

Localized Collection of Airborne Analytes: A Transport Driven Approach to Improve the Response Time of Existing Gas Sensor Designs

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The detection of single binding has been a recent trend in sensor research introducing various sensor designs where the active sensing elements are nanoscopic in size. Currently, transport and collection of airborne analytes for gas sensors is either diffusion based or non-localized and it becomes increasingly unlikely for analytes to interact with sensing structures where the active area is shrunk, trading an increased sensitivity with a slow response time. This report introduces a corona discharge based analyte charging method and an electrodynamic nanolens based analyte concentration concept to effectively transport airborne analytes to sensing points to improve the response time of existing gas sensor designs. Localized collection of analytes over a wide range, including microscopic particles, nanoparticles, and small molecules, is demonstrated. In all cases, the collection rate is several orders of magnitudes higher than in the case where the collection is driven by diffusion. The collection scheme is integrated on an existing SERS (surfaceenhanced Raman spectroscopy) based sensor. In terms of response time, the process is able to detect analytes at 9 ppm (parts per million) within 1 s. As a comparison, 1 h is required to reach the same signal level when diffusion-only-transport is used.

1. Introduction

The desire to detect and identify trace amounts of airborne analytes, including combustible or toxic gases, small molecules, particles, viruses or bacteria with ever increasing sensitivity and selectivity continues to be one of the main drivers in sensor research.^[1–3] While the variety of sensing principles continues to grow, most principles share a common feature which is the requirement that the analyte adsorbs on the sensor surface or

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interacts chemically or physically with the sensing element for signal transduction to take place. For example, adsorption and analyte interaction is critical in sensors that use an electrochemically active surface,^[4] surface catalysis,^[5] a mesoporous metal-semiconductor-metal network.^[6] a chemically sensitive field effect transistor,^[7] a resonant mechanical beam,^[8] or optical methods such as fluorescence microscopy^[9] and SERS (surface-enhanced Raman spectroscopy),^[10,11] to name a few. A recent trend has been to increase the sensitivity to a point where it is possible to detect single binding events. Here the common approach has been to reduce the active sensor size, for example using nanometer sized transistors,^[12] resonating cantilevers,^[13] surface plasmons,^[14] and nanogaps.^[15] While it is possible to detect single binding events through the introduction of these highly miniaturized sensing points, the efficient transport of the airborne analytes to point-like struc-

tures has been a critical factor to improve the response time. Commonly, transport is driven by diffusion which is not the best approach. Specifically, basic gas laws provide a simple formula to calculate the number of analyte particles that impinge on a surface

$$N = R_{\rm i} A \Delta t = \frac{8.33 \times 10^{22} P_{\rm i}}{\sqrt{TM}} A \Delta t \tag{1}$$

where R_i is impingement rate (number m⁻² s⁻¹), P_i is partial pressure (Pa) of the analyte in a gas mixture which increases with its concentration, *T* is temperature (K), *M* is its molar mass (kg mol⁻¹), *A* is sensing area exposed to the analyte (m²), and Δt is exposure time (s). Considering Equation 1 there is a downside when the active sensor size is reduced to an extremely small value since the total number of analyte particles that actually interact with a point-like sensing structure approaches zero. In other words, it becomes increasingly unlikely for an analyte molecule to "find" and interact with an ever increasingly small sensor, trading an increased sensitivity with a slow response time.



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Instead of relying on diffusion-only-transport, this report evaluates the use of a directed force to overcome this problem and to transport the analyte from a distance away to predetermined sensing points at a higher rate. The approach is inspired in part by prior research in the aerosol community which has developed transport strategies to collect airborne particles using convection,^[16] thermophoretic,^[17] magnetic,^[18] and Coulomb forces.^[19,20] Among these candidates, Coulomb force based concepts have found a wide range of applications ranging from the collection of dust particles in air purifier and electrostatic filters^[21] to the manipulation of molecules in mass spectrometry.^[22] Most of these precipitation concepts including a cold substrate (thermophoretic)^[17] or an electrically biased metal plate (electrostatic precipitator)^[19-22] collect the materials over a relatively large surface and effective localized collection on nanoscopic sensing points has not yet been reported. One exception but outside of the field of sensors is employed in xerographic and nanoxerographic printers^[23,24] which use a charge patterned surface to attract nanoparticle locally as supposed to globally. Particular the recently gained knowledge in the field of Nanoxerography^[25–27] is relevant since it has become evident that localization of nanoparticles is possible with sub 100 nm lateral resolution. While the application^[23-27] was in the field of printable electronics it inspired the presented research

