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Flexible Plasmonic Sensing Substrates and their application in Explosive Sensing
by
Sang hyun Justin Bae

A thesis presented to the School of Engineering
of Washington University in St. Louis in partial fulfillment of the
requirements for the degree of
Master of Science

May 2017

Saint Louis, Missouri

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Acknowledgments

I would like to first thank Dr. Srikanth Singamaneni his guidance. His exemplary work ethic, expertise and experience greatly impacted my research.

I would also like to thank Ms. Sirimuvva Tadapelli and Mr. Keng-Ku Liu as well as the members of the Soft Nanomaterials Laboratory for their help and support.

Special thanks go to the Office of Naval Research.

Lastly, I would like to thank the students, staff, and distinguished faculty within the Mechanical Engineering and Materials Science department for helping me through this process.

Sang hyun Justin Bae

Washington University in St. Louis

May 2017

Dedicated to my family and friends for their support.

ABSTRACT

Flexible Plasmonic Sensing Substrates and their application in Explosive Sensing

by

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Master of Science in Mechanical Engineering

Washington University in St. Louis, 2017

Research Advisor: Professor Srikanth Singamaneni

With an increasing use of improvised explosive devices in combat and terrorism, there is an urgent need for novel methods of trace explosive detection that can provide an inexpensive and effective solution. This study focuses on the development of such platform using flexible surface enhanced Raman scattering (SERS) substrates. Gold nanorods(AuNR) functionalized with peptides selective to explosive molecules, trinitrotoluene(TNT) and dinitrotoluene (DNT) were immobilized on various substrates to fabricate a flexible SERS substrate. The peptide conjugated AuNRs can detect TNT and DNT vapors, and the cysteamine conjugated nanorods could detect TNT in aqueous solution down to 100 nM.

Additionally, we also proposed the design of a 3D structures to improve the sensitivity of SERS detection.

The synthesis of 3D nanostructures involves the growth of zinc oxide nanowires on paper substrates, followed by the adsorption of gold nanorods on the ZnO nanowires. The resulting structure had a higher surface area and higher number of AuNRs within the laser footprint compared to paper adsorbed with AuNRs enabling and are expected to exhibit higher SERS enhancement. The ZnO-AuNR paper substrate showed higher SERS sensitivity than planar silicon and plasmonic paper surfaces. The unique design of zinc oxide – paper hybrid substrate improved the sensitivity of SERS based detection. The advances in the development of unique SERS substrates and the design of the recognition elements for explosive detection is a critical step towards to the design of SERS based chemical sensors.

Chapter 1

Background

1.1 Need for Development

The detection of explosive like trinitrotoluene (TNT) and dinitrotoluene (DNT) is imperative in counter-insurgency and counter-terrorism activities. The detection of TNT is especially important because TNT is widely used because of its low melting point, stability, low sensitivity to stimuli such as impact, friction, temperature, and its relatively safe methods of manufacture [1]. The detection of DNT is also an important target for explosive detection since it is an intermediate in the manufacture of TNT [2]. The environmental effects of these nitroaromatic groups are debilitating, not to mention that the effect they have on human health is detrimental [3,4].

In the status quo, various spectrometry techniques such as ion mobility spectrometry or mass spectrometry, and chromatography techniques such as gas chromatography are used to detect these compounds [5]. These techniques often require bulky and expensive machinery, and are time consuming, thus are ineffective in rugged environments including but not limited to the battlefield [5]. Among the more recently developed techniques, surface enhanced Raman spectroscopy (SERS) provides an incredibly powerful for chemical sensing because it requires significantly less sample preparation, can be portable, and can sense single molecular compounds, and is very robust and can be used in harsh conditions [6,7,8]. These advantages of SERS can be further bolstered by the wide spectrum of application of flexible and stable substrates such as paper. [ref] Paper provides ideal, low cost platform for chemical detection because it is commonly found in most regions, is biodegradable,

and is non-toxic [9,10]. In fact, this group has already reported the use and advantages of paper based SERS substrates.[9,10,11] Paper based SERS substrates have significant advantages over their rigid counterparts such as high specific surface area, excellent wicking properties, and cost reduction[11].

1.2 LSPR and SERS

Plasmons are collective and cohesive oscillations of free electrons at the interface of a metallic substance and dielectric material [12]. In a metal, countless free electrons exist that can react easily to external stimulus, such as an electromagnetic wave. In the case of nanoscale metal colloids, these plasmons are localized, hence they are called localized surface plasmons. When localized plasmons are excited by the irradiation of electromagnetic waves, they are stimulated into an excited vibrational state to first release the energy of the excitation to return to ground state. The frequency of this energy release is highly dependent on the morphology of the nanoparticles and the dielectric environment around the nanoparticles, which means the amounts of energy absorbed and then released depends on the vibrational energy of the molecule near the nanoparticles [13,14]. This phenomenon is called a Raman Scattering. During Raman scattering, there is an energy transfer between the EM wave(light) source and the molecule under irradiation. The amount of energy that is transferred is unique to the molecular structure, which means the frequency of light that is scattered is also unique to the molecular structure. Raman spectroscopy capitalizes on such resonances, called Localized Surface Plasmon Resonance(LSPR) to identify the chemical structure of the compounds under study.

The disadvantage with Raman spectroscopy is that the available area for scattering, called the scattering cross-section, is $\sim 10^{-30} \text{ cm}^2$, which is almost 14 magnitudes smaller than a typical fluorescent dye [6]. In fact, it requires more than one hour to sense a single Raman photon from a 1 um^2 sample under 100 mW of light irradiation [6]. To remedy this, SERS is used to amplify the signal. To amplify the

Raman signal, the analyte needs to be near metallic nanoparticles including but not limited to gold or silver. When the localized surface plasmons of these metallic nanoparticles are excited with an electromagnetic wave with a frequency that matches the frequency of the plasmons, the electromagnetic wave is scattered or absorbed. This frequency is called the resonance frequency. SERS enables researchers to harness this resonance to amplify the signal by a factor of 10^8 for an ensemble of molecules and as much as 10^{15} for single molecules [15]. SERS is incredibly powerful because it is a label free and nondestructive technique that is relatively insensitive to the wavelength of excitation and suffers no interference from water. The robustness of SERS makes it an attractive choice for analyte detection, and an effort to improve the limit of sensitivity and develop a platform that is reliable, reproducible and uniform.

Chapter 2

Plasmonic Solution Sensing of Commonly Used Explosive Compounds

2.1 Introduction

In this chapter, we report results from cysteamine and peptide modified SERS substrate for the selective detection of TNT. Utilizing peptides as recognition elements over antibodies has significant benefits such as the enhanced chemical and environmental stability of peptides compared to antibodies [16]. We utilized gold nanoparticles with surfaces modified with cysteamine or TNT specific binding peptides, then adsorbed them to paper to fabricate SERS substrates for TNT sensing in solution. Cysteamine modified AuNR based SERS substrate could detect aqueous solutions of TNT down to concentrations of 100 nM. The substrate also shows relatively small standard deviation, given the simplicity in its fabrication. TNT and DNT specific binding peptides were also tested as functionalities.

2.2 Sample Preparation

2.2.2 Gold Nanorod Synthesis

Gold nanorods (AuNR) were chosen as the nanostructure to be adsorbed to paper because of their high refractive index sensitivity leading to a drastic increase in the relative scattering efficiency [17,18]. Their optical properties can also be easily changed by tuning the aspect ratio, thus changing the LSPR wavelength. [19,20] AuNR were synthesized using a modified seed-mediated approach [21]. Gold seed

solution was first prepared by reducing 10 mL of 0.25mM HAuCl₄ in a 0.1 M aqueous cetyltrimethylammonium bromide(CTAB) solution under magnetic stirring at 800 rpm. 0.75 mL of 10 mM freshly prepared ice-cold Sodium borohydride(NaBH₄) was added to reduce HAuCl₄ to produce the seeds, where the color of the seed solution would change from golden yellow to brown. Growth solution prepared by mixing 0.9 mL 10 mM HAuCl₄, 19 mL of 0.1 M CTAB, 0.2 mL of 10 mM Silver nitrate(AgNO₃), 0.11 mL of 0.1M ascorbic acid, and 24 ul of seed solution then left in the dark undisturbed for 14 hours. The color of the resulting mixture changed to green once the synthesis was complete. Before use, the solution was centrifuged at 8000 rpm for 20 minutes to remove excess CTAB, then dispersed in nanopure water. This centrifugation was repeated twice. The resulting LSPR extinction spectrum of the AuNR showed its characteristic longitudinal peak at ~670 nm and transverse peak at ~510 nm.

a

2.2.3 Synthesis of 2D SERS Substrate

1. Paper-based SERS substrates

The synthesized AuNRs were adsorbed onto laboratory grade filter paper (Whatman grade No.1, 180 uM thick) by immersing a strip of paper in a 2mL centrifuge tube filled with 1.8 mL of twice washed, either conjugated or non-conjugated AuNR solution. The filter paper was left in the nanorod solution overnight, then removed from the solution. Once removed, the paper was then washed with nanopure water to release any loosely bound nanorods, then were dried with a stream of nitrogen.

2. Silicon-based SERS Substrates

AuNRs were adsorbed on (3-Mercaptopropyl) trimethoxysilane (MPTES) modified silicon substrates. The silicon substrates were first cleaned with piranha solution (mixture of 3:1

sulfuric acid : hydrogen peroxide), thoroughly washed with nanopure water and dried with a stream of nitrogen, then immersed in 1% MPTES solution in ethanol for an hour. The substrates were then removed from the MPTES solution, placed in ethanol for 30 minutes to remove excess MPTES, then rinsed with ethanol, then water. The washed substrates were dried for 30 seconds with a stream of nitrogen. Once the substrates were completely dry, they were exposed to an aqueous solution of AuNRs and left overnight. After the AuNRs were adsorbed to the silicon, the substrates were washed thoroughly with nanopure water to remove any loosely bound nanorods, then dried with a stream of nitrogen.

2.2.4 Functionalization

1. TNT/DNT binding peptide

Selective binding peptides with the sequence HPNFSKYILHQR (DNT peptide) and WHWQRPLMPVSI (TNT peptide) were purchased from Genscript. The peptide sequence was found using the phage display technique [44]. The selective binding peptides were modified with three glycine groups and once cysteine group at the C terminus to impart conformational stability and chemically conjugate with the surface of gold through a Au-SH chemical bond. 1mM solution of both peptides were made in 100 uL quantities in centrifuge tubes, then frozen at -20°C to be used in the future. The tubes were thawed before each use. Increments of 2uL of peptide solution were added to 1mL of AuNR solution until the local surface plasmon resonance (LSPR) shift no longer occurred. The resulting peptide-conjugated AuNR solution was adsorbed to the different substrates, respectively.

2. Cysteamine

10 μ L of 10 mM aqueous solution of cysteamine was added to 10mL of once-centrifuged AuNR solution, then placed on the shaker for 4 hours to be conjugated. Once shaking was complete, the solution was centrifuged at 8000 rpm for 10 minutes to remove excess CTAB. Respective substrates (paper and silicon) were exposed to the resulting solution for adsorption.

3. p-aminothiophenol (pATP)

5 μ L of 10 mM pATP solution in ethanol was added to 10mL of twice centrifuged gold nanorods in aqueous solution and placed on the shaker for 2 hours to be conjugated [36]. The conjugated nanorods were adsorbed onto filter paper overnight.

4. PEGylation of AuNR (HS-PEG-NH₂)

10 μ L of 1mM of amine-PEG-thiol(HS-PEG-NH₂) was added to 10mL of once-centrifuged AuNR solution and placed on the shaker overnight. Then the solution was centrifuged at 8000rpm for 10 minutes to remove excess CTAB and unreacted HS-PEG-NH₂, then redispersed in water.

