Plasmonic hotspots in air : an omnidirectional three-dimensional platform for stand-off in-air sers sensing of airborne species

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Plasmonic Hotspots in the Air: Omnidirectional and Three-dimensional Platform for Stand-off In-air SERS Sensing of Airborne Species**

Gia Chuong Phan-Quang,[1] Hiang Kwee Lee,[1,2] Hao Wen Teng,[1] Charlynn Sher Lin Koh,[1] Barnabas Qinwei Yim ,[1] Eddie Khay Ming Tan,[3] Wee Lee Tok,[3] In Yee Phang,[2,3,] Xing Yi Ling[1]**

Abstract: *Molecular-level airborne sensing is critical for early prevention of disasters, diseases and terrorism. Currently, most 2D surface-enhanced Raman spectroscopy (SERS) substrates used for air sensing have only one functional surface and exhibit poor SERS active depth. Here, we introduce 'aerosolized plasmonic colloidosomes' (APC) as airborne plasmonic hotspots for direct in-air SERS measurements. Our APC functions as a macro-scale 3D and omnidirectional plasmonic cloud that receives laser irradiation and emits signals in all directions. Importantly, it brings about an effective plasmonic hotspot in ~2.3 cm lengthscale, which affords 100-fold higher tolerance to laser misalignment along the z axis comparing with 2D SERS substrates. Our APC exhibits extraordinary omnidirectional property and demonstrates consistent SERS performance independent of laser and analyte introductory pathway. Furthermore, we showcase the first in-air SERS detection in a stand-off condition at 200 cm distance, highlighting the immense applicability of our 3D omnidirectional plasmonic cloud for remote airborne sensing in threatening/inaccessible areas.*

Airborne sensing of explosive vapors, chemical hazards and pathogens is critical for early recognition and prevention of disasters, diseases and terrorism.[1] Generally, airborne sensing is performed using methods such as gas chromatography,[2] photoelectric/ionization detectors,[3] and nanomechanical sensors.[4] Despite their widespread usage, these conventional methods do not provide direct and specific molecular fingerprints of target analytes.[5] The identification and differentiation of gas molecules with similar physical properties remain challenging yet crucial to prevent potential false signals from interferences.[6] As a solution, surface-enhanced Raman spectroscopy (SERS) has been employed as a general detection technique that provides instantaneous molecular fingerprints read-out,[7] for the trace detection of various species present in the air using ultrasensitive substrates.[8] However, SERS sensing of airborne species often require additional molecular collection systems such as electrodynamic precipitation or fluidic stream to accumulate airborne molecules to the SERS substrates.[1b, 9] These substrate-based platforms are further limited by the need for stringent laser focal and directional alignment during measurements – any slight deviation of laser path or its focal point can result in dramatic decrease in signal intensity.[10]

To overcome these pressing problems, an omnidirectional and three-dimensional (3D) SERS platform is ideal for airborne detection within an extended volume due to their ability to receive laser irradiation and transmit signals in all directions. We hypothesize that incorporating plasmonic nanoparticles within an isotropic aerosol to form a 3D plasmonic 'cloud' can function as a macro-scale omnidirectional SERS platform to tackle the aforementioned issues of 2D substrates.[11] Such plasmonic clouds are independent to laser angle alignment and have advantageous flexibility in dynamic gas phase environment, permitting the detection of analyte molecules introduced from any direction. On the other hand, 2D substrates have merely one functional surface where only analytes deposited on the specific surface can be detected. Moreover, aerosols extending up to centimeter-scale can be easily produced using a commercial spray device, allowing the formation of macroscale 3D plasmonic volume with high tolerance to laser misfocus. Hence, aerosols of plasmonic nanoparticles have immense potential to couple with stand-off Raman devices for remote sensing in dangerous/inaccessible areas where accurate laser positioning from meter-range distances remains non-trivial.