to evaluate if it is possible to employ similar schemes to the field of sensing of airborne species including small molecules. As a results this article reports and applies a localized electrodynamic precipitation concept to collect, spot and detect airborne species in predetermined locations with sub 100 nm lateral resolution, which can further concentrate the analytes and improve the response time of prior results.^[28,29] Specifically we introduce a new general approach which uses a corona discharge based analyte charging method in combination with an electrodynamic lens based analyte collection concept to transport airborne analytes to precise points on a surface to improve the response time of existing gas sensor designs by several orders of magnitude. The process, referred to as "corona/ lens-based-collection", enables us to transport analytes from a space that is centimeters away to specific sensing points on a surface with a minimal spot size approaching 100 nm. The approach is widely applicable demonstrating localized collection of i) microscopic particles (Kentucky blue grass pollen, 20 µm in diameter, $\approx 3 \times 10^{17}$ Dalton), ii) inorganic nanoparticles (CdSe nanoparticles, 4 nm in diameter, $\approx 1.4 \times 10^5$ Dalton), all the way down to iii) small organic molecules (Alq₃, 459.43 Dalton; anthracene, 178.23 Dalton; benzenethiol, 110.19 Dalton). In all cases we find that the collection rate is several orders of magnitudes higher than in the case where the corona/lens-based-collection is turned off and where collection is driven by diffusion FULL PAPER

only. To demonstrate and quantify how this general strategy improve the response time of an existing gas sensor design, the collection scheme is integrated on an existing SERS based sensor that is sensitive to the adsorption of benzenethiol. The particular SERS sensor employs the standardized AgFON (Ag film over nanosphere) substrate.^[30] We compare the results with and without corona/lens-based-collection and find that SERS signal is enhanced by three orders of magnitudes as a result of increased collection efficiency. In terms of response time, the process is able to detect analytes at 9 ppm (parts per million) within 1 s. As a comparison, 1 hour is required to approach the same signal intensity in the case where diffusion-only-transport (current standard) is used. The report also addresses the question of concentration ratio as a function of lens diameter whereby smaller diameters increase the concentration ratio.

2. Results

2.1. Corona/Lens-Based-Collection Procedure

Figure 1 describes the procedure of corona/lens-basedcollection. The airborne analyte enters the system from the left. When compared to conventional point to conducting plate



Figure 1. Schematic of advanced analyte transport and collection using corona discharge in combination with an electrodynamic lens based concentrator. Uniform collection across an extended charge dissipating sensor surface (bottom left) is extended to localized concentration and collection (bottom right) using a negatively charged dielectric. Corona discharge is used to charge the analyte particles (red) and the dielectric thin film (green) negatively, primarily through the attachment of electrons (insert). The depicted fringing field is a consequence of the buildup of surface charge and acts as an electrodynamic funnel. Analyte collection and concentration occurs at predetermined charge dissipating sensing points. The term "surface sensor" is used as a placeholder for all types of sensors that require analyte transport and adsorption on a sensing surface for signal transduction to take place.





Figure 2. A CAD drawing of the collection chamber and micrographs of corona/lens-basedcollection of various analytes representing a wide range of molecular weights (from 3×10^{17} to 1×10^2 Dalton). a) Insulating acrylic chamber with gas inlet, gas outlet, pointed electrode, sample port and sample tray. b) Optical microscope image of locally collected Kentucky blue grass pollen. c–e) Fluorescent microscope images of locally collected CdSe quantum dots, Alq₃ and anthracene. f,g) SEM images of locally collected tobacco smoke and benzenethiol. Inserts show SEM closeups. The scale bars are 200 µm in (b) and 1 µm in (c–g).

corona discharge experiments,^[31] this report adds a patterned dielectric thin film with openings to the conductive plate to form a single or arrays of lensing structures. The purpose of the introduced dielectric lensing structures is to provide an electrodynamic funnel to transport the analyte from a distance away to desired sensing points on a surface with sub 100 nm placement accuracy. The purpose of the corona based charging system is to achieve a high degree of charging, which in combination with the electrodynamic lens based transport, increases the localized collection rate of the analyte far



