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Rapid detection of TNT in aqueous media by selective label free surface enhanced Raman spectroscopy

Arniza K.M. Jamil, Emad L. Izake *, Arumugam Sivanesan, Peter M Fredericks

Nanotechnology and Molecular Sciences Discipline, Faculty of Science and Engineering, Queensland University of Technology, 2 George St., Brisbane 4001, QLD, Australia

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ABSTRACT

We report rapid and ultra-sensitive detection system for 2,4,6-trinitrotoluene (TNT) using unmodified gold nanoparticles and surface-enhanced Raman spectroscopy (SERS). First, Meisenheimer complex has been formed in aqueous solution between TNT and cysteamine in less than 15 min of mixing. The complex formation is confirmed by the development of a pink colour and a new UV–vis absorption band around 520 nm. Second, the developed Meisenheimer complex is spontaneously self-assembled onto unmodified gold nanoparticles through a stable Au–S bond between the cysteamine moiety and the gold surface. The developed mono layer of cysteamine-TNT is then screened by SERS to detect and quantify TNT. Our experimental results demonstrate that the SERS-based assay provide an ultra-sensitive approach for the detection of TNT down to 22.7 ng/L. The unambiguous fingerprint identification of TNT by SERS represents a key advantage for our proposed method. The new method provides high selectivity towards TNT over 2,4 DNT and picric acid. Therefore it satisfies the practical requirements for the rapid screening of TNT in real life samples where the interim 24-h average allowable concentration of TNT in waste water is 0.04 mg/L.

1. Introduction

Nitroaromatic explosives have significant detrimental effects on national security, ecological environment, and human health [1]. 2,4,6-Trinitrotoluene (TNT) is the most widely used explosive in industry and military/terrorist activities. TNT is widely used in landmines and under water blasting, leading to the contamination of soil and ground water. The treatment of TNT pollution in soil and waste water is always difficult and expensive to remedy [2,3]. Human exposure to TNT pollution may lead to anemia and abnormal liver function especially when the exposure to the pollutant is for prolonged periods of time [4]. To be able to protect the civilian and military population, it is very important to develop a detection method which is rapid, simple, sensitive, and can be used by first responders in field for the identification of TNT threats, whether to the environment or human safety.

A variety of methods are currently available for the detection of TNT [5]. These methods include fluorescence spectroscopy [6,7], infrared spectroscopy [8,9], luminescence spectroscopy [10–15], chromatography [16,17], ion mobility spectrometry [18], neutron activation analysis [1], immunochemistry [19–21], electrochemistry [22–27], molecularly imprinted polymers [28–30], immunoassays [31–33]. However most of these techniques are expensive, non-portable and potentially limited by extensive sample preparation [1,34]. For example, mass spectrometry requires isolation and purification of the analyte usually by chromatography.

Surface Plasmon spectroscopy has been recently utilized for the detection of TNT in aqueous solution [35–38]. Also biosensors that utilize the displacement of an anti- TNT antibody from a surface-confined immune-complex by TNT and the transduction of the dissociation of the antibody by SPR, have been demonstrated in the literature [39,40]. These TNT sensors detect the binding of the molecule by measuring the change in the refractive index at the interface between a metallic layer with a fixed receptor and a dielectric medium (e.g. analyte in aqueous solution). Therefore, they are vulnerable to nonspecific interactions [37,41].

Nanomaterial-based electrochemical sensors were also demonstrated for the detection of TNT. These sensors take advantage of the redox activity of the nitro groups within the nitro aromatic explosives [42]. Electrode materials such as graphene [43], polyguanine-SiO_2 [44], meso porous SiO_2 [45], ordered meso porous carbon [46] have been used for the detection of TNT in various media.

Recently UV–vis methods that utilize the use of gold nanoparticles for the detection of TNT were also demonstrated. In these methods, a primary amine such as 1,2-ethylenediamine or cysteamine is used to

* Corresponding author. Tel.: +61 7 3138 2501; fax: +61 7 3138 1804.
E-mail address: e.kiriakous@qut.edu.au (E.L. Izake).

