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Raman Spectra Evaluation of Gold Nanoparticles Composite Interaction with Nerve Agent Simulant

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ABSTRACT

Raman spectroscopy is one of many reliable methods to detect chemicals' presence and traces in the environment. Raman enhancement for organophosphorus nerve agents is crucial considering its lethality in low concentration. In the present study, we evaluate Raman detection towards dimethyl methyl phosphate (DMMP), a colorless organophosphate chemical on selected substrates and environments. The role of AuNPs in providing surface-enhanced Raman scattering signals and graphene oxide as interaction templates are discussed in the interest of analysing various DMMP contaminations. Our study shows that DMMP's Raman modes were enhanced by gold nanoparticles (AuNPs) coated cellulose film indicating the potential of this substrate. In aqueous measurement, the D band to G band intensity ratio of AuNP/graphene was seen to produce a significant increase in sensitivity towards DMMP compared to graphene oxide dispersion. These Raman signatures can be used to understand molecules-substrate surface interactions that will be beneficial to chemical and optical sensor development. The current system also shows the potential to identify 1000 ppm DMMP which is difficult by typical infrared spectroscopy.

1. Introduction

Exposure and misuse of organophosphate compounds originated from insecticides, drugs and chemical warfare agents (CWA) are a potential hazard to health and the environment [1]. CWA organophosphate nerve agents are highly toxic and capable of accelerating acute symptoms to death within minutes of poisoning. Chemical detection is one of the four counter strategies (deter, detect, delay, and defend) used by national security to protect the vulnerable against this threat typically by employing various sensing instruments ranging from electrical, optical, radioactive, electrochemical, mass spectrometric and other possible methods [2]. As an optical method, Raman spectroscopy is useful as complementary to infrared spectroscopy in which the latter probes molecular absorption at specific vibrational frequencies that causes a change in the dipole moment while Raman relies on

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the change in the polarizability of a molecule at the Raman shift frequencies at which the molecule scatters radiation. Though the typical cross-section of Raman scattering is only $\sim 10^{-29}$ cm^2 per molecule, signal enhancement by means of electronic resonance and electromagnetic resonator allows better sensitivity in detection as far as a single molecule detection [3-5].

Surface enhanced Raman spectroscopy (SERS) was first reported by Fleischmann and co-workers in 1974 whose intense Raman signal arose from pyridine adsorption on Ag electrodes. After that, Raman application in surface adsorption studies rapidly grew contributing to surface plasmon excitations mainly observed in Ag, Au and Cu based structures [3,6]. Signal enhancement was also reported by other metals such as Pt, Fe, Co and Ni, however, on a lesser scale. Gold (AuNP) and silver (AgNP) nanoparticles are known as feasible substrates to detect dimethyl methyl phosphate (DMMP), an organophosphate known as a simulant of Sarin [7,8]. These substrates are believed to provide high electromagnetic enhancement and chemical affinity towards the target molecule while avoiding band interference with responsible functional groups [4,7]. Mode selection by SERS substrates provides additional information on molecule symmetry when adsorbed to a surface which differs when it is in freeform [9].

Metal incorporated grapheneous materials such as graphene oxide (GO) and reduced graphene oxide (rGO) is employed as optical based biosensors due to signal enhancement by charge transfer from porous graphene to metal [5,10-12]. Metal alone has poor adsorption of biomolecules, but with graphene addition as a composite, adsorption efficiency increases and creates a stronger electric field at the interface [6,10]. An investigation by Rattan *et al.,* [13] has shown that AuNPs functioned as electron mediators for the transfer of electrons from rGO to NO_2 gas as a highly efficient gas sensor. The high surface area of graphene and GO-based materials facilitates the adsorption of target molecules, and their sensing capability can be derived from the favorability of π-π interactions occurring within the aromatic rings [14]. The same graphene surface plays a key role in making AuNPs efficiently integrated and decorated, thus, its influence in optical detection will be highly interesting as well.

Known for its practicability, the handheld Raman device is suitable for in-situ/real-time identification of dangerous chemical residues in solid, liquids and gaseous forms. The use of enhancement methods in handheld Raman devices is rarely reported. In this paper, the feasibility of the system to identify DMMP using several AuNPs coated surfaces as SERS substrates has been demonstrated. Similar techniques were also employed to investigate the role of metal nanoparticles in improving analyte adsorption by graphenes. Our evaluation of Raman spectra can provide a better understanding of AuNP/graphene surface interactions under ambient and aqueous conditions and provide recommendations for utilizing nanomaterials for chemical detection.