beyond levels reported so far.^[28,29] Depicted is the case where the analyte (red dots) is surrounded by N2 (blue dots) which unless stated otherwise represents the carrier gas we used. From an analyte collection point of view we compared two designs: i) one where the collection is uniform across extended surface region (global sensing region, bottom left) and ii) one where the analyte is delivered to certain sensing points (localized sensing points, bottom right). The delivery to certain sensing points involves the introduction of electrodynamic lens arrays which are defined by a patterned dielectric layer (green) with openings to a charge dissipating sensing device layer. The actual dimensions will be discussed later. To charge and transport the analyte to predetermined locations. a corona discharge surrounding a pointed electrode is used.[32,33] In brief, positive ionization occurs within a fairly thin ionizing plasma region,^[34] where the electric field is sufficiently strong to cause the emission of electrons through the photoelectric effect which subsequently produce positive gaseous species and secondary electrons through impact ionization.[32] Beyond this region, the electric field diminishes rapidly and electrons with energy lower than the ionization energy will attach to neutral analyte particles yielding negatively charged analyte particles (non-ionizing plasma region). These negatively charged species move downwards through the depicted unipolar region (negative) until they reach the grounded or positively biased sensing structures. In the case where the dielectric layer is introduced, the dielectric becomes negatively charged through the deposition of electrons. The subsequent buildup of charge leads to the depicted fringing field which under steady state condition diverts the charged analyte to the desired charge dissipating sensing points.^[23] These predetermined sensing points can hold any conductive surface sensor including a SERS sensor discussed later.

2.2. Corona/Lens-Based-Collection of Various Analytes

Figure 2 provides a CAD drawing of the collection chamber and micrographs of the samples testing the collection of various analytes ranging from 3×10^{17} to 1×10^2 Dalton. In the depicted set of experiments, optical, fluorescence and scanning electron microscopy was used as a detection method to provide a visual response of the analyte distribution. All analyte collection experiments use the collection chamber depicted in Figure 2a which was machined out of an insulating acrylic block to provide a 3

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 $cm \times 3 cm \times 3 cm$ cavity, a 10 mm in diameter gas inlet, a 3 mm in diameter gas outlet, a pointed copper electrode 5 mm above the sample, a sample port and a sample tray. In the particular set of experiments, periodic electrodynamic lens arrays were used. The lens arrays are defined using a patterned 500 nm thick layer of insulating photoresist (s1805, Microposit) with 200 µm square (Figure 2b) or 1 µm circular (Figure 2c-g) openings to a flat silicon substrate. All chips were 5 mm wide and 10 mm long. All analytes were introduced to the testing chamber using 2000 sccm (standard cubic centimeters per minute) of N₂ as a carrier gas (Supporting Information, Figure S1). The SEMs and optical/fluorescent micrographs illustrate the range of analyte particles that can be collected. Specifically, we tested gas mixtures (aerosols) containing large microscopic particles Kentucky blue grass pollen (20 μ m in diameter, \approx 3 \times 10¹⁷ Dalton, Figure 2b), fluorescent CdSe nanoparticles (4 nm in diameter, $\approx 1.4 \times 10^5$ Dalton, Figure 2c), all the way down to small molecules such as fluorescent Alg₃ (459.43 Dalton, Figure 2d), fluorescent anthracene (178.23 Dalton, Figure 2e), non-fluorescent tobacco smoke (nicotine, tar, etc., Figure 2f), and non-fluorescent benzenethiol (110.19 Dalton, Figure 2g).

From an experimental point of view the following general observation were made: First, independent of analyte type or size, it is possible to transport, concentrate, and collect the various analytes at predetermined sensing points using the introduced corona/lens-based-collection process which is remarkable considering the large range of analytes we tested. In terms of molecular weight the results represent a range of 3×10^{17} to 1×10^2 Dalton. Second, the structures and at least some of the relevant physical properties remain intact. For example: i) shape of the pollen particles; ii) fluorescent characteristics of the CdSe quantum dots, Alq3 molecules and anthracene molecules; and iii) spectral response due to Raman scattering (detailed later), remain intact. Third, the localized collection rate is large compared to the commonly used approach where the particles deposit randomly on the surface by diffusion-only-transport. In the case of benzenethiol, discussed in more detail below, the collection rate was determined to be 3 orders of magnitude faster than diffusion. This is remarkable since it means that the response time in a sensor application will be improved. The faster transport and concentration reduce the required collection time from hours to seconds. In the depicted results 5 s was used for CdSe quantum dots and Alq₃ and 1 second for the remaining samples. To reach such short exposures times it was necessary to use a special chamber design depicted in Figure 2a which uses a sample tray that can be shifted back and forth between two sealed positions. In the particular design the corona discharge occurs only as the grounded sample is shifted to the exposure position which is underneath the negatively biased -5 kV tip electrode. Moreover, we monitored the actual exposure current and time using an oscilloscope that measures the voltage drop across a 1 k resistor that is connected in series with the high voltage source. The discharge currents were 1300, 260, 380, 1000, 125, 600 µA in the case of pollen, CdSe quantum dots, Alq₃, anthracene, tobacco smoke, benzenethiol, respectively (Supporting Information, Figure S2).