2.3 Results and Discussion

Gold nanorods with aspect ratio of ~ 2.5 were synthesized using a seed mediated approach. The UV-vis extinction spectrum of the nanorods revealed two characteristic bands corresponding to longitudinal(677nm) and transverse(513nm) peak (Fig. 2.1). The nanorods were first conjugated with TNT peptide recognition element in aqueous solution, then adsorbed to silicon substrates. The conjugation of the peptide recognition elements was monitored by observing the LSPR shift of the aqueous AuNR solution pre-and post-conjugation. The spectrum showed a 2.5 nm red shift in the longitudinal peak of the TNT peptide recognition element conjugated nanorods in aqueous solution (Fig. 2.1A), and a relatively shorter, 1.5nm shift in the longitudinal peak of the DNT peptide recognition element conjugated solution (Fig. 2.1B). This shift in the LSPR spectrum shows a successful conjugation of the peptide recognition elements.

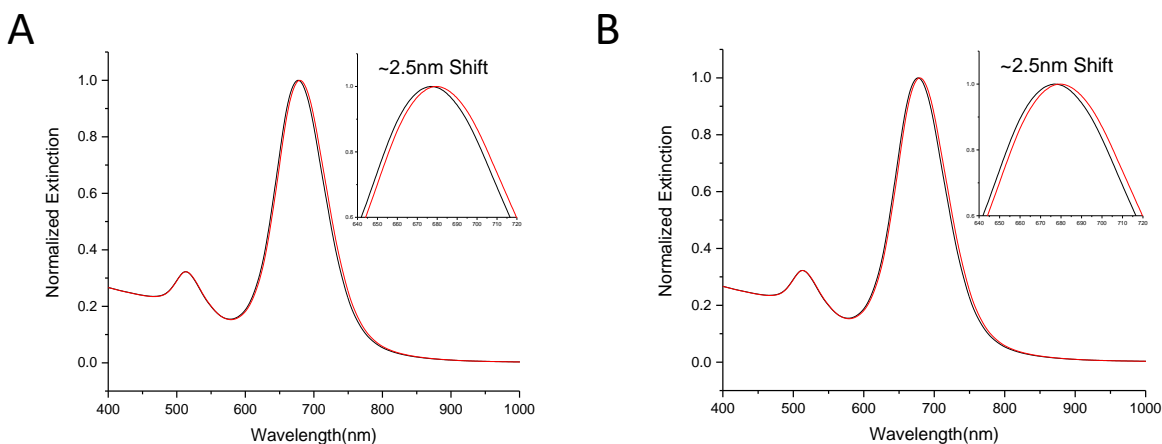


Figure 2.1 – (A)UV-vis spectra of wavelength from 400nm to 1000nm of AuNR solution before and after TNT recognition peptide element conjugation. The characteristic longitudinal peak shows a ~ 2.5 nm red shift (B)UV-vis spectra of AuNR solution from 400nm to 1000nm before and after DNT recognition peptide element conjugation. The characteristic longitudinal peak shows a ~ 1.5 nm red shift

Exposure to 900 μL of 100 μM TNT solution of TNT peptide conjugated AuNR for 1 hour to confirm the functionality of the TNT peptide recognition element. The samples were thoroughly rinsed with water once exposure was complete. SERS spectra were collected for both the TNT solution exposed and control samples using Raman spectroscopy with 785 nm wavelength laser. The peaks were normalized to the silicon peak at $\sim 949\text{ cm}^{-1}$ exhibited by both the control and the exposed samples. The TNT exposed sample shows a sharp Raman band at 1350 cm^{-1} , corresponding to $-\text{NO}_2$ stretching modes of TNT (Figure 2.1). Also, the normalized spectra of the control sample exposed to nanopure water and TNT, respectively, show a large difference between the peak height at 1350 cm^{-1} .

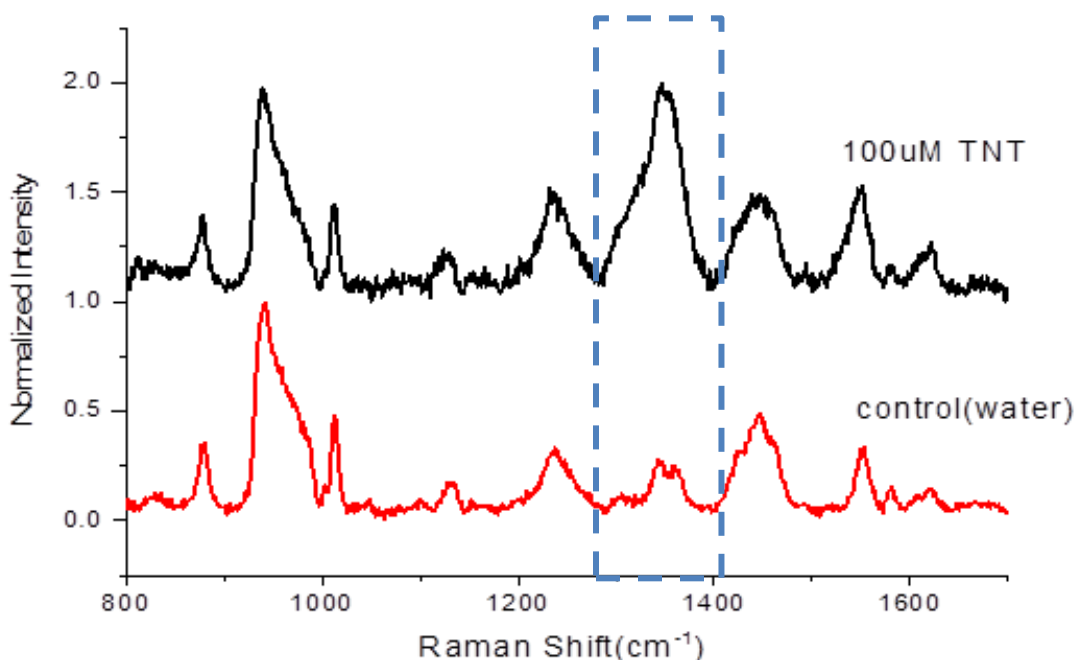


Figure 2.2 - SERS spectra obtained from the nanorods-adsorbed silicon substrates with and without TNT exposure. 100 μM TNT exposed substrate was compared against the control sample, which was TNT peptide conjugated AuNR adsorbed silicon substrates exposed to nanopure water for equal amount of time.

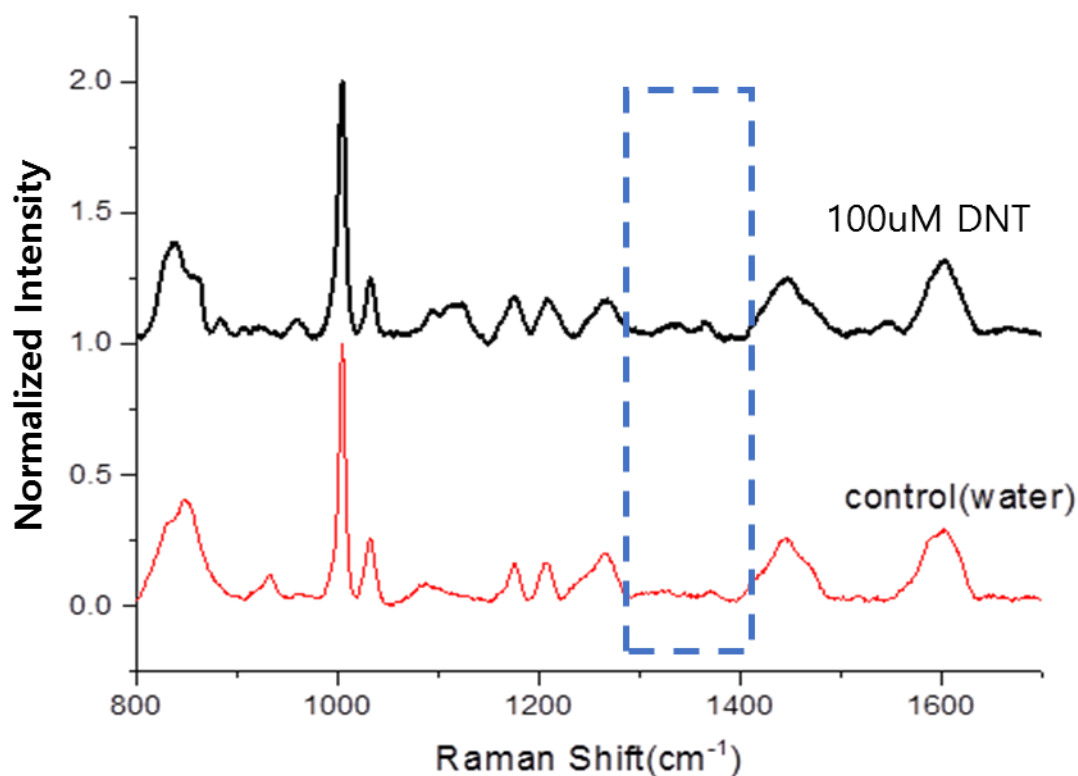


Figure 2.3 - SERS spectra obtained from the silicon substrates adsorbed with nanorods functionalized with DNT selective binding peptides. 100uM DNT exposed substrate was compared against the control sample, which was DNT peptide conjugated AuNR adsorbed silicon substrates exposed to nanopure water for equal amount of time.

Although the control sample does have a peak at 1350 cm^{-1} , the large difference in normalized SERS intensity suggests that the TNT peptide is adsorbing TNT molecules to the surface of the nanorods successfully. The through rinsing of the TNT exposed sample ensures that there is no free unbound TNT molecules, since TNT is water soluble at lower temperature, and suggests that the peptides have

chemical affinity to the TNT molecules. Literature published from this group suggests that TNT has very low specific binding affinity to gold nanorods [10]. Figure 2.3 suggested that there is little interaction between the peptide and the DNT molecules, because negligible change was observed from the SERS spectra of the control and explosive exposed samples.

The conjugated nanorods were also adsorbed to filter paper and left overnight. SEM image(Fig. 2.4) showed even adsorption of nanorods on the paper surface without large scale aggregation or patchiness. Once adsorbed, the paper substrates exhibited a dark green color corresponding to the size and wavelength of the nanorod solution. The AuNR adsorbed paper substrates were dried with a stream of nitrogen, then cut into 2 mm x 2 mm squares and exposed to 900 uL of TNT solution with varying concentration. From fig. 2.5, it is shown that the height of the 1350 cm^{-1} peak is monotonically increasing versus the concentration of TNT. However, it is observed that other peaks are increasing as well. Also, the peak at 1350 cm^{-1} of the control sample is exhibited, therefore at lower concentrations TNT binding to substrates are harder to detect.