2. Methodology

2.1 Sample Preparation

Graphene oxide (GO dispersion in H_2O, 4 mg/ml), gold (III) chloride hydrate ($HAuCl_4$, 99.995% trace metal basis), sodium citrate and ascorbic acid were purchased from Sigma Aldrich. Deionized water was prepared by a Milli-Q Plus system (Millipore). GO aqueous dispersion was prepared by 30 min sonication of 1:30 of GO:deionized water. Gold nanoparticles (AuNPs) were reduced from aqueous $HAuCl_4$ using sodium citrate. One pot reduction of AuNP-graphene was prepared according to our previous investigation [15]. Briefly, 100 ml of GO dispersion and 20 ml of 0.01 M $HAuCl_4$ were mixed and stirred before adding 30 mg of ascorbic acid. After that, the solution was heated to 95°C and kept for 90 min under vigorous stirring, resulting into AuNP/graphene composite.

The substrates were carefully prepared to provide homogenous AuNPs deposition. Silane treated quartz substrate in reference [15] was dip coated in aqueous AuNPs for 24 h to produce AuNPs coated glass while AuNPs coated Whatman paper was collected by filtering the same aqueous AuNPs using a conical glass funnel and Whatman paper No.1. The substrates were subsequently left to dry for 48 h. For the AuNPs cellulose film, cellulose acetate powder was stirred in acetone at ambient for 6 h prior to the addition of the aqueous AuNPs. The mixture continued to stir until homogenous before it was poured onto glass petri dishes and left to dry. The films can be peeled away when the solvent is completely dried.

2.2 FTIR and Raman Measurements

FTIR study was carried out with attenuated total reflectance accessory configuration in the mid-IR range provided by the Perkin Elmer Frontier IR instrument. Resolve Handheld Raman Analyzer by Agilent Technologies was used to obtain Raman spectra. The laser is 830 nm with a maximum irradiance of 475 mW. All spectra were collected in 350 cm^{-1}-2000 cm^{-1} spectral range, 1 cm^{-1} spectral resolution and in back-scattering geometry. The technology provided by the Raman system allows chemical identification through its container. Dimethyl methyl phosphonate ($CH_3P(O)(OCH_3)_2$, M_W=124.8 gmol^{-1}) was purchased from Sigma-Aldrich. The analyte was used without purification. DMMP of 1000 ppm, 5000 ppm, 10 000 ppm, 20 000 ppm, 50 000 ppm and 70 000 ppm dilutions were made with deionized water. These dilutions were lightly shaken and dropped into samples or substrates before Raman measurement was taken. The distance between the Raman nose and the substrates was approximately 1 cm apart.

3. Results and Discussion

3.1 Identification of DMMP and Diluted DMMP Using FTIR and Raman

Figure 1 shows FTIR spectra obtained after pure DMMP and diluted DMMP solution were dropped onto the ATR surface. This condensed phase of DMMP consistently agreed with Neupane *et al.,* [16] with the strongest absorption observed at 1050.1 cm^{-1} for asymmetric stretching of P–O–C, P=O stretching mode located at 1274 cm^{-1}, and lastly, C–H stretching modes appearing around 2800–3100 cm^{-1}. Also presented in the figure is a compilation of P–CH_3, P–O and P–O–CH_3 stretching/bending modes around 700-800 cm^{-1}, the fingerprint region. The subset of Figure 1 shows spectra of 1000 ppm and 5000 ppm diluted DMMP which presents none of these strong features, indistinguishable from typical ATR-FTIR spectra measured from water.