The locally collected analyte amount is found to be related to the diameter and pitch of the lens forming elements. Figure 3 presents results to investigate the amount of analyte as a function of opening size and pitch. The images show SEM images (left) next to corresponding AFM topography scans (right) of a sample exposed to a benzenethiol gas mixture containing 9 ppm benzenethiol in N₂ for 1 second. The depicted nanolens arrays in this study were prepared using an e-beam lithography patterned 90 nm thick layer of PMMA with circular openings (3 µm, 2 µm, and 1 µm in Figure 3a and 8 µm, 6 µm, 4 µm, 2 µm, and 1 µm in Figure 3b) on a silicon substrate. Generally, we find that the locally collected analyte amount increases with a reduced opening size. In the illustrated Figure 3a the thickness of the precipitates increases from 25 nm, to 57 nm, to 180 nm with 3 μ m, 2 μ m, and 1 μ m openings, respectively. Table 1 provides a more detailed analysis of the AFM data and provides the average diameter, height, and volume of the precipitates in the three regions. Interestingly, in terms of volume each point collects about the same amount. In other words a constant material flux is "squeezed" into exceedingly small areas yielding tall structures containing the analyte. All patterns we have tested so far followed this general trend. The material concentration factor is roughly inversely proportional to the opening (Supporting Information, Figure S3), which means that it is possible to adjust the concentration ratio and consequently response time in a gas sensor application to a desired value.

The case of the benzenethiol is particular interesting for further studies since it is substantially different from the other analytes we tested. The CdSe quantum dots, Alq₃, and anthracene are fluorescent substances that simplified the detection which is not the case for benzenethiol. The benzenethiol is the smallest analyte in the test series. Most importantly it is a liquid at room temperature (vapor pressure: 1.4 mmHg at 300 K). However, the recorded precipitates discussed in Figure 3 were solid which means that the substance cannot be pure benzenethiol. The recorded deposits formed as a result of exposure to a gas mixture containing 9 ppm benzenethiol in N2. However, this does not completely eliminate the potential of oxidation. Moreover, the samples are exposed to air for further characterization. In air benzenethiol decomposes and produces sulfur oxides, biphenyl, diphenyl sulfide and dibenzenethiophene,^[35] which are all solids at room temperature; such reactions are not integral part of the collection process presented here since they will occur in a diffusion-only-transport as well. Nevertheless, it is interesting since it raises the question of whether or not benzenethiol is present in the precipitates which will be evaluated in the following section where we integrate the localized transport mechanism with a SERS based gas sensor.

 Table 1. Average precipitation amount collected in 1 second in terms of diameter, height, and volume based on Figure 3a.

	Ø 3 μm openings	Ø 2 μm openings	Ø 1 µm openings
Diameter [µm]	2	1.2	0.7
Height [nm]ª)	25 (36 monolayers)	57 (81 monolayers)	180 (257 monolayers)
Volume [µm³]	0.079	0.064	0.069

^{a)}We used 0.7 nm as a monolayer thickness^[35] to provide a relative measure of the height in terms of number of monolayers.

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1μm 200nm 1μm 200nm C C C C C 00000 00000 0000 000000 0 1µm 200nm 10um 200nm 10µm

Figure 3. Behavior of analyte concentration as a function of opening size and pitch. a) SEM images (left) and corresponding AFM topography scans (right) showing localized collection of benzenethiol using 10 × 10 arrays of 90 nm deep wells on a 4 μ m pitch with 3 μ m, 2 μ m, and 1 μ m diameter openings and corresponding 25 nm, 57 nm, 180 nm analyte collection height. b) SEM image (left) and AFM topography scans (right) of a different region with 8 μ m, 6 μ m, 4 μ m, 2 μ m, and 1 μ m diameter openings. In the tested range, the observed analyte concentration factor is roughly inversely proportional to the opening area.



