



High sensitive setup of gold nanorods substrates for explosives detection using surface enhanced Raman spectroscopy

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Abstract

Surface enhanced Raman spectroscopy (SERS) is a sensitive analytical technique that has been widely utilised for detection of trace levels of organic species. The detection of trace levels of poor vapour pressure molecules such as explosives is a critical challenging due to the low concentration of adsorbed molecules on the surface sites of the SERS substrate. In this work, gold nanorods were fabricated with analyte samples and provided highly sensitivity of SERS detection along with low limit-of-detection (LOD) for explosives down to μM of 2,4-dinitrotoluene (DNT) and nM of both 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) with highly specificity. The sensitivity of the detection was developed by optimising the adsorption of the molecules on nanorods sites, where nanorods and analyte solution were mixed followed by rigorous stirring. This procedure allowed extra molecules to be adsorbed on the nanorods surface, thus, high SERS enhanced has been observed with high specific identification of target probes. This approach showed a powerful method for rapid detection of explosives based SERS technique especially for illicit samples, where the enhancement factor calculated for analytes was in the range 3.17×10^8 to 2.69×10^{11} .

Keywords: Surface-enhanced Raman spectroscopy, Gold nanorods, Explosives, Enhancement factor, R6G.

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1. Introduction

Since the discovery of Surface enhanced Raman scattering (SERS) phenomena in 1974, it has become a powerful and highly sensitive technique specially for trace-samples identification [1, 2]. SERS was used effectively for detection of a wide range of analytes including biological, illicit and environmental samples [3–6]. The enhancement of Raman signals occurs by amplification of scattering photons for molecules placed on or close approximate on substrate, and most reported nanostructures that provide the highest SERS enhancement those materials containing noble metal nanoparticles that display plasmonic bands, such as golds and silver nanostructures [7,8]. The accepted interpretation of SERS enhancement mechanism attributed to two proposed mechanisms, electromagnetic, and charge transfer mechanisms [9]. In the electromagnetic enhancement mechanism (EM), resonance excitation of free electrons in metallic nano particles causes collective oscillation (localised surface plasmon resonance - LSPR), that leads to enhance surface polarisation and thus contributing to promote the Raman scattering intensity of adsorbed molecules on the nanoparticle site [10]. On the other hand, chemical enhancement mechanism (CM) involves charge transfer process between the metallic nanoparticle and the adsorbate [11]. However, among both mechanisms, most of the amplification of the Raman signal enhancement attributed to

the EM, with unremarkable contribution of CM [2,7,12]. Recently, advanced studied on some non-metallic substrates reported high chemical enhancement, such as on N-doped graphene substrate, where the total enhancement factors were comparable to those reported on metallic substrates [13]. The reputation for SERS being effective was due to the fact that it could detect a single molecule, making it the most ultra-sensitive analytical method available. This meant that it found favour among other applications as it was able to provide molecular information on a single detected molecule. However, the main issue with the SERS that needed further advancement was the reproducibility of the sample substrate [14]. The reproducibility of the signal depends on the shape and size, as well as the separation, of the nanoparticles. According to studies conducted by Tantra and others, there are ongoing efforts to improve the reproducibility of SERS signals, with some success [15]. SERS enhancement factor can be as high as 10^{11} near interparticle gaps which known as hot spots, where the electromagnetic field can be maximised, however, the surface- averaged enhancement is always a few order of magnitude lower [16]. Therefore, for accurate evaluation of the SERS substrate efficiency, several spot must be recorded at multi spot on the substrate, and then average measurement is the EF calculated. For obtaining homogeneous enhancement over the whole substrate, there are reproducible SERS substrates can be prepared by

lithographic or patterning techniques, but these methods are cost as well as require further facilities for preparation. Therefore, preparing, nanomaterials in solution approaches are more flexible, cost-effective. Not only this, but also EFs that obtained on lithographic substrates are often lower than these reported on self-assembled colloidal particles [17]. For explosives detection using SERS technique, great number of substrates have been fabricated, provided a various enhancement factors. These substrates include noble metal, semi-conductors and hybrids of metallic- semiconductor substrates [18–22]. However, most of the high efficient enhancement for explosives among all were obtained on metallic substrates that is due to the poor vapor pressure of explosives compared to other probe such as dyes, thus explosive molecules require strong mechanism to enhance their Raman signals, and that can be achieved by electromagnetic mechanism which can be mainly obtained by using noble-metal substrates such as gold or silver [23,24]. In this work, gold nanorods were used as SERS substrates for trace levels of explosives samples with very limit of detection (LOD) and high selectivity for all examined explosives (DNT, TNT and RDX). The fabricated AuNRs substrate activity was first evaluated using a model analyte, Rhodamine-6G (R6G), with excellent enhancement factors (1.32×10^{11}) with limit of detection below 10^{-12} M. Similar trend has observed for selected explosives DNT, TNT and RDX, as they exhibited limit of detection of 10^{-12} M, 10^{-9} M and 10^{-9} M respectively, these results accomplished with highly specificity for all analytes. EF was calculated for all explosives and shown high values which revealed the strong enhancement for Raman signals and present an applicable approach for explosives identification at trace levels, as EFs for explosives reported in this study were 2.69×10^{11} for the 10^{-12} M sample of DNT, and 5.19×10^8 and 8.25×10^8 for 10^{-9} M of TNT and RDX samples respectively.