Here, we introduce 'aerosolized plasmonic colloidosomes' (APC) as an omnidirectional 3D platform that serves as in-air SERS hotspots for the identification of airborne molecules in their native environment. An aerosol containing plasmonic colloidosomes is first introduced into the air using an aerosolizer, where its physical properties such as spatial dimensions and stability are evaluated. We further examine the SERS characteristic of our APC clouds, exemplifying them as a macro-scale 3D SERS active volumes that extends over several centimeters required for omnidirectional SERS measurement. Comparison with conventional 2D substrates further highlights that our APC exhibits >100-fold larger SERS-active volume crucial to circumvent laser misalignment issue typical in in-air detection. When coupled with stand-off Raman system, our APC notably represents the world's first proof-of-concept in-air SERS sensor for remote detection of airborne species up to 200 cm away. Our work lays the foundation for the development of remote air sensing technology, which is especially critical for defense and security sectors.

To prepare omnidirectional 3D plasmonic clouds for in-air SERS, we first fabricate plasmonic colloidosomes and subsequently aerosolize them using a commercial nanosprayer device (Figure 1A, B). Briefly, plasmonic colloidosomes of an average diameter and standard deviation of (7 ± 3) µm are fabricated by emulsifying a water/hexane system using single-crystalline Ag nanocubes (edge length ~120 nm) as building blocks (Figure S1, S2A).[12] Our plasmonic colloidosomes are spherical and possess multilayer shells composed of (10 ± 3) Ag nanocube layers, giving rise to a high density of SERS hotspots (Figure S2B, S2C).[8,12-13] Subsequently, we transfer the as-synthesized colloidosomes to an aerosolizer disk that uses high-rate vibration at a regularity of 1 GHz to eject aerosols containing colloidosomes. APC is produced instantly in the form of a mist, and can spread up to ~8 cm away from the nozzle within ~1 second upon activation of the device (Figure 1B; Figure S3).

[*][1] Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University
21 Nanyang Link, Singapore 637371
E-mail: xyling@ntu.edu.sg

[2] Institute of Materials Research and Engineering
Agency for Science, Technology and Research (A*STAR)
2 Fusionopolis Way, Innovis, #08-03, Singapore 138634
Email: phangiy@imre.a-star.edu.sg

[3] Technospex Pte Ltd, 1092 Lower Delta Road
#04-01 Tiong Bahru Industrial Estate, Singapore 169203.

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Upon collection of the aerosolized contents, a large portion of colloidosomes have retained their original shape and size (7 ± 3) µm (Figure 1C, 1D; Figure S4). This indicates that they can withstand the physical impacts of the expulsion process through the aerosolizer nozzle (Figure S5). We estimate