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modify the surface of gold nanoparticles (GNPs), and the amine capped GNPs were applied for the detection of TNT by UV–vis spectroscopy [47–50]. In these models the donor–acceptor interaction between the amine-capped nanoparticles and TNT result in the aggregation of the nanoparticles and, in effect, a colour shift from red to blue. This visual colorimetric detection is attractive because the detection results can be easily read out by the naked eye. However these colorimetric methods suffer from the uncertain identity of the detected analyte since the aggregation of nanoparticles and colour change can be influenced by various compounds. For example the colour change associated with the detection of TNT is similar to that of codeine, melamine, organic dithiols and pesticides [51–56]. Also the change in ionic strength or pH of the sample can induce aggregation and colour change. Therefore the above methods carry the risk of false positive identification especially for samples of complex matrices [57,58].

Another nanoparticle-based technique takes advantage of the ability of metal nanoparticles to quench emission from nearby fluorescent compounds [59]. In this sensors the presence of the analyte is detected by the change in the intensity of emission from the fluorescent molecule attached to the detection platform [59–63]. Goldman et al. [64] developed nanoscale sensing assemblies that are based on fluorescence resonance energy transfer (FRET) for the detection of 0.5 nM TNT in soil samples. The sensor consisted of anti-TNT specific antibody fragments attached to a hydrophilic quantum dot (QD) via metal-affinity coordination. A dye-labelled TNT analogue pre-bound in the antibody binding site quenches the QD photoluminescence via proximity-induced FRET. The disadvantage of this model is that it uses an antibody which requires carful procedures for functionalization onto the QD as well as proper storage of the functionalized QD. Kartha developed sensitive method for the detection of TNT down to 0.23 ppq using nano fibres [65]. These nano fibres experience fluorescence quenching in the presence of nitroaromatic compounds. However, the nano fibre sensor is non-specific to TNT and responds to other closely related structures such as 2,4,6 trinitrophenol (picric acid) and dinitrotoluene (DNT) [66]. Recently, Senthamizhan et al. developed a nano fibre for detecting 1 ppb of TNT in water with high selectivity over 2,4 DNT [67]. A disadvantage of using optical nano fibres is the fact that surface interactions, such as van der Waals and Casimir-Polder, may affect both the resonance line shape and the central position in relation to free-space studies [68]. Ma et al. [69] recently demonstrated a fluorescent paper Sensor that utilizes 8-hydroxyquinoline aluminum (Alq3)-based fluorescent composite nanospheres for the detection of nitroaromatic explosives at the ng/mL detection limit.

Surface-enhanced Raman spectroscopy (SERS) has been considered for the sensitive detection of nitro-aromatic explosives [70,71]. When the analyte molecules are adsorbed on roughened metal surfaces, their Raman signals are greatly amplified due to enhanced electromagnetic fields within the immediate vicinity of the metal upon excitation of Plasmon resonances by photon interaction as well as charge transfer processes between the metal and the adsorbed molecule [1]. The SERS enhancement effect overcomes the low sensitivity problem inherent in conventional Raman spectroscopy allowing even single molecule detection [72]. The distinct ability to obtain molecular recognition of an analyte at very low concentrations in aqueous environment allows SERS to be a unique technique for ultrasensitive biological and chemical analysis as well as environmental sensing [73,74]. Numerous SERS substrates have been developed for the detection of nitroaromatic explosives [55,59,75–78]. By incorporating a specific chemical moiety on the SERS surface, one can target the detection of TNT present in a complex sample mixture at ultra trace level without the need to physically separate out other interfering species [79]. Molecules such as cysteine, L-cysteine methyl ester, 2-aminothiophenol, BSA have been recently used to form Meisenheimer complexes with TNT and enable the SERS detection of TNT [11,76,77,80–82].

In this article we report the detection of ultra trace amounts of TNT by surface enhanced Raman spectroscopy after the rapid formation of a coloured Meisenheimer complex between TNT and cysteamine in aqueous medium. The complex formation is confirmed by visual inspection and UV–vis spectroscopy. Using this method, we were able to directly detect TNT in aqueous media with high selectivity over the common interfering molecules 2,4 DNT and picric acid. The quantification limit of the method was found to be 22.7 ng/L. By combining high sensitivity and selectivity that are offered in this method, we enhance the accuracy and reliability of our detection technique.