2. Experimental section

2.1 Chemicals and materials

Gold (III) chloride trihydrate $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (99.9%), Silver nitrate AgNO_3 (99+ %), sodium borohydride NaBH_4 (99%), L-ascorbic acid AA (99+ %), cetyltrimethylammonium bromide- CTAB (99%), and Rhodamine -6G -R6G (99%) were purchased from Sigma-Aldrich and used as received. Explosives (2, 4-Di Nitro Toluene DNT, 2, 4, 6- Tri Nitro Toluene TNT, and Cyclotrimethylenetrinitramine RDX) samples were provided by Forensic Chemistry laboratory at King Fahad Security College. Powder samples of explosives used as received for reference Raman spectra recording, and for the SERS measurements, explosives samples were diluted in ethanol to a certain concentration as explained in this manuscript from 10^{-3} M to 10^{-12} M for DNT samples, and from 10^{-3} M to 10^{-9} M for TNT and from 10^{-5} M to 10^{-9} M for RDX. All aqueous solutions used in this study were prepared using deionized water (18.3 M Ω .cm).

2.2. Synthesis of Gold Nanorods

AuNRs were prepared following reported method with some modification [25]. In such a procedure, two steps were performed to prepare gold nanorods.

2.2.1. First step, preparation of Seed solution

CTAB solution (5 mL, 0.20 M) was mixed with 5.0 mL of 0.00050M of HAuCl_4 . To the stirred solution, 0.60 mL of ice-cold 0.010 M NaBH_4 was added, which resulted in the formation of a brownish yellow solution. Then seed solution was stirring vigorously for continued for 2 minutes, then kept at 25°C.

2.2.2. Second step, growth of NRs using the prepared seeds

As following; CTAB (5 mL, 0.20 M) was added to (0.15 mL) of 0.0040 M AgNO_3 solution at 25°C, then 5.0 mL of 0.0010 M HAuCl_4 was added, mixed solution was mixed gently, followed by adding of a solution 70 μL of 0.0788 M ascorbic acid as a mild reducing agent changes the growth solution from dark yellow to colorless. The final step was adding 12 μL of the seed solution to the growth solution at 27-30 °C. The solution colour was changed gradually within 10-20 min. The temperature of the nanorods growth medium was kept constant at 27-30 °C for the rest of the synthesis process. This procedure produces homogeneous and pure nanorods NRs with an average 50 nm length and 10 nm width, as shown in the results below. Prepared nanorods were then washed 3 times in DI water then re-spread in pure DI water and kept safe at 4°C. Purified suspension nanorods were then used as prepared for preparation of SERS substrates.

2.3. SERS substrate Preparation

SERS substrates were prepared by mixing AuNRs and analyte samples, then centrifugation the mixture followed by drop- casting onto borosilicate glass slides. Depositing AuNRs solution followed by the analyte solution was tested, and mixing both solution then stirring mixture was also tested, were the latter was found more efficient for SERS detection especially for explosives samples, while both method were slightly similar for R6G with higher observed signals for the mixture producer. For all data for explosives here, the mixing procedure was used, in such procedure, 100 μL of ethanolic analyte solutions at the given concentrations were mixed with 100 μL of the AgNRs in ethanol. Mixed was then stirred variously for 10 minutes, mixture then was, drop-cast onto borosilicate glass and left dried in air for 5 minutes prior SERS measurements.

2.4. Instrumentations

Raman spectroscopy studies were carried out using a Renishaw 1000 spectrometer coupled to a microscope with 50 \times objective lens and equipped with a 633-nm laser. The laser spot size was ca. 4.4 μm^2 . The Raman system was calibrated using a silicon reference. The acquisition time was 10 s with one accumulation for all measurements. UV/Vis spectroscopy was carried out using a Perkin Elmer Lambda 125 UV/Vis/NIR instrument. Transmission electron microscopy (TEM) images and selected area electron diffractograms (SAEDs) were obtained using a high resolution TEM Jeol 2100 with a LaB-6 source operating at an acceleration voltage of 200 kV. Micrographs were recorded on a Gatan Orius Charge-coupled device (CCD).

3. Result and discussion

AuNRs were prepared using seed and growth procedure following a method adapted from the literature [25]. In such procedure, HAuCl_4 was used as a gold precursor and NaBH_4 as a reducing agent and CTAB were used as a surfactant to control the growth of the

Au seeds in the presence of AgNO_3 . CTAB was used as a capping agent due to its suitability as a surfactant for synthesis of gold nanorods. A CTAB known to form rod-shaped particles that growth on spherical seeds prepared initially, this made CTAB preferable as a capping agent compared to citrate capping agent. Once the reducing agent (NaBH_4) was added, the mixture was stirred vigorously; this is to insure simultaneous production of all Au nuclei, and obtained homogeneous distribution of the seeds in the entire solution volume. This resulted into seed solution with brownish yellow colour solution. These seed was used to produce gold nano rods, with involvement of ascorbic acid as a reducing agent for AuNRs growth to control the shape of the prepared nanorods. As during the growth solution, gold ions released in the forms of Au(III) and Au(I) to form Au(0) at the end of the formation process. Using seeds approach help getting high quality Au reduction as the presence of Au nuclei in the solution act as a catalyst. The reducing agent was used for nanorods growth is ascorbic acid, as it still the most popular for rods growth. As upon addition of ascorbic acid to the mixture solution of HAuCl_4 and CTAB, Au(III) ions were reduced to Au(I) which observed by turning solution colour into colorless, this is due to the disappearance of the ligand-to-metal charge transfer band for orbital d^{10} metal center of Au(I) [26]. This procedure provided nanorods with resonance absorption band covering a broad near infrared range, which is suitable for Raman enhancement techniques. To characterize the synthesised AuNRs, UV-Vis spectra for AuNRs were recorded for the 300 -1000nm region for 50 μL of the colloidal solution in 4mL DI water, where localize surface plasmon resonance (LSPR) was observed at 827 nm, and a small peak at 510 nm was observed which is belongs to the Au seeds, as shown in Figure (1). While TEM images were also recorded to observe the nanorods dimension, length and thickness of the rods, where the average length is in the range of 50 nm, and around 10 nm in thickness, Figure (1-inset).

