Microfluidic/SERS Detection of Trace Explosives

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We have developed a chemical detector combining Free-Surface microfluidics (FSF) with surface-enhanced Raman spectroscopy (SERS) to measure air-borne molecules with extremely high sensitivity (parts per trillion) and molecular specificity. The free-surface of a microfluidic material stream allows polar airborne molecules to absorb directly into a microchannel flow, and provides a barrier to non-polar, water-insoluble airborne molecules. Explosives molecules are polar and readily absorb into the microchannel flow, whereas many interferent molecules do not absorb. Once absorbed into the flowing liquid within the microchannel, the explosives molecules combine with SERS-active nanoparticles, thereby enhancing the Raman signal by approximately 8-10 orders of magnitude.

The molecules adsorbed into the microchannel flow are detected with surface-enhanced Raman spectroscopy (SERS), an effect first observed in 1978[i], which is a highly amplified form of Raman spectroscopy that occurs when molecules reside near appropriately nanostructured surfaces of certain metals. Aside from the alkali metals, silver, gold or copper are ideal SERS-enabling metals, less ideally indium, aluminum and platinum and even less so other metals. Currently, the best reported results are obtained when the SERS-active substrate is composed of closely arrayed, interacting nanoparticles or nanostructures so constructed as to allow the analyte or a portion thereof to occupy small crevices between particles with dimensions in the range 0.5 to 40 nm. The enhancement in signal and therefore in analysis sensitivity brought about by placing the analyte in close proximity to the SERS-active materials is large (up to ~7-10 orders in magnitude), so large that Raman spectroscopic signals arising from single analyte molecules or a small number of analyte molecules may be recorded under favorable circumstances[ii]. This feature makes SERS potentially among the most sensitive analysis techniques with molecular identification capabilities. Moreover, Raman is a vibrational spectroscopy that can provide molecular identity and quantification.

SERS-Based Substrates for Explosives Detection offers the potential for high sensitivity and molecular specificity in a field-portable platform. To date, most SERS applications for explosive vapor and particle detection have used nano-engineering SERS-active substrates that are exposed directly to air. This approach has achieved ppb sensitivity levels of DNT (Spencer et al.) [iii]. Baker & Moore[iv] review advancements in

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SERS for detecting trace materials. The performance characteristics of nano-engineered SERS-active substrates is an area of ongoing research in the SERS community.

Instead of using a nano-textured SERS-active substrate exposed directly to air, we have taken a novel approach, whereby the SERS enhancement is produced when colloidal Ag nanoparticles suspended in a microfluidic channel aggregate under the influence of the analyte (such as an explosive molecule). As a result of the nanoparticle synthesis process, ions such as citrate or nitrate are weakly and non-specifically bonded to the silver nanoparticle surface. This maintains a semi-stable colloidal suspension. However, when certain analyte molecules (such as aromatic nitro- compounds) are introduced to the colloidal solution, which form stronger bonds to the Ag nanoparticles than the original surface ions, the surface ions are replaced by the analyte molecules. This process is further amplified via the redeployment of the electrical double layer associated with the surface ions, thereby allowing more analyte to bind to the Ag nanoparticles. The aggregation process is illustrated in Fig. 4.

As with many molecules, all the explosive molecules we have tested to date interact in solution with Ag particles, and replace the charged species present at the surface of colloidal metal particles[v] promoting aggregation of the metal (silver) nanoparticles into closely packed clusters ideal for SERS. Initially monomers are formed, followed by dimers, then trimers, and higher order aggregates.
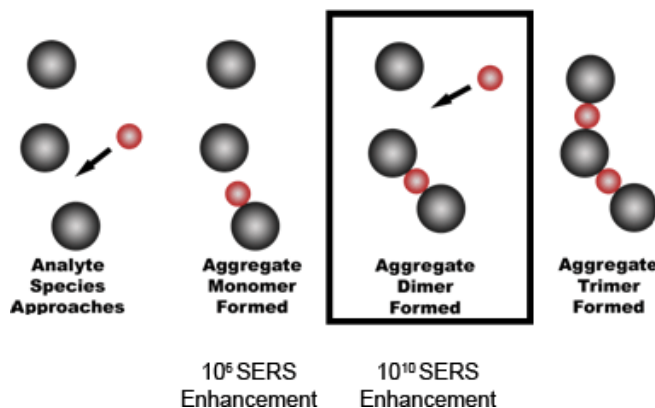

Analyte Species Approaches   Aggregate Monomer Formed   Aggregate Dimer Formed   Aggregate Trimer Formed

10^6 SERS Enhancement 10^{10} SERS Enhancement

Figure 1. The aggregation process of Ag colloidal particles to create the SERS effect. When the colloidal Ag particles interact with analyte (e.g. explosive) molecules, monomers are initially formed. The SERS enhancement of an aggregate monomer is approximately 10^6, which is similar to SERS substrates. Within a few seconds, dimers are formed, and the SERS enhancement increases by additional four orders of magnitude to approximately 10^{10}

Molecules bound to a single nanoparticle (monomer) exhibit SERS enhancements ~10^6. In our microfluidic system, the nanoparticle monomers aggregate to dimers then to larger aggregates within a few seconds. As a result, we achieve SERS enhancements approximately 4 orders of magnitude larger than what monomers[vi] produce. This provides the very high sensitivity that is exhibited by the detector.

