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Fabrication of reusable and low-cost sers substrate for explosives detection

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Abstract. Surface-enhanced Raman Spectroscopy (SERS) is a highly sensitive and powerful analytical technique for molecular identification and analysis and is used in various fields. SERS uses the plasmonic effect on the surface of specific substrates, such as grating plasmonic, to enhance the Raman signal of the sample. However, the fabrication of grating structures as substrates is challenging and often comes with high costs. This research presents an approach to address this challenge by developing a low-cost SERS substrate using DVDs as a grating-based substrate coated with gold thin film. The fabricated substrate will be used as a SERS substrate to detect explosives: trinitrotoluene (TNT), Tetryl, Research Department Explosive (RDX), and pentaerythritol tetranitrate (PETN). According to our research, the concentration of explosives that can be detected is up to 0.01M for TNT, PETN, and Tetryl and 0.1M for RDX. Furthermore, a reusability test was conducted for the SERS substrate from DVD by cleaning the substrate using an acetone solution. Based on the results of the reusability test, the substrate can be reused up to three times. The periodicity of grating used is 713 nm, the thickness of the gold thin film used is 50 nm, and the depth of grating is 29.43 nm.

1 Introduction

An explosion is an event that occurs due to pressure caused by a sudden increase in volume and the release of a large amount of energy. Explosions can happen due to chemical reactions. For example, an explosion caused by trinitrotoluene (TNT) decomposition or nuclear reactions, such as the Chernobyl nuclear tragedy in 1986 [1]. Terrorist using explosive as a weapon to endanger national security and often targets civilians. The increase in terrorism using explosives emphasizes the significance of Explosive Trace Detection (ETD) due to the

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growing utilization of Home-Made Explosives (HMEs). Therefore, there is a need to improve existing Explosive Trace Detection (ETD) technology [2].

Raman spectroscopy is an analytical method to analyze complex mixtures and molecules quantitatively [3]. Raman spectroscopy provides detailed chemical properties and molecular information, even for samples with similar chemical properties and structures that are difficult to distinguish [4]. It is widely used in various fields, such as medical applications, food ingredients analysis, narcotics detection and many other areas. The signals of Raman spectroscopy are very weak due to the nature of the Raman scattering process itself [5]. SERS is a development of Raman spectroscopy that significantly enhances the weak Raman signal of molecule [5].

SERS is a highly sensitive and powerful molecular identification and analysis technique used in various fields. SERS uses the plasmonic effect on the surface of specific substrates, such as grating plasmonic, to enhance the Raman signal of the sample [6]. However, the fabrication of grating structures as a substrate is difficult and often comes with high costs, and currently, few reported SERS substrates can be reused [7].

This paper presents an approach to address this challenge by fabricating a reusable and low-cost SERS substrate using DVD as a grating-based substrate coated with gold thin film. The produced substrate will be used for the detection of explosives; Trinitrotoluene (TNT), Tetryl, Research Department Explosive (RDX), and Pentaerythritol Tetranitrate (PETN).

2 Materials and Methods

The fabricated SERS substrate (Figure 1) is made from DVD-RW plus GT-PRO Multi Speed 4x with a capacity of 4.7 GB. The DVD outer layer must be separated to obtain a grating layer by using a knife razor tool. Subsequently, the separated DVD layer is cut into 1 cm x 1 cm size.