3.1. SERS measurements

SERS spectra were recorded for the explosives using gold nanorods as a substrate. An excitation laser line with a wavelength of 633nm (He-Ne) was applied with an exposure time of 10 seconds. Prior to recording of the Raman and SERS spectra of analytes, Raman spectra were collected for pure gold nanorods deposited on a microscope slide to determine the effect of impurities and aggregation of the nanoparticles on the Raman signals- data has not been shown here- which showed no clear signals in the vibrational fingerprint region of the analytes, makes the nanorods substrate a suitable candidate for enhancing Raman signals of explosives.

3.2. Characterisation of SERS activity of AuNRs substrates

The SERS substrate preparation via mixing nanorods colloidal solution and analytes then centrifugation them encouraged the formation of AuNRs clusters and increases the hotspot population across the film. The efficiency of this substrate was initially evaluated using different concentrations of Rhodamine 6G (R6G), namely 10^{-7} , 10^{-8} , 10^{-9} , 10^{-10} and 10^{-12} M (Figure 2). Rhodamine-6G (R6G) has a unique Raman active mode, thus it used for the characterization and testing the sensitivity and activity of our approach of nanorods SERS substrates. R6G is a fluorescent

organic molecule with a molar mass of 479.02 gmol^{-1} , and a density of 1.26 g/cm^3 and has an absorption band at 528 nm, which is not in resonance with the laser source used in our experiments (633 nm), however it has a conveniently large Raman cross-section ($d\sigma/d\Omega$) of ca. 1×10^{-27} $\text{cm}^2\text{sr}^{-1}$ (ca. 1×10^{-18} $\text{cm}^2\text{sr}^{-1}$ for single molecule SM-SERS). It has been widely utilized as a probe molecule for SERS and SERRS as well as single molecule-SERS and other techniques as it is a well-known molecule and fully characterized by SERS [27]. Solutions of R6G were prepared at several concentrations, then mixed with colloidal solutions AuNRs in ethanol. The resulting mixture was in the ratio of 2:1 for the Rh-6G: colloidal solution. This was used to develop final concentrations of the analyte mentioned above. The resulting mixture was drop cast on glass slides and then air dried for SERS measurements. SERS enhancement for R6G samples was observed, demonstrating that analytes can bind properly to the AuNRs, as Figure (2) shows SERS spectra of the R6G with characteristic bands at 612 cm^{-1} (C-C-C ring in-plane bend), 768 cm^{-1} (C-H out-of-plane bend), 1179 cm^{-1} (C-H in-plane bend), 1311 cm^{-1} (C-O-C stretch), and 1362, 1511, 1649 cm^{-1} (aromatic C-C stretch), which are all clearly observed even at low concentrations (10^{-12} M). No impurities resulted from synthesis residues (CTAB, ascorbic acid, etc) Raman modes were observed as gold nanorods were washed with ethanol and water to insure a removal organic residues. Overall, high sensitivity SERS spectra were collected on AuNRs even at lower applied 10^{-12} M concentration, the specificity still of high quality, indicating that maximising adsorption of analyte molecules on or close approximate to the nanorods site is a crucial step that bind more molecules to the surface, resulting to maximise the total enhancement.

3.3. SERS Measurement of Explosives

Following testing the activity of SERS substrates set-up on gold nanorods using R6G, SERS measurements were conducted for three analytes of explosives, 2,4,6- di nitro toluene (DNT), 2, 4, 6- trinitrotoluene (TNT), and Cyclotrimethylenetrinitramine (RDX). 5 diluted solutions of DNT were prepared and SERS spectra were collected for each on NRs in three different spots to insure the reproducibility, then averaged spectrum plotted. Figure (3) shows Raman spectrum for solid neat DNT along with SERS spectra of diluted DNT samples at concentrations of 10^{-3} M to 10^{-12} M. As figure (3) shown, Raman and SERS spectra of DNT deposited on AuNRs substrate from different concentrations in ethanol up to the pecomolar range. Raman signals were analysed, as bands at ~800 and 1170-1190 cm^{-1} are assigned to out-of-plane C-H and C-N, and in-plane H-C-C modes respectively, whereas bands at ~1350-1390 and 1560 cm^{-1} are assigned to symmetric and asymmetric stretching modes of NO_2 respectively, and The band at 1615 cm^{-1} is attributed to stretching of aromatic ring- NO_2 and the band at high frequency ~2995 cm^{-1} is attributed to aromatic C-H stretching mode. Overall, SERS data for DNT samples exhibited high sensitivity even at low concentration 10^{-12} M, as the main mode at ~1350-1390 cm^{-1} can be observed, showing the advantage of our SERS set- up in this work. This concentration is lower than the case of vapour concentration, therefore, this method can be applicable for real-time test for explosives, and other illicit samples especially low vapour pressures samples. On the other hand, SERS on AuNRs have been tested for most well-known explosive 2, 4, 6- tri nitro

