayora et al., 1997; Fu et al., 2017; Ofner et al., 2016). For instance, Craig et al (Craig et al., 2015) first applied it to atmospheric aerosol particles and showed rich vibrational spectra for individual submicron particles with Ag nanoparticles (NPs) as SERS substrates. Recently Fu et al., (Fu et al., 2017) used commercial
- 10 Klarite for a chemical component study of individual atmospheric aerosols, and further increased substrate sensitivity by an enhancement factor of 6. However, continued improvements of the feasibility and practicality of SERS spectroscopy are needed to probe the most important individual particles affecting the climate and human health (Ault and Axson, 2016) (Ofner et al., 2015). Our previous work focused on NP design and fabrication (Sun et al., 2016b) for SERS detection of environmental pollution in solution, such as mercury ions (Sun et al., 2016a), hexavalent chromium (Lv et al., 2016b)
- 15 2017), polycyclic aromatic hydrocarbons (Du et al., 2016), and polybrominated diphenyl ethers (Sun et al., 2014). These studies will provide the theoretical and experimental basis for the application of SERS technology in the atmospheric sciences.

The purpose of the present study was to effectively identify fine particles (with an aerodynamic diameter of less than 2.5 μ m, PM_{2.5}) collected on a winter haze day by using a novel SERS method. We selected Ag foil as the

20 SERS substrate and sampling film as an alternative to the traditional quartz filter, Teflon filter, and Al foil. Moreover, the SERS effect of the Ag foil was studied with a finite-difference time-domain (FDTD) simulation accompanied with a SERS experiment for crystal violet (CV). We built a spectral library by further scanning pure reagents related to three main types of components from PM_{2.5}. Based on our observation, the morphology and typical chemical components (e.g., soot, nitrates, and sulfates) of size fractioned PM_{2.5} captured on a heavy haze 25 day in Beijing, China, were successfully identified.

2 Experiment section

30

2.1 Single particle collection The sampling site was located on the campus of Tsinghua University, Beijing, China (116.33°E, 40.01°N), as reported in our previous studies (Hu et al., 2016a). Knowledge of the size distribution of PM is essential in modeling PM formation processes in atmospheric aerosol processes and is useful for developing emissions control strategies. A single particle collection and analysis system for size-fractionated aerosols was set up by combining a

Dekati Low Pressure Impactor (DLPI) instrument and confocal Raman spectroscopy (Fig. 1). For PM particle collection, the







DLPI was operated at a flow rate of 10 L·min⁻¹. The collection time was selected according to the Air Quality Index (AQI, http://www.aqistudy.cn) of the Olympic Center Station in Beijing to ensure particle monodispersion (Hu et al., 2016a). The DLPI has 13 stages and a backup filter, which can collect particles based on size classification by aerodynamic diameter as follows: > 10 μ m, 6.8–10 μ m, 4.4–6.8 μ m, 2.5–4.4 μ m, 1.6–2.5 μ m, 1.0–1.6 μ m, 0.65–1.0 μ m, 0.40–0.65 μ m, 0.26–0.40 μ m, 0.17–0.26 μ m, 0.108–0.17 μ m, 0.060–0.108 μ m, 0.030–0.060 μ m, and <0.030 μ m.

2.2 Chemicals and materials

All reagents were of analytical grade and used without further purification. CV was purchased from Aldrich Scientific Ltd. (China). The chemicals for the Raman spectra library were purchased from Sinopharm Chemical Reagent Co., Ltd (China).

2.3 Apparatus

10 For the micro-Raman analysis of single PM_{2.5} particles, an inVia Renishaw confocal Raman microspectrometer (Renishaw, Gloucestershire, UK) coupled to a Leica microscope was used. Various excitation lasers (532 nm, 633 nm, and 785 nm) and magnification lenses (100×, 50×, 20×, and 5×) were used to perform the measurements. Data acquisition was carried out using the Wire 3.4 software package. The AFM images of Ag foil were obtained in tapping mode using a Veeco Dimension 3100 AFM with a Nanoscope IVa controller.