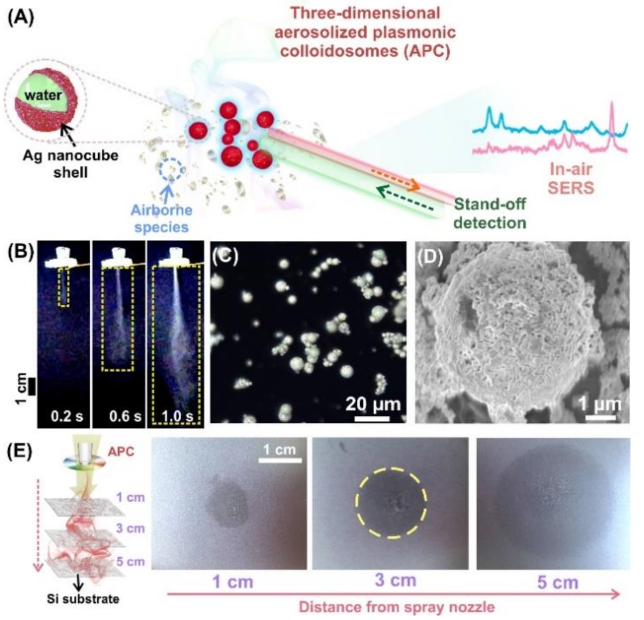

Figure 1. **Aerosolized plasmonic colloidosomes (APC).** (A) Schematic illustrating plasmonic colloidosomes as a 3D plasmonic cloud for stand-off SERS measurement of airborne species. (B) Digital image of the plasmonic mist dispensed from the aerosolizer. (C) Microscopic image of aerosolized colloidosomes collected in a hexane solution after spray. (D) SEM image of a colloidosome collected on a Si substrate after spray. (E) Digital images showing APC's cross-sectional coverage area (yellow-dash circle in second image) obtained by depositing the aerosol on Si substrates at 1, 3 and 5 cm away from the aerosolizer nozzle (as illustrated in the 3D scheme).

that a concentration of 68000 colloidosomes/cm^3 (equivalent to 10^9 Ag nanocubes/cm^3) is introduced within the APC volume per second (Supporting Information 1), providing substantial quantity of SERS hotspots in the air for the subsequent in-air detection. In addition, we obtain circular coverage areas of APCs with diameters of 0.8, 1.5 and 3.0 cm by depositing the aerosol on Si substrates at 1, 3 and 5 cm away from the aerosolizer nozzle (Figure 1E, S4). Notably, the circular cross-sections of APCs also suggest their omnidirectional property, where the three-dimensional cloud of APCs indicates that the plasmonic hotspots are available in all directions for in-air analyte detection. Such property is highly advantageous for in-air sensing of airborne species that are typically randomly dispersed.

The major advantage of APCs over 2D SERS substrates lies within its 3D effective plasmonic volume over centimeter-scale. To demonstrate and characterize the SERS active volume and sensitivity along the spatial axes of APC, we simultaneously record the 1077 cm^{-1} fingerprint of 4-MBT-functionalized APCs across the corresponding x, y, and z axes at 500 µm step intervals as they are sprayed into a detection chamber (4-MBT acts as signalling molecule, Figure 2A,B, S6, supporting information 2). Upon projection of the intensity profiles along the axes, we obtain a large 3D SERS active volume with ~2.3 cm in the vertical spray direction (y-axis, main axis of the spray) and ~ 1.0 cm and ~ 0.98 cm in in x- and z-axes, respectively (full-width half-maximum (FWHM) of intensity profiles, Figure 2B, Figure S7). While this cuboid shape is modelled after the spray in the chamber and does not fully represent the standalone plasmonic cloud, it still affirms that the SERS-active volume of our APC clouds is three-dimensional and extends over centimeter-scale regions, a significant leap from conventional 2D SERS substrates with micro-scale SERS active depth. It is also critical to design a SERS platform that possesses higher tolerance to laser misfocus, and can produce consistent signal readout over larger region in z-axis. Notably, the FWHM of the intensity profile along the z-axis for APC is calculated at up to 9.8 mm (0.98 cm,