toluene (TNT), where four diluted solutions at molar concentrations of 10^{-3} , 10^{-5} , 10^{-7} and 10^{-9} M were prepared and SERS spectra were collected for each. Figure (4) shows the Raman spectrum of neat solid TNT and SERS spectra of TNT samples deposited on AuNRs substrates. From Figure (4), 10^{-3} M solution of TNT had the highest enhancement, with extra signals beyond Raman signals of pure TNT, some of these extra signals matched IR modes of TNT, which means modification of the surface selection rules, and also SERS effects either through electromagnetic or chemical enhancement mechanism might contribute for such enhancement of these extra signals. Overall, the main band at 1361 cm^{-1} was observed for all samples which corresponded to the NO_2 symmetric, C-N stretching, $\nu(\text{NO}_2, \text{C-N})$ modes, while the band at 1210 cm^{-1} was also observed in all samples but with small shift toward lower frequencies which assigned to C-H (ring) in plane bend, ring breathing, $\delta(\text{C-H})$, $\nu(\text{C-H})$. In addition, bands at 792 and 822 cm^{-1} were observed clearly down to the 10^{-7} M, and can be distinguished for the lower concentrated sample at 10^{-9} M, where they assigned for C- CH_3 stretching, 2,4,6 NO_2 scissors, $\nu(\text{C-CH}_3)$ and 2,4,6 scissors, sc (NO_2) modes respectively. Band at 1532 cm^{-1} was enhanced in all samples except 10^{-9} M sample, while the band at 1616 cm^{-1} was enhanced strongly in all samples, where those bands assigned to NO_2 Asymmetric stretching, $\nu(\text{a NO}_2)$ and 2,6 NO_2 Asymmetric stretching, $\nu_{2,6}(\text{a NO}_2)$ modes respectively. It is clear that 10^{-3} M of TNT had shown the highest enhancement compared to other samples, which mainly attributed to the high number of molecules adsorbed on the Au substrates which increase the chance of maximizing the hotspot leading to obtain strong enhancement. For lower concentration samples, other factors affect the overall enhancement, such as the orientation of molecules that adsorbed on the AuNRs sites, as lower concentration results in more freedom of molecules orientation, where the part of the molecules towards the hotspot will be enhanced more than the other part in the other direction.

SERS measurements were also done for Cyclotrimethylenetrinitramine (RDX), as it is a well-known explosive used in military operations and in terror attacks, and it is frequently detected in soils and groundwater close to military places due to its long persistence [28]. For comparison and tracking the SERS signals for RDX, Raman measurements were collected for crystals of RDX as a reference, and the Raman spectrum has shown a number of signature peaks of RDX, where the most intense are the Raman band at $\approx 882\text{ cm}^{-1}$ which attributed to the stretching mode of the RDX Ring. Another band at 1215 cm^{-1} and a number of lower intensity bands between 1200 cm^{-1} and 1500 cm^{-1} also give a fingerprint spectrum of RDX, these bands correspondent to a stretching of N-N and symmetric stretching of NO_2 modes. SERS spectra were then recorded for three diluted samples of RDX in ethanol. 10^{-5} M, 10^{-7} M and 10^{-9} M deposited on AuNRs. Figure (5) shown Raman spectrum of pure crystal RDX sample and SERS spectra of aforementioned RDX diluted samples. SERS spectrum RDX

samples shown remarkable enhancement especially for signature peaks. The most intense peak was observed at approximately 882 cm^{-1} that attributed to the asymmetric stretch breathing mode of the RDX ring. The peak at 1215 cm^{-1} was also strongly enhanced in all three samples, which corresponded to CH_2 scissoring, and N-N stretch stretching modes. However, a small shift in its frequency was observed due to the surface selection rules and the electromagnetic effects on the nanostructure surface. The signal at around 1650 cm^{-1} was also enhanced in all three samples that attributed to asymmetric NO_2 stretching; however, it has shown some shift due to the reasons mentioned previously. Overall, there are a number of factors that affect the sensitivity and reproducibility of SERS. The most important one discussed in this work are the properties of the nanoparticles substrates. The shape and size of the nanoparticles as distributed in the substrate affect the sensitivity of the SERS. In the tests conducted, the Au nanorods of were randomly distributed and later deposited on the glass slides for air drying and SERS measurements. As a result, the detection sensitivity of the samples was reduced with the limit being 10^{-12} M for the R6G and 10^{-12} M for DNT and TNT, and 10^{-9} M for RDX. Since R6G molecules are large and have, they resulted in a high scattering with a lower cross section area of the molecules, thus, even at picomolar of R6G, SERS enhancement was remarkable compared to DNT and TNT samples. The sensitivity of the SERS could be improved through close packing of the nanorods. The enhancement of the nanostructures (AuNRs in this work) is mainly affected by electromagnetic enhancement mechanism (EM) and chemical enhancement (CT). The two processes involve generating electrons across the analyte, as more deposited molecules, higher enhancement can be obtained. For lower concentrations, the enhancement factors were recorded high, and it is a common phenomenon to have EFs that are higher with low concentrated solutions. This can be attributed to the nature of the EF formula. The recorded values for the concentrations show varying values of the EF across different concentrations, as shown in table (1). Furthermore, to examine the reproducibility of our AuNRs substrates for explosives detection, mapping of the substrate carried out for 10^{-7} M sample of DNT, where SERS spectra were collected on different spots as shown in figure (6). Mapping of diluted sample of DNT showed good reproducibility and proper enhancement for all collected spectra that indicated an efficient distribution of hotspots, however, close inspection of SERS spectra in Figure (6) shows slight discrepancy in band intensities but unnoticeable for detection and identification purposes. Such observation confirm the validity of this method for detection of traces explosives, which will contribute for reducing false alarm during testing samples in security points.

3.4. Calculation of enhancement factor EF

The Enhancement Factor (EF) was calculated on gold nanorods colloidal solutions as SERS substrates using the analytical enhancement factor.