2. Experimental

2.1. Reagents

Hydrogen tetrachloroaurate ($HAuCl_4 \cdot 4H_2O$), trisodium citrate, cysteamine hydrochloride, 2,4-dinitrotoluene (2,4 DNT), 2,4,6-trinitrophenol (picric acid), sodium hydroxide, acetonitrile, ethanol and methanol were purchased from Sigma Aldrich (USA). All chemicals and solvents were of analytical grade and were used without further purification. 2,4,6-trinitrotoluene (TNT) standard (1 mg/mL in 1:1 acetonitrile:methanol) was purchased from Merck (Australia). All dilutions were made using deionised water (18.2 MΩ cm) from a Millipore water purification system.

2.2. Gold nanoparticle synthesis

Au NPs were prepared according to the standard citrate reduction method [83,84]. Typically, 30 mL of 0.1% $HAuCl_4$ was heated to boiling point. Next, 180 μL of 1% sodium citrate was added to the boiling solution. During heating, the colour of the solution changed from yellow to red. The solution was further heated with stirring for another 15 min before being left undisturbed to cool at room temperature. The Plasmon properties and average size of the prepared gold nanoparticles were characterized by UV–vis spectroscopy and high resolution transmission electron microscopy (Hr-TEM).

2.3. Preparation of Meisenheimer complex with TNT

Cysteamine stock solution (2×10^{-4} M) was prepared in Milli-Q water. In order to obtain the free base form of cysteamine, the pH of the solution was then adjusted to pH 8.5 with 0.01 M aqueous sodium hydroxide. To develop the Meisenheimer complex, equal volumes of TNT and cysteamine standard solutions (2×10^{-4} M) were mixed together. The mixture is allowed to stand for till its colour changes from colourless to pink then screened by UV–vis spectroscopy. UV–vis spectra are collected at 1 min intervals for 15 min in order to determine the optimum time for the complete formation of the cysteamine-TNT complex.

2.4. Detection of TNT by surface enhanced Raman spectroscopy (SERS)

TNT standard solutions in the concentration range 2×10^{-4}–2×10^{-9} M were prepared by serial dilutions. Equal volumes of a TNT standard solution and cysteamine stock solution were mixed and allowed to stand for 30 min to develop cysteamine-TNT complexes at various concretions of TNT. A 100 μL of the TNT-cysteamine complex is then mixed with 900 μL of the GNPs colloid. Therefore the TNT concentration range in the final preparations is 10^{-5}–10^{-10} M.

2.5. Interference study

To determine the selectivity of the method towards TNT over other nitroaromatic compounds, standard solutions (2×10^{-4} M) of 2,4-DNT (in ethanol) and picric acid (in deionised water) were prepared. Equal volumes of 2,4-DNT or picric acid and cysteamine stock solution are mixed and allowed to stand for 30 min. The mixtures were then screened by UV–vis spectroscopy. For SERS measurements, equal volumes of 2,4-DNT or picric acid (2×10^{-5} M) and cysteamine stock solution were mixed, allowed to stand for 30 min then 100 μL of the DNT/cysteamine or picric acid/cysteamine solution is mixed with 900 μL and the mixture screened by SERS.

2.6. Instrumentation

UV–vis measurements were carried out in the wavelength range 250–800 nm using the Agilent Cary 60 UV–vis spectrometer (Agilent Technologies, USA). The gold nanoparticles were characterized using the JEM-2100 F Transmission Electron Microscope. Raman spectra were collected on the Renishaw inVia Raman Microscope using NIR excitation. A 785 nm laser beam was used for excitation. The applied laser power was 0.1% of maximum power of the laser source (450 mW). Spectra were collected using a 50 objective lens over a wavelength range from 500 cm^{-1} to 2000 cm^{-1} using 10 accumulations of 10 s exposure times each for a minimum of six independent measurements.