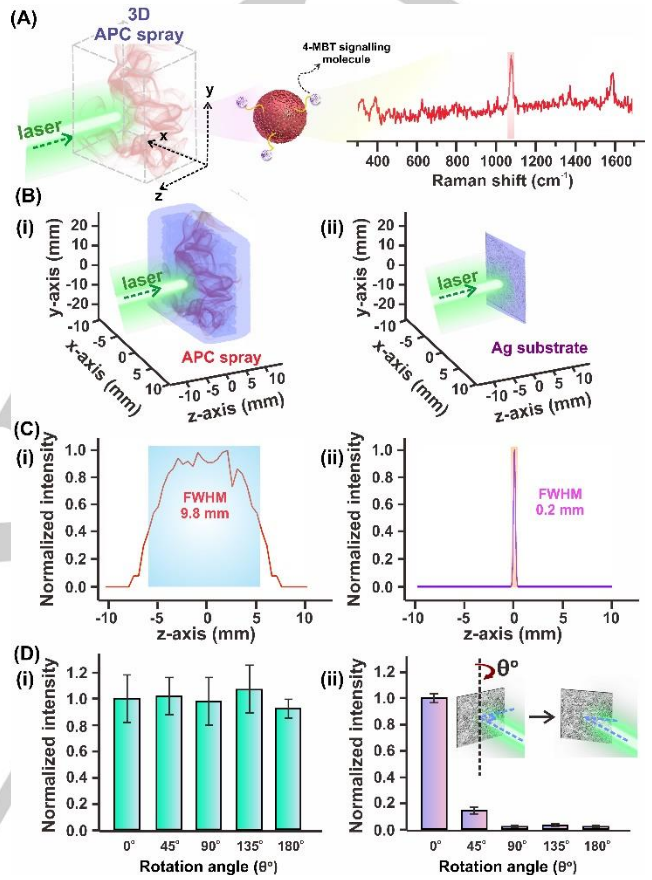

Figure 2. **3D characteristic of APC.** (A)Schematic illustration on the spread of APC (with 4-MBT) in the x, y, and z directions. (B – D) Comparison of SERS detection capabilities between (i) APC and (ii) 2D substrate based on different parameters. (B) SERS active volume along x, y, z axes, (C) SERS intensity of 4-MBT signal observed when laser focal point is moved along z-axis (D) SERS intensity recorded when each platform is rotated at different angles from the original position with respect to laser beam

Figure 2C). In our control experiments with 2D SERS substrate, the SERS active volume along the z-axis is measured at only ~200 µm in FWHM of the intensity profile. Based on the above results, it is clear that the effective 3D SERS active layer of APC is 100-fold superior to that of conventional 2D substrates. This unprecedented centimeter-scale 3D focal volume is a breakthrough from the conventional focal plane, and provides immense flexibility in laser focal alignment, which is especially crucial for in-air SERS measurements. On a side note, we observe that even after the nozzle is turned off, 4-MBT signals are still detectable after ~2 s (Figure S8, Video S1), indicating the airborne suspension time of APC last up to 2 s. Nevertheless, we choose to constantly introduce APC into the detection chamber to maximize the in-air hotspot density.

The omnidirectional property of APC gives it uniformity and reproducibility in SERS performance in all directions, rendering it independent on the angle of laser irradiation. To examine this unique property, we measure the SERS signals by rotating the injection angle of APCs along the y-axis from 0 to 180^o with respect the laser beam (Figure 2A; Figure S6), thus exposing different sides of the APC to the laser pathway. We obtain consistent 4-MBT signals from APC clouds with a relative standard deviation of 5% when we systematically rotate the APC injection angles at 0^o, 45^o, 90^o, 135^o and 180^o along the y-axis (Figure 2D). In contrast, 2D substrates exhibits highest intensity only when the substrate surface is directly facing the laser beam (original position, 0^o) and a 45^o rotation leads to a 90% decrease in signal intensity (Figure 2D(ii)). These observations highlight the importance of APC's 3D SERS volume to operate uniformly in all directions, offering significantly higher tolerance to laser directional misalignment compared to a 2D substrate.