15 2.4 FDTD calculations

The electromagnetic (EM) field intensity distribution on the Ag foil was simulated using the FDTD method. The FDTD Solutions software package (Lumerical Solutions Inc., Vancouver, Canada) was used to perform the computational calculations and numerical analysis. The mesh size was 1 nm. The simulation time was 1000 fs. Ag NPs with a diameter of 5 nm and distance of 1 nm were set according to the AFM analysis results.

20 3 Results and discussion

3.1 Sampling film for Raman signal enhancement

In previous studies, for aerosol chemical components and individual particle analysis, the main types of PM collecting included quartz filter, Teflon filter, Nylon filter and Polyester film (He et al., 2001). In addition, Ag foil and Al foil, which widely used in the materials field, were also used for PM collection (Hu et al., 2016; Eom et al., 2014). In this study, four

25 types of commercial filters were selected for $PM_{2.5}$ collection and Raman analysis, including Ag foil, Al foil, traditional quartz filter, and Teflon filter. $PM_{2.5}$ samples were simultaneously collected on October 18, 2016 (16:00 in the afternoon, $PM_{2.5} = 148 \ \mu g \cdot m^{-3}$), and could be clearly observed on the four films (Fig. 2A–D). Images taken under the microscope of the Raman instrument indicated that the blank Teflon film and quartz filter had rough surfaces (Fig. 2E–F), which could cause







interference with the particle morphology identification (Fig. 2I–J). The flat surfaces of the Al and Ag foils provided suitable backgrounds that facilitated particle observation (Fig. 2G–L).

Raman signals of 25 random points for $PM_{2.5}$ were further collected on Al foil and Ag foil. The average Raman peak intensity of 1589 cm⁻¹ on the Ag foil was found to be 4,500 a.u., about an order of magnitude higher than the intensity of 418 a.u. on the Al foil (Fig.3). In addition, Raman peaks close to 987 cm⁻¹ and 1040 cm⁻¹ were also identified on Ag foil (inset of Fig. 3). The result indicated more Raman peaks and higher intensities can be obtained on Ag foil compared to Al foil. Since SERS effects generally occur when molecules are attached to nanometer-sized noble metals, such as gold and silver structures (Schlucker, 2014), we hypothesize that the Ag foil worked here both as a $PM_{2.5}$ SERS substrate and a $PM_{2.5}$

10 3.2 SERS effect of Ag foil

collection film in the following experiments.

To validate the SERS effect of Ag foil, we further simulated the distribution of the local electric field following the FDTD methods. FDTD simulations have been used extensively to study the optical properties of NPs, as reported in leading scientific publications (Li et al., 2010; Klinkova et al., 2014; Liu et al., 2015). The FDTD model was set up for Ag foil according to the AFM results with a surface roughness of Ag NPs of about 5 nm (Fig. 4A–C). The FDTD results indicated

- 15 the local EM field was greatly enhanced between Ag NPs (Fig. 4B–D). The SERS enhancement factor (EF), as estimated from $E_{local, max}/E_0^4$ (Gopinath et al., 2009), was about 4.6×10^4 . The FDTD simulations provided theoretical support for the significant SERS enhancement of the Ag foil substrate. CV was used as a Raman probe at different concentrations. The SERS spectra exhibited strong Raman bands corresponding to CV at 924, 1184, 1379, and 1628 cm⁻¹ (Fig. 4E, F). The detection limit was determined to be about 1×10^{-6} M. The EF factor was 4.3×10^4 , as calculated using the following
- 20 equation: $\text{EF} = (I_{\text{SERS}}/I_{\text{RS}})$ ($C_{\text{RS}}/C_{\text{SERS}}$), where $I_{\text{SERS}} = \text{SERS}$ intensity at 1628 cm⁻¹, $I_{\text{RS}} = \text{normal Raman intensity}$ at 1628 cm⁻¹, and $C_{\text{RS}}/C_{\text{SERS}} =$ the CV concentration ratio in normal Raman over the SERS sample (Le Ru et al., 2007). Generally, both EM and charge-transfer (i.e., chemical) enhancements contribute to the overall SERS enhancement (Hu et al., 2007). However, the experimental SERS enhancement factor in this work (4.3 × 10⁴) was very close to the FDTD simulation result (4.6 × 10⁴), indicating that the SERS effect of Ag foil was mainly due to the EM mechanism, which did not involve the
- 25 formation of chemical bonds between the analyte and substrate. Thus, the SERS effect results experimentally and theoretically indicate that Ag foil can function as an effective SERS substrate for aerosol particles from real environmental samples. Therefore, Ag foil had the advantage that it could not only give low background readings, but also enhance the signal intensity in the Raman analysis.