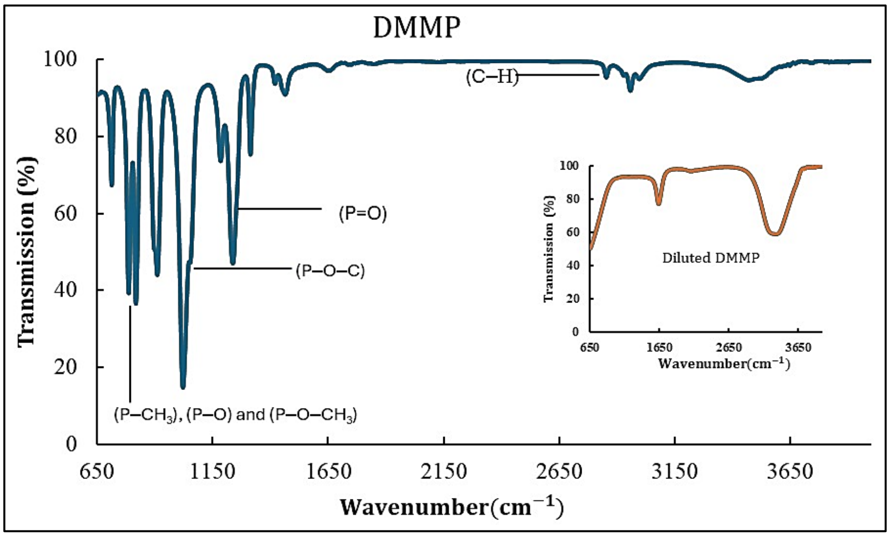


Fig. 1. ATR-FTIR spectrum of undiluted DMMP solution and 5000 ppm DMMP dilution (subset). Water dominated infrared absorption peaks which interfered identification

Upon closer inspection of the spectra, we recognized ~0.5 % absorption change at similar vibration regions for DMMP. Raman spectra of DMMP show a strong peak belonging to the phosphate group vibrational mode located at 715 cm^{-1} for both undiluted and diluted DMMP (Figure 2). This peak can be observed in a spectrum of 5000 ppm DMMP without strong interference by water. This unique feature in Raman suppressed the strongest bond observed in FTIR and provided a complementary investigation of the functional group analysis together with IR spectroscopy.

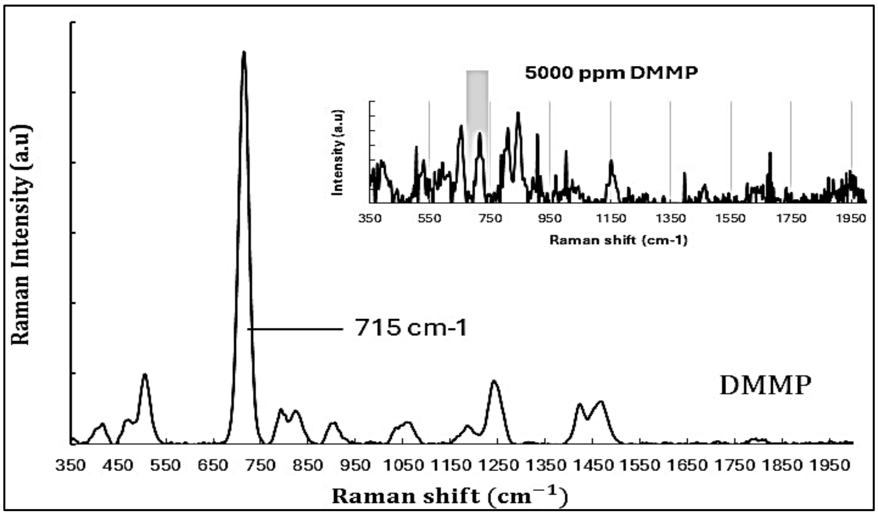


Fig. 2. Raman spectra of undiluted DMMP and 5000 ppm DMMP dilution (subset)

3.2 Raman Quantification of DMMP

Firstly, the quantification analysis has to be established for the Raman system. The calibration plot as shown in Figure 3 was produced using two different DMMP dilutions. Raman peak of 715 cm^{-1} previously identified as DMMP has increased by 5 times with 5000 DMMP dilution. Lafuente *et al.*, [7] have established this peak as a monitoring peak in their Raman study. This linear correlation implied that the current method assessment is suitable for quantification purposes. Bear in mind, there are several other environmental factors that should be accounted for when taking the measurement such as the distance between the laser nose cone and the sample, type and thickness of substrates and others. These factors were consistently controlled throughout the experiments.