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2.3. Corona Discharge Driven Transport Integrated on an Existing SERS Gas Sensor: Response Time Improves by Three Orders of Magnitude

The following section demonstrates and quantifies how this general strategy improves the response time of an existing gas sensor design. Specifically we integrated the collection scheme on an existing SERS based sensor that is sensitive to benzenethiol. As far as we know, prior SERS based gas sensors used diffusion to transport the analyte to the sensing surface. Figure 4 compares the coronabased-collection scheme with the diffusion-only-transport (current standard) in case of a SERS sensor and shows schematics of the testing conditions (top), next to corresponding Raman microscopy intensity maps at 1573 cm⁻¹ (middle), and resulting spectra (bottom). The particular SERS sensor employs an AgFON substrate, which is considered the standard in the field of SERS detection. In brief, the AgFON surface enhancing layer is a closely packed self-assembled layer of 200 nm in diameter silica nanospheres where the top half is coated with 20 nm/180 nm Cr/ Ag film. To maintain the original state of the AgFON surface the collection concept was first tested without the integration of the dielectric lensing structures discussed before. Instead it used only the corrugated nanostructured Cr/Ag film. This film supports the application of the required voltage between the pointed electrode and the substrate and no additional modifications are necessary. All substrates were 5 mm wide and 10 mm long. Analog to prior experiments we used the 9 ppm of benzenethiol in N₂; prepared using 10 sccm of N₂ flowing through a benzenethiol containing bubbler further diluted using 2000 sccm of N₂ (Supporting Information, Figure S1). The Raman intensity at 1573 cm⁻¹ was recorded under four exposure conditions: a) 1 s long exposure using diffusion-only-transport vielding 1-2.5 counts (red, 2 was used in the relative comparison), b) 1 second long exposure using corona-based-collection under -4 kV (135 µA) yielding 230 counts (blue, 115 times more), c) 1 second long exposure using corona-based-collection under -5 kV (450 µA) yielding 570 counts (green, 285 times more), and d) 1 h long exposure using diffusion-only-transport yielding 470 counts (black, 235 times more).



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the two experiments (green and black plots) is virtually identical. Identical signal-tonoise level means that the process does not degrade or improve the inherent noise level of the sensor itself, which is what one would expect. Only the response time is improved due to a faster transport of the molecules to the sensor. Identical spectral response also means that the collection process maintains some of the relevant physical properties. The locations of the three major peeks remain consistent with the published values for benzenethiols.^[10] Considering the additional results presented in Figure 4, we conclude that the solid precipitates previously discussed in Figure 3 contain the analyte as well; this was an open point in the discussion before.

2.4. Further Enhancements Using the Electrodynamic Lens Based Concentration Concept

The integration of the nanolens concept on the SERS sensor was found to be more challenging than originally thought. In analogy to Figure 2, it requires the integration of a dielectric layer with openings to AgFON surface layer. While we have tested several methods involving standard photolithography it has become evident that the required spin coating, development, and washing steps quench the plasmonic properties of the AgFON thin film we intended to maintain. An alternative working method is presented in Figure 5; here a 0.5 mm thick PDMS film with an opening of 1 mm (Figure 5b) and subsequently 0.5 mm (Figure 5c) was used as the lens forming element (Supporting Information, Figure S5). The reason to use PDMS is that it creates a good contact upon placing it onto the SERS layer, it can be removed during optical characterization, it can be reused, and most importantly it will not alter the sensing area; a disadvantage is the relative large size of the lens forming element. Like in the previous experiment (Figure 4) the sensor was exposed to 9 ppm

of benzenethiol in N2 for 1 s and the SERS data was recorded using identical recording conditions. Figure 5 (bottom) depicts the corresponding Raman microscopy intensity map of benzenethiol at 1573 cm⁻¹ band shift and spectra without and with application of the lensing layer. This result extends the size of the lens forming element to the mm-range (the opening sizes presented previously ranged from 200 µm to 1 µm). Despite this difference the results show the same general trend whereby the signal intensity increases from 570 to 1725 and 2445 counts with the introduction and reduction of the opening size. This represents 285, 862, 1222 times the signal

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illustrating schematics of the testing conditions (top), next to corresponding Raman microscopy intensity maps at 1573 cm⁻¹ (middle), and resulting spectra (bottom): a) diffusion-only-transport with 1 second long exposure, Raman intensity is close to zero and an insert provides details; b) corona-based-collection (-4 kV) with 1 second long exposure; c) corona-based-collection (-5 kV) with 1 second long exposure; d) diffusion-only-transport with 1 hour long exposure. Raman intensity maps show raw unprocessed data recorded at 1573 cm⁻¹ using the same microscope settings. Raman spectra represent an average recorded by the instrument over a 5 μ m imes5 µm sized region; an offset (up down) correction has been applied for the spectra to overlap at the beginning of the graph; peak height measurement and relative comparison is not effected.