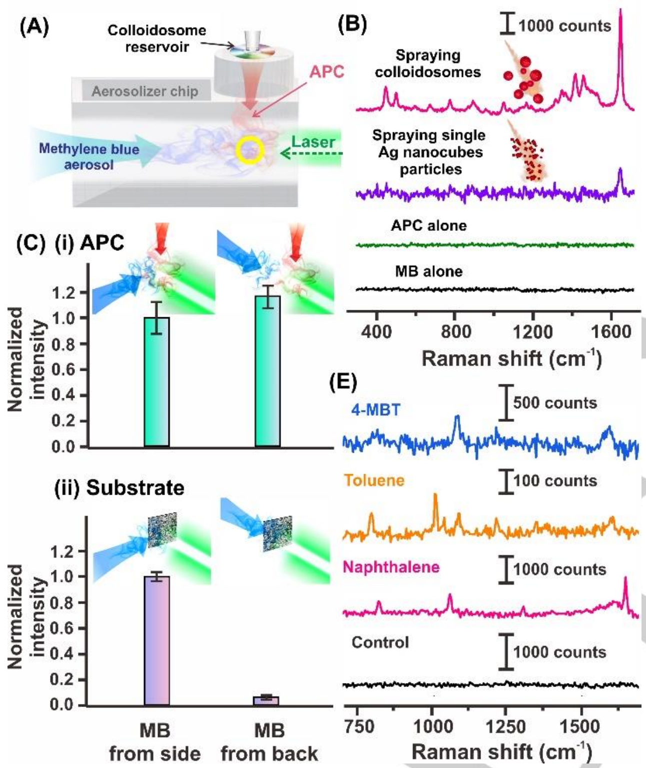

Figure 3. **In-air detection of airborne species.** (A) Experimental setup for SERS detection of methylene blue aerosol using APC (yellow dashed-circle indicates laser illumination spot). (B) Comparison of SERS performance of our 3D colloidosome with control experiment using single Ag nanocubes. (C) SERS intensity of MB (0.5 µmol) when MB is introduced from the back and side of (i) APC and (ii) substrate. The intensity is based on the characteristic fingerprint at 1630 cm^{-1}. (E) SERS spectra of other airborne species detected using APC ('control' refers to blank APC without any analyte introduced)

The in-air SERS performance of our APCs is further evaluated by detecting various aerosolized liquid analytes, an important class of airborne species that is commonly encountered in medical diagnosis (saliva),[14] environmental monitoring (haze and mist),[15] and defense (sprayed nerve and biological agents).[16] Our detection model uses aerosolized methylene blue (MB) as probe molecules, where blank aerosolized plasmonic colloidosomes are the substrate-less SERS platforms. Typically, 5 µmol MB aerosols (in ethanol) and a 500 µL suspension of 4.8 mg APCs (in hexane) are introduced simultaneously into the detection chamber from two separate inlets; one from side and one from top (Figure 3A). The SERS signals are collected instantaneously in mid-air where the aerosolized colloidosomes and MB come into direct contact and mixing (yellow dash-circle in Figure 3A). We obtain SERS spectra with distinct fingerprints of MB including C-N-C deformation modes at 456 and 503 cm^{-1}, and aromatic C-C stretching at 1630 cm^{-1}, respectively (Table S1).[17] When 5 µmol aerosolized MB is introduced into the detection chamber, the vibrational mode centered at 1630 cm^{-1} exhibits a SERS intensity of ~ 5900 counts/s. (Figure S9). The featureless spectra obtained just by spraying APC (without MB) or MB (without Ag) clearly affirms that the aforementioned signals arise from the successful in-air SERS detection of MB molecules using APCs (Figure 3B). This SERS response also demonstrates that our in-air APCs are able to interact effectively with aerosolized liquid analytes. On the other hand, aerosolized Ag nanocubes only give rise to 1500 counts of signal when MB aerosols of the same concentration is used (Figure 3B, Figure S9). Furthermore, aerosolized plasmonic colloidosomes are capable of detecting MB down to 0.5 nmol (~ 450 counts, Figure S9), giving rise to an analytical enhancement factor (AEF) of 1.8 × 10^5 (Figure 3C). In contrast, single Ag particle spray can only achieve a detection limit of 5 µmol MB, with AEF value of only 36 (Figure S10, Supporting Information 3). These results demonstrate that APC outperforms single Ag particles, and is a superior platform for in-air SERS sensing owing to their unique multilayered Ag shells, to effect manifold SERS hotspots due to plasmonic couplings and thus increasing hotspot-analyte interaction in a highly dynamic in-air environment.