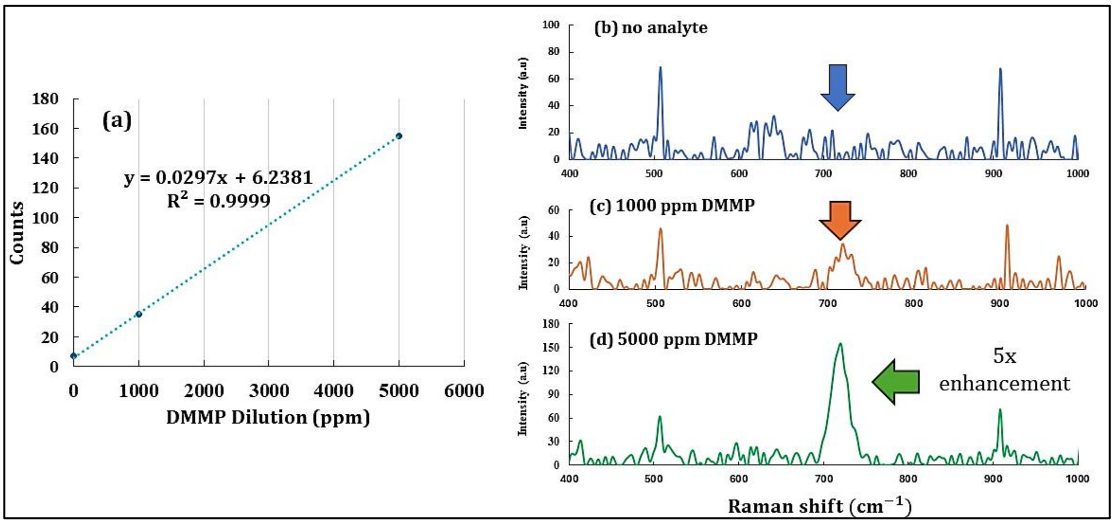


Fig. 3. (a) Calibration plot of DMMP dilutions and Raman spectra (b) Clean substrate (c)1000 ppm DMMP (d) 5000 ppm DMMP

Interference from the Raman signal is possible with a certain choice of substrates in addition to low concentration or weak signal contribution from the compound of interest. Two common substrates found in the laboratory were used to demonstrate substrate interference in Raman identification. In the case of DMMP assessment in Figure 4, we found the broad Raman signal from the glass substrate centred at 700 cm^{-1} overlapped with the most prominent Raman peak of DMMP. The presence of dominant peaks from other regions can also affect the sensitivity of analytes such as shown in Raman spectra obtained from Whatman paper. A large contribution from C-O vibrational modes in some way has added to the difficulty of distinguishing the 715 cm^{-1} peak from the spectra of 5000 ppm DMMP dilution. Thus, there is a need to employ Raman enhancement strategies when obtaining both qualitative and quantitative analysis of the analyte.

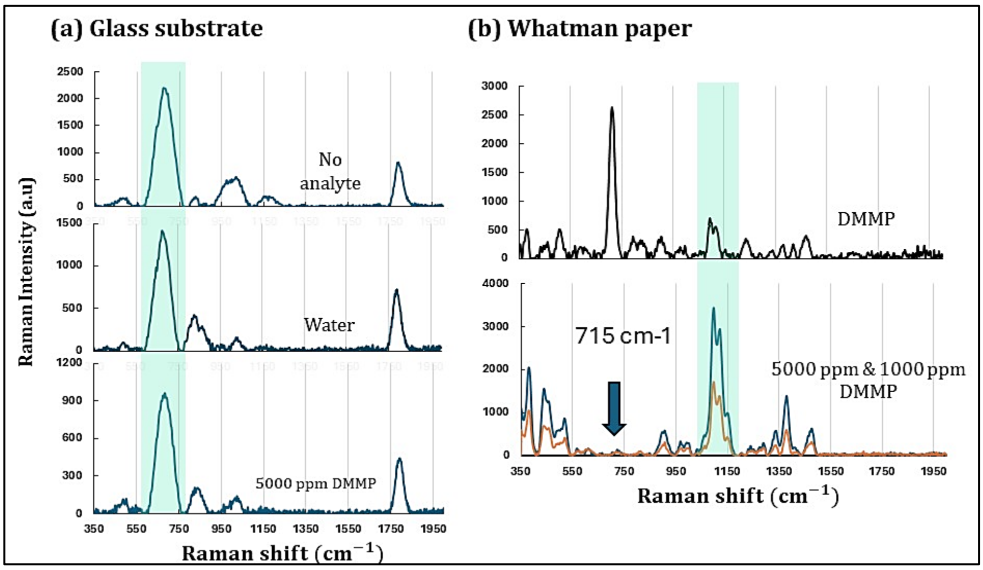


Fig. 4. Some Raman spectra of analytes collected (a) Glass substrate (b) Whatman paper

3.3 Raman of DMMP from AuNPs Cellulose Film

Cellulose film is a solution for flexible and free-standing substrate, hence, is proposed as an SERS substrate. In this investigation, AuNPs cellulose film is reproduced from Khalaf *et al.,* [17]. Figure 5 shows the UV-Vis absorption spectrum of the AuNPs cellulose film which enclosed both absorption peaks of cellulose around 270 nm and the SPR peak of AuNPs centered around 580 nm. Since the SPR does not neither coincides nor is close to the energy of the incident photon, there is no possibility of resonant Raman scattering in our method [18,19].