3.3 Optimization of signal identification for PM_{2.5}

30 One challenge that must frequently be overcome for Raman microspectroscopy is auto-fluorescent emissions from the particle itself after excitation by the Raman laser (Ault and Axson, 2016). To minimize the absorption and subsequent







fluorescent emissions, three laser wavelengths (532 nm, 633 nm, and 785 nm) were tested for the SERS spectra acquisition. The results indicated that a higher spectral quality was obtained at a wavelength of 532 nm (Fig. S1). This may be explained by the phenomenon that Raman signals can be greatly enhanced when the laser excitation line is moved close to the peak of the localized surface plasmon resonance band (Tan et al., 2013).

- 5 To identify the chemical species of particulate matter, measured Raman spectra (band wavenumber and relative intensities) with a flat baseline are needed for comparison with spectra in established libraries (Batonneau et al., 2006). Although several printed compendia of Raman spectra and characteristic frequencies are available (Nakamoto, 2008; Griffiths, 1991; Schrader, 1989; Dollish et al., 1974) and electronic versions are beginning to emerge, specialized libraries for particular problems are required to mitigate differences in instrumental functions. Based on our previous studies, PM_{2.5} is composed of various
- 10 chemical species, which can be divided into three main groups based on bulk analysis: (1) inorganic ions; (2) carbonaceous species; and (3) trace elements (Cheng et al., 2016; Xu et al., 2017). By scanning the pure reagents related to the main types of components mentioned above, we built a spectral library for the PM_{2.5} analysis (Fig.S2, Table S2). In the case of inorganic ions, spectra for 14 types of nitrates (Fig. S2A), nine types of sulfates (Fig. S2B), and seven types of ammonium salts (Fig. S2C) were obtained. For carbonaceous species, two types of graphene were collected (Table
- 15 S2). Trace elements could not be directly detected by Raman spectroscopy due to their small scattering cross section, and thus, nine types of oxides were added (Table S2).

3.4 Physicochemical analysis of individual PM_{2.5}

We performed an aerosol particle collection on a heavy haze day (June 1, 2017) with a $PM_{2.5}$ concentration of 301 µg·m⁻³. The particles on the Ag collection film were divided into 13 stages, and we selected four stages with diameters in the range

- 20 of 0.4–2.5 μm to study, because the highest resolution of the instrument was 0.7 um (Table S1). The two-dimensional optical images from the Raman microscope clearly show particles of various sizes, physical states, and morphologies (Fig. 5A–D). The size distribution measured with the Nano Measurer software corresponded well with the theoretical values (Fig. 5E–H, Table S1). Most of the particles in the four diameter stages were monodispersed with irregular shapes and mixed states. This single PM_{2.5} particle collection method provided a basis for the SERS analysis.
- For the SERS analysis, 60 spectra of particles on the Ag foil of the 1.6–2.5 μm stage were randomly selected (Fig. 6A). Five main peaks near 979 cm⁻¹, 1045 cm⁻¹, 1051 cm⁻¹, 1350 cm⁻¹, and 1589 cm⁻¹ were observed. The peaks at 1350 cm⁻¹ and 1589 cm⁻¹ in the PM_{2.5} samples are similar to the standard graphitic band (especially activated carbon) (Rosen and Novakov, 1977). The pronounced G- and D-band Raman emissions of the peaks reflect the nano-crystalline order within soot NPs (Niessner, 2014). A peak close to 979 cm⁻¹ was attributed to vibration of the sulfate ion (SO₄²⁻) (Fig. S2B, Table S2). Two geaks at 1045 cm⁻¹ and 1051 cm⁻¹, present in some samples, were attributed to the vibrations of the nitrate ion (NO₃⁻)
 - 5





5

(Fig.S2A, Table S2). There were many small peaks between 1250 cm⁻¹ and 1750 cm⁻¹ in the Raman spectra of the PM_{2.5} particles, possibly from organic components (Cordeiro and Corio, 2009; Kuo et al., 2011).