Figure 2 illustrates the integrated free-surface microfluidic platform combined with SERS for molecular-specific detection. The free-surface flow utilizes surface tension to create pressure-driven flow. Once absorbed in the fluid in the microfluidic channel, the airborne molecules or particles adsorb on the silver nanoparticles, causing them to aggregate. This leads to a greatly-enhanced SERS effect. As the particles advect downstream, colloidal particles continue to aggregate: monomers form dimers, and dimers form trimers, etc. A Raman system can probe the free-surface channel anywhere along the stream and can therefore select the streamwise position where the maximum concentration of dimers is present. This allows us to measure a wide variety of explosive vapors and particles, including DNT, TNT and picric acid.
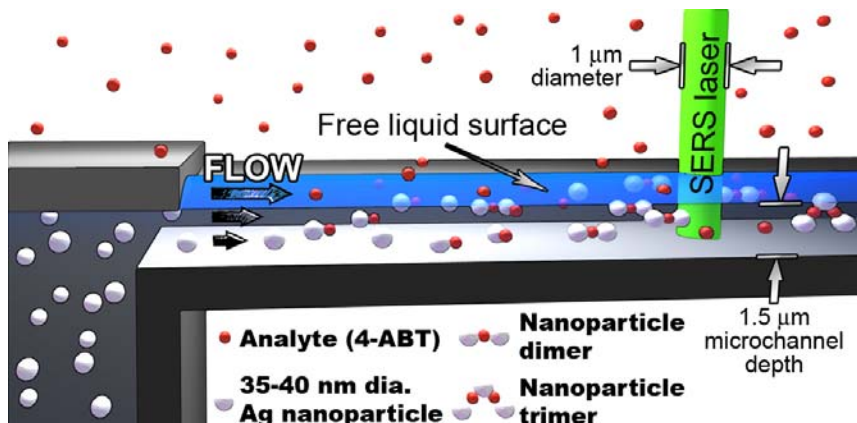

Figure. 2. A solution of silver nanoparticles flows towards a 514nm laser for Raman spectroscopy. The nanoparticles aggregate around molecules adsorbed from the nearby atmosphere, causing electromagnetic amplification of the Raman signal.

Current explosives detectors and SERS-active substrates exposed to air become degraded and are spoofed by contamination from ambient chemicals such as gasoline & jet fuel vapor, shoe polish, and perfume. We have tested DNT in saturated vapor (parts per thousand) of volatiles such as gasoline, ethanol, acetone, toluene and acetone, and observed no degradation in signal as a result of the interferents. For comparison, we also measured 2,4-DNT directly in solution with Ag nanoparticles. The resulting SERS spectrum agrees very well with other 2,4-DNT measurements in vapor phase in the presence of air and saturated gasoline vapor (which is parts per 1/3). We also observe clear differences between the spectra obtained from 2,4-DNT and 2,6-DNT.

A preliminary experiment is described below to demonstrate the operation of our SERS-based microfluidic system for high sensitivity detection of airborne explosives. Gas-phase sensing was tested by establishing a low partial pressure of 4-aminobenzenethiol (4-ABT) (a molecule similar in structure to TNT) in the vicinity of the microchannel by placing a solid sample of the 4-ABT approximately 3 cm from the open sol flow within a containment box (10 cm diameter × 0.6 cm tall) which helped collect the 4-ABT vapor. The central portion of the flowing colloidal solution (with a cross-section approximately

1 µm diameter by 1.5 µm deep) was monitored by confocal Raman spectroscopy. The 50 mW continuous wave 514.5 nm (SpectraPhysics 164) laser was focused through a 50x lens for 1 second. A typical Raman spectrum of 4-ABT is shown in Figure 7. The sol exposure time to 4-ABT increases linearly with position down the microchannel since the flow velocity is steady and maps to microchannel position as $t = x_e/v_c$, where t is sol exposure time to the gaseous species, x_e is the streamwise sol travel distance since exposure, and v_c is the average colloid flow velocity in the microchannel. The flow adds another degree of freedom to SERS analysis whereby the distance from $x_e = 0$ to the interrogation position corresponds to substrate exposure time to analyte.
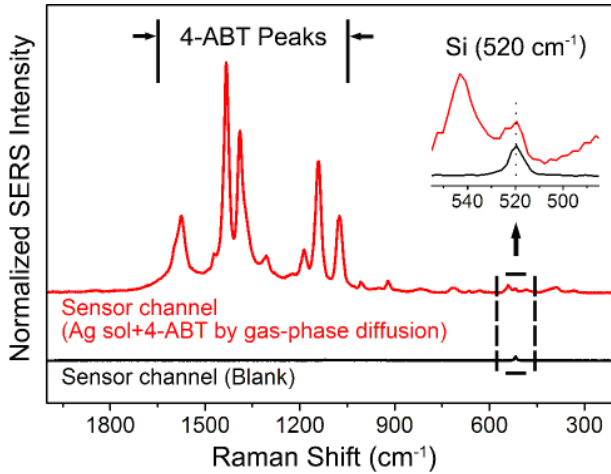