Raman spectra collected from AuNPs coated cellulose film before and after 5000 ppm DMMP dilution dropped onto the surface are presented in Figure 6(a). No substantial signal was observed when using a pristine cellulose surface as the analyte quickly adsorb onto the film layer. Apparently, AuNPs content has reduced the hydrophilicity of cellulose which increases its reusability with the liquid analyte several times. In addition, several Raman peaks appeared aside from the prominent 715 cm^{-1} peak where their origin can be traced back to the pure DMMP spectrum seen in Figure 2. These moderately strong peaks manifested in the cellulose-based film due to clean background interference from the substrates. The shift of positions of DMMP's fingerprint peaks can be analysed further to investigate the molecular geometry of the DMMP-Au complex formed during interaction [7].

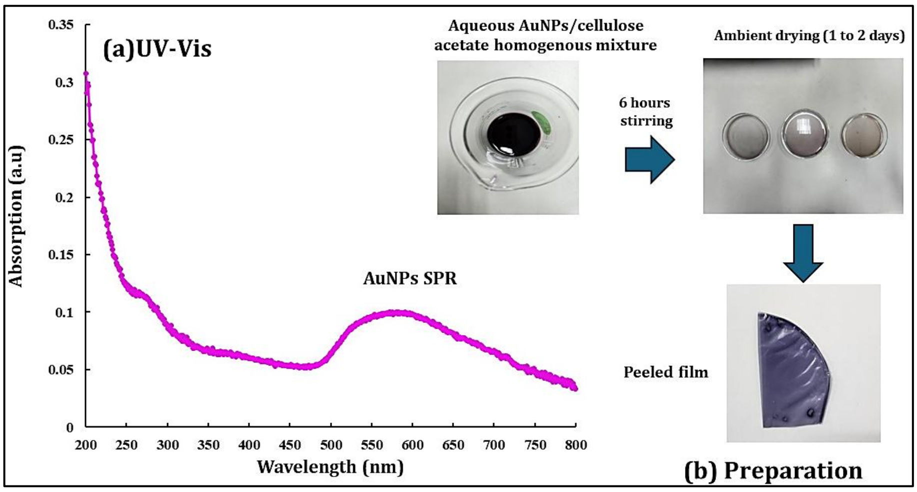
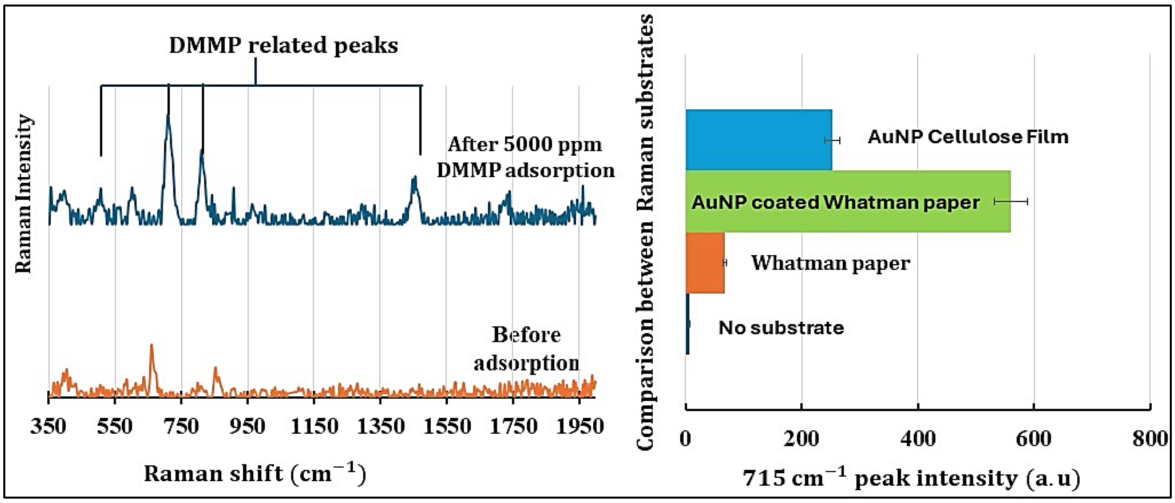


Fig. 5. (a) UV-vis absorption spectrum of AuNPs cellulose film (b) Preparation steps to produce the film



(a) (b)

Fig. 6. (a) Raman spectra obtained before and after 5000 ppm DMMP was dropped onto the AuNPs cellulose film (b) Comparison of DMMP's Raman peak from different substrates tested in this study