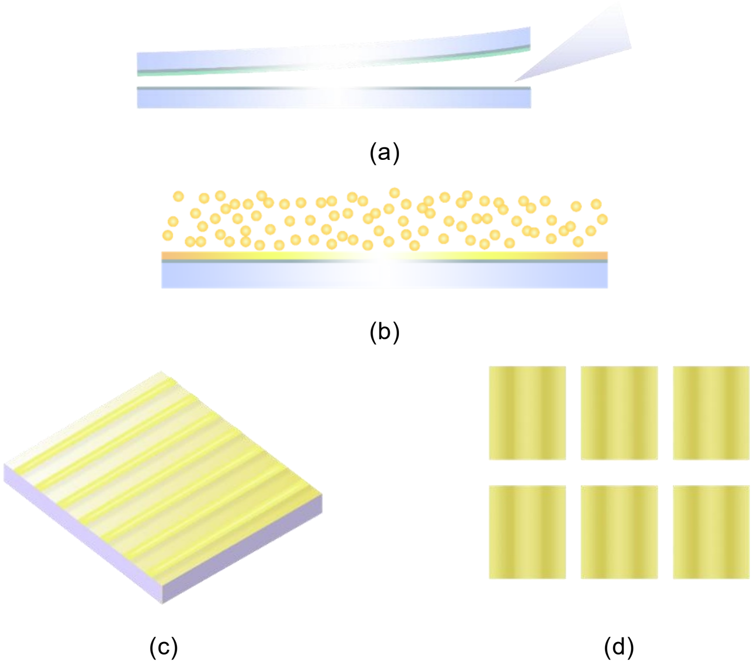


Fig. 1. Preparation steps to fabricate SERS substrates. (a) separation, (b) sputtering of gold thin film, (c) fabricated SERS substrate, (d) coated substrate.

The substrate was then coated with gold thin film using the Ion Beam Sputtering (IBS). The substrate was placed in an MC1000 Ion Sputter Coater, the parameters used for this coating process are 10 mA plasma current and a coating rate of 5 nm per minute. The sputtering process took 10 minutes to obtain a layer of gold thin film with a thickness of 50 nm.

Raman characterization of the SERS substrate is performed by measuring the Raman spectra of explosive materials using a Raman spectrometer. The Raman spectrometer used is The MacroRAMTM Raman Spectrometer with a laser wavelength of 785 nm. The laser power used is 10% (4.5 mW) and an exposure time of 5 seconds (1 exposure per second). We were using AFM (Atomic Force Microscopy) and SEM (Scanning electron Microscopy) to observe the substrate structure.

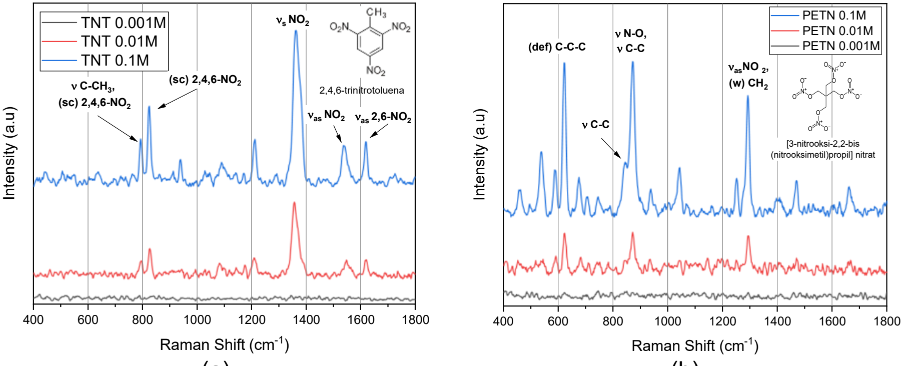
The samples used are 0.1 M, 0.01 M, and 0.001 M of TNT, PETN, RDX, and Tetryl. The samples used are explosives in a solid phase dissolved in acetone. The sample was prepared by drop-and-dry technique at room temperature.

For the reusability test, the substrate is cleaned by using acetone, and the Raman measurements were performed on the substrates to ensure no residual sample remained on the substrate surface. After that, the explosives sample is dropped onto the substrate to check whether the substrate can be used repeatedly or not.