The highest intensity of $v(NO_3^-)$ for the atmosphere was about 10,000 a.u. around 1045 cm⁻¹ (Fig. 6B). The highest intensities of two previously reported works for real particles were about 500 a.u. (Craig et al., 2015) at 1370 cm⁻¹ and about 300 a.u. (Fu et al., 2017) at 1039 cm⁻¹, respectively. The SERS intensity can be influenced by the chemical concentration in

- aerosol sample, but our PM_{2.5} particles were collected on a heavy haze day (PM_{2.5} = 301 μg·m⁻³), the PM_{2.5} mass was only about three times higher than that in the reported work (PM_{2.5} index of 91) (Fu et al., 2017). After eliminating the influence of chemical concentration, the SERS intensity in this study for v(NO₃) is still 7-11 times higher than the highest EF of 8-30 reported in previous SERS studies (Craig et al., 2015; Fu et al., 2017). This indicates that our work has made great
 improvements on the sensitivity of the SERS technique for PM_{2.5} study, with an EF factor of at least 56.
- The Ag foil with nanoscale gaps is desirable for SERS detection of target $PM_{2.5}$ with highly localized regions of enhanced electromagnetic fields (Fig.7A). Those highly localized regions, also called "hot spots", usually occur at gaps between two adjacent coupling metal NPs with a distance of a few nanometers (Ge et al., 2013). When $PM_{2.5}$ particles were collected on Ag foil, the particles were positioned on the hotspots of Ag NPs, which facilitated Raman signal enhancement. Figure 7B
- 15 exhibits a typical example of a fine particle collected on a winter haze day in Beijing. The point-by-point Raman scanning acquisition over $5 \times 5 \ \mu\text{m}^2$ area around a fine particle with a step of 0.5 μ m, generates a set of 100 pixel spectra. A careful analysis of each spectrum indicates that typical spectra are characteristic of mixtures with particularly severe spectral overlap. The four main peaks of SO₄²⁻, NO₃⁻, and soot near 979 cm⁻¹, 1051 cm⁻¹, 1350 cm⁻¹, and 1589 cm⁻¹ were observed (Fig. 7C-F). The Raman images demonstrate a mixture of SO₄²⁻, NO₃⁻, and soot in fine particle.
- 20 Typical chemical components (e.g., soot, nitrate, and sulfate) could be identified by this method. However, organic component identification is a great challenge due to the varied composition of aerosol particles and the trace concentrations of organic compounds. To solve this problem, on one hand, we need to have more information about organics in these particles with the help of other powerful techniques, such as mass spectrometry, while on the other hand, the optimization of the SERS substrate for greater sensitivity is also needed. In addition, efforts should be made to develop the
- 25 SERS method for quantitative analysis of chemical components of particles to better understand the interface reaction process.

4 Conclusions

Our results show that Ag foil can act as both a collection film and SERS substrate, reducing background noise while enhancing the signal intensity of the Raman spectra. The SERS EF factor of Ag foil was studied experimentally and

30 theoretically and has a value of the order of ~ 10^4 . The enhancement effect was reduced for real aerosol particles, because only the particle surface could make contact with the SERS substrate. Nevertheless, the highest intensity of v(NO₃⁻) for the atmosphere was still about 10000 a.u. around 1045 cm⁻¹. The SERS intensity in this study for v(NO₃⁻) is 7-11 times higher







than the highest EF of 8-30 reported in previous SERS studies (Craig et al., 2015; Fu et al., 2017). This indicates that our work has made great improvements on the sensitivity of the SERS technique for $PM_{2.5}$ study, with an EF factor of at least 56. We believe that our study makes a significant contribution to individual particle analysis because the proposed method can be effectively used to analyze particulate matter, and could further provide the basis for haze formation mechanisms and

5 governance policies.

