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Detection of volatile organic compounds by surface enhanced Raman scattering

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ABSTRACT

We present the detection of volatile organic compounds directly in their vapor phase by surface-enhanced Raman scattering (SERS) substrates based on lithographically-defined two-dimensional rectangular array of nanopillars. The type of nanopillars is known as the tapered pillars. For the tapered pillars, SERS enhancement arises from the nanofocusing effect due to the sharp tip on top. SERS experiments were carried out on these substrates using various concentrations of toluene vapor. The results show that SERS signal from a toluene vapor concentration of ppm level can be achieved, and the toluene vapor can be detected within minutes of exposing the SERS substrate to the vapor. A simple adsorption model is developed which gives results matching the experimental data. The results also show promising potential for the use of these substrates in environmental monitoring of gases and vapors.

Keywords: Surface Enhanced Raman Scattering, spectroscopy, sensing, nanostructures

1. INTRODUCTION

There is need for compact, field-deployable, sensitive, and molecule-specific detection techniques for volatile organic compounds (VOCs) such as toluene due to their prevalence as ozone-producing air-pollutants as well as importance in certain national security applications. The VOCs have found widespread use in industry, particularly as solvents; and yet they possess significant health risks to humans and there is thus strong interest in their rapid detection in the vapor phase. Surface-enhanced Raman scattering (SERS) is attractive for this purpose because of its high sensitivity, molecule-specific fingerprinting and compatibility with real-time, in-situ remote sensing [1, 2]. There is also increasing interest in using SERS for gas and vapor detection and sensing [3-6]. The substrate on which the SERS is performed is often the critical component for successful detection and identification of the targeted molecules. The common ways to produce SERS-active substrates such as thin metal island films [7], electrochemical roughening [8], metallic nanoparticles [9], and self-assembly [10] often results in structures that are random in nature and/or are limited in control of their structural geometry. This can lead to issues with uniformity, reproducibility and repeatability that hinder the large-scale use of SERS. It is also difficult to optimize the geometry of these substrates to attain the maximum possible enhancement. A solution to these challenges is through the use of substrates that are precisely defined regular nanostructures obtained by lithography [11, 12]. Furthermore, a lithographically-defined SERS substrate can offer more degree of freedom in the design and tuning of its geometrical parameters, thereby allowing optimization that can lead to higher SERS enhancement factor.

By exposing Ag-coated tapered nanopillars SERS substrate to toluene in the vapor phase, strong SERS signals are directly observed at various substrate temperatures ranging from -10 C to 40 C. Results from kinetics studies of the SERS signal show that the toluene adsorption saturates to a certain coverage level at temperatures above its dew point and the SERS data conform to Langmuir model of monolayer adsorption. At temperature below the dew point, the SERS kinetics exhibit more complicated behavior, and is consistent with a multilayer adsorption process as the toluene vapor condenses onto the substrate. Furthermore, our data shows that the adsorption is strongly dependant on concentration of the toluene vapor. A theoretical model of the adsorption process on our substrate is developed which enables us to quantitatively extract physical insight from the data and thus deduce fundamental limits of detection of the device. The methodology and model can be extended to other analytes of interest such as inorganic gases and explosives.

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We have developed SERS substrates based on lithographically-defined two-dimensional rectangular array of nanopillars. As these substrates are created by well-established, high-precision planar nanofabrication techniques and processes, their geometrical parameters can be precisely controlled and fine-tuned, thereby allowing optimization of their performance. Another advantage of lithographically-defined SERS substrates is that they can be fabricated with high uniformity and reproducibility over large area, and are well-suited for mass-production. In addition, these nanopillars are closely-spaced (pitch = 350 nm here) and thus allow for a very high density of SERS 'hotspots' that can be pre-defined. In principle, the hotspot density is only limited by the resolution of nanolithography, which is itself constantly improving due to demands of the semiconductor industry.