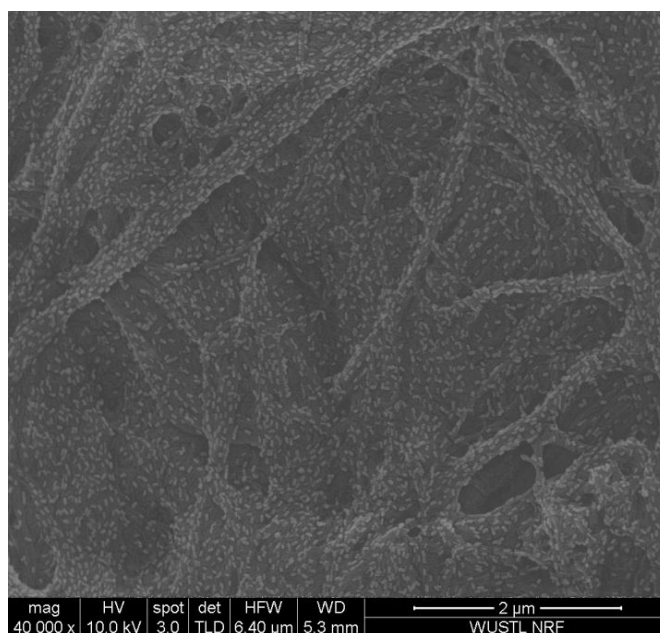


Figure 2.4– SEM image of gold nanorods with LSPR spectrum of 670nm adsorbed on paper substrates

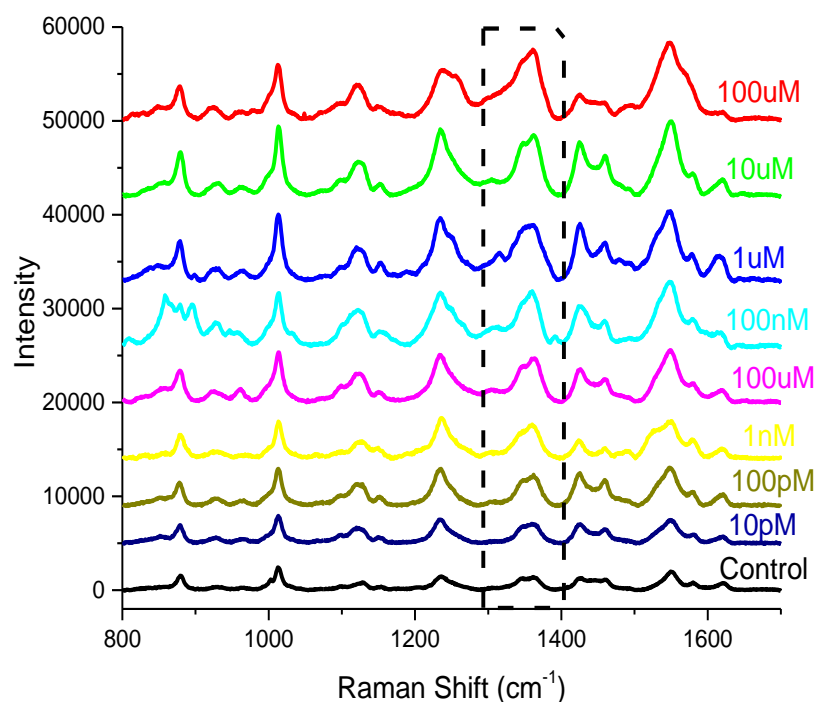


Figure 2. 5 – Raman spectra acquired from TNT specific binding peptide conjugated AuNR-paper substrates. These substrates were exposed to 0 pM, 10 pM, 100 pM, 1 nM, 10 nM, 100 nM, 1 μM , 10 μM and 100 μM in the range of 800-1700 cm^{-1} . Most peaks were found to have a monotonously increasing trend versus concentration of TNT solution.

The benefits of a stable, flexible, and inexpensive substrate such as filter paper is too great to abandon. Paper substrates offer a 3D scaffolding structure, as well as innate microfluidic channels that can deliver the analytes near the electromagnetic hot spots on the tips of the nanorods [10]. Ergo, other functionalities capable of selectively or even partially selectively binding with TNT was needed to construct a SERS sensor. Several chemical functionalities that are reported to have specific and/or

partial affinity to nitroaromatic groups, such as cysteamine, p-aminothiophenol (pATP), polyethylene glycol (PEG) were selected to be functionalized on the nanorod surfaces [22,23,24]. The selected chemicals were conjugated with the nanorods in aqueous media. Once the functionalities were conjugated to the nanorod surfaces, the LSPR spectrum of the conjugated nanorod solutions showed a ~ 5 nm red shift for AuNR-PEG-NH₂, ~ 1 nm red shift for pATP and ~ 1.5 nm red shift for cysteamine, as shown in fig.2.6. The nanorods were then adsorbed to the paper similarly to the peptide conjugated rods. As a preliminary test, the functionalized substrates were exposed to 900 μ L of 100 μ M aqueous TNT solution for 1 hour.

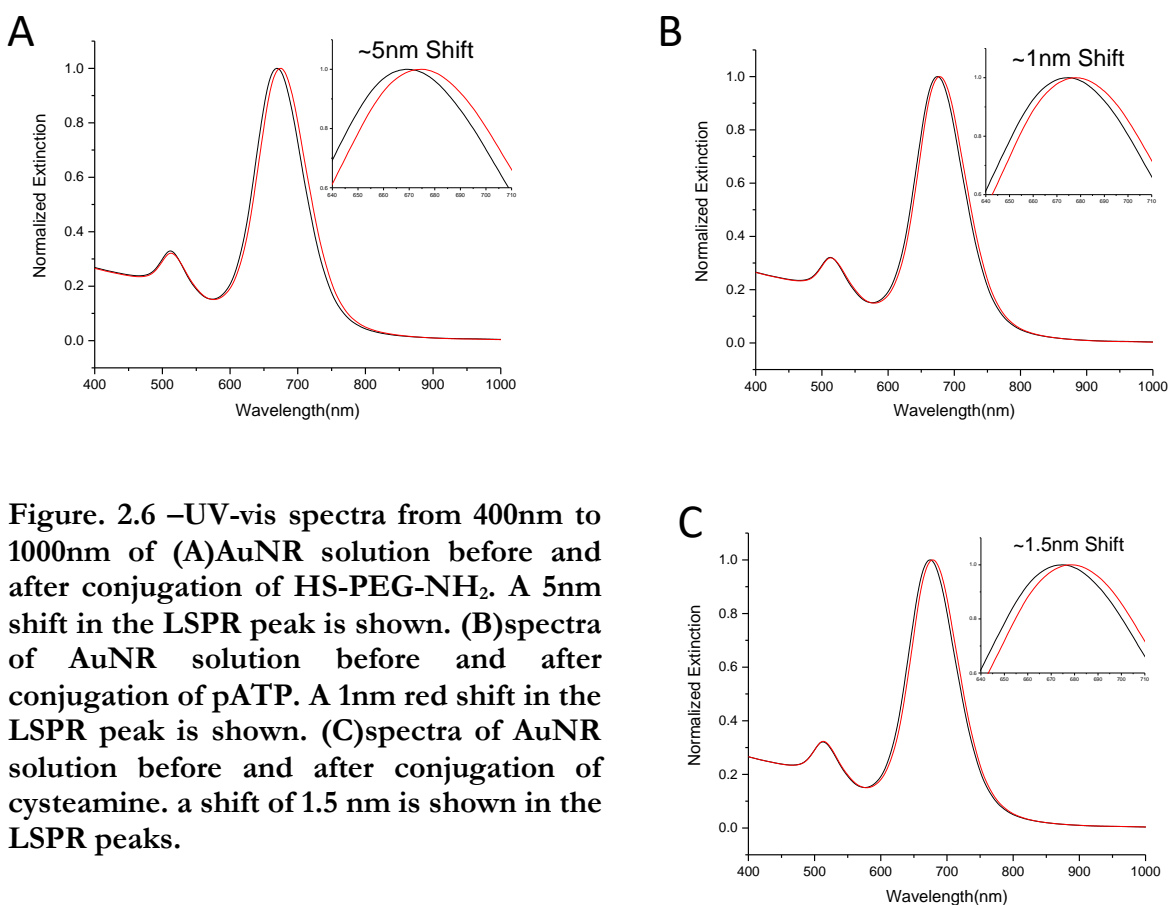


Figure. 2.6 –UV-vis spectra from 400nm to 1000nm of (A)AuNR solution before and after conjugation of HS-PEG-NH₂. A 5nm shift in the LSPR peak is shown. (B)spectra of AuNR solution before and after conjugation of pATP. A 1nm red shift in the LSPR peak is shown. (C)spectra of AuNR solution before and after conjugation of cysteamine. a shift of 1.5 nm is shown in the LSPR peaks.

When the 'TNT' exposed samples were compared to the control samples, pATP and PEG showed little or no difference in the spectra, signifying no partial or specific binding of the 'TNT' to the chemicals. However, cysteamine conjugated samples showed a clear difference in the 1350 cm^{-1} peak. The 'TNT' exposed sample showed a 400% greater peak height compared to the control sample that was submerged in nanopure water. There is still a 1350 cm^{-1} peak on the SERS spectrum from the control **A** sample from cellulose, but the difference is deemed large enough for the cysteamine functionalized AuNR- paper to be used as a SERS substrate.

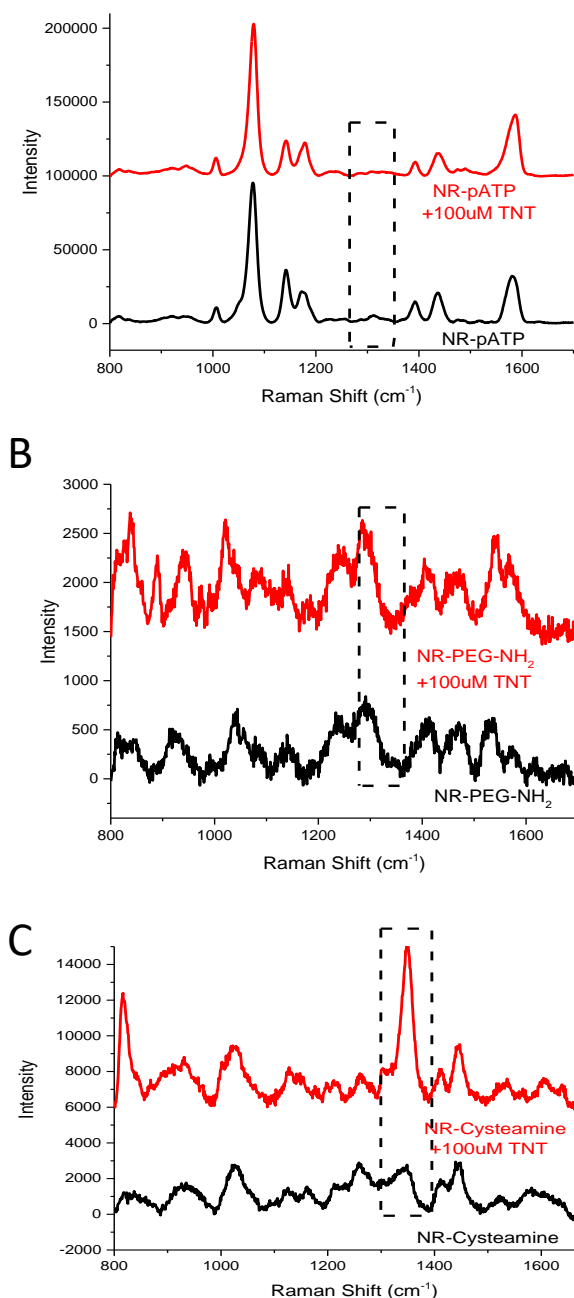


Figure 2.7 – (A) pATP
functionalized nanorods were adsorbed to paper, then exposed to water and an aqueous solution of 900 μL of 100 μM TNT. The difference between the two spectra is insignificant. **(B) PEG** functionalized nanorods were adsorbed to paper, then submerged in 100 μM TNT and water. There is little difference between the two spectra. **(C) Cysteamine conjugated** nanorods show large difference in the 1350 cm^{-1} peak of the SERS spectra.

It was confirmed that cysteamine is selectively binding to TNT by rinsing the samples thoroughly with water. TNT is reported to have a widely varying solubility in water that ranges from 100 mg/L to 200 mg/L [25] which corresponds to 440 μM to 881 μM . Therefore at 100 μM concentration, rinsing thoroughly with water is sufficient to wash all free molecules of TNT for accurate testing.