Acknowledgements: The authors thank Dr. Chuanyong Jing (State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences) for providing the chemicals for the Raman spectra database set up. We acknowledge the financial support of the National Science and Technology Program of China

10 (2014BAC22B01, 2016YFC0202700, and 2017YFC0211601) and the National Natural Science Foundation of China (81571130090).

References

Adachi, K., Chung, S. H., and Buseck, P. R.: Shapes of soot aerosol particles and implications for their effects on climate, J. Geophys. Res.-Atmos., 115, 4447-4458, doi: 10.1029/2009jd012868, 2010.

- 15 Ault, A. P., Zhao, D., Ebben, C. J., Tauber, M. J., Geiger, F. M., Prather, K. A., and Grassian, V. H.: Raman microspectroscopy and vibrational sum frequency generation spectroscopy as probes of the bulk and surface compositions of size-resolved sea spray aerosol particles, *Phys. Chem. Chem. Phys.*, 15, 6206-6214, doi: 10.1039/c3cp43899f, 2013. Ault, A. P., and Axson, J. L.: Atmospheric aerosol chemistry: spectroscopic and microscopic advances, *Anal. Chem.*, 89, 430-452, doi: 1021/acs.analchem.6b04670, 2017.
- Ayora, M. J., Ballesteros, L., Pérez, R., Rupérez, A., and Laserna, J. J.: Detection of atmospheric contaminants in aerosols by surfaceenhanced Raman spectrometry, *Anal. Chim. Acta*, 355, 15-21, doi: 10.1016/S0003-2670(97)81607-8, 1997. Batonneau, Y., Sobanska, S., Laureyns, J., and Bremard, C.: Confocal microprobe Raman imaging of urban tropospheric aerosol particles, *Environ. Sci. Technol.*, 40, 1300-1306, doi: 10.1021/es051294x, 2006. Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., and Carmichael, G.: Reactive nitrogen
- 25 chemistry in aerosol water as a source of sulfate during haze events in China, *Sci. Adv.*, 2, e1601530, doi: 10.1126/sciadv.1601530, 2016. Cordeiro, D. S., and Corio, P.: Electrochemical and photocatalytic reactions of polycyclic aromatic hydrocarbons investigated by Raman spectroscopy, *J. Braz. Chem. Soc.*, 20, 80-87, doi: 10.1590/S0103-50532009000100014, 2009. Craig, R. L., Bondy, A. L., and Ault, A. P.: Surface Enhanced Raman Spectroscopy Enables Observations of Previously Undetectable Secondary Organic Aerosol Components at the Individual Particle Level, *Anal. Chem.*, 87, 7510-7514, doi:
- 30 10.1021/acs.analchem.5b01507, 2015. Dockery, D. W., and Pope, C. A.: Acute respiratory effects of particulate air-pollution. Ann. Rev. Public Health., 15, 107-132, doi: 10.1146/annurev.pu.15.050194.000543, 1994. Dollish, F. R., Bentley, F. F., and Fateley, W. G.: Characteristic Raman frequencies of organic compounds. Microelectron. J., 37, 395-403, 1974.
- 35 Du, J., Xu, J., Sun, Z., and Jing, C.: Au nanoparticles grafted on Fe₃O₄ as effective SERS substrates for label-free detection of the 16 EPA priority polycyclic aromatic hydrocarbons. *Anal. Chim. Acta*, 915, 81-89, doi: 10.1016/j.aca.2016.02.009, 2016. Eom, H. J., Gupta, D., Li, X., Jung, H. J., Kim, H., and Ro, C. U.: Influence of collecting substrates on the characterization of hygroscopic properties of inorganic aerosol particles. *Anal. Chem.*, 86, 2648-2656, doi: 10.1021/ac4042075, 2014. 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

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2017-303 Manuscript under review for journal Atmos. Meas. Tech. Discussion started: 13 November 2017

© Author(s) 2017. CC BY 4.0 License.





Griffiths, P. R.: The handbook of infrared and Raman characteristic frequencies of organic molecules; *Academic Press: London, U.K.*, 1991.