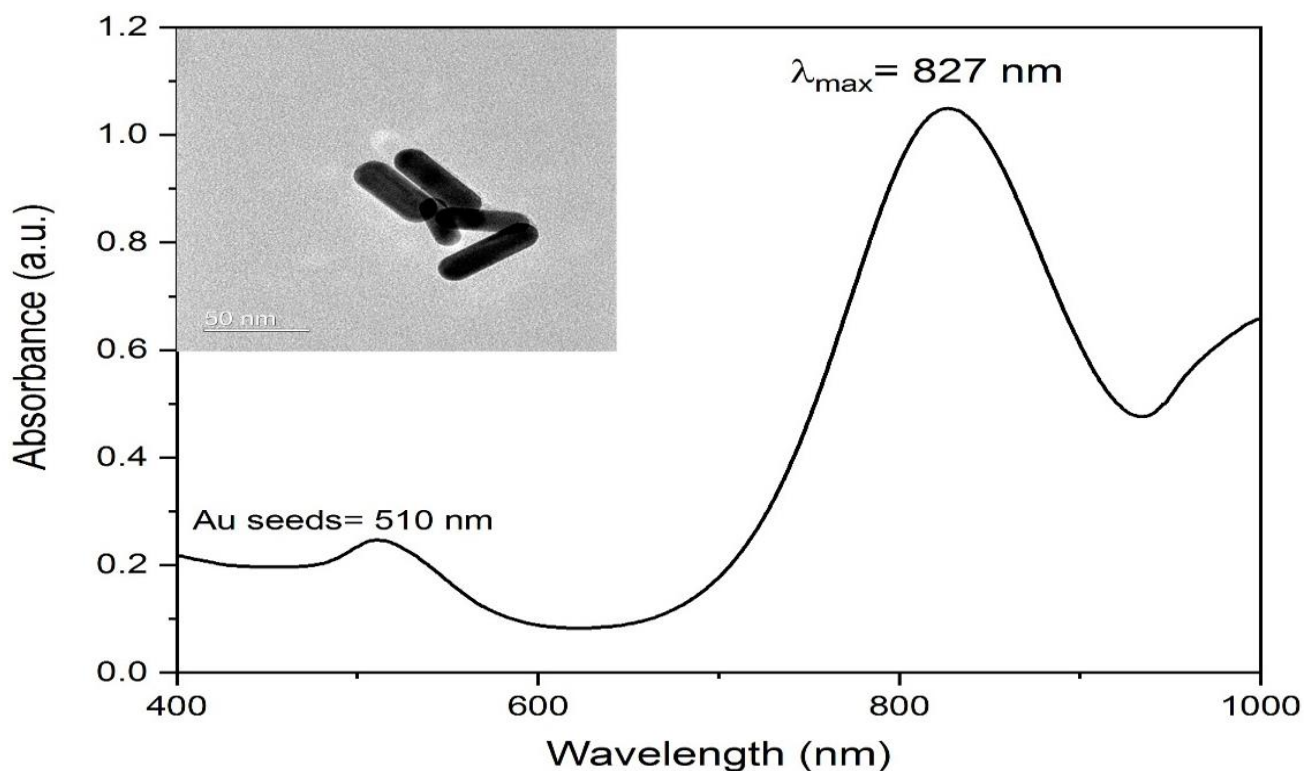


Figure 1: UV-Vis absorption spectrum of gold nanorods. The surface plasmon resonances (SPR) absorption peak observed at 827 nm, and a peak at 510 nm for gold nano seeds. The spectrum was obtained at room temperature. The inset shows TEM images of gold nanorods at a scale of 50 nm.