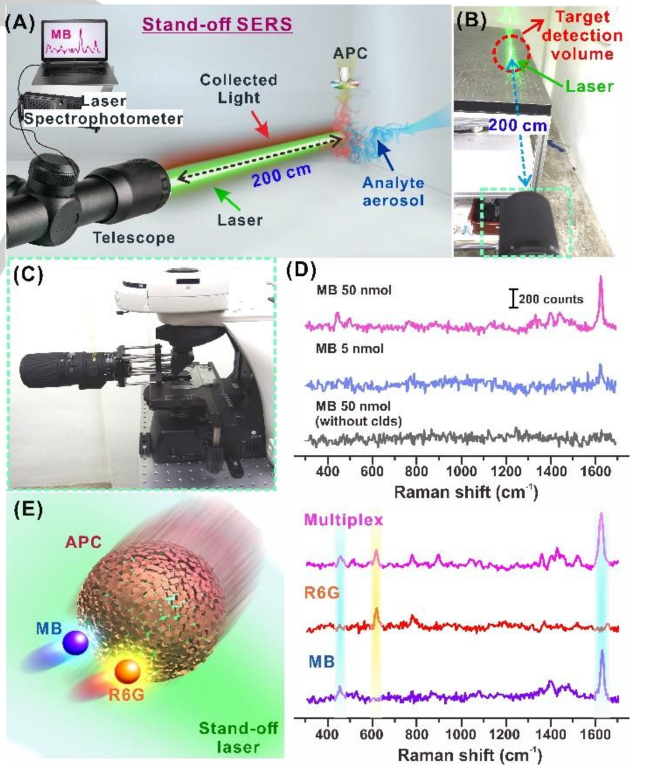

Figure 4. **Stand-off SERS detection.** (A, B) Scheme and digital image depicting the set-up of stand-off SERS for detection of methylene blue aerosol using APC. (C) Digital image of telescope lens used for stand-off detection. (D) SERS spectra of different methylene blue amount introduced into air per second, detected with APC using our set-up shown in (B). (E) Scheme and SERS spectra of in-air multiplex detection of both methylene blue (MB) and rhodamine 6G (R6G) by APC. The characteristic peaks of MB (456, 1630 cm^{-1}) and R6G (620 cm^{-1}) are highlighted in blue and yellow respectively.

Airborne species are usually non-static and could be highly dynamic due to environmental conditions such as wind and air disturbance. Hence, an isotropic SERS platform increases the flexibility and feasibility in detection, eradicating the need for substrate alignment or positioning. To demonstrate the isotropic property of our APCs, we systematically vary the direction from which MB aerosol is introduced into the APC spray. In our set-up, MB aerosol (0.5 µmol) is sprayed from the side and the back of SERS chamber. The APC affords highly reproducible and consistent SERS signals (~2000 counts) regardless of the analyte direction (Figure 3C, S11). In contrast, control 2D Ag substrate has only one active side and thus displays a dramatically poorer SERS performance. For instance, the 2D SERS substrate is only able to detect MB when the analyte is introduced from the side (~3000 counts), but not able to efficiently interact with the analyte (MB intensity < 50 counts) when it is introduced from the back. This result again exemplifies the importance of APC's 3D nature to achieve omnidirectional SERS detection of airborne species. Moreover, we are also able to perform the in-air identification of several volatile molecules such as 4-MBT vapors (vapor pressure, P_{MBT} = 0.807 mmHg), toluene and naphthalene aerosols (Figure 3D, Table S2-4 for peak assignments). Among the analytes, we notice that the colloidosomes generally produce better intensity with large conjugated analyte (methylene blue) and absorbing thiol 4-MBT. Nevertheless, we are able to differentiate each airborne molecule by their characteristic SERS fingerprints, thus highlighting the strength of SERS in providing molecular-level identification to circumvent false positive commonly encountered in commercial air sensors.