Using diffusion-only-transport the collection rate is fastest in the beginning (a few counts per second) and slows down over time following a time-dependent Langmuir kinetics approximated by 500 counts × $(1 - \exp(-\frac{t}{18 \min}))$ (Supporting Information, Figure S4). Independent of this detail we find that the corona-based-collection is always several orders of magnitudes faster. For example, to obtain the same Raman signal intensity observed using a 1 second long collection using a corona current of 450 µA (Figure 4c) requires more than one hour using diffusion-only-transport (current standard, Figure 4d). The spectral response and noise level of

1μm 1µm 1μm 600 573 0 100 200 300 400 500 600 Counts Intensity (counts) ,075 Counts 990 1620 rel. 1/cm 0 990 1080 1170 1260 1350 1440 1530 1620 Raman shift (rel. 1/cm) Figure 4. SERS sensor comparing diffusion-only-transport with corona-based analyte collection,



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Figure 5. Schematics and experimental results comparing different dielectric electrodynamic lens based concentration concepts: a) coronabased-collection (–5 kV) with 1 s long exposure without a lens (identical to condition (c) in Figure 4); b) corona/lens-based-collection (–5 kV) with 1 s long exposure with a Ø1 mm PDMS lens; c) corona/lens-based-collection (–5 kV) with 1 s long exposure with a Ø0.5 mm PDMS lens. The corresponding Raman microscopy intensity maps at 1573 cm⁻¹ and resulting spectra were recorded in the center of the nanostructured sensor surface in (a) and center of the opening in (b,c). Like in Figure 4, Raman spectra represent an average recorded by the instrument over a 5 μ m × 5 μ m sized region. Instrumental settings were identical to the results presented in Figure 4 and a relative comparison between the two experiments is possible.

recorded using diffusion-only-transport where we recorded 1-2.5 counts (2 was used in the relative comparison) during the same time.

3. Conclusions

We generally find that diffusion-only-transport (current standard) is several orders of magnitude slower when compared with the corona/lens-based-collection process. While the experimental results are clear, there are two open questions on the theory when we compare:



i) the actual charge dissipation rate *J*_{current} of charged species (corona/lens-based-collection)

$$J_{\text{current}} = \frac{I_{\text{corona}}}{A_{\text{local}}} = \begin{cases} 5.6 \times 10^{15} e \text{ cm}^{-2} \text{s}^{-1} \text{ In Figure 5, condition (a)} \\ 4.7 \times 10^{17} e \text{ cm}^{-2} \text{s}^{-1} \text{ In Figure 5, condition (b)} \\ 1.9 \times 10^{18} e \text{ cm}^{-2} \text{s}^{-1} \text{ In Figure 5, condition (c)} \end{cases}$$
(2)

ii) with the impingement rate R_i of neutral analyte molecules based on Equation 1 (diffusion-only-transport)

$$R_{i,diffusion} = \frac{8.3 \times 10^{22} P_i}{\sqrt{TM}} \xrightarrow{9 \text{ ppm}=0.9 \text{ Pa}}_{300 \text{ K},110.19 \text{ g mol}^{-1}} > 1.3 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$$
(3)