Like the 'TNT' peptide conjugated samples, cysteamine conjugated AuNR-paper was exposed to different concentrations of aqueous 'TNT' solutions with concentrations ranging from 100nM to 100 uM to demonstrate its sensing capabilities. Six different locations on the paper substrate was chosen for the spectra to be measured and to ensure the reliability of the SERS substrate, then these samples of AuNR- paper exposed to different concentrations of 'TNT' all exhibited the 1450 cm^{-1} peak coming from cellulose, therefore each spectrum was normalized against this cellulose peak to determine an accurate trend in the increase of peak height. The normalized spectra showed a monotonously increasing 1350 cm^{-1} peak height with increasing concentration. The monotonic increase in the normalized counts of the 1350 cm^{-1} peaks are more evident in the zoomed view of the spectrum. The 1350 cm^{-1} peak from cellulose was still present, but the cysteamine showed more utility than the 'TNT' peptides because the peak height at higher concentrations were sufficiently high that there was a noticeable difference between 'TNT' exposed samples and the control sample. We also postulate that the compact size of cysteamine helped to keep the 'TNT' molecules closer to the gold nanorods thus invoking a stronger SERS signal [26].

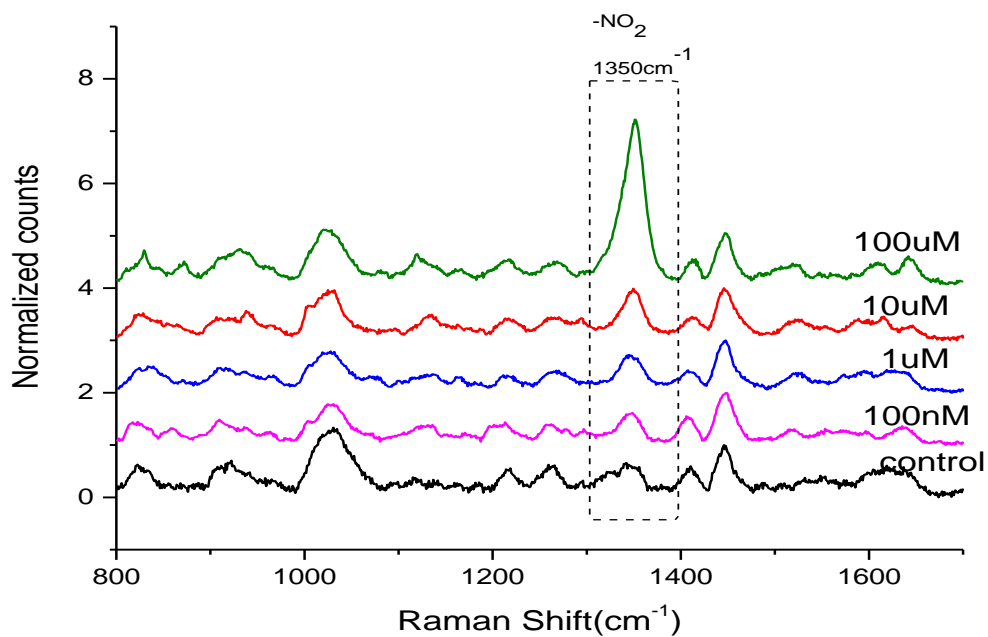


Figure 2.8 – SERS spectra obtained from cysteamine-AuNR-paper substrates exposed to different concentrations of aqueous TNT solution ranging from no TNT to 100 μM. Monotonous increase in peak height according to TNT concentration is observed.

The detection limit was found to be 100 nM, but with possible improvements such as the change in shape of the nanostructure adsorbed to paper and a higher density of nanorods per unit area, it is plausible that the detection limit could be lowered.

The normalized mean peak height from the cysteamine- AuNR-paper samples exposed to TNT solutions were plotted against the concentration in a logarithmic scale and the standard deviations of each sample set were represented in the plot by error bars.

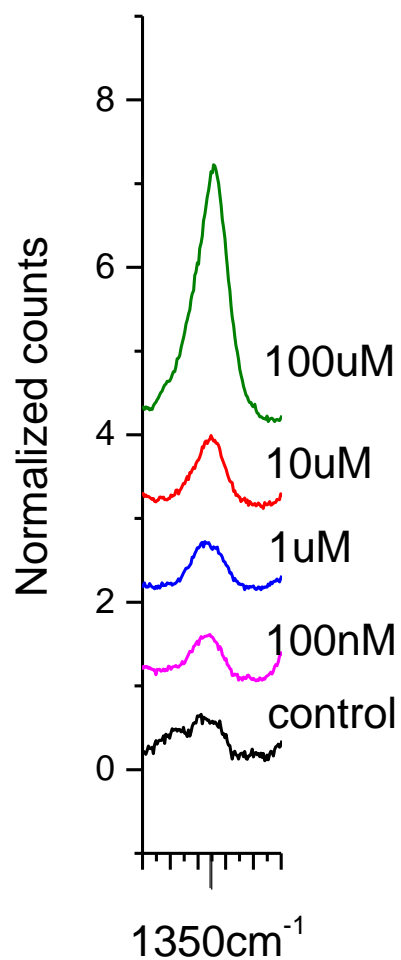


Fig. 2.9 - Zoomed spectrum of fig. 2.8 in the range of 1300–1400 cm⁻¹

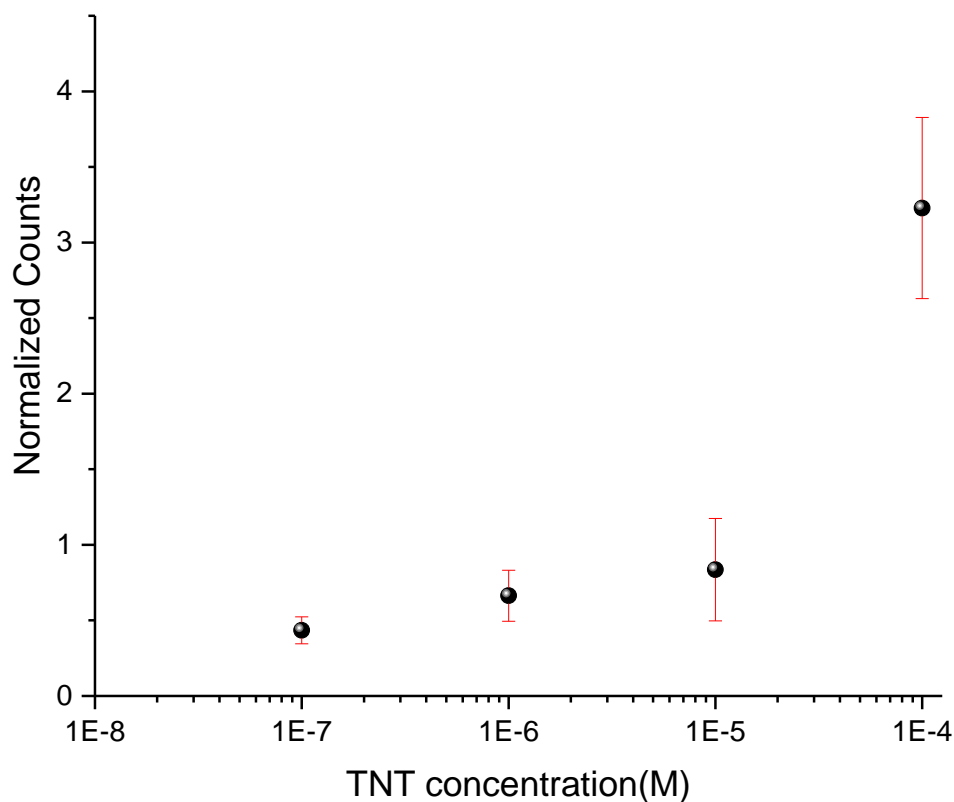


Figure 2.10 Mean normalized counts of the 1350 cm^{-1} peak intensity of each cysteamine-AuNR-paper samples exposed to different concentrations of aqueous TNT plotted against concentration on a logarithmic scale. The error bars represent standard deviation.

In conclusion, it is demonstrated that paper with adsorbed gold nanorods conjugated with cysteamine can serve as a SERS detection platform for trace TNT detection. The fabrication of such sensing platforms is inexpensive, flexible and environmentally friendly. The 3D scaffolding structure of cellulose fibers serve to put a high density of nanorods under the laser, while also serving as an effective path to deliver the analyte to the vicinity of the nanorod

Chapter 3

Plasmonic Vapor Sensing of Commonly Used Explosive Compounds

3.1 Introduction

Real world applications demand that the SERS platform be versatile, especially for detection of explosives. Battlefield and counterterrorism usage of such explosive sensing platforms can be greatly bolstered if the sensors have vapor sensing capabilities, but this difficult to achieve since the vapor detection of TNT and DNT is especially challenging due to their low vapor pressures [27]. Conventional methods of detecting trace TNT and its predecessor DNT often involves expensive and large spectroscopy and chromatography instruments [5], which makes applications in harsher conditions unrealistic. In chapter two, we propose a simpler, inexpensive, and versatile method of detecting TNT and DNT vapor using gold nanorod as SERS media. This platform utilizes a similar platform that was used for solution detection in chapter 2, where the gold nanorod is modified with different functionalities, then adsorbed onto paper substrates.

The gold nanorod surfaces were modified with peptide recognition elements. Once the nanorod surfaces were modified, they were adsorbed to flexible substrates such as silk films and filter paper. Silk film is an exceptional material for SERS substrate and a sustainable material in optics and photonics, electronics and optoelectronic applications due to its biocompatibility and strength [28,29] AuNR modified with both the TNT and DNT peptide recognition elements, respectively, showed effectiveness in detecting TNT and DNT explosive vapor. The samples were enclosed in a sealed

container with solid explosive powder, where the entire container was heated on a hot plate set to 60°C. Inside this container, the samples were compartmentalized and segregated away from the explosive powders and never made physical contact. We report that after an hour of enclosure in the sealed container, both DNT and TNT peptide recognition elements showed capabilities to detect explosive vapor through the change in the 1350 cm⁻¹ peak height. To investigate the vapor sensing capabilities of the peptide conjugated nanorods adsorbed on various substrates, the following preparations and experiments were done.

3.2 Sample Preparation

1. Silk film substrate fabrication

Silk film substrates were fabricated using the following instructions [30,31]. *Bombyx mori* silkworm cocoons were exfoliated to extract silk fibroins. The silkworm cocoon was cut open, and the dead worm was removed. The fibroins were cut into 1 cm x 1 cm squares and peeled into thin sheets. The thin sheets were boiled in 1L of 0.02M aqueous sodium carbonate solution to be formed into a well dispersed silk fibroin fibers. The fibers were rinsed with nanopure water for 20 minutes. The rinsing process was repeated three times. The fibers were dried in a fume hood. 10 mL of 9.3 M lithium bromide(LiBr) per 1 gram of silk fibroin was used to dissolve the fibroin at 60°C for 4 hours. Once the fibroins were dissolved, they were dialyzed with nanopure water in a dialysis tube for 48 hours, where the water was replaced six times during the dialysis. The dialyzed solution was centrifuged at 9000 rpm for 20 minutes, at 4°C, to remove impurities. The centrifugation was repeated twice. 200 uL of the supernatant solution was put in a weight boat and dried to determine the weight percentage of the silk.

The supernatant solution was diluted according to calculation to 2% silk(mass/volume). Silk substrates were prepared by spin-coating 2% polystyrene dispersed in toluene on silicon substrates⁹ to form a sacrificial layer, at 2000 rpm for 1 minute, then spin coating another layer of silk (2%) on top of the PS layer. The entire substrates were then immersed in methanol for 5 minutes to crosslink the silk. The prepared silk substrates were then exposed to an aqueous solution of gold nanorods overnight.