The Tapered Nanopillars (TNP) substrates are designed to have tapered pillars with sharp tip on top (ideally, cones) and are over-coated with metal (e.g. Ag) deposited at an angle. They have previously shown SERS enhancement factor of around 10^8 [14] due to the nanofocusing effect. SERS experiments were carried out on these substrates using toluene vapor as the analyte. There is important need for compact, field-deployable, sensitive, and molecule-specific detection techniques for volatile organic compounds (VOCs) such as toluene due to their prevalence as air-pollutants as well as importance in national security applications. The VOCs have found widespread use in industry, particularly as solvents; and yet they possess significant health risks to humans and there is thus increasing interest in their rapid detection. Our results show that saturated toluene vapor can be detected effectively at room temperature by the TNP substrate and there is promising potential for the use of these substrates in detecting VOCs.

2. EXPERIMENTS

2.1 Fabrication of nanopillars SERS substrates

The nanopillars substrate was fabricated by holographic interference lithography [15] over 4-inch fused silica wafers that are coated with half-micron thick photoresist. The laser wavelength for the lithography is 413 nm and the dose is around 40 mJ/cm^2. The resultant photoresist structure is a two-dimensional periodic array of pillars with pitch of 350 nm and diameter of 150 nm. The exposed wafers are cleaved into smaller pieces for subsequent processing. The patterned photoresist acts as the etching mask in a subsequent step of ion beam milling.

To obtain the tapered pillars, the silicon dioxide is over-etched in the ion beam milling process. As there is side-way etching, an undercut will start to develop under the photoresist. Through careful testing and calibration, the desired tapered pillar shape with sharp tips on top can be achieved. Pillar height can be varied between 250 nm to 1000 nm. A 40 nm layer of silver (Ag) was then e-beam evaporated onto it at an angle of 30^0 to make it SERS-active.

2.2 Bubbling of Toluene

Nitrogen carrier gas was fed using Teflon tubings and bubbled into toluene liquid (Sigma-Aldrich, purity > 99.9 %) held in a glass bubbler at a temperature of 20 ^{0}C. The flow is controlled by a regulator set at 2 psi. The toluene vapor is assumed to saturate the resultant gas mixture [16]. This gas mixture was then fed into a gas cell (Linkam THMS600) with our SERS substrate placed on top of a temperature-controlled stage inside the gas cell. The gas flow is continuous and exits from the gas cell into an exhaust.

2.3 Spectroscopy

For the toluene vapor measurement using the TNPs, a diode-pumped solid state laser (OEM Lasers) emitting at 532 nm was used. A Kaiser Optics fiber probe (MK II) delivers the laser light through a window on the gas cell, and the Raman signal was collected by the same fiber probe. The delivered laser power after the fiber probe is measured to be 4 mW. Focusing is achieved by vertically moving the gas cell, which is fixed on a precision x-y-z translational stage. The SERS signal is fed into a grating based spectrometer (Kaiser Optics), which spectrally dispersed the signal onto a TE-cooler-cooled (-70 ^{0}C) CCD camera (Princeton Instruments). Data collection was done through the WinSpec software.

3. RESULTS AND DISCUSSION

3.1 SERS of toluene vapor using Ag-coated tapered nanopillar (TNP) substrate

The Ag-coated TNP substrates have previously shown enhancement factor of around 10^8 with benzenethiol (BT) monolayer [14]. As toluene has a similar molecular structure as BT, we continued on to use the TNP substrate for detecting toluene vapor. It is also previously reported that out of several metal coatings, Ag provides the largest enhancement for toluene vapor and a number of other organic molecules [3], suggesting that it is more favorable to binding with the molecules.

The SERS spectrum of toluene vapor (mixed with N_2 as the carrier gas) obtained at substrate temperature of 25 ^{0}C using the TNP substrate are shown in fig. 1. The concentration of the toluene vapor in the gas mixture is estimated to be around 3% (by partial pressure) assuming that the toluene vapor saturates the N_2 carrier gas in the bubbling process. The spectrua were taken every 2 mins. after the toluene/N_2 gas mixture flows for 15 mins. The laser wavelength is 532 nm and the measured laser power is 4 mW. The data acquisition time is 60 secs.