3. Results and discussion

3.1. Development of Meisenheimer complex

Cysteine and cysteamine have high affinity to form Meisenhimer complexes with TNT. In this work we choose cysteamine as small molecule, of only 2 carbon atoms, to interact with TNT and form a donor–acceptor molecule. The small chain length of cysteamine makes it very suitable capturing molecule for the detection of TNT by SERS since the TNT moiety of the cysteamine-TNT complex will be very close to the surface of the metal substrate used in the SERS testing. Depending on the pH of the cyteamine solution, it may predominantly exist in one of three ionic forms: the positively charged form ($HS–CH_2–CH_2–NH_3^+$), the zwitterionic form ($S–CH_2–CH_2–NH_3^+$), and the negatively charged form ($S–CH_2–CH_2–NH_2$) [85]. In a neutral aqueous medium (pH 7), the zwitterionic form of cysteamine interact with the water molecules so that there are two hydrogen bonds with the cysteamine molecule, that is, sulphur atom to hydrogen atom of water and from oxygen to hydrogen of the positively charged amino group. As a result the cysteamine molecule may adopt to a gauche confirmation where the sulphur and amino groups are engaged in a cyclic structure via a water molecule bridge [85]. Therefore, the cysteamine molecule at pH 7 is incapable of forming a stable Meisenhimer complex with TNT than when it is in an alkaline medium (pH > 7) where the non-cyclic form ($S–CH_2–CH_2–NH_2$) predominates. The development of 1:1 Meisenheimer complex between alkaline cysteamine solution (pH8.5) and TNT is indicated by the colour change from colourless to pink upon the addition of aqueous cysteamine to the TNT solution (Fig. 1). The UV–vis spectrum of the formed complex is depicted in Fig. 2a. As shown by the figure, the formation of the cysteamine-TNT complex results in the development of a new band at 520 nm. Fig. 2b depicts the development of the cysteamine-TNT complex with time. As indicated by the figure, the complex is formed rapidly which is evident by the increase in the signal intensity at 520 nm. The change in the absorbance of the 520 nm band becomes insignificant after 11 min which indicates the complete formation of the complex.

Fig. 1. Development of 1:1 cysteamine-TNT Meisenheimer complex in aqueous medium at pH 8.5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The Meisenheimer complex between an electron-deficient nitroaromatic compound and an electron-rich amine is a resonance-stabilized intermediate structure formed during a nucleophilic aromatic substitution reaction. For TNT, the three nitro groups act as strong electron-withdrawing groups that activate the molecule to nucleophilic substitution [79,83–88]. Therefore in the presence of cysteamine (electron-rich nucleophile), a donor–acceptor complex is formed by the addition of a lone pair of electrons from cysteamine to the aromatic ring of TNT [89,90]. Fig. 3 depicts the mechanism for the TNT-Cysteamine complex development in aqueous solution. The developed σ anion complex is stabilized through resonance stabilization by the three electron-withdrawing nitro groups [77]. The nucleophilic addition at the ring carbon of TNT leads to the formation of a highly conjugated anion that absorbs light in the visible range and, therefore, develops a pink colour as well as the absorption band at 520 nm [89–91].

3.2. SERS detection of TNT

For the SERS fingerprinting and quantification of ultra trace amounts of TNT in aqueous solutions, we utilized label-free gold nanoparticles (GNPs). We elected gold over silver since the later is exposed to oxidation in aqueous media which would lead to loss of the SERS effect [92]. The Plasmonic properties of the bare GNPs were characterised by UV–vis spectroscopy. The nanoparticles exhibited a characteristic absorption band at 530 nm. Fig. 4 depicts the TEM measurement of the nanoparticles and the size distribution curve. The nanoparticles were found to be of spherical shape with an average size of 58 ± 9.4 nm.