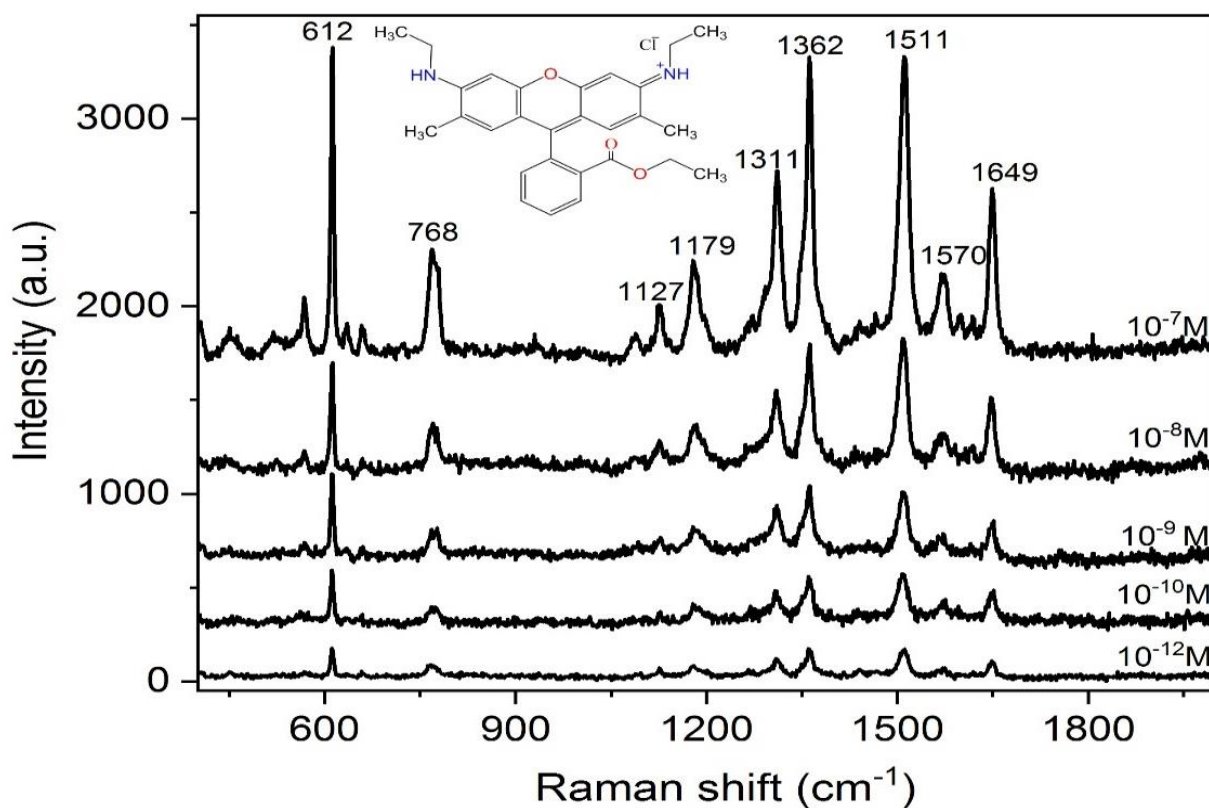


Figure 2: Surface enhanced Raman spectroscopy spectra of 10^{-7} , 10^{-8} , 10^{-9} , 10^{-10} and 10^{-12} M of R6G solutions deposited on gold nanorods substrates. Frequencies of characteristic peaks were shown on the top spectrum along with the chemical structure of the analyte.

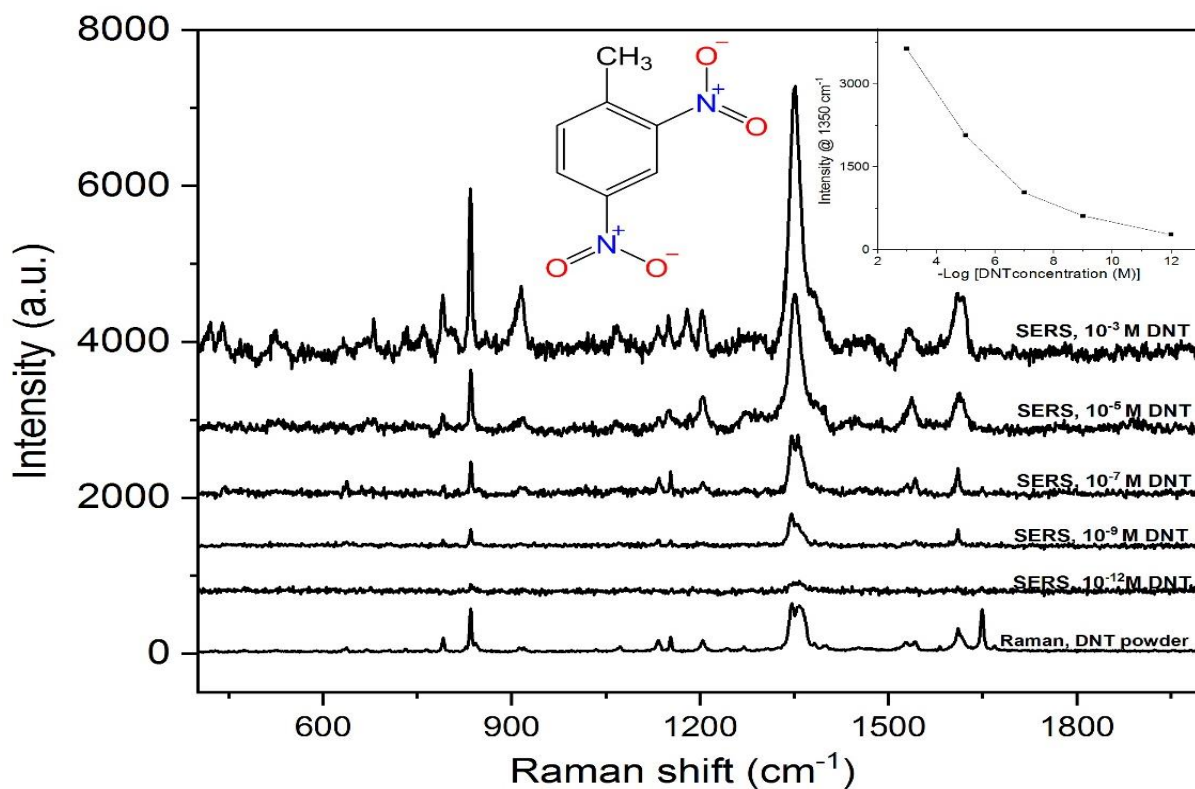


Figure 3: Raman and SERS spectra of 2, 4-di nitro toluene (DNT) on gold nanorods substrates from different concentrations in ethanol in the range 10^{-3} M to 10^{-12} M. The inset shows the relation between SERS intensity of the band 1350 cm^{-1} of DNT and samples concentration.