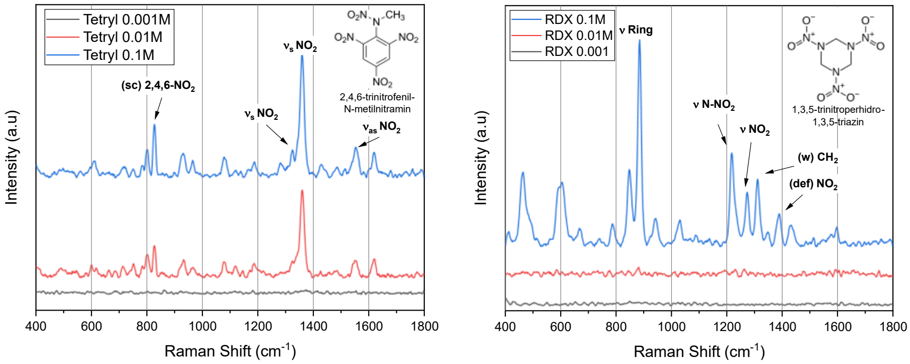
3 Result and Discussion

3.1 Limit of Detection Test

Figure 2 shows the Raman spectra of TNT, Tetryl, PETN, and RDX on SERS substrate. The concentrations of TNT, Tetryl, PETN, and RDX used are 0.1 M (blue line), 0.01 M (red line), and 0.001 M (black line). As shown in Figure 2, when the concentration of the samples decreases to 0.01 M and 0.001 M, the intensity of the peaks in the Raman spectrum decreases or becomes undetectable because the number of particles that vibrated also reduces along with a decrease in the sample's concentration. For TNT, PETN, and Tetryl, as the concentration is decreased, the peak intensities decrease, and some peaks become undetectable. However, for the RDX sample, no Raman spectrum was observed when the concentration of the sample was decreased. For a concentration of 0.001 M, no Raman spectrum is obtained for any of the samples.



(a) (b)



(c) (d)

Fig. 2. The Raman spectra of explosives (a) TNT, (b) PETN, (c) Tetryl, and (d) RDX are shown with varying concentrations of 0.1M, 0.01M, and 0.001 M.

As can be seen in blue line Figure 2 (a), the strong peak of TNT appears at Raman shift of 793 cm^{-1}, 825 cm^{-1}, and 1362 cm^{-1}. Raman shifts and vibrational modes for the Raman spectrum of TNT can be seen in Table 1. When the concentration of TNT decreases to 0.01 M (red line in Figure 2 (a)), the intensity of the peak decreases, and the peak at 940 cm^{-1} is not detected. When the concentration is decreased to 0.001 M (black line in Figure 2 (a)), no Raman spectrum is detected.

Table 1. Assignment of Vibrational Mode of TNT Raman Spectra [8,9].

Raman Shift (cm^{-1})		Vibrational Mode
Ref	Exp	
1617	1619.75	$2,6-NO_2$ Asymmetric stretch
1536	1537.94	NO_2 Asymmetric stretch
1362	1362.32	NO_2 Symmetric stretch
1212, 1089	1212.39, 1089.88	$C-H$ (ring) In-plane bend
940	942.173	$C-H$ (ring) out-plane bend
825	825.105	$2,4,6-NO_2$ Scissoring
793	795.565	$C-CH_3$ Stretching, $2,4,6-NO_2$ Scissoring

PETN molecule consists of carbon atom bonds, nitrogen and oxygen atom bonds forming nitrate groups, and nitrate groups with carbon atom bonds. From PETN Raman spectra result (Figure 2 (b) blue line), the strong peaks appear at the Raman shift of 622 cm^{-1}, 844 cm^{-1}, and 872 cm^{-1}. Raman shift and vibrational modes for the Raman spectrum of PETN can be seen in Table 2. When the concentration of PETN decreases to 0.01 M (red line in Figure 2 (b)), the intensity of the peak decreases, and the peak at 1044 cm^{-1}, 1251 cm^{-1}, and 1469 cm^{-1} are difficult to distinguish from noise. When the concentration is decreased to 0.001 M (black line in Figure 2 (b)), no Raman spectrum is detected.