Table 1 summarizes Raman spectra evaluation when 5000 ppm of DMMP analyte was introduced to the surface of different substrates. Dominant Raman signal from glass is seen within the same range of DMMP should appear for AuNPs coated glass sample, while the 715 cm^{-1} peak of DMMP materialized more clearly for AuNPs coated Whatman paper compared to the uncoated one. This Raman enhancement by the AuNPs coated Whatman paper is visualised in Figure 6(b) where its intensity is around 9 times of Raman intensity obtained from the uncoated paper. Nevertheless, this enhancement ratio is much lower than typically achieved by SERS perhaps due to technical limitations in the handheld system and the rough surface of Whatman paper that produced many scattering centres. Inefficient detection from AuNPs coated glass substrate is because of the insufficient film coverage on the glass surface, thus can be improved by exploring other deposition methods. We also implored the possibility of insufficient AuNPs aggregation formation that should have manifested as a dark red color colloid, thus the present AuNPs can pose inadequate material for SERS study [18].

Table 1
Observation from different Raman substrates for DMMP identification

Substrate	Observation
AuNPs coated glass.	Dominant Raman contribution from glass.
AuNPs coated Whatman paper.	Strong 715 cm^{-1} peak was observed.
AuNPs cellulose film.	Several fingerprint peaks belonging to DMMP appeared.

3.4 Raman of DMMP from Graphene- and AuNP/Graphene in Aqueous Environment

Raman of graphene is one of the fundamental data indicating the quality of graphene in terms of structure, conductivity and presence of dopants [20]. Intensity ratio, I_D/I_G measured from the intensity of defect, D band (~1350 cm^{-1}) and graphene, G band (~1580 cm^{-1}) are the basis of the degree of inter-defect distance in graphene [20,21]. The G band is related to vibrations of sp^2 domains and several defect-associated bands while the D band arises when there are defective sites in the C aromatic lattice [21]. Previous research has established graphene's role as substrate, building block and also Raman probe in hybrid combination with metal nanoparticles [6]. At ambient, the surface of graphene is a weakly interacting surface, therefore chemical sensing can only be derived from its functionalization [14]. Surface interaction between graphene and DMMP was done in an aqueous environment where the hydrophobic nature with the dispersant must be considered, and their interaction will be evaluated using G and D bands of graphene. We believe that this environment gives valuable insights towards the future making of SERS substrate.

Figures 7(a) to 7(c) show Raman spectra obtained from different GO volumes mixed with 2 ml pure DMMP analytes. The dispersed GO was contained in the plastic test tube (Figure 7(d)) and positioned in front of the nose cone of the Raman spectrometer as shown in Fig. 7 (e). Large background noise was detected in the spectra, fortunately, the D and G bands of the GO became more prominent with increasing GO volumes. This linear proportionality is illustrated in Figure 7(f) using G band intensity because of its position and overlapping intensity which is less susceptible to any defects on graphene planes.