Fig. 1 shows that while many of the characteristic Raman peaks of toluene are recognizable in the SERS spectrum, it is somewhat different from the Raman spectrum. The characteristic Raman peaks of toluene at 1002, 1031, 1605 (due to C=C stretching) were shifted slightly in the SERS spectrum to 994, 1024, and 1594, respectively. The 1210 peak in the bulk Raman spectrum (due to ring-CH3 stretching) maintained its position in the SERS spectrum, but is broadened. Interestingly, the 522 (ring deformation) and 789 (ring-CH3 stretching) peaks in the bulk Raman spectrum were suppressed in the SERS spectrum (and may be shifted), while a new, broad band at 637 appears. This band is very repeatable, and it is not previously reported. It is not clear at this point if it is due to the shifting of the 622 Raman peak (ring deformation). These features strongly suggest that the SERS spectrum is not due to the Raman scattering of liquid toluene condensed onto the TNP substrate, but is indeed due to adsorbed toluene molecules that interact with the Ag surface to shift original peaks as well as produce new peaks.

Furthermore, the kinetics of the various SERS peaks were given in fig. 2. The results show that the toluene vapor SERS signal increases monotonically with time and saturates after around 12 mins. at substrate temperature of 25 ^{0}C. The SERS signal also increases with decreasing substrate temperature.

The SERS spectra at various substrate temperatures were given in fig. 3 and the kinetics of the 994 peak was given in fig. 4. At 0 ^{0}C, which is well below the condensation temperature, there is visibly condensation of the toluene onto the substrate after around 10 mins. The 3 strongest peaks in the SERS spectrum are still apparent and persistent even after the toluene vapor flow is stopped and the sample kept in pure N_2 for 3 days. Nevertheless, they can be completely purged out by heating the sample at around 110 ^{0}C for 5 mins. These features suggest that the SERS signal can be dynamically controlled by thermal adsorption and desorption cycle.

It is known that a sharp metallic tip can confine electromagnetic field tightly at its tip due to the lightening rod effect, leading to large localized field enhancement [19]. The metallic coating on the TNPs provides the support for excitation of surface plasmons resonances for the lightening rod effect. The TNP thus serves as a nano-focusing device that adiabatically focus the light energy onto the tip of the pillars. This nano-focusing effect thus creates the SERS “hot spots” [20] necessary for the electromagnetic field enhancement. Simulation results by density functional theory have previously shown that the interaction between a binding organic molecule and metal surface can lead to a shift in Raman peaks and contribute additional enhancement to the SERS signal due to presence of a strong electrostatic built-in field [21]. This interaction can thus lead to drastic changes in SERS spectrum as compared to Raman spectrum. Current work includes extending the application of the TNPs to other gases.

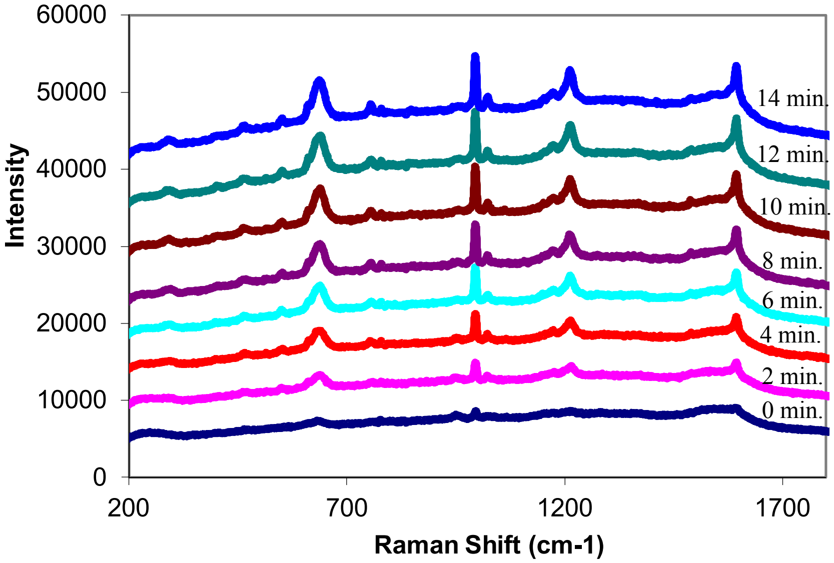

Fig. 1. Temporal Evolution of toluene vapor SERS spectrum at 25 ^{0}C.