Table 2. Assignment of Vibrational Mode of PETN Raman Spectra [8, 10, 11].

Raman Shift (cm^{-1})		Vibrational Mode
Ref	Exp	
1469	1469.64	CH_2 Scissoring
1292	1294.21	NO_2 Asymmetric stretch, CH_2 wagging
1251	1251.56	$C-H$ Bending stretch
1044	1044.14	$C-C$ Bending
872	874.094	$N-O$ Stretching, $C-C$ Stretching
844	842.776	NO_2 Scissoring
676	678.304	$N-O$ Stretching, $C-C$ Stretching
622	624.07	$C-C-C$ Deformation, $C-C$ Stretching
587	591.759	$O-NO_2$ Rock, $C-C$ Bend
538	538.981	C_5 Skeletal, CH_2 Wagging, $N-O$ Stretching

The molecular adsorption behavior on the substrate surface plays a critical role in determining the Raman cross-section, where any reduction in molecular adsorption leads to a corresponding attenuation in the signal intensity. This phenomenon is particularly evident in the SERS spectrum of PETN, specifically at the Raman shift of 1294.21 cm^{-1}. While standard library references[12] typically identify this peak as the most dominant for PETN, our experimental measurements show a lower relative intensity. This discrepancy is attributed to the specific adsorption orientation and the unique interfacial interactions between the PETN molecules and the gold-coated DVD grating, which likely differ from the conditions found in bulk phase or standard library spectra. Consequently, these variations in peak intensity provide a clearer physical interpretation of how the molecular alignment on the nanostructured surface influences the resulting Raman enhancement.

From the Tetryl Raman spectra result (Figure 2 (c) blue line), the strong peaks appear at the Raman shift of 827 cm^{-1}, 1325 cm^{-1}, 1358 cm^{-1}, and 1552 cm^{-1}. Based on the figure, the Raman spectra of TNT and Tetryl have similarities, but there is a shoulder peak at the Raman shift of 1325 cm^{-1}, and no peak appears at 1325 cm^{-1} in Raman spectra of TNT. This is because Tetryl and TNT are nitroaromatic compounds with different functional groups attached to their aromatic rings [13, 14]. Raman shifts and vibrational modes for the Raman spectrum of Tetryl can be seen in Table 3. When the concentration of Tetryl is decreased to 0.01 M (red line in Figure 2 (c)), the intensity of the peak is decreased, and the shoulder peak is not clear. When the concentration is decreased to 0.001 M (black line in Figure 2 (c)), no Raman spectrum is detected.

Table 3. Assignment of Vibrational Mode of Tetryl Raman Spectra [9].

Raman Shift (cm^{-1})		Vibrational Mode
Ref	Exp	
1617	1619.75	$2,6-NO_2$ Asymmetric stretch
1552	1554.02	NO_2 Asymmetric stretch
1358	1360.49	NO_2 Symmetric stretch
1325	1323.74	NO_2 Symmetric stretch
1078	1078.47	$C-H$ (ring) In-plane bend

930	934.422	$C - H$ (ring) out-plane bend
827	829.035	$2,4,6 - NO_2$ Scissoring
801	801	$C - CH_3$ Stretching, $2,4,6 - NO_2$ Scissoring