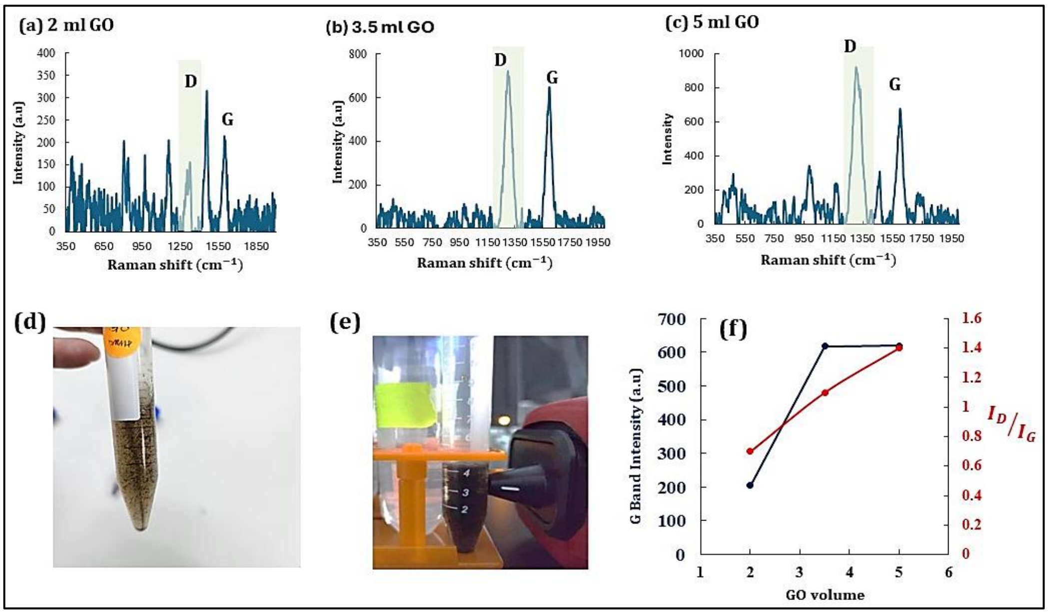


Fig. 7. Raman spectra from GO colloid samples (a) 2 ml GO + DMMP (b) 3.5 ml + DMMP (c) 5 ml + DMMP (d) Sample plastic tube containing mixture of GO and DMMP (e) The sample is positioned directly to the nose cone of the Raman system (f) Relationship between graphene band intensities with the GO volume

On the other hand, the D band intensities change drastically in ratio to the G band with increasing GO volume. Increasing I_D/I_G is often associated with an increase in carbon to oxygen ratio, and also expanding interlayer distance between graphene basal planes [21]. The change from 0.7 to 1.4 can be related to graphene surface preferential toward DMMP molecules over water molecules. The 2 ml GO possessed less surface area for DMMP occupation compared to 3.5 ml and 5 ml GO. Large amounts of DMMP molecules on the graphene surface may also affect surface charge which leads to the drastic increase of I_D. Interestingly, we did not obtain similar results when the same experiment was repeated with 5000 ppm DMMP dilution which indicated insensitivity detection by GO.

Figure 8 shows the spectra obtained by the AuNP/graphene composite that implied remarkable sensitivity toward DMMP. It was seen that the I_D/I_G ratio increased from 0.99 to 1.79 as the higher concentration of DMMP was added subsequently onto the same sample. This different turn out when AuNP/graphene was used to substitute the GO means that AuNP incorporation is a crucial factor in enhancing the sensitivity of DMMP adsorption on graphene surfaces. Firstly, a relatively high ratio of AuNP/graphene in Figure 8(a) indicates nanoparticles were successfully anchored on graphene edges [15,22]. The presence of AuNPs within the graphene planes posed a weaker van der Walls interaction as observed from the formation of crumpled graphene sheets in the HRTEM image from Kasim *et al.,* [15]. This graphene structural disorder induced larger interlayer distance in graphene stacks compared to GO. The already weakly interacting graphenes will disperse further after more DMMP molecules are added to the composite. The preferential of DMMP to be adsorbed on the aromatic rings will cause the increase of D band intensity as seen in Figure 8(b) to 8(e).

In summary, the increase of D band intensities could be directly related to the increase of graphene interlayer spacing that reduces bulk aggregation of rGO. AuNPs doping assisted re-aggregation mechanism even at low DMMP concentration. This microscopic explanation can be used to produce selectivity of material against different analytes which are subject to their polarity and hydrogen bonding interactions.