Stand-off Raman spectroscopy is an analytical tool that is often used in operational scenarios whereby the spectrometer is separated from dangerous (explosion/disaster) or inaccessible (waterfall/mountainous) sample sites.[10a] Using a Raman spectrometer equipped with long distance objective lens (Figure 4A-C, S12), we successfully perform an in-air stand-off SERS detection of aerosolized MB upon its interaction with APC at a distance of 200 cm (~ 600 counts and ~ 200 counts for 50 nmol and 5 nmol respectively, Figure 4D). On the other hand, a featureless spectrum is obtained when signals are collected from MB aerosol in the absence of APC, indicating stand-off Raman alone does not yield sufficient signals for trace analyte detection. Moreover, quantitative multiplex spectra exhibiting characteristic vibrational features of MB (1630 cm^{-1} peak) and R6G (620 cm^{-1} peak, Table S5) are obtained when a mixture of 50 nmol of MB and 5 nmol of rhodamine 6G are sprayed with APC (Figure 4E). This demonstrates the immense potential in the development and application of APC for real-life sensing of airborne samples, which often contain more than one chemical species. To our knowledge, this is the first in-air stand-off SERS sensing demonstration in a substrate-less manner. While the overall sensitivity and detection limit of the aerosol platform is not superior in comparison to static substrates due to the vigorous spraying condition, the ensemble benefits enabled by APC effectively eliminates the need of tedious laser focusing processes. Collectively, these insights are important for the further development of stand-off, substrate-less SERS technology in identifying explosives/ hazardous compounds in inaccessible sites.

In conclusion, we demonstrate aerosolized plasmonic colloidosomes (APC) as a 3D plasmonic cloud containing ~10^9 Ag nanocubes/cm^3 for in-air SERS detection of airborne species. The APC serves as an omnidirectional plasmonic active cloud that extend over centimeter -lengthscale. Our platform directly tackles the poor SERS-active depth and laser focal misalignment tolerance issues of conventional 2D SERS substrates. Its omnidirectionality property also brings about consistent SERS signals independently of laser and analyte introductory pathways. Importantly, we demonstrate the substrate-less multiplex detection of airborne liquid aerosols in a stand-off detection from a distance of 200 cm. These collective advantages of APC as an in-air SERS platform open up new horizons in fundamental SERS research, as well as detection technology in general for on-site and remote applications in environmental analysis and terrorism control.

Keywords: colloidosomes, stand-off Raman spectroscopy, airborne sensing, in-air surface-enhanced Raman scattering, aerosol.