For the SERS detection of TNT, the analyte was reacted with cysteamine with TNT, to develop a Meisenheimer complex that is then immobilized onto the GNPs colloid (Section 2.4). The SERS spectrum of 10^{-6} M TNT is depicted by Fig. 5. As indicated by the figure, the diagnostic spectral lines of TNT at 793 cm^{-1} (C–H out-of-plane bend), 826 cm^{-1} (ring deformation), 1215 cm^{-1} (C–H ring bend and in-plane rocking) 1350 cm^{-1} (symmetric nitro stretching) and 1613 cm^{-1} (2,6-NO_2, asymmetric ring stretch) were detected with excellent match to the TNT reference spectrum [77,93,94]. This unambiguous fingerprint identification of TNT represents a key advantage for our proposed method.

For the SERS quantification, various concentrations of TNT were screened with each measurement repeated 6 times ($n = 6$). Fig. 6a, depicts the Raman signal at 1350 cm^{-1} of TNT within the concentration range 10^{-5}–10^{-10} M (spectra were normalised and background subtracted for comparison purposes). Fig. 6b depicts the relationship between the Raman signal intensity @ 1350 cm^{-1} and the concentration of TNT solution. The relationship between TNT concentration and the SERS signal intensity (Fig. 6b) is linear within the concentration range 10^{-7}–10^{-10} M TNT ($R^2 = 0.9866$) and the lower limit of TNT quantification was found to be 0.1 nM (22.7 ng/L).

The success of the proposed method in detecting very low concentrations of TNT is underlined by our approach to develop the cysteamine-TNT complex in solution prior to its immobilization onto the GNPs for SERS measurements. Glembocki et al. [95] attempted the detection of TNT using cysteamine-coated gold and silver substrates where they developed a monolayer of the amine

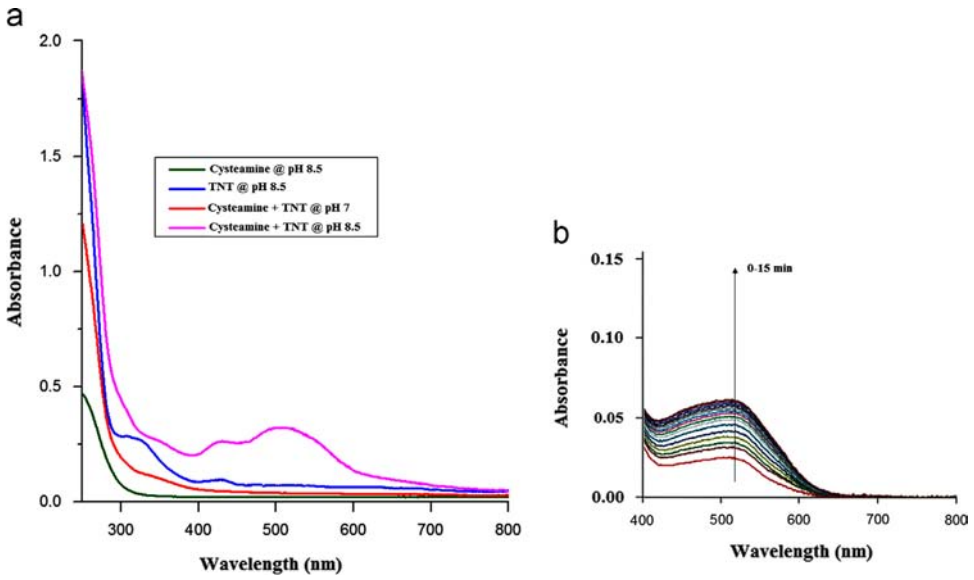

Fig. 2. (a) UV–vis absorption spectrum of the aqueous 1:1 Meisenheimer complex between cysteamine and TNT and (b) the development of the complex with time.

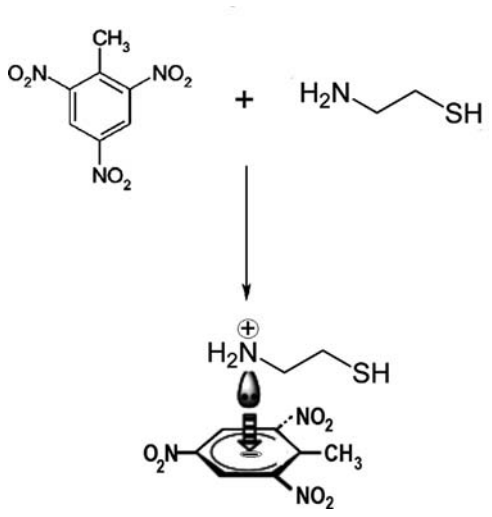

Fig. 3. Mechanism for the formation of 1:1 cysteamine-TNT Meisenheimer complex.