2. TNT/DNT peptide (post-adsorption conjugation)

Pre-adsorption conjugation techniques were unsuccessful on silk substrates, therefore the nanorods were adsorbed on silk first, then conjugated post-adsorption. AuNR-Silk substrates were exposed to 100 μ M aqueous peptide solutions and were left overnight. The substrate was rinsed with nanopure water, then placed in covered containers to dry.

3. Exfoliation of Silk Films

The silk substrates could later be immersed in toluene to dissolve the sacrificial layer and exfoliate the silk layer, which could be used as a chemical detection tattoo for other platforms, such as insects. To exfoliate the silk film off the silicon, the edges of the peptide-AuNR-silk film on silicon was scratched with a metal pin to cut the silk film to desired size. The entire substrate was then immersed in toluene in a glass petri dish. Within ten minutes, the sacrificial PS layer was dissolved in toluene, and the film floated off the silicon. The silk film, now suspended in toluene, was transferred into a petri dish filled with nanopure water using a 10mL pipet. Once the film was re-suspended in water, excess toluene was evaporated spontaneously. The water suspended film was transferred to the wings of a locust by dipping the wings on the film.

4. Anesthetizing Locusts

The locusts were put in a clear plastic cup with conventional lids with openings for plastic straws. The plastic straw opening was connected to a CO₂ gas source using a clear tube. The locusts were then exposed to a stream of CO₂ for 30 seconds [32]. The locusts excreted brownish black liquid from their mouths, but was otherwise unharmed. Once the locusts stopped moving, they were immobilized with copper wires and cellophane tape onto a glass slide. The locusts started moving and breathing within several minutes.

3.3 Explosive Vapor Sensing Results

TNT/DNT binding peptide conjugated nanorod adsorbed paper, as well as TNT/DNT binding peptide functionalized nanorod adsorbed silk membranes were fabricated, then exposed to TNT and DNT vapor respectively. Two different small petri dish with 3cm diameter was placed inside a bigger petri dish with 12cm diameter. One petri dish contained 5 mg of solid explosive powder which was either DNT or TNT, corresponding to the affinity of peptide or functional group on the nanorod to the analyte. The analyte and the sensor substrates were separated to prevent solid explosive powder from contacting the substrates. The entire setup of two petri dishes inside a bigger petri dish was sealed using parafilm, then put on a hot plate where the temperature was set to 60°C. The petri dish was left on the hot plate for an hour, then removed. No explosive vapor generators were used. The control samples were heated on the hot plates as well at the same condition, but without the explosive powder. The SERS spectra of the control and the explosive vapor exposed samples were collected using Raman spectroscopy

The SERS spectra of the DNT exposed silk substrates show a peak at 1350 cm⁻¹ corresponding to the NO₂ stretching mode, whereas the control sample does not exhibit any peak at 1350 cm⁻¹. The

difference is more apparent on the magnified spectra, as shown in fig.3.1(B), where there is a clear and noticeable difference in peak height between the control sample and the DNT exposed sample. The silk substrates did not exhibit any innate peak at 1350 cm^{-1} contrary to the paper substrates which had an innate peak that was interfering with the TNT peak (chapter 2).

Similarly, the SERS spectra obtained from TNT vapor exposed samples showed a peak at 1350 cm^{-1} whereas the spectra obtained from control samples did not. The difference is more pronounced on the magnified spectra.

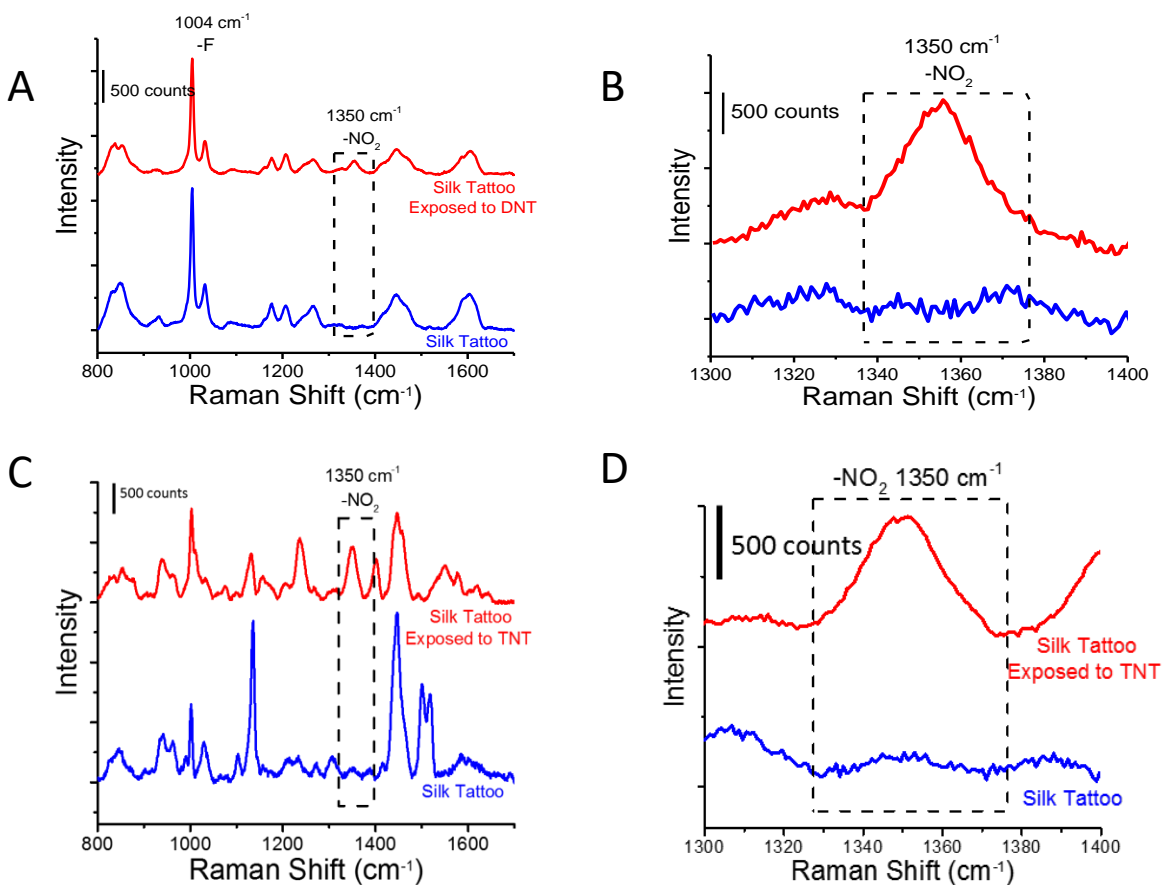


Figure 3.1 - (A) SERS spectra of DNT vapor exposed and control silk substrates. (B) Magnified SERS spectra of DNT exposed and control silk substrates 1300 cm^{-1} to 1400 cm^{-1}

(C) SERS spectra of silk substrates with and without TNT vapor exposure. (D) Magnified SERS spectra from 1300 cm^{-1} to 1400 cm^{-1} in Figure 3C.

The conjugated AuNR adsorbed silk film on silicon substrates showed SERS peaks corresponding to TNT and DNT just by being enclosed in the same container as the explosive powders at slightly elevated temperatures, without the generation of an explosive vapor pulses using vapor generators.

The silk films could also be exfoliated off the silicon substrates, then adhered to the wings of locusts. SERS spectra of the control and the TNT exposed films were measured off the wings of a live locust. The exfoliation and the re-adherence of the silk film suggests that the AuNR-silk film can be attached to smaller platforms such as robots, drones or even glossy surfaces of insect exoskeletons to allow for explosive vapor detection in hard to reach places or otherwise inaccessible locations. The vapor exposed silk films exhibit sharp, noticeable peak at 1350 cm^{-1} . The height of the NO_2 band on the SERS spectra between the explosive vapor exposed films and the control samples show a clear difference, as shown by the grey boxes on fig. 3.2

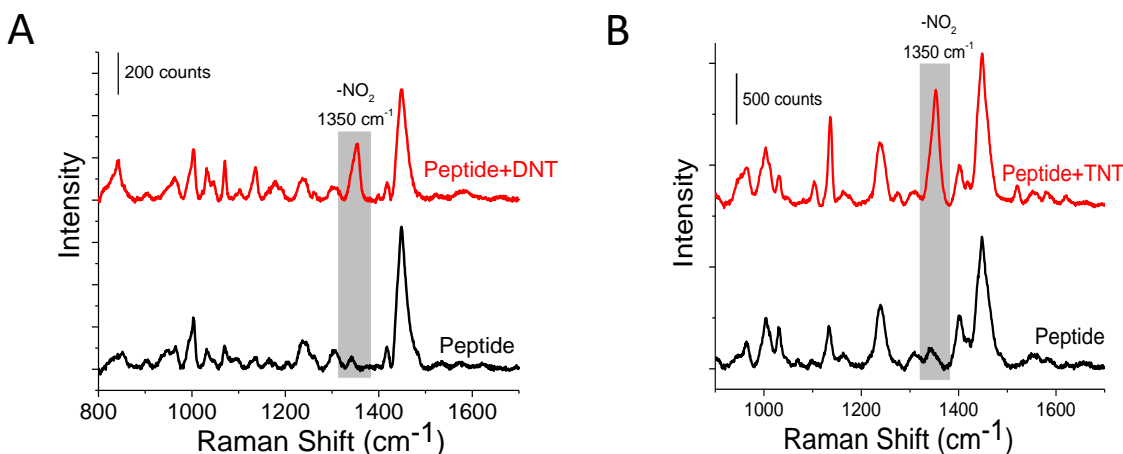


Figure. 3.2 – (A) SERS spectra of DNT vapor exposed and control silk substrates that were adsorbed to live locusts. (B) SERS spectra of TNT vapor exposed and control silk substrates that were adsorbed to live locusts

Both TNT and DNT binding peptide conjugated nanorods were adsorbed to paper, respectively, and exposed to explosive vapor like the silk samples. In both the TNT and DNT peptide sensing paper substrates, the height of the 1350 cm^{-1} band showed considerable difference between the control and the vapor exposed samples. This highlights an application of the peptide recognition element SERS substrate as a possible explosive vapor detection sensor in the form of vapor filters, since the substrates are fabricated with widely used filter paper that is permeable to vapor.

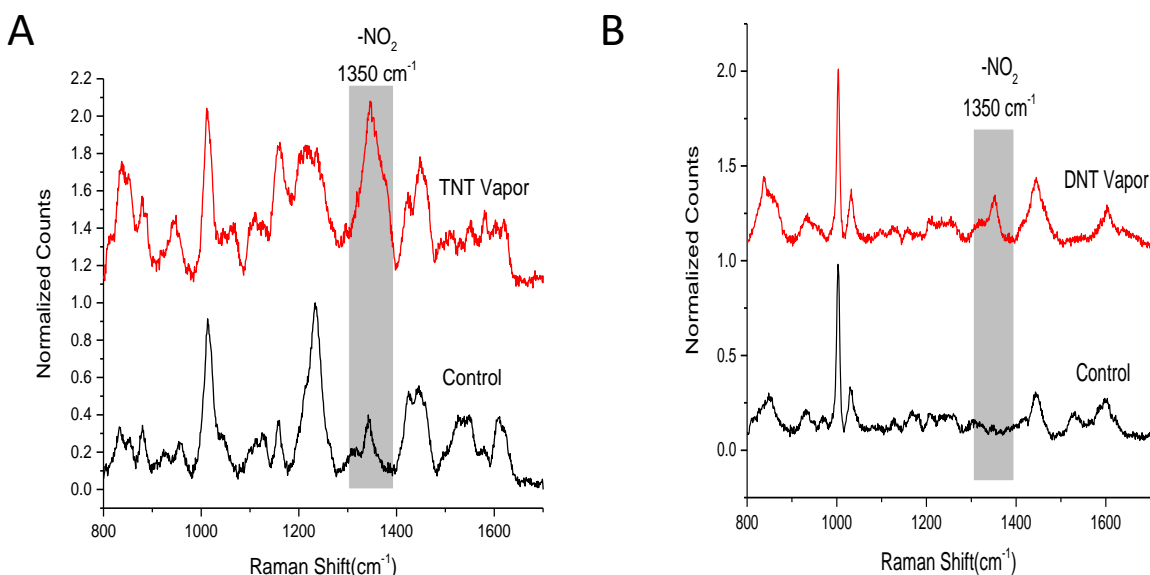


Figure 3.3 (A) SERS spectra of TNT vapor exposed and control TNT binding peptide recognition element modified nanorods adsorbed to paper (B) SERS spectra of DNT vapor exposed and control DNT binding peptide recognition element modified nanorods adsorbed to paper

In this chapter, we have demonstrated peptide recognition element based AuNR – flexible substrate systems using silk films and filter paper that is able to detect explosive vapor without the use of vapor generators. We have also shown that the silk film substrate can be used in the form of silk tattoos on locusts to detect explosive vapor in hard to reach places. The paper substrates, which were shown to be ineffective in detecting explosive in solution, successfully detected explosive vapor, hinting an application as SERS detectors for explosive vapors in the form of filters.