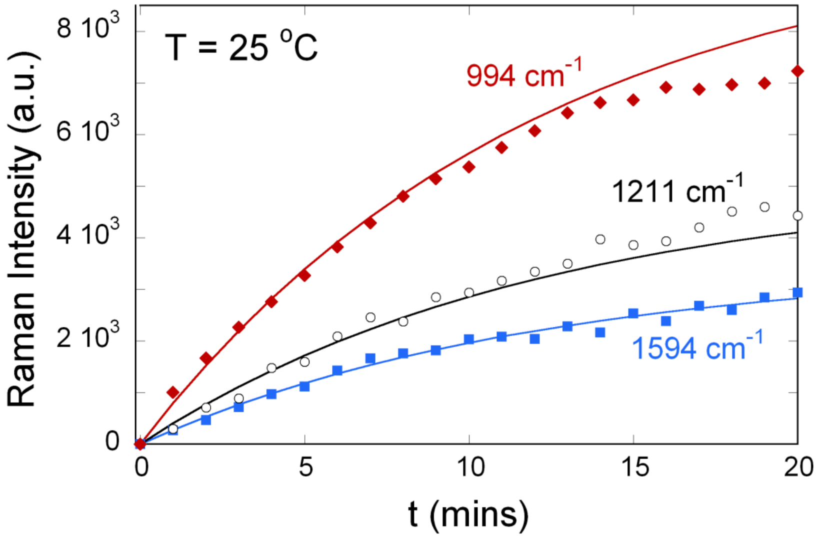

Fig. 2. Kinetics of SERS peaks of toluene vapor adsorbed onto TNP substrates

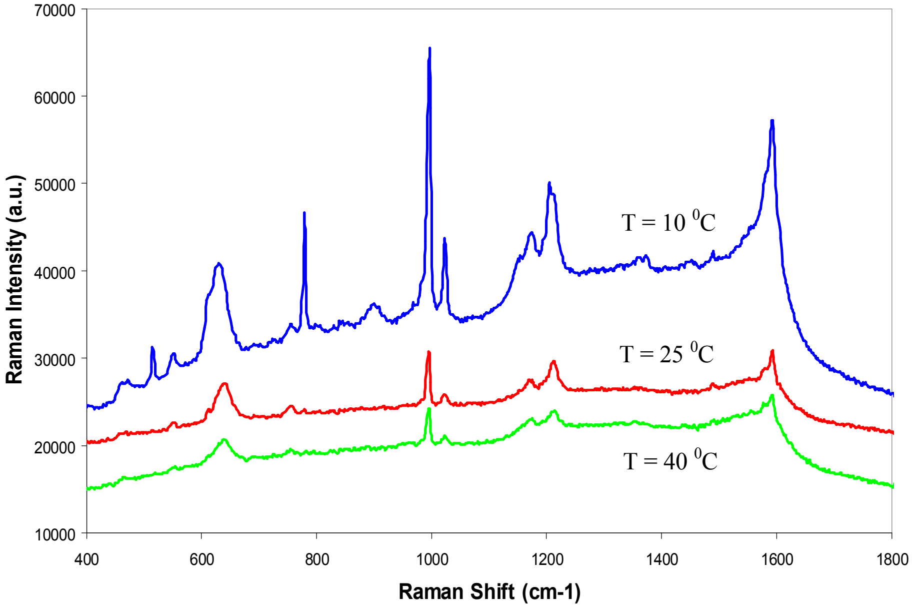

Fig. 3. Toluene Vapor SERS at various substrate temperatures

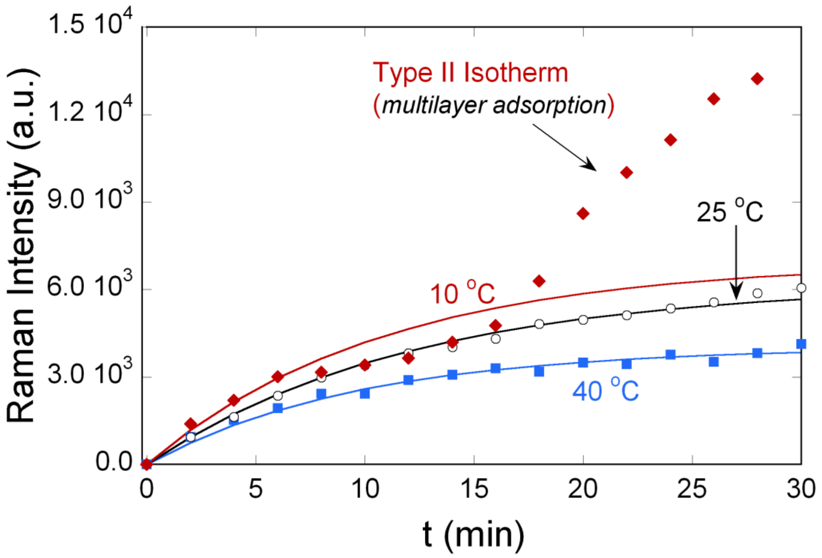

Fig. 4. Kinetics of 996 cm^{-1} peak at various substrate temperatures

3.2 Modeling of toluene molecule adsorption on silver

A simple 1-site model for the adsorption and desorption of toluene molecules on/from the silver SERS substrate can be developed. It assumes that the silver surface is uniform with only a single type of binding sites. Since all analytes are in identical binding configurations in this simple model, the SERS intensity is proportional to the analyte coverage.

The adsorption and desorption times are given by:

$$\tau_{ads} = \frac{\sqrt{2\pi m k_B T}}{p \alpha s}\ ; \tag{1}$$

$$\tau_{des} = \frac{h}{k_B T}\frac{\Lambda^2}{\alpha}\frac{\{Z_{vib}(\nu_{eff})\}^6}{Z_{rot}}\exp(\Delta E_{binding}/k_B T) = A(T)\exp(\Delta E_{binding}/k_B T) \tag{2}$$

The fractional surface coverage as a function of time (t) and equilibrium coverage θ_{eq} are then given by:

$$\theta(t) = \frac{\tau_{des}}{\tau_{ads}+\tau_{des}}\left[1-\exp\{-t(1/\tau_{ads}+1/\tau_{des})\}\right]; \tag{3}$$

$$\theta_{eq} = \lim_{t\to\infty}\theta(t) = \frac{\tau_{des}}{\tau_{ads}+\tau_{des}} \tag{4}$$

where the symbols are defined as:
θ = Fractional monolyer coverage
t = Time
τ_{ads}, τ_{des} = Adsorption & desorption times
T = absolute temperature, k_B = Boltzmann constant