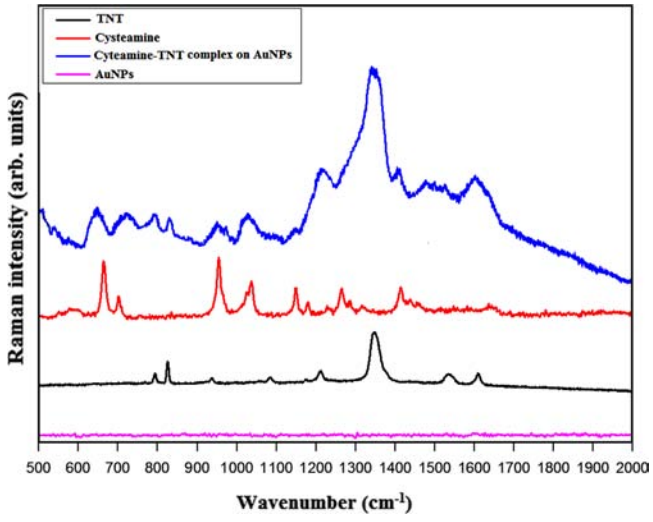

Fig. 5. Raman spectrum of 10^{-6} M TNT. The TNT solution was first reacted with cysteamine then with unmodified GNPs for the SERS detection.

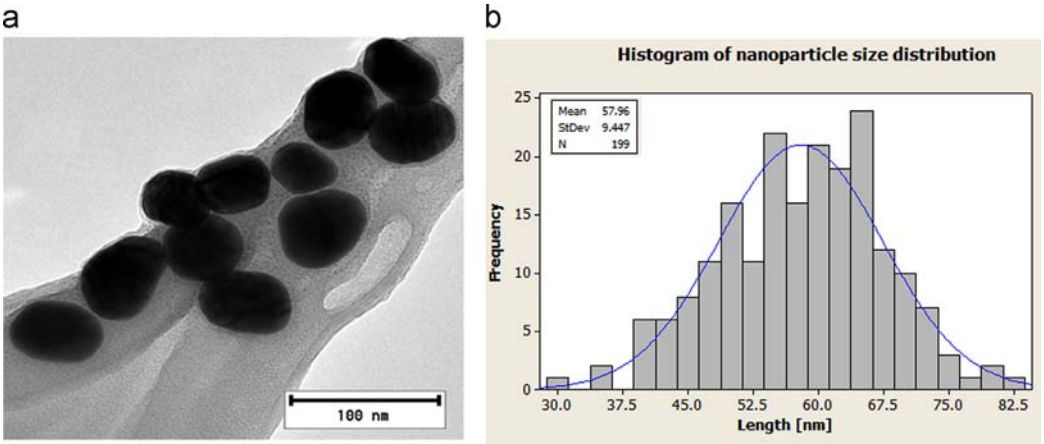

Fig. 4. (a) TEM and (b) size distribution of unmodified gold nanoparticles.