Halvorson, R. A., and Vikesland, P. J.: Surface-enhanced Raman spectroscopy (SERS) for environmental analyses. *Environ. Sci. Technol.*, 44, 7749-7755, doi: 10.1021/es101228z, 2010.

- 5 He, K., Yang, F., Ma, Y., Zhang, Q., Yao, X., Chan, C. K., Cadle, S., Chan, T., and Mulawa, P.: The characteristics of PM_{2.5} in Beijing, China. *Atmos. Environ.*, 35, 4959-4970, doi: 10.1016/S1352-2310(01)00301-6, 2001. Hu, G., Feng, Z., Li, J., Jia, G., Han, D., Liu, Z., and Li, C.: Adsorption of ethanediamine on colloidal silver: A surface-enhanced raman spectroscopy study combined with density functional theory calculations, *J. Phys. Chem. C*, 111, 11267-11274, doi: 10.1021/jp071066k, 2007
- 10 Hu, J., Duan, F., He, K., Ma, Y., Dong, S., and Liu, X.: Characteristics and mixing state of S-rich particles in haze episodes in Beijing, *Front. Environ. Sci. Eng. Chin.*, 10, doi: 10.1007/s11783-016-0861-y, 2016. Klinkova, A., Therien-Aubin, H., Ahmed, A., Nykypanchuk, D., Choueiri, R. M., Gagnon, B., Muntyanu, A., Gale, O., Walker, G. C., and Kumacheva, E.: Structural and optical properties of self-assembled chains of plasmonic nanocubes. *Nano Lett.*, 14, 6314-6321, doi: 10.1021/nl502746h, 2014.
- 15 Kneipp, K.: Surface-enhanced Raman scattering and biophysics. J. Phys. Condens. Matter., 14, R597-R624, doi: 10.1088/0953-8984/14/18/202, 2002.

Kuo, S. C., Tsai, Y. I., Tsai, C. H., and Hsieh, L. Y.: Carboxylic acids in PM2.5 over Pinus morrisonicola forest and related photoreaction mechanisms identified via Raman spectroscopy, *Atmos. Environ.*, 45, 6741-6750, doi: 10.1016/j.atmosenv.2011.08.007, 2011.

- Le Ru, E., Blackie, E., Meyer, M., and Etchegoin, P.: Surface enhanced Raman scattering enhancement factors: a comprehensive study, *J. Phys. Chem. C.*, 111, 13794-13803, doi: 10.1021/jp0687908, 2007.
- Li, J. F., Huang, Y. F., Ding, Y., Yang, Z. L., Li, S. B., Zhou, X. S., Fan, F. R., Zhang, W., Zhou, Z. Y., Wu, D. Y., Ren, B., Wang, Z. L., and Tian, Z. Q.: Shell-isolated nanoparticle-enhanced Raman spectroscopy, *Nature*, 464, 392-395, doi: 10.1038/nature08907, 2010.
- Li, W., Sun, J., Xu, L., Shi, Z., Riemer, N., Sun, Y., Fu, P., Zhang, J., Lin, Y., Wang, X., Shao, L., Chen, J., Zhang, X., Wang, Z., and Wang, W.: A conceptual framework for mixing structures in individual aerosol particles, *J. Geophys. Res.-Atmos.*, 121, 13784-13798, doi: 10.1002/2016jd025252, 2016.

Liu, X., Lebedkin, S., Besser, H., Pfleging, W., Prinz, S., Wissmann, M., Schwab, P. M., Nazarenko, I., Guttmann, M., Kappes, M. M., and Lemmer, U.: Tailored surface-enhanced Raman nanopillar arrays fabricated by laser-assisted replication for biomolecular detection using organic semiconductor lasers, *Acs Nano*, 9, 260-270, doi: 10.1021/nn506589a, 2015.

Lv, B., Sun, Z., Zhang, J., and Jing, C.: Multifunctional satellite Fe₃O₄ -Au@TiO₂ nano-structure for SERS detection and photo-reduction of Cr(VI). *Colloids Surf.*, *A*, 513, 234-240, doi: 10.1016/j.colsurfa.2016.10.048, 2017.