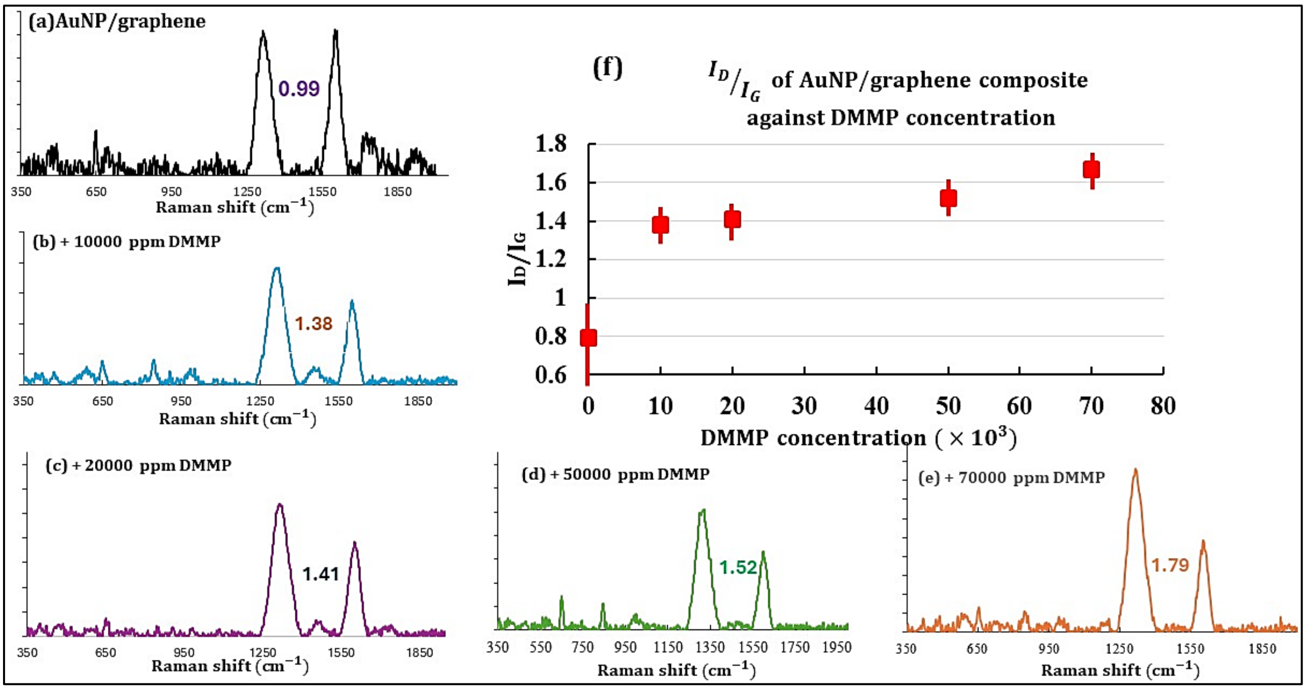


Fig. 8. Raman spectra of (a) AuNP/graphene composite (b) to (e) The composite after mixed with DMMP dilutions (f) The plot of I_D/I_G ratio in Raman spectra from AuNP/graphene aqueous samples as a function of different concentration of DMMP dilutions

The fact that the D band to G band intensity ratio of AuNPs/graphene show remarkable sensitivity towards DMMP dilutions compared to GO indicated that the former can provide better sensing surface in optical detection. The non-linear relationship shown in the graph also implied that the variation between the I_D/I_G ratio and the DMMP concentration may reach the point of saturation after certain additions and, hence might require more optimization for this material strategy. Under these circumstances, no sensing event related to charge transfer from Au to graphene is detected. Charge transfer between molecules should manifest in the amplification of Raman signals belonging to DMMP. Another challenge in achieving a SERS signal in the form of a one-pot reduction of AuNP/graphene is the inhomogeneous accumulation of particles on the edges where there is a higher presence of oxygen functional groups (-OH and –COOH) compared to basal planes [5].

Lastly, the reliability of this evaluation is presented in the form of an average relative standard deviation of I_D/I_G at 5% as the measurements from the aqueous sample were taken repetitively over 8 minutes. The result is shown in Figure 9. This test shows that the AuNP/graphene composite remained stable even after several laser radiation. The reliability and stability of both the measurement technique and the sensing material are crucial in the detection of nerve agent chemicals and as demonstrated from this study, both components have the potential to be explored in defence and security applications.

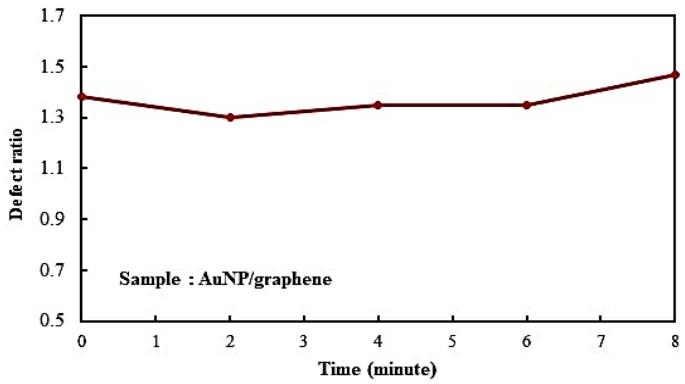


Fig. 9. Stability test for Raman measurement taken from AuNP/graphene samples in aqueous environment

4. Conclusions

The interaction between gold nanocomposites and DMMP in various forms was studied using Raman spectra. The Raman system is not a conventional method to yield quantitative information, but we evaluate its qualitative reliability with the SERS method. Based on this result, we highlight some vibrational modes that are crucial in organophosphate identification. The issue of overlapping vibrational modes due to interference from substrates may hinder Raman measurement, nevertheless, it is believed that by optimizing graphene and gold nanoparticle sizes, the method can deliver more accurate analysis in chemical trace identification. DMMP identification in AuNP/graphene composite in an aqueous environment yields promising results in probing molecule adsorption on graphene surfaces due to preferential interaction in analytes.

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