Chapter 4

3D Paper- Zinc Oxide Plasmonic Substrate

4.1 Introduction

SERS spectra measurements depend highly on the nanoparticle shape, structure and density. Ideally, the analytes must be near the nanoparticles (within 10nm), the nanoparticles must be of sufficient size to have localized surface plasmons, and must be high density [33,34] To improve the sensitivity of SERS substrates, it is imperative that researchers improve upon these criteria. We propose a three-dimensional SERS substrate that can be constructed from paper and zinc oxide, that will provide higher density of nanorods under the target area illuminated by the SERS laser.

Zinc Oxide is a metal oxide semiconductor with a large band gap of ~ 3.3 eV. The material properties of Zinc Oxide provide numerous benefits as a construction material for a 3D SERS substrate. It is easily fabricated in solution, can be assembled into various morphologies, and is optically transparent, which makes it ideal for 3D structure fabrication as well as a wave guide for the incident electromagnetic wave during SERS[38, 39]

The construction plan is as follows – zinc oxide nanowires will be grown on filter paper, and gold nanorods will be adsorbed to the zinc oxide nanowires. This provides a 3D scaffolding where there is more nanorod under the unit area of illumination. The zinc oxide can also act as a wave guide because of its optical qualities, therefore enhancing the SERS signal when the substrate encounters the analyte [35]

4.2 Sample Preparation

4.2.1 Zinc Oxide Seeds

20 mL of 4 mM zinc acetate solution with 20 mL of ethanol, heated at 70°C for 30 minutes, then cooled to room temperature. 20 mL of 4 mM sodium hydroxide solution was mixed with the cooled zinc acetate solution and hydrolyzed at 60°C for 2 hours. Whatman grade No.1, 180 μ m thick filter paper was cut into 1 cm by 2 cm rectangles and dipped into the colloidal zinc oxide seed solution, then dried. This dipping process was repeated 5 times [41,43].

4.2.2 Growing Zinc Oxide (ZnO) Nanowires on Paper

The dipped and dried filter paper, now adsorbed with colloidal zinc oxide particles, were put in a growth solution made by mixing 10 mL of 30 mM zinc nitrate solution and 10 mL of 30 mM hexamethylenetetramine(HMTA). The container was sealed and put in an oil bath at 90°C for 6 hours, then cooled. The paper, now with grown ZnO nanowires protruding in a radial direction from the cellulose fibers, were taken out and dried [42].

4.2.3 Adsorbing AuNR to ZnO nanowires

The ZnO-paper was immersed in 1% P2VP solution in ethanol for 1 hour, then removed from the P2VP solution, submerged in ethanol for ten minutes, rinsed with ethanol, then dried. Once the paper was completely dry, it was immersed in aqueous solution of AuNR and left overnight for the nanorods to adsorb onto the paper. Once the nanorods were adsorbed, the paper exhibited green with specks of white from the ZnO. The paper substrates were dried in air in a covered container.

4.3 Results and Discussions

The SEM image of the finished 3D substrate showed no large-scale aggregation of nanorods on the surface of cellulose. It also showed that the nanorods were successfully adsorbed to the surface of the ZnO nanowires. P2VP residue is observed on the surface of the cellulose, but the nanorod density is still high and the rods are well dispersed. No lumps were observed.

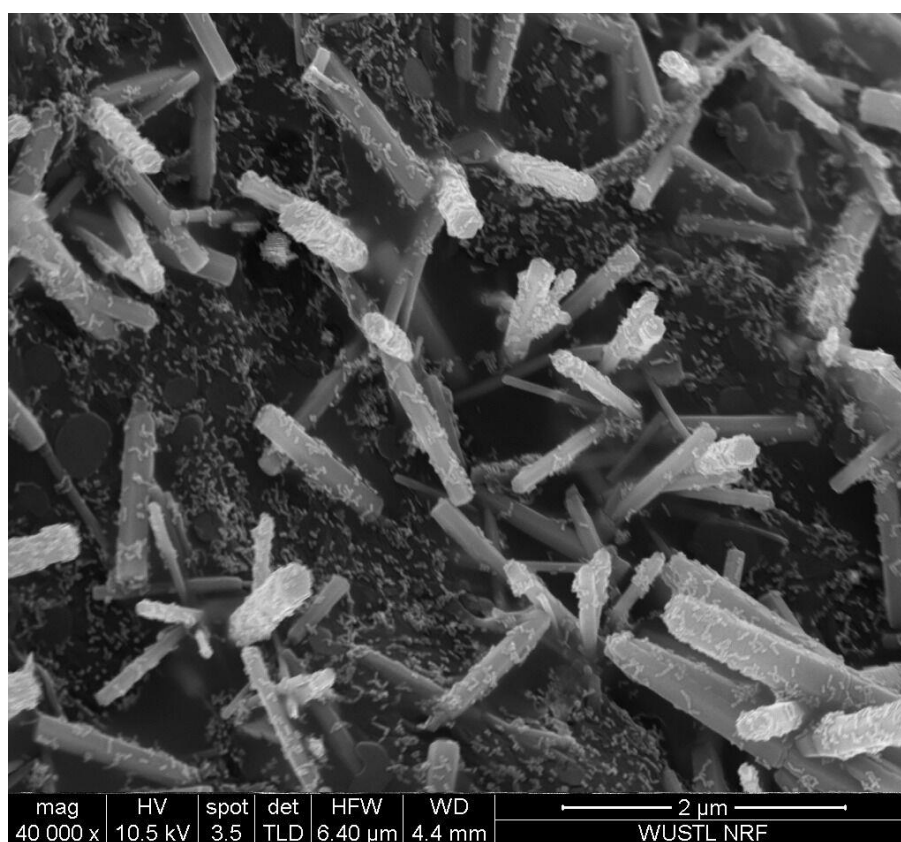


Figure 4.1 – SEM image of AuNR-ZnO-Paper substrate.

The AuNR-ZnO-Paper substrates were cut into 2 mm by 2 mm squares and exposed to 900 uL of 1 mM BDT for 1 hour. The SERS spectra of the BDT exposed samples measured using Raman

spectroscopy with a 785 nm laser, 15 second exposure time at 10% laser power were compared against the spectra of AuNR-Paper and AuNR- Silicon with identical exposure conditions.

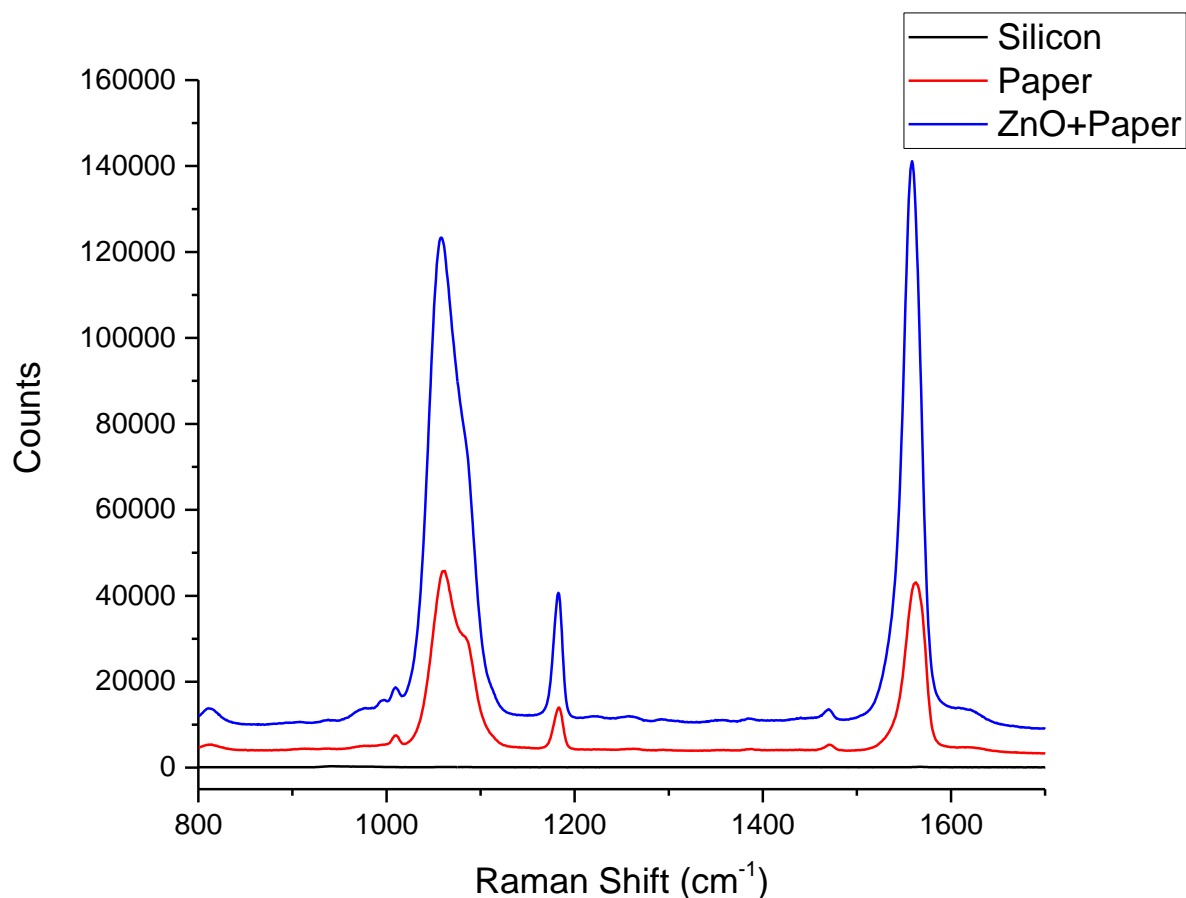


Figure 4.2 - SERS spectra of AuNR adsorbed on silicon, AuNR adsorbed on paper, and AuNR adsorbed on ZnO+Paper substrates after exposure to 900 uL of 1 mM BDT for 1 hour.

The differences between the height of the peaks corresponding to BDT is obvious. At 1560 cm^{-1} , the largest peak corresponding to BDT, ZnO+Paper substrates show 400% peak height enhancement compared to the paper substrates. The silicon substrates show such a small magnitude of signal compared to other substrates. The power of the 785nm laser was limited to 10 percent and the

exposure time was also limited to 15 seconds because otherwise the peak height of the AuNR+ZnO+paper samples would be too great for the SERS equipment to measure. Nevertheless, it is shown that the signal from the ZnO modified paper substrate is far greater.