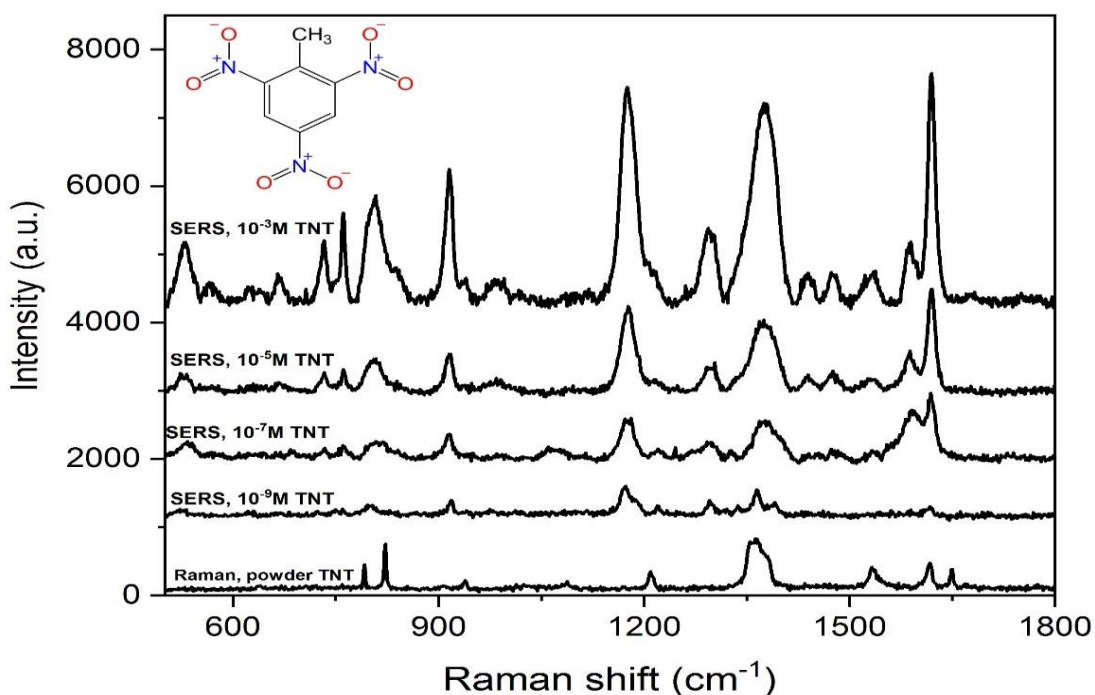


Figure 4: Raman spectrum of powder TNT and SERS spectra of TNT solutions on gold nanorods substrates at different concentrations in ethanol namely 10^{-3} , 10^{-5} , 10^{-7} , and 10^{-9} M. SERS spectra shown high sensitivity on AuNRs for almost the whole Raman mode of TNT, with shift of some bands due to the selection surface selection rules of SERS.

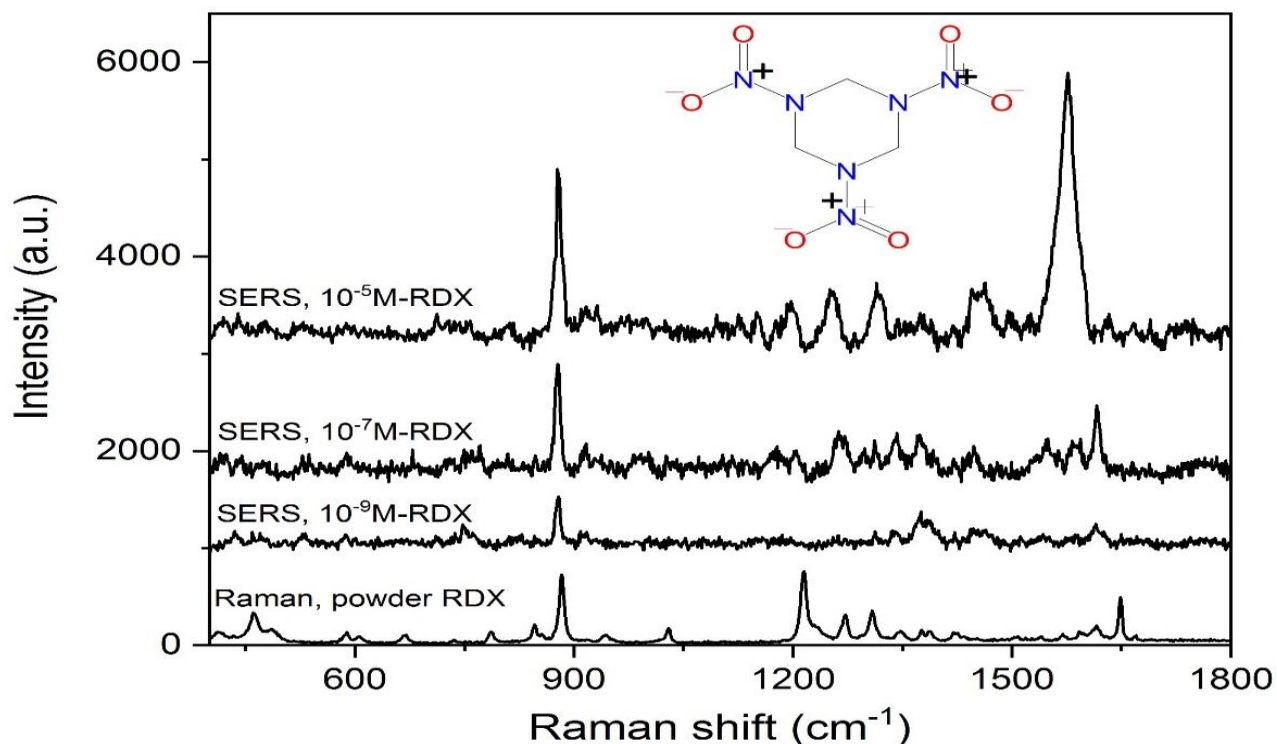


Figure 5: Raman spectrum of neat RDX, and SERS spectra of 10^{-5} , 10^{-7} , 10^{-9} M of RDX on AuNRs. A sharp peak at $\sim 882\text{cm}^{-1}$ was strongly enhanced which corresponds to the symmetric ring-breathing mode, the band at 935 cm^{-1} attributed to ring stretching and N-O deformation. Bands at 1274 cm^{-1} corresponded to scissoring of CH_2 and stretching vibration of N-N, 1330 cm^{-1} attributed to CH_2 wagging, the band at 1397 cm^{-1} asymmetric stretching NO_2 where the band at 1649 cm^{-1} is attributed to asymmetric stretching of NO_2 .