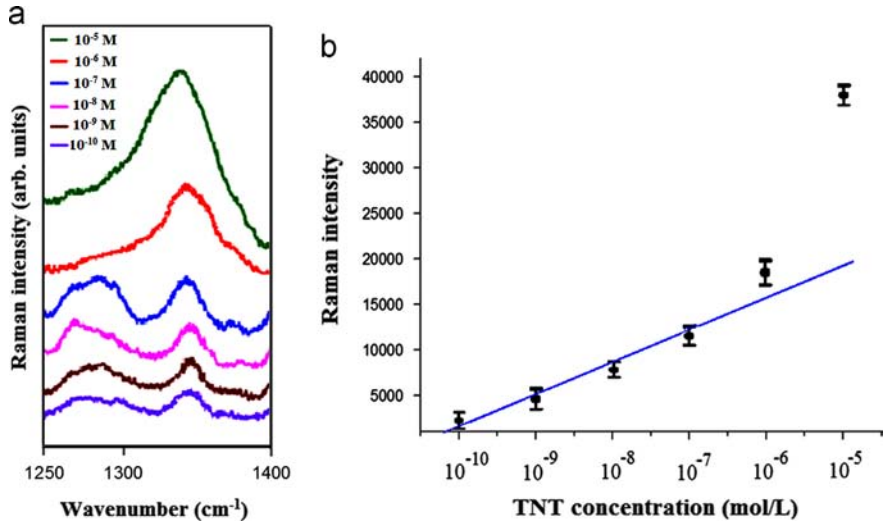

Fig. 6. Quantification of ultra trace amounts of TNT in aqueous solution (a) Raman signal of TNT @ 1350 cm^{-1}, (b) the relationship between the signal intensity and concentration. The error bars indicate the standard deviation from 6 measurements.

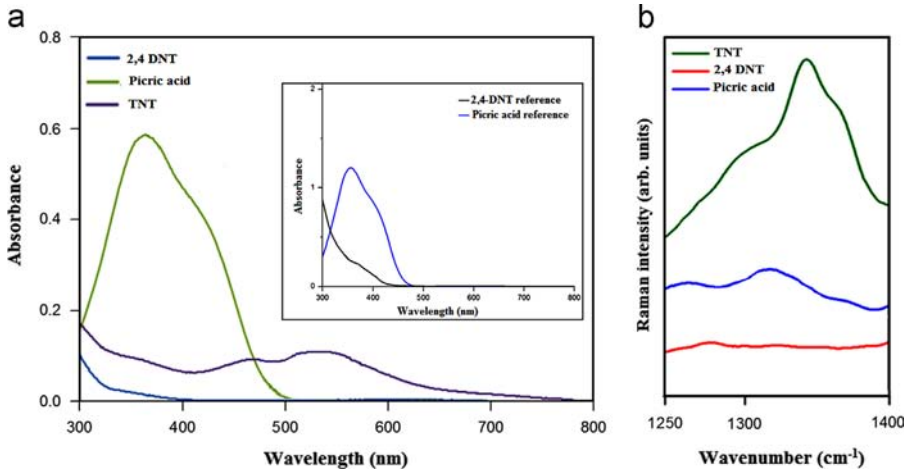

Fig. 7. (a) UV–vis absorption spectra and (b) Raman spectra of cysteamine/ TNT, cysteamine/DNT and cysteamine/ picric acid mixtures. The final TNT concentration for the UV–vis measurements was 10^{-4} M and for the SERS measurements 10^{-6} M. The inset depicts the reference UV–vis spectra of 2,4-DNT and picric acid.

onto the metal surface then used the modified substrate to detect TNT. However their detection strategy faced serious challenges that made the SERS detection of TNT almost impossible and non reproducible. They attributed the unreliable measurements in their experiment to the fact that cysteamine molecules on gold surface exist mainly in a gauche configuration. In this configuration the cysteamine binds to the metal surface from both the thiol and amine ends [96]. This causes the cysteamine molecule to bend parallel to the metal surface and the amino group of cysteamine is no longer able to interact with TNT. Therefore the Meisenheimer complex cannot be formed and the SERS detection of TNT fails. To the contrary, our approach allows the amino groups to react first with TNT in solution and the resulting complex, when added to the GNPs, can only bind to the gold surface via the free thiol group of the cysteamine moiety to form a stable Au–S bond [97].

Moskovits [98] and Creighton [99] explained that the molecule's Raman vibrations that have larger component of polarizability in the direction normal to the surface experience high SERS enactment by the substrate. On the other hand, the least enhanced modes are those whose Raman tensor components involve the two axes in the plane of the surface [100]. Therefore, the large SERS enhancement of the TNT Raman bands and the low quantification limit that are observed in our SERS measurements may be attributed in part to the immobilization of the TNT molecule, via the cysteamine linker, in an upward position with its molecular plane almost vertical with respect to the metal surface [96,100].