Nakamoto, K.: Infrared and Raman spectra of inorganic and coordination compounds, part A and part B, two volume set, 6th edition. Sex. Transm. Infect., 85, 182-186, doi: 10.1002/0470027320.s4104, 2006.

Nelson, M. P., Zugates, C. T., Treado, P. J., Casuccio, G. S., Exline, D. L., and Schlaegle, S. F.: Combining Raman chemical imaging and scanning electron microscopy to characterize ambient fine particulate matter. *Aerosol Sci. Technol.*, 34, 108-117, doi: 10.1080/02786820120709, 2001.

Niessner, R.: The Many Faces of Soot: Characterization of Soot Nanoparticles Produced by Engines, Angew. Chem.-Int. Edit., 53, 12366-12379, doi: 10.1002/anie.201402812, 2014.

 Ofner, J., Kamilli, K. A., Eitenberger, E., Friedbacher, G., Lendl, B., Held, A., and Lohninger, H.: Chemometric analysis of multisensor hyperspectral images of precipitated atmospheric particulate matter. *Anal. Chem.*, 87, 9413-9420, doi: 10.1021/acs.analchem.5b02272,
 2015.

Ofner, J., Deckertgaudig, T., Kamilli, K. A., Held, A., Lohninger, H., Deckert, V., and Lendl, B.: Tip-enhanced Raman spectroscopy of atmospherically relevant aerosol nanoparticles, *Anal. Chem.*, 88, 9766-9772, doi: 10.1021/acs.analchem.6b02760, 2016. Pöhlker, C., Wiedemann, K. T., Sinha, B., Shiraiwa, M., Gunthe, S. S., Smith, M., Su, H., Artaxo, P., Chen, Q., and Cheng, Y.: Biogenic

potassium salt particles as seeds for secondary organic aerosol in the Amazon, *Science*, 337, 1075-1078, doi: 10.1126/science.1223264,
 2012.

Posfai, M., Xu, H. F., Anderson, J. R., and Buseck, P. R.: Wet and dry sizes of atmospheric aerosol particles: An AFM-TEM study, Geophys. *Res. Lett.*, 25, 1907-1910, doi: 10.1029/98gl01416, 1998.

Rosen, H., and Novakov, T.: Raman-scattering and characterization of atmospheric aerosol-particles. *Nature*, 266, 708-710, doi: 10.1038/266708a0, 1977.

50 Schlucker, S.: Surface-enhanced Raman spectroscopy: concepts and chemical applications. *Angew. Chem. Int. Ed.*, 53, 4756-4795, doi: 10.1002/anie.201205748, 2014.

Schrader, B.: Raman/infrared atlas of organic compounds, VCH, 1989.

Sobanska, S., Hwang, H., Choel, M., Jung, H.-J., Eom, H.-J., Kim, H., Barbillat, J., and Ro, C.-U.: Investigation of the chemical mixing state of individual Asian dust particles by the combined use of electron probe X-ray microanalysis and Raman microspectrometry. *Anal.*

55 Chem., 84, 3145-3154, doi: 10.1021/ac2029584, 2012.



Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2017-303 Manuscript under review for journal Atmos. Meas. Tech. Discussion started: 13 November 2017

© Author(s) 2017. CC BY 4.0 License.





Sobanska, S., Falgayrac, G., Rimetz-Planchon, J., Perdrix, E., Bremard, C., and Barbillat, J.: Resolving the internal structure of individual atmospheric aerosol particle by the combination of Atomic Force Microscopy, ESEM-EDX, Raman and ToF-SIMS imaging. Microchem. J., 114, 89-98, doi: 10.1016/j.microc.2013.12.007, 2014.

Sun, Z., Du, J., Lv, B., and Jing, C.: Satellite Fe₃O₄@SiO₂-Au SERS probe for trace Hg²⁺ detection. RSC Adv., 6, 73040-73044, doi: 5 10.1039/c6ra15044f, 2016a.