We have demonstrated that the ZnO modified paper substrates exhibit a greater signal than the paper or silicon substrates, and it is suspected that the reason for this enhancement is because the zinc oxide nanowires spread in a radially outward direction from the cellulose fibers. This orientation helps to increase the surface area of the nanorods under the area of irradiation by the 785nm laser. It is also probable that the optical qualities of the zinc oxide can guide the light waves near the gold nanorods. The appeal of this platform is that the even if the paper is doped with zinc oxide, it still retains its flexible properties, while enhancing the SERS amplification greatly. Also, it is manufactured from relatively inexpensive materials that can easily be found in the lab. This platform is applicable for use as filters for vapor detection, swabs for solution and solid detection. Coupled with the functional chemicals and peptides shown above, the gold nanorod adsorbed zinc oxide on paper substrates will be a powerful tool for explosive detection.

Appendix

Supporting Information

S.1 Materials

All chemicals, unless otherwise mentioned, were purchased, and used without further purification. Cetyltrimethylammonium bromide (CTAB), chloroauric acid, ascorbic acid, sodium borohydride, silver nitrate, cysteamine, p-aminothiophenol were purchased from Sigma Aldrich. Amine PEG thiol(SH-PEG-NH₂) was purchased from Jenkem technology. Selective binding peptides with the sequence HPNFSKYILHQR (DNT peptide) and WHWQRPLMPVSI (TNT peptide) were purchased from Genscript

S.2 Characterization

TEM image was obtained with field emission TEM (JEM-2100F, JEOL) or JEOL 2010 LaB6 at an accelerating voltage of 200 kV. Samples were prepared by drying a drop of the solution on a carbon-coated grid previously made hydrophilic by glow discharge.

UV-vis extinction spectra were collected using a Shimadzu 1800 spectrophotometer. Raman spectra of all samples were collected using a Renishaw inVia confocal Raman spectrometer mounted on a Leica microscope with 50X objective (NA = 0.40) in the range of 700–1600 cm⁻¹ for 30 seconds of exposure at 50% laser power for ZnO free samples and 10 seconds of exposure at 10% laser power for ZnO samples. The samples were excited with 785 nm wavelength diode laser coupled to a holographic notch filter.

Scanning electron microscope(SEM) images were obtained using a FEI Nova 2300 Field Emission SEM at an accelerating voltage of 10 kV. The paper was gold sputtered for 60 second before SEM imaging.

S.2.1 TEM Characterization

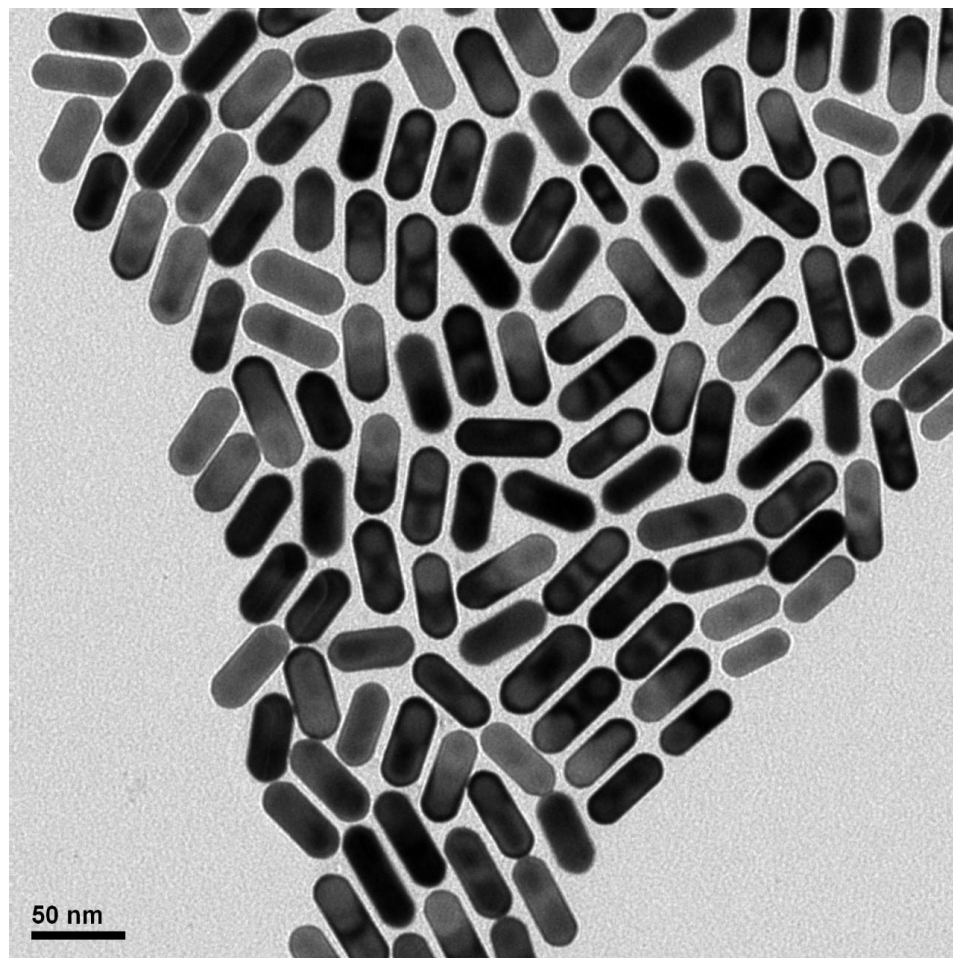


Figure. S.1 – TEM image of AuNR with a LSPR peak at 670nm

S.2.2 SEM Characterization

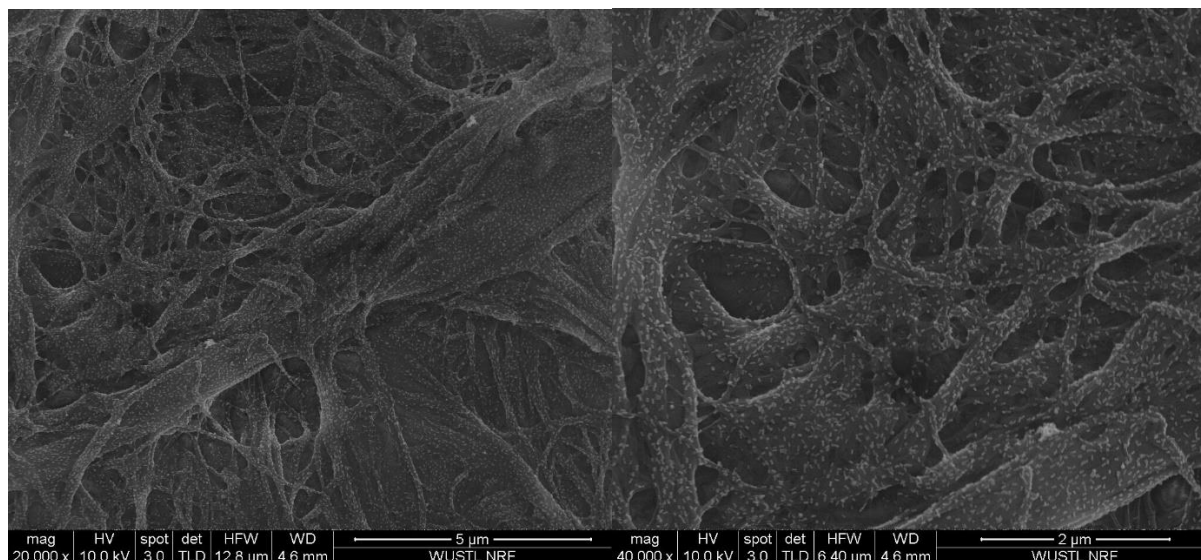


Figure S.2– SEM image of gold nanorods with LSPR peak at 670nm adsorbed on paper substrates.

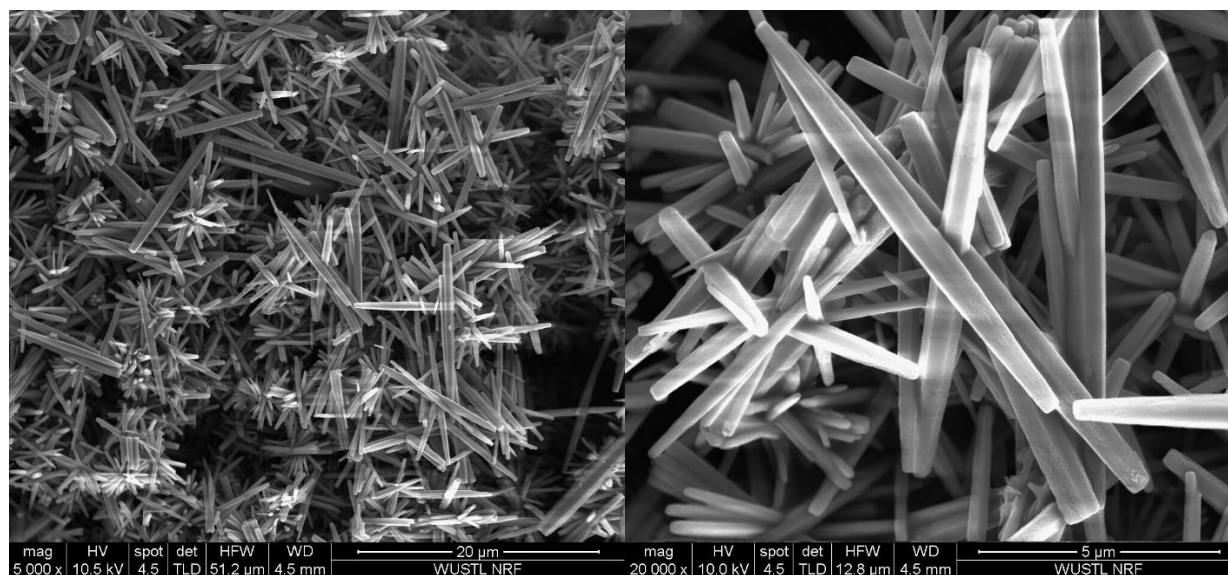


Figure S.3 – SEM image of zinc oxide nanowires grown on Paper.

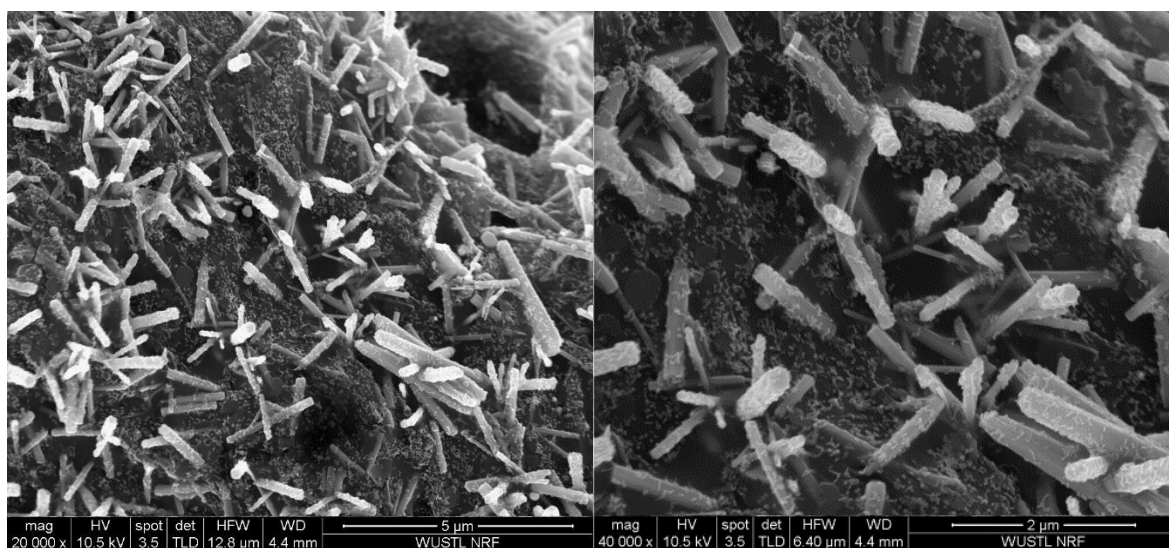


Figure S.4 – SEM image of AuNR adsorbed to zinc oxide nanowires grown on paper using P2VP.