A recent report indicated the detection of TNT by gold meso flower shaped nanoparticles (MFs). The authors indicated the detection limit of TNT per a single MF to be 0.015 zeptomoles [11]. However, a 100 ng/L TNT solution was effectively used for the measurement. In addition, under colorimetric conditions the LOD of the reported method was found to be higher than 44 μM [50]. A more recent report indicated the detection of 1 pM TNT using dumbbell nano probes [1]. However, the authors used a complex technique for the synthesis of the nano probes. In addition, the analysis involves multi-step process that requires 24 h for the development of a Meisenheimer complex with L-cysteine and an additional 24 h for the development of dumbbell hot spots for the SERS detection of TNT. Therefore, the overall time of 48 h renders the TNT detection by this method as impractical. Despite the higher detection limit of our proposed method (22.7 ng/L), the present method satisfies the practical requirements for the rapid screening of TNT in real life samples where the interim 24-h average allowable concentration of TNT in waste water is 0.04 mg/L [65,101,102].

3.3. Interference study

In order to determine the selectivity of the proposed method towards TNT detection over other nitroaromatic compounds, we investigated the interaction between 2,4 DNT and picric acid with cysteamine. The structure of Picric closely resembles that of TNT. Picric acid is also used for metal etching and in the dye, leather, and glass industries. Trace amounts picrate anion can exist in water and soil as a pollutant [103]. 2,4-DNT is found to be unavoidable impurity in military grade TNT [104]. Therefore it is very important to confirm the selectivity of the analytical method towards TNT over picric acid and 2,4-DNT in order to avoid false identification.

For the interference study, equal volumes of cysteamine stock solution and 2,4-DNT and picric acid were reacted under the given experimental conditions (Section 2.5). The resulting mixtures were examined by visual inspection, UV–vis and SERS. The visual inspection did not indicate any colour change after 30 min of the reaction. Also the UV–vis spectra of the 2,4-DNT/cysteamine and picric acid/cysteamine mixtures did not show any change to the absorption spectra of DNT or picric acid (Fig. 7a). The SERS spectra of the cysteamine/2,4-DNT and cysteamine/picric acid mixtures are depicted in Fig. 7b and indicate the absence of the characteristic symmetric nitro stretching Raman signal of nitroaromatic compounds @ 1350 cm^{-1}. The absence of the band @ 1350 cm^{-1} is attributed in part to the formation of a passive cysteamine monolayer onto the gold nanoparticles [96,105]. This layer neither allows for the adsorptions of 2,4-DNT or picric acid onto the gold surface nor the formation of a Meisenheimer complex and hence the absence of the SERS signal. These results are also in agreement with the reported literature on the inability of 2,4-DNT and picric acid to form stable Meisenheimer complexes with primary amines [47,49,50,62,77].

4. Conclusion

Herein we present a simple and rapid approach to the detection of trace amounts of TNT in aqueous media. The new method involves the development of a cysteamine-TNT Meisenheimer complex in solution. The TNT anion in the developed complex is highly stable due to resonance stabilization through the three NO_2 groups of TNT. Due to the high conjugation in the cysteamine-TNT system, the complex develops a pink colour in solution as well as a characteristic UV–vis absorption band at 520 nm. The immobilization of the formed complex onto the GNPs surface takes place rapidly via the formation of a favoured Au–S bond between the cysteamine moiety of the complex and the gold surface. Therefore a self assembled monolayer is formed, within 30 min, onto the gold surface to bring the TNT molecule in an upward position to the enhancing metal surface and hence the SERS detection of TNT down to 22.7 ng/L. The new method is selective towards TNT over 2,4-DNT and picric acid. Therefore it satisfies the practical requirements for the rapid unambiguous screening of TNT in real life samples where the interim 24 h average allowable concentration of TNT in waste water is 0.04 mg/L. The new sensor can be used for the rapid screening of TNT residues in soil, water, on metallic surfaces (e.g. implements used to synthesis TNT and prepare improvised device, car carrying a bomb), on suspected packages, post explosion debris (crime scene investigation).

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