First, looking at the actual collection rate using Equation 2 and the SERS signal in Figure 5, we noticed that the SERS signal is not directly proportional to the amount of analyte adsorbed on the surface. For example, the opening in condition (c) collects roughly 339 times more material locally than the SERS sensor without lensing structure in condition (a). Yet the signal increases only by a factor of 5. At the same time we believe that Equation 2 is correct since previous discussed AFM measurements found that the material concentration factor is roughly inversely proportional to the opening area (Figure 3). The only explanation as to why the signal increased by only a factor of 5 is that the SERS signal is already saturated due to excessive analyte coverage. It is known that the EM fields associated with the excitation of plasma oscillations decays within a few molecular distances from the surface^[35] which explains the observed non-linear response. In the overall theme of things this is perhaps a small detail considering that the signal counts increased by 3 orders of magnitudes when compared to diffusion-onlytransport. Second, it is interesting to compare the calculated impingement rate of neutral analyte molecules (diffusion-onlytransport) in Equation 3 with the charge dissipation rate of charged species (corona/lens-based-transport) in Equation 2. Doing so we find that the impingement rate is larger than the charge dissipation rate in condition (a) and (b) or on the same order as in condition (c). At first one would anticipate that this cannot be correct. However, it is an important reminder since it points out that the impingement rate is not equal to the rate of analyte adsorption; instead a sticking coefficient smaller than 1 needs to be considered. Many molecules including organothiols reacting with a noble metal surfaces suffer from a low sticking probability.^[36,37] For example, the benzenethiol initial sticking coefficient is calculated to be 1.50×10^{-5} ; the detailed derivation can be found elsewhere.^[10] So considering diffusion-only-transport mechanism the rate of molecular adsorption is approximately 10¹³ cm⁻² s⁻¹, which is sufficiently smaller than the rate of charge dissipation which was on the order of 10^{15} cm⁻² s⁻¹ without lens, and 10^{17} cm⁻² s⁻¹ with a single 1 mm in diameter lens, and 10¹⁸ cm⁻² s⁻¹ with a single 0.5 mm in diameter lens. We should also point out that the rate of charge dissipation is not equal to the rate of analyte uptake in the corona/lens-basedcollection case; there should also be a sticking coefficient in this case. In any event the introduced corona/lens-based-collection mechanism leads to a much faster analyte collection rates

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which means that the sticking coefficient in this case has to be larger than diffusion-only-transport value of 1.50×10^{-5} .

Based on the current results the introduced corona/lensbased-collection approach increases the amount of locally collected material by at least 3 orders of magnitude. While this appears an incredibly large number we think that this is a conservative estimate. For example in terms of increased signal intensity the corona/lens-based-collection method led to a 3 orders of magnitude higher signal when compared to the diffusion-only-transport. Considering that the SERS signal saturates under excessive material coverage the intensity measurement would suggest that the actually collected material exceeds the 3 orders of magnitude estimate. For example, if we go back to the AFM height measurement where we used 1 µm sized lens arrays on a 4 µm pitch, the deposits were 257 monolayers tall and formed within 1 s. If we compare this height and time with a diffusion-only-transport case where it takes at least 1 minute for a monolayer to form (using a molecular absorption rate of 10¹³ cm⁻² s⁻¹ identical to previously published values and a monolayer packing density of $\approx 6.8 \times 10^{14}$ cm⁻² on flat Ag^[10] we receive a 4 orders of magnitude faster transport. The previously used wording of "at least three orders of magnitudes" reflects this knowledge.

In conclusion, various nanostructured sensors currently aim for or claim single molecular detection by a reduction of the active sensor size. An equally important challenge, however, can be found in the question "whether the analyte will find the nanoscopic sensing sites". The reduction in the size will ultimately require research on methods which enable localized analyte delivery. The reported corona/lens-based-collection concept is a first step in this direction. The approach is not limited to the SERS sensor or analytes that we have tested in this study and should provide equal improvements in terms of response time in other sensor designs. Others adapting this concept should anticipate at least 3 orders of magnitude improvement in response time over system that use diffusion-only-transport. Moreover, the ultimate level of improvement is not yet known. This would require testing of a wider range of opening sizes and pitch distances in terms of the lens design. It would also be beneficial to test a wider range of analyte molecules with poor or high sticking coefficients. We also see a potential for the introduction of an active matrix type analyte collection system that collects analytes at various points on a substrate at different times. The minimal 1 s long exposure time is presently a practical limitation and not representative of the minimal exposure time that is required to identify the various analytes and concentrations we tested in this study.