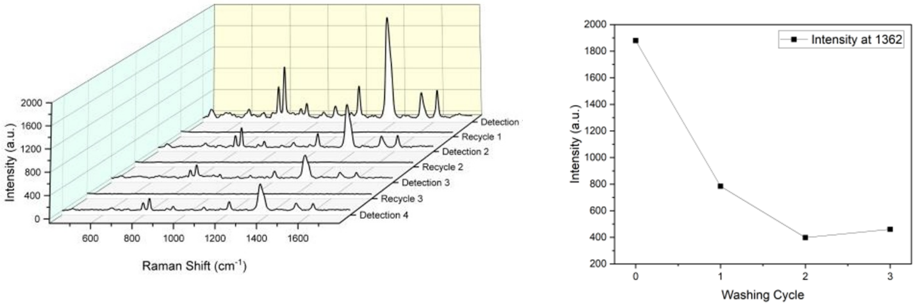
In the RDX Raman spectra (Figure 2 (d) blue line), the strong peaks appear at the Raman shift of 885 cm^{-1}, 1218 cm^{-1}, 1273 cm^{-1}, 1310 cm^{-1}, and 1387 cm^{-1}. Raman shift, and vibrational modes for the Raman spectrum of RDX can be seen in Table 4. The peak at 1218 cm-1 is a characteristic of the vibrational mode of the nitramine group [10]. When the concentration of RDX is decreased to 0.01 M (red line in Figure 2 (d)) and 0.001 M (black line in Figure 2 (d)), no Raman spectrum is detected.

Table 4. Assignment of Vibrational Mode of RDX Raman Spectra [9, 10].

Raman Shift (cm^{-1})		Vibrational Mode
Ref	Exp	
1596	1596.72	NO_2 Asymmetric stretch
1431	1433.44	$CH_2 - N$ Deformation
1387	1389.76	NO_2 Asymmetric stretch
1310	1389.76	NO_2 Symmetric vibration
1273	1275.7	NO_2 Stretching
1218	1218	$N - NO_2$ Stretching
944	944.109	$N - O$ Deformation
885	885.807	$N - N$ Symmetric ring breathing
848	850	CH_2 rocking, $C - N - C$ Deformation
787	789.643	$N - O$ Deformation
605	605.991	NO_2 Wagging

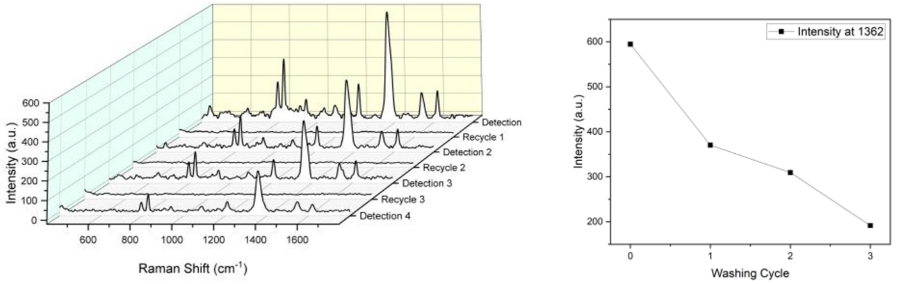
3.2 Reusability Test of SERS Substrate

To evaluate the reusability of SERS substrates, a reusability test was conducted by cleaning the used substrates with acetone. After cleaning, Raman measurements were performed on the substrates to ensure no residual sample remained on the substrate surface. As observed in Figures 3, all peaks in the Raman spectrum reappeared upon reusing the substrate, albeit with a decrease in peak intensity. This phenomenon arises from enhancements in low sample concentrations that depend on the detected molecular locations. SERS enhancements rely on hot spots and the distribution of sample molecules [15]. Therefore, Raman measurement results may vary from one measurement point to another. The SERS substrate can be reused up to three times.