[1] a) F. Röck, N. Barsan, U. Weimar, *Chemical Reviews* **2008**, *108*, 705-725; b) E.-C. Lin, J. Fang, S.-C. Park, F. W. Johnson, H. O. Jacobs, *Nature Communications* **2013**, *4*, 1636; c) J. Wang, L. Yang, B. Liu, H. Jiang, R. Liu, J. Yang, G. Han, Q. Mei, Z. Zhang, *Analytical Chemistry* **2014**, *86*, 3338-3345.
[2] C. Taylor, F. Lough, S. P. Stanforth, E. C. Schwalbe, I. A. Fowlis, J. R. Dean, *Analytical and Bioanalytical Chemistry* **2017**, *409*, 4247-4256.
[3] B. Miccoli, V. Cauda, A. Bonanno, A. Sanginario, K. Bejtka, F. Bella, M. Fontana, D. Demarchi, *Scientific Reports* **2016**, *6*, 29763.
[4] a) P. Xu, X. Li, H. Yu, T. Xu, *Sensors* **2014**, *14*, 19023; b) T. S. Biswas, N. Miriyala, C. Doolin, X. Liu, T. Thundat, J. P. Davis, *Analytical Chemistry* **2014**, *86*, 11368-11372.
[5] R. L. Grob, E. F. Barry, *Modern Practice of Gas Chromatography*, Wiley, **2004**.
[6] Y. Xiao, A. A. Lubin, A. J. Heeger, K. W. Plaxco, *Angewandte Chemie* **2005**, *117*, 5592-5595.
[7] a) G. C. Phan-Quang, H. K. Lee, X. Y. Ling, *Angewandte Chemie International Edition* **2016**, *55*, 8304-8308.
[8] a) Z. Zhang, W. Yu, J. Wang, D. Luo, X. Qiao, X. Qin, T. Wang, *Analytical Chemistry* **2017**, *89*, 1416-1420; b) M. Alba, N. Pazos-Perez, B. Vaz, P. Formentin, M. Tebbe, M. A. Correa-Duarte, P. Granero, J. Ferré-Borrull, R. Alvarez, J. Pallares, A. Fery, A. R. de Lera, L. F. Marsal, R. A. Alvarez-Puebla, *Angewandte Chemie International Edition* **2013**, *52*, 6459-6463; c) S. Yang, X. Dai, B. B. Stogin, T.-S. Wong, *Proceedings of the National Academy of Sciences* **2016**, 113, 268-273; d) S. Wang, L. L. Tay, H. Liu, Analyst 2016, 141, 1721-1733.
[9] B. D. Piorek, S. J. Lee, J. G. Santiago, M. Moskovits, S. Banerjee, C. D. Meinhart, *Proceedings of the National Academy of Sciences* **2007**, *104*, 18898-18901.
[10] a) J. Moros, J. A. Lorenzo, K. Novotný, J. J. Laserna, *Journal of Raman Spectroscopy* **2013**, *44*, 121-130; b) B. Zachhuber, C. Gasser, E. t. H. Chrysostom, B. Lendl, *Analytical Chemistry* **2011**, *83*, 9438-9442;
[11] a) V. Sivaprakasam, M. B. Hart, J. D. Eversole, *The Journal of Physical Chemistry C* **2017**, *121*, 22326-22334; b) O. Okponyia, B. M. Williams, K. Patton, D. A. Stuart, in *SPIE Defense, Security, and Sensing, Vol. 8366*, SPIE, **2012**, p. 9.
[12] G. C. Phan-Quang, H. K. Lee, I. Y. Phang, X. Y. Ling, *Angewandte Chemie* **2015**, *127*, 9827-9831.
[13] G. C. Phan-Quang, E. H. Z. Wee, F. Yang, H. K. Lee, I. Y. Phang, X. Feng, R. A. Alvarez-Puebla, X. Y. Ling, *Angewandte Chemie International Edition* **2017**, *56*, 5565-5569.
[14] D. Musso, C. Roche, T.-X. Nhan, E. Robin, A. Teissier, V.-M. Cao-Lormeau, *Journal of Clinical Virology* **2015**, *68*, 53-55.
[15] Y. J. Kaufman, D. Tanré, O. Boucher, *Nature* **2002**, *419*, 215.
[16] J. E. Mondloch, M. J. Katz, W. C. Isley Iii, P. Ghosh, P. Liao, W. Bury, G. W. Wagner, M. G. Hall, J. B. DeCoste, G. W. Peterson, R. Q. Snurr, C. J. Cramer, J. T. Hupp, O. K. Farha, *Nature Materials* **2015**, *14*, 512.
[17] H. K. Lee, Y. H. Lee, I. Y. Phang, J. Wei, Y.-E. Miao, T. Liu, X. Y. Ling, *Angewandte Chemie* **2014**, *126*, 5154-5158.

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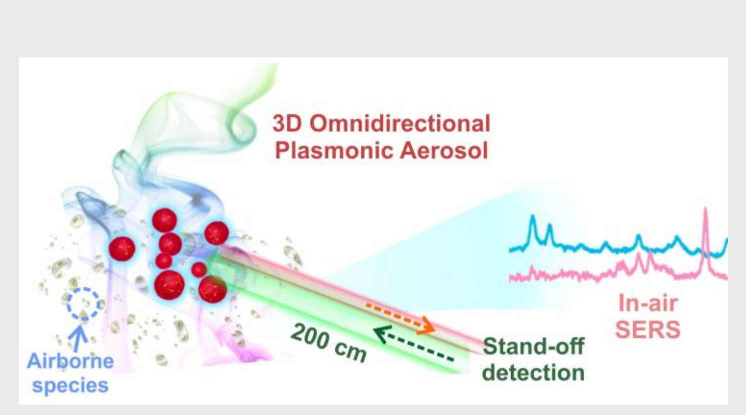

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