Sun, Z. L., Du, J. J., Yan, L., and Jing, C. Y.: Rapid detection of 2,2 ',4,4 '- tetrabromodiphenyl ether (BDE-47) using a portable Aucolloid SERS sensor. J. Raman Spectrosc., 45, 745-749, doi: 10.1002/jrs.4554, 2014.

Sun, Z. L., Du, J. L., Yan, L., Chen, S., Yang, Z. L., and Jing, C. Y.: Multifunctional Fe₃O₄@SiO₂-Au satellite structured SERS probe for charge selective detection of food dyes. ACS Appl. Mat. Interfaces., 8, 3056-3062, doi: 10.1021/acsami.5b10230, 2016b.

Tan, T. X., Tian, C. G., Ren, Z. Y., Yang, J., Chen, Y. J., Sun, L., Li, Z. T., Wu, A. P., Yin, J., and Fu, H. G.: LSPR-dependent SERS 10 performance of silver nanoplates with highly stable and broad tunable LSPRs prepared through an improved seed-mediated strategy. Phys. Chem. Chem. Phys., 15, 21034-21042, doi: 10.1039/c3cp52236a, 2013.

Xu, L., Duan, F., He, K., Ma, Y., Zhu, L., Zheng, Y., Huang, T., Kimoto, T., Ma, T., and Li, H.: Characteristics of the secondary watersoluble ions in a typical autumn haze in Beijing, Environ. Pollut., 227, 296-305, doi: 10.1016/j.envpol.2017.04.076, 2017.

15 Zhang, G., Han, B., Bi, X., Dai, S., Huang, W., Chen, D., Wang, X., Sheng, G., Fu, J., and Zhou, Z.: Characteristics of individual particles in the atmosphere of Guangzhou by single particle mass spectrometry. Atmos. Res., 153, 286-295, doi: 10.1016/j.atmosres.2014.08.016, 2015

Zhou, Q., Pang, S. F., Wang, Y., Ma, J. B., and Zhang, Y. H.: Confocal Raman studies of the evolution of the physical state of mixed phthalic acid/ammonium sulfate aerosol droplets and the effect of substrates. J. Phys. Chem. B, 118, doi: 6198-6205, 2014.

20

25

30

35

40

45

50







Figure 1. Schematic diagram of the SERS strategy for size-fractionated collection and physicochemical analysis of individual PM_{2.5} aerosol particles using a Raman analysis system.



Figure 2. Images of the films and aerosols collected on (A, I) Teflon filter, (B, J) quartz filter, (C, K) Al foil, and (D, L) Ag foil. Images of blank film for (E) Teflon filter, (F) quartz filter, (G) Al foil, and (H) Ag foil.









Figure 3. Average Raman spectrum of 25 random points for PM_{2.5} particles on Al foil (black) and Ag foil (red). The inset provides a magnified view of the average Raman spectrum for fine particles on Ag foil.



Figure 4. (A) AFM image, and (B) surface roughness of Ag foil. (C) FDTD model and (D) simulation results for Ag foil as SERS substrate. (E) SERS spectra of CV on Ag foil with concentrations from 1×10^{-2} M to 1×10^{-6} M. (F) Raman spectra of CV on a silicon wafer with concentrations of 1×10^{-2} M.

10

5







Figure 5. Optical images of aerosol obtained on Ag foil with particle diameters of (A) 0.40–0.65 μm, (B) 0.65–1.0 μm, (C) 1.0–1.6 μm, and (D) 1.6–2.5 μm. (E–H) The size distribution of the particle samples in A–D, respectively.



Figure 6. (A) SERS spectra of 50 randomly selected points of aerosols on Ag foil. (B) Raman intensity for the peaks near 979 cm⁻¹, 1045 cm⁻¹, 1051 cm⁻¹, 1350 cm⁻¹, and 1589 cm⁻¹.

10









Figure 7. (A) Schematic of a fine particle impacted onto a SERS Ag foil substrate. (B) Optical image, and (C-F) Raman images of a single fine particle with peaks near 979 cm⁻¹ (red), 1051 cm⁻¹ (yellow), 1350 cm⁻¹ (green) and 1589 cm⁻¹ (purple). The scale bars represent 1000 nm.

5