4. Experimental Section

Aerosol Preparation: Various types of aerosols were used in this study. Specifically, we tested gas mixtures (aerosols) containing large microscopic particles Kentucky blue grass pollen (Sigma-Aldrich), fluorescent CdSe nanoparticles (Lumidot), all the way down to small molecules such as fluorescent Alq₃ (Sigma-Aldrich), fluorescent anthracene (Sigma-Aldrich), non-fluorescent tobacco smoke (nicotine, tar, etc.), and non-fluorescent benzenethiol (Sigma-Aldrich). The corresponding aerosol preparation methods are (Supporting Information, Figure S1): i) Pollen (a loose powder) was carried into the collection chamber using 2000 sccm N₂ flow. It is used to show collection ability of an allergenic substance. ii) Alq₃/CdSe quantum dots containing aerosol was generated using atomization. Specifically, Alq₃ (5 mg) was first dissolved in tetrahydrofuran (THF, 1 mL) solution. The solution was then dropped on an atomizer (an ultrasonic vibrating mesh) at a constant rate. The atomization rate was approximately 0.01 mL s^{-1} . The aerosol was further diluted with 2000 sccm N₂ which also serves as a carrier gas to transport the analyte into the collection chamber. The calculated concentration (using 459.43 Dalton) was ≈73 ppm. The aerosol containing CdSe quantum dots were prepared using the same method. Here a CdSe quantum dots solution (5 mg mL⁻¹ in toluene) were used. The atomization rate was approximately 0.01 mL s^{-1} which was further diluted with 2000 sccm N_2 . The calculated concentration (using 1.4×10^5 Dalton) was 238 ppb (parts per billion). iii) Anthracene containing aerosol was generated by thermal evaporation. Anthracene is a white solid in powder form with a melting point of 210-215 °C. In this experiment, anthracene was thermal evaporated at 250 °C. The evaporation rate was estimated to be 0.2 mg s⁻¹ by measuring the weight reduction in certain amount of time. The carrier gas was 2000 sccm N₂. The calculated concentration (using 178.23 Dalton) was ≈750 ppm. iv) Tobacco smoke containing aerosol was generated using smoldering. A cigarette was smoldered at a constant rate using 10 sccm air. The smoke was then diluted using 2000 sccm N₂. We have not further analyzed the composition of the aerosol which is known to contain more than 2000 chemicals. A primary constituent is tar and nicotine which are soft solid and liquid like substances at room temperature. v) Benzenethiol containing aerosol was generated using a bubbler based evaporation. Specifically, the benzenethiol was introduced using a conventional bubbler approach with a flow rate of 10 sccm N_2 in the bubbler line. The vapor pressure of benzenethiol is 1.4 mmHg at room temperature which is equivalent of 1800 ppm of benzenethiol molecules inside the bubbler

and 9 ppm after dilution with 2000 sccm N₂. *AgFON Substrate Fabrication*: Silicon wafers were first put in HF solution for 30 s to remove the native oxide. The wafers were rinsed in acetone, methanol, IPA, DI water, and further cleaned in piranha etch at 120 °C for 30 min, and then in 5:1:1 ratio of H₂O:NH₄OH:H₂O₂ for 30 min to make the surface hydrophilic. Surfactant-free, silica nanosphere suspensions (Bangs Laboratories, Inc., 200 nm, 4 wt%) was further diluted in ethanol (1:1 volume ratio), which served as a spreading agent. The suspension was dropped onto a water surface which yields a surface layer of silica beads. The Langmuir-Blodgett method was used to compact the beads and to transfer the beads to the target wafer. After drying the surface for 30 minutes, the AgFON standard substrate was completed through e-beam evaporation of 20 nm/180 nm Cr/Ag films to form the plasmonic cap layer.

PDMS Lens Fabrication: 184 silicone elastomer base (Sylgard, 20 g) and 184 silicone elastomer curing agent (Sylgard, 2 g) were well mixed in a plastic cup. The cup was then placed in a desiccator to degas for 30 minutes. The mixture was then slowly poured into a petri dish followed by another 30 min degas process. The amount of the mixture was controlled so that the thickness of the film was kept 0.5 mm. The PDMS was then cured in an oven at 70 °C for an hour. After curing, the film was cut into 5 mm wide and 10 mm long pieces. The lens was made on PDMS film by a 1 mm or 0.5 mm hole punch (Supporting Information, Figure S5).

SERS Characterization: SERS spectra and corresponding Raman microscopy intensity maps were acquired using a confocal Raman microscope system (Witec Alpha 300R) equipped with an objective lens (Nikon 100×, 0.90 NA in air). A 514 nm argon ion laser was used as a laser source, which was set to a constant power of ~2 mW for all SERS measurements in this report. The scattered light was analyzed using a 600 mm⁻¹ spectrometer grating with a spectral resolution of about 3 cm⁻¹. The collection area was defined by a 5 μ m ×5 μ m region with a 10 × 10 sampling density. The collection spectrum was analyzed using a VIS-NIR spectrophotometer (Ocean Optics, USB4000 VIS-NIR spectrometer, QR400–7-UV–vis reflection probe). The reflectance absorption spectrum of AgFON was collected and used for the chosen wavelength (514.5 nm).



Supporting Information

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Supporting Information is available from the Wiley Online Library or from the author.

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