m = Mass of a Toluene molecule
p = Partial pressure of incoming gas
α = Adsortion area/ Toluene molecule
s = sticking coefficient; could be T-dependent
Z_{vib}, Z_{rot} = Vibrational and Rotational partition functions
Λ = Thermal de Broglie wavelength
$\Delta E_{binding}$ = Binding energy of Toluene to the Ag surface.

Table 1. Computed parameters from adsorption model

	10 °C	25 °C	40 °C
s (sticking coeff)	$1.70\text{x}10^{-10}$	$1.38\text{x}10^{-10}$	$1.15\text{x}10^{-10}$
τ_{ads} (min)	11.1	14.0	17.2
τ_{des} (min)	434.6	91.2	22.4
θ_{eq}	0.98	0.87	0.56

From the calculations, the binding energy of toluene to silver nanopillars is ~ 18.9 kcal/mol, which is nearly half-way between DFT-computed values using GGA (~ 7 kcal/mol) and LDA (~ 30 kcal/mol). The sticking coefficient is 4-5 *orders-of-magnitude* smaller than that for a strongly chemisorbed molecule such as benzenethiol (somewhat consistent with the binding energy being about a factor of half smaller). The sticking coefficient appears to *decrease* with *increasing* temperature. This effect is completely opposite to that observed for benzenethiol.

4. CONCLUSIONS

Toluene vapor can be detected by the Ag-coated TNP substrates at room temperature. The observed toluene vapor SERS spectrum shows slightly shifted Raman peaks as well as new strong SERS band at 637 cm^{-1}. The results show the promising potential for these types of substrates in robust, high-sensitivity environmental sensing using SERS for detecting chemicals and gases.

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