References

- [1] R. Boopathy and C.F. Kulpa, "Trinitrotoluene (TNT) as a Sole Nitrogen Source for a Sulfate Reducing Bacterium *Desulfovibrio* sp. (B Strain) Isolated from an Anaerobic Digester," *Current Microbiology* Vol.25(1992) pp 235-241
- [2] S. Nishino, J. Spain, H. Lenke, and H. Knackmuss, "Mineralization of 2,4- and 2,6-Dinitrotoluene in Soil Slurries," *Environ. Sci. Technol.* 1999, 33, 1060-1064
- [3] Elizabeth P. Burrows, David H. Rosenblatt, Wayne R. Mitchell, David L. Parmer, "Organic explosives and related compounds: Environmental and Health Considerations," US army biomedical research and development laboratory, technical report No.8901
- [4] Juhasz AL, Naidu R, "Explosives: fate, dynamics, and ecological impact in terrestrial and marine environment," *Rev Environ Contam Toxicol.* 2007; 191:163-215.
- [5] R. Bharadwaj, S. Mukherji, "Gold nanoparticle coated fibre optic probe for localized surface plasmon resonance based detection of explosive vapours," *Sensors and Actuators B* 192 (2014) 804-811
- [6] H. Lee, Y.D. Suh, "Recent trends in nano Raman spectroscopy," *Polymer science and technology* Vol. 23, No. 4
- [7] H. Lee, S. M. Jin, Y.D. Suh, "Single-molecule surface-enhanced Raman spectroscopy: a perspective on the current status," *Phys. Chem. Chem. Phys.*, 2013, 15, 5276-5287
- [8] K. M. Mayer and J. H. Hafner, "Localized surface plasmon resonance sensors," *Chem. Rev.* 2011, 111, 3828-3857

- [9] C.H. Lee, L. Tian, and S. Singamaneni, "Highly sensitive surface enhanced Raman scattering substrates based on filter paper loaded with plasmonic nanostructures," *Anal. Chem.* 2011, 83, 8953-8958
- [10] S. Z. Nergiz, N. Gandra, L. Tian, "Biomimetic SERS substrate: peptide recognition elements for highly selective chemical detection in chemically complex media," *J. Mater. Chem. A*, 2013, 1, 6543-6549
- [11] Tian, Limei, Jeremiah J. Morrissey, Ramesh Kattumenu, Naveen Gandra, Evan D. Kharasch, and Srikanth Singamaneni. "Bioplasmonic paper as a platform for detection of kidney cancer biomarkers." *Analytical chemistry* 84, no. 22 (2012): 9928-9934.
- [12] A. Modinos "Secondary Electron Emission Spectroscopy," *Field, Thermionic, and Secondary Electron Emission Spectroscopy* pp 327-345
- [13] Willets, Katherine A., and Richard P. Van Duyne. "Localized surface plasmon resonance spectroscopy and sensing." *Annu. Rev. Phys. Chem.* 58 (2007): 267-297.
- [14] Link, Stephan, M. B. Mohamed, and M. A. El-Sayed. "Simulation of the optical absorption spectra of gold nanorods as a function of their aspect ratio and the effect of the medium dielectric constant." *The Journal of Physical Chemistry B* 103, no. 16 (1999): 3073-3077.
- [15] J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao and R. P. Van Duyne, "Biosensing with plasmonic nanosensors," *Nature Mater.*, vol. 7, p. 442, 2008.
- [16] Tadepalli, Sirimuvva, Zhifeng Kuang, Qisheng Jiang, Keng-Ku Liu, Marilee A. Fisher, Jeremiah J. Morrissey, Evan D. Kharasch, Joseph M. Slocik, Rajesh R. Naik, and Srikanth Singamaneni. "Peptide Functionalized Gold Nanorods for the Sensitive Detection of a Cardiac Biomarker Using Plasmonic Paper Devices." *Scientific reports* 5 (2015).

- [17] R. D. Near, and M. A. El-Sayed, "Rapid and efficient prediction of optical extinction coefficients for gold nanospheres and gold nanorods," J. Phys. Chem. C 2013, 117, 24960-23955
- [18] K. S. Lee and M. A. El-Sayed, "Dependence of the Enhanced Optical Scattering Efficiency Relative to That of Absorption for Gold Metal Nanorods on Aspect Ratio, Size, End-Cap Shape, and Medium Refractive Index," J. Phys. Chem. B, vol. 109, p. 20331, 2005.
- [19] Huang, Xiaohua, Svetlana Neretina, and Mostafa A. El-Sayed. "Gold nanorods: from synthesis and properties to biological and biomedical applications." *Advanced Materials* 21, no. 48 (2009): 4880-4910.
- [20] Becker, Jan, Andreas Trügler, Arpad Jakab, Ulrich Hohenester, and Carsten Sönnichsen. "The optimal aspect ratio of gold nanorods for plasmonic bio-sensing." *Plasmonics* 5, no. 2 (2010): 161-167.
- [21] B. Nikoobakht and M. A. El-Sayed, "Preparation and growth mechanism of gold nanorods using seed-mediated growth method," *Chem. Mater.*, vol. 15, p. 1957, 2003.
- [22] R. Bharadwaj, S. Mukherji, "Gold nanoparticle coated U-bend fibre optic probe for localized surface plasmon resonance based detection of explosive vapours," *Sensors and Actuators B* 192 (2014) 804-811
- [23] S. Dasary, D. Senapati, and P. Chandra Ray, "Highly sensitive and selective dynamic light-scattering assay for TNT detection using p-ATP attached gold nanoparticle," *ACS applied materials & interfaces*, vol. 2, No.12, 3455-3460, 2010
- [24] T. Thambi, D. S. Lee, and J. H. Park, "Poly (ethylene glycol)-b-poly(lysine) copolymer bearing nitroaromatics for hypoxia-sensitive drug delivery," *Acta Biomaterialia*, Volume 29, 1 January 2016, Pages 261–270

- [25] K. S. Ro, et al, and D. Roy, "Solubility of 2,4,6-Trinitrotoluene (TNT) in Water," J.Chem. Eng. Data, 1996, 41 (4), pp 758-761
- [26] Tian, Limei, Enze Chen, Naveen Gandra, Abdenmour Abbas, and Srikanth Singamaneni. "Gold nanorods as plasmonic nanotransducers: distance-dependent index sensitivity." Langmuir 28, no. 50 (2012): 17435-17442.
- [27] D.S. Moore, Instrumentation for trace detection of high explosives, Rev. Sci.Instrum. 75 (2004) 2499.
- [28] Hakimi, Osnat, David P. Knight, Fritz Vollrath, and Pankaj Vadgama. "Spider and mulberry silkworm silks as compatible biomaterials." Composites Part B: Engineering 38, no. 3 (2007): 324-337.
- [29] Tao, Hu, David L. Kaplan, and Fiorenzo G. Omenetto. "Silk materials—a road to sustainable high technology." Advanced materials 24, no. 21 (2012): 2824-2837.
- [31] Rockwood, Danielle N., Rucsanda C. Preda, Tuna Yücel, Xiaoqin Wang, Michael L. Lovett, and David L. Kaplan. "Materials fabrication from Bombyx mori silk fibroin." Nature protocols 6, no. 10 (2011): 1612-1631.
- [31] Jin, Hyoungh-Joon, and David L. Kaplan. "Mechanism of silk processing in insects and spiders." Nature 424, no. 6952 (2003): 1057-1061.
- [32] Theresa L. Nilson, Brent J. Sinclair and Stephen P. Roberts, "The effects of carbon dioxide anesthesia and anoxia on rapid cold-hardening and chill coma recovery in *Drosophila melanogaster*," J Insect Physiol. 2006 Oct; 52(10): 1027–1033.
- [33] R. Kattumenu, C.H.Lee, L.Tian, and S. "Nanorod decorated nanowires as highly efficient SERS-active hybrids," J.Mater.Chem., 2011, 21, 15218
- [34] L. Greene, D. Tan, J. Goldberger, and P. Yang, "General route to vertical ZnO nanowire arrays using textured ZnO seeds," Nano letters, 2005, vol. 5, No. 7, 1231-1236

- [35] A. E. Kandjani, M. Mohammadtaheri, A. Thakkar, V. Bansal, “Zinc oxide/silver nanoarrays as reusable SERS substrates with controllable ‘hot-spots’ for highly reproducible molecular sensing,” *Journal of Colloid and Interface Science*, Volume 436, 15 Dec 2014, pg 251-257
- [36] Shenfei Zong, Zhuyuan Wang, Jing Yang, and Yiping Cui, “Intracellular pH Sensing Using p-Aminothiophenol Functionalized Gold Nanorods with Low Cytotoxicity,” *Anal. Chem.*, 2011, 83(11), pp 4178–4183
- [37] Junping Zhong, Liewei Wen, Sihua Yang, Qun Chen, Da Xing, “Imaging-guided high-efficient photoacoustic tumor therapy with targeting gold nanorods,” *Nanomedicine: Nanotechnology, Biology and Medicine*, Volume 11, Issue 6, August 2015, Pages 1499–1509
- [38] Fugang Xu, Yue Zhang, Yujing Sun, Yan Shi, Zhiwei Wen, and Zhuang Li, “Silver Nanoparticles Coated Zinc Oxide Nanorods Array as Superhydrophobic Substrate for the Amplified SERS Effect,” *J. Phys. Chem. C*, 2011, 115 (20), pp 9977–9983
- [39] Muhammad A. Khan, Timothy P. Hogan, B. Shanker, “Gold-coated zinc oxide nanowire-based substrate for surface-enhanced Raman spectroscopy,” *Journal of Raman Spectroscopy*, Volume 40, issue 11, November 2009, pp 1539-1545
- [40] Godhuli Sinha, Laura E. Depero, and Ivano Alessandri, “Recyclable SERS Substrates Based on Au-Coated ZnO Nanorods,” *ACS Appl. Mater. Interfaces*, 2011, 3 (7), pp 2557–2563
- [41] Lori E. Greene, Matt Law, Dawud H. Tan, Max Montano, Josh Goldberger, Gabor Somorjai, and Peidong Yang, “General route to vertical ZnO nanowire Arrays using Textured ZnO seeds,” *Nano Lett.*, 2005, 5 (7), pp 1231–1236
- [42] Afsal Manekkathodi, Ming-Yen Lu, Chun Wen Wang, Lih-Juann Chen, “Direct Growth of Aligned Zinc Oxide Nanorods on Paper Substrates for Low-Cost Flexible Electronics,” *Adv. Materials*, Volume 22, Issue 36, pp 4059–4063

- [43] Mayuree Jaisai, Sunandan Baruah,corresponding and Joydeep Dutta, “Paper modified with ZnO nanorods – antimicrobial studies,” Beilstein J Nanotechnol. 2012; 3: 684–691
- [44] Justyn W. Jaworski, Digvijay Raorane, Jin H. Huh, Arunava Majumdar, and Seung-Wuk Lee, “Evolutionary Screening of Biomimetic Coatings for Selective Detection of Explosives,” Langmuir 2008, 24, 4938-4943

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