Figure 3. Characteristic 4-ABT spectrum obtained by SERS in the open channel sol microflow (red line). Background SERS spectrum of the bare channel with no sol or 4-ABT present (black line). SERS measurements were collected over a 1 second integration period with ~50 mW of laser power.
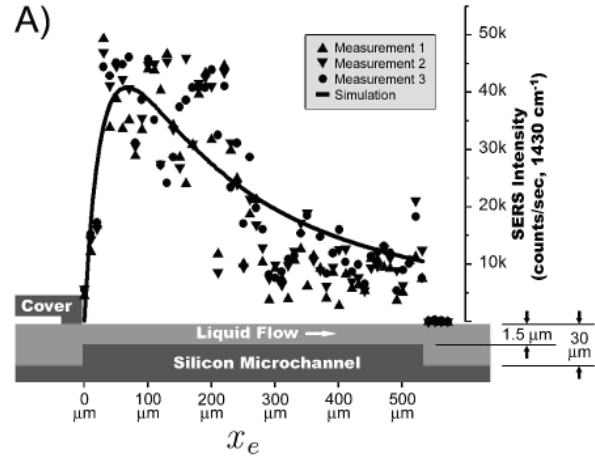
Figure 4. The measured SERS intensity is shown above a diagrammatic side view of the microchannel (triangles, inverted triangles, circles). The aggregation simulation (solid line) assumes SERS intensity is due exclusively to nanoparticle dimers.

The magnitude of the 1435 cm⁻¹ Raman band of the 4-ABT as a function of distance down the microchannel is shown by symbols in Fig. 4. The flowing liquid was covered for values of $x_e < 0$ to avoid premature sol exposure to gas-phase analyte. The flow was uncovered for values of $x_e > 0$, allowing sol exposure to analyte at a gaseous concentration of 4-ABT we estimate to be ~300 µM. Nanoparticle transport is dominated by convection since the microsystem Peclet number is $Pe = v_c L /D = 5.4 \times 10^3$, where L is a typical length scale, and D is the nanoparticle diffusivity. Three independent SERS intensity measurements were taken stepwise at 10 µm intervals between microchannel positions $x_e = 0$ µm and $x_e = 570$ µm. Diffusion-driven exposure of the flowing sol to 4-ABT eliminated the need for manual sample injection, producing an autonomous environmental chemical sensor.

The surface-enhanced Raman signal intensity is greatly increased in the 1.5 µm deep region of the microchannel system. In this region, the microchannel depth is matched to the penetration depth of the SERS excitation laser and the collection optics. Furthermore,

confinement of analyte to the thin liquid flow eliminates signal losses from diffusion of analyte away from the interrogation region. The sensor signal diminishes in the $30 \, \mu m$ deep downstream fluid reservoir at values of $x_e > 530 \, \mu m$. In this region, a slower bulk flow rate results from a twenty-fold increase in depth, causing the rapid formation of larger and therefore less SERS-active nanoparticle clusters.

Nanoparticles are known to aggregate when exposed to species such as the 4-ABT used in this study[vii], whereby single nanoparticles tend to aggregate around species of dissimilar charge in solution forming larger and larger aggregates. Figure 4 shows a maximal SERS response between distances of $x_e \sim 50 \, \mu m$ to $x_e \sim 150 \, \mu m$. The average velocity was $v_c = 60 \, \mu m/s$, corresponding to sol exposure times of 1 - 3 s to generate the maximum SERS signal intensity.

In conclusion, a free-surface microflow was designed to operate as an explosives vapor detector by the use of SERS. The flowing nanoparticle suspension within the microflow produces the surface enhancement of Raman spectroscopy needed to accurately detect and identify explosive vapors which diffuse into the channel. By designing a microsystem which produces a flowing microstream at a fixed velocity, the nanoparticle aggregates interrogated at a fixed position within the microchannel are on average exposed to the gas-phase analyte for a fixed period of time. Since the nanoparticle aggregation effect is a temporal process controlled by nanoparticle aggregation kinetics, the degree of nanoparticle aggregation is a function of position along the streamwise direction of the microflow. Therefore the maximal SERS intensity can be obtained by scanning the streamwise direction of the microflow to determine the position at which the nanoparticle aggregate structure is mostly dimers, which produce the greatest SERS intensity in comparison to non-dimerized nanoparticle aggregates.

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