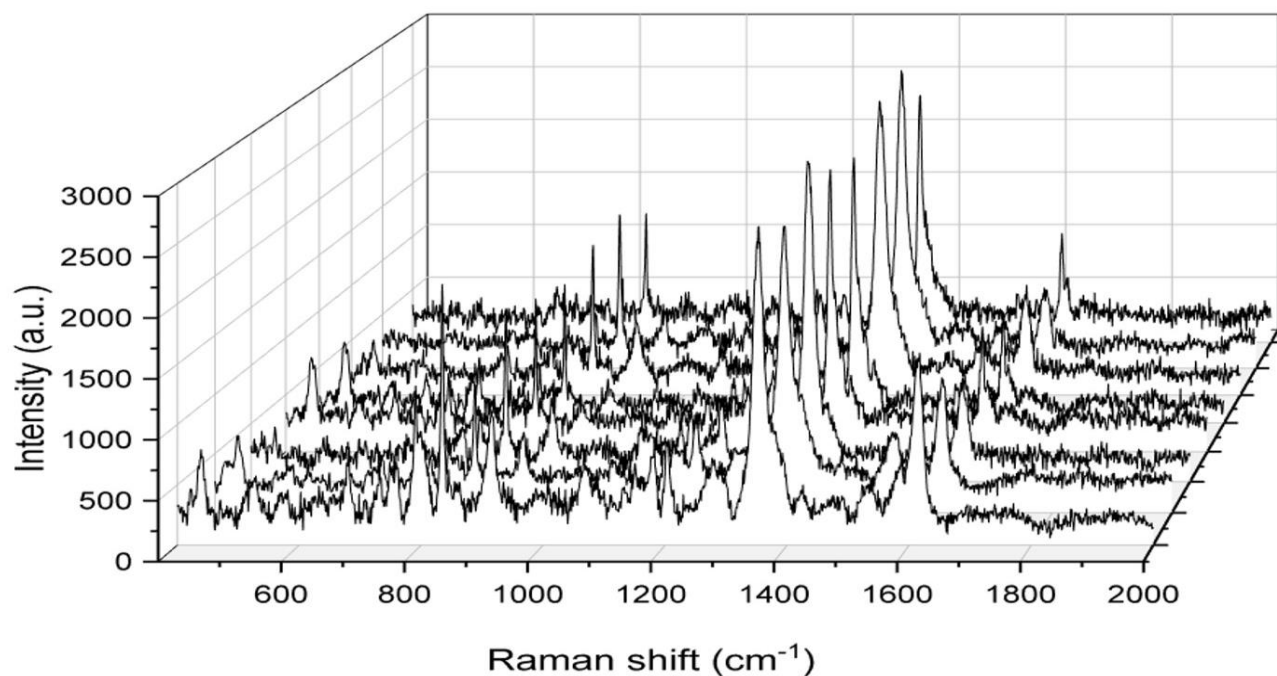


Figure 6: Mapping of SERS spectra of DNT from a 10^{-7} M solution across a AuNRs substrate, shown great reproducibility for SERS measurements in all selected spots that were selected randomly across the substrate.

Table 1: Calculated Enhancement Factors (EF) for R6G and DNT, TNT and RDX explosives on AuNRs substrates.

Sample	Signals (cm ⁻¹)	Bands intensities (a.u.)		Enhancement Factor EF
		Raman	SERS	
R6G, 10 ⁻⁹ M	1511	1294	411	3.17×10 ⁸
R6G, 10 ⁻¹² M	1511	1294	171	1.32×10 ¹¹
DNT, 10 ⁻⁹ M	1350	640	447	6.98×10 ⁸
DNT, 10 ⁻¹² M	1350	640	172	2.69×10 ¹¹
TNT, 10 ⁻⁹ M	1361	793	412	5.19×10 ⁸
RDX, 10 ⁻⁹ M	882	726	599	8.25×10 ⁸

This can be defined by the follows formula equation (1) [29]:

$$AEF = \frac{I_{SERS} \times C_{RS}}{I_{RS} \times C_{SERS}} \quad (\text{equation. 1}) \quad [4]$$

Where I_{SERS} and I_{RS} are the intensities of SERS and Raman bands respectively as shown in Table (1), and C_{RS} , and C_{SERS} are the corresponding analyte concentrations in the Raman and SERS measurements, respectively.

4. Conclusions

In this work, a simple but sensitive SERS substrate based on AuNRs has been demonstrated for the detection of ultra-trace concentrations of explosives. The substrate provided high sensitivity and specificity and allowed detection of picomolar concentrations of DNT, and nanomolar levels of TNT and RDX, three model explosive materials. The SERS enhancement factor when using R6G as a model molecule with high Raman cross-section was estimated at 1.32×10^{11} , and enhancement factors of 2.69×10^{11} , 5.19×10^8 and 8.25×10^8 are given for DNT, TNT and RDX respectively. The SERS substrate preparation procedure here has allowed detecting trace levels of explosives with high specificity, where mixing analytes with nanorods colloids allowed more molecules deposition on nanorods surfaces with remarkable spectral resolution of key fingerprint regions, this step improve the overall detection procedure that may have potential for stand-off detection of explosives.

Conflicts of interest

There are no conflicts to declare.

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