(a) Spectrum Raman of TNT 0.1 M

(b) Intensity at 1362 cm^{-1} of Spectrum Raman of TNT 0.1 M



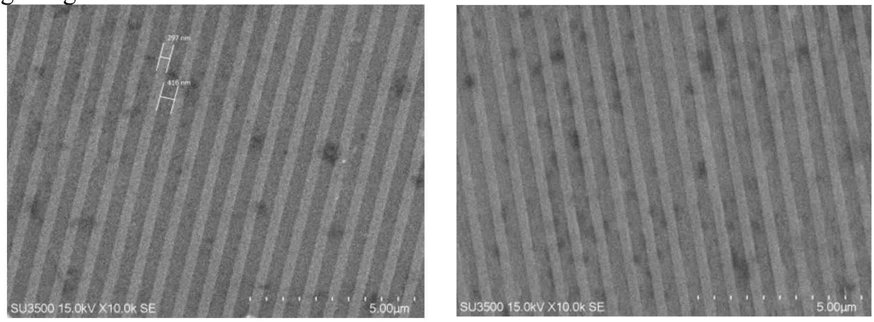
(c) Spectrum Raman of TNT 0.01 M

(d) Intensity at 1362 cm^{-1} of Spectrum Raman of TNT 0.01 M

Fig. 3. Result of reusability of SERS substrate with 3 cycles. (a) and (c) represent the Raman spectra of measurement results. Recycle is the condition when the sample is dropped to the substrate, and detection is the condition after substrate has been cleaned. (b) and (d) represent the Raman spectra intensity at specific Raman shift for each sample.

3.3 SEM and AFM Characterization for SERS Substrate

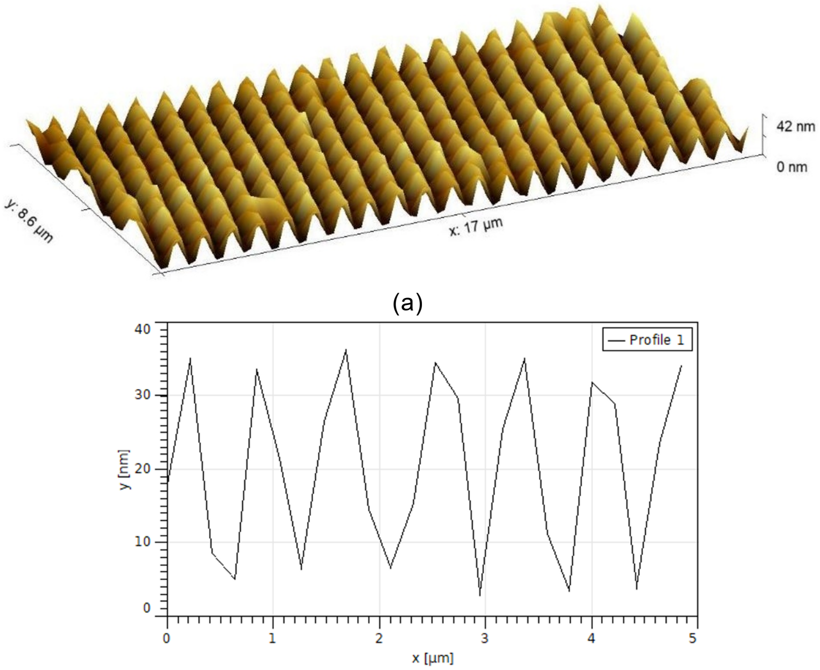
Scanning Electron Microscope (SEM) (Figure 4) and Atomic Force Microscope (AFM) (Figure 5) were performed on the fabricated SERS substrate to observe the grating structure of the substrate. Based on the SEM result, the grating structure has a period of 713 nm, and the thickness of the coated gold thin film is 50 nm. Based on the AFM result, the depth of grating is 29.43 nm.



(a)

(b)

Fig. 4. SEM images showing grating structure of a gold-coated DVD substrate for (a) unused substrate and (b) triple-use substrate.



(a)

(b)

Fig. 5. AFM topographic image of DVD substrate showing the grating structure of DVD layered with gold thin film (a) and AFM profile measurements perpendicular to the grating to show the depth of the grating (b).

4 Conclusions

The fabrication of SERS substrates using DVDs coated with gold thin film has been successfully achieved. The periodicity of the grating used is 713 nm, the thickness of the gold thin film used is 50 nm, and the grating depth is 29.43 nm. The detectable concentration of explosive materials is up to 0.01 M for TNT, PETN, and Tetryl, while for RDX, it is 0.1 M. The SERS substrate can be reused up to three times after the substrate has been cleaned.

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