

Synthesis, Characterization, and Experimental Investigation of Surface Activity of Surface Enhanced Raman Scattering Substrates using Trinitrotoluene (TNT)

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Abstract

Surface-enhanced Raman scattering (SERS) was used for detecting low concentration of Trinitrotoluene molecules or TNT ($C_7H_5N_3O_6$) by using three different substrates such as Colloidal silver solution, filter paper and aluminum foil in which all of them containing or coated by silver nanoparticles separately. We used various techniques such as ultraviolet-visible spectroscopy, dynamic light Scattering, scanning electron microscopy, X-ray diffraction and energy dispersive X-ray spectroscopy to characterize the samples. Enhancement factors were investigated to show effectiveness of the SERS effect of the substrates. We figured out that the activity of the synthesized substrates is very operative for enhancing the Raman signal.

Keywords: Surface Enhanced Raman Scattering (SERS); Colloidal silver, Silver-coated filter paper; Trinitrotoluene (TNT) ($C_7H_5N_3O_6$)

Introduction

Ever since the Surface-enhanced Raman scattering (SERS) was observed by Fleischmann et al. [1] in 1974 in which the enhancing of Raman signal is occurred, it was established that this effective and selective technique has remarkable advantages. The analysis of molecule structure in absorption of molecule on metal nanoparticles, its interaction with the used substrate and even its direction can be derived [2-4].

In studying the SERS effect, different reasons were attributed to extraordinary enhancement of Raman signal's intensity. At the beginning, the growing of roughed substrate area and later in 1977 as Jean Marie and his colleagues explained, growing the cross section of Raman scattering were attributed to enhanced Raman signal [5].

Nowadays, two major categories are considering describing the intensity proportion of inelastic light scattering in SERS; electromagnetic coupling enhancement and chemical enhancement mechanism. The electromagnetic coupling enhancement is the dominant effect and is due to localized surface plasmon resonance (LSPR) [6]. LSPR is an optically excited electron wave resonance state on the surface of a nanostructure, which can increase both elastic (Rayleigh) and inelastic (Raman) light scattering from the sample [7]. The chemical enhancement mechanism is caused by molecular charge-transfer interactions between the molecule and the metallic surface [8,9]. Together, these mechanisms of enhancement increase the Raman intensity to a point where SERS can be used for applications which require greater molecular sensitivity. Another important factor is the selection rules. When a molecule is absorbed on the gold, silver, or other noble metals, its symmetry is decreased, and this leads to weaken the selection rules. As a result, more frequencies than those in the ordinary Raman spectroscopy are found [10-12]. In SERS applications and experiments, the main parameter is the choice of the appropriate substrate. The chosen SERS active substrates are almost belong to three major categories [13]:

- I. Metallic electrodes: These types have great contribution in evolution of SERS effect.
- II. Metal nanoparticles in solution: Such as the first group, these

types have high importance in sensing of SERS. Colloids are the proper candidates to produce the LSPR effect.

III. Nanostructured substrates: There are two methods for obtaining these types:

- (a) By using colloidal solution which containing metal nanoparticles and deposition of metal nanoparticles onto chosen substrates via drying or evaporation of solvent.
- (b) By using the nanostructured manufacturing techniques to produce the nanostructured surfaces of metal.

Here, we provide a detailed statement about manufacturing of the two types of main SERS active substrates;

- I. Colloidal silver nanoparticles.
- II. The filter paper and foil of Al which both covered by silver nanoparticles.

To characterize the latter the scanning electron microscopy (SEM) was used. To define the size of nanoparticle and Also plasmon absorption monitoring of nanocrystals which formed in colloidal silver, dynamic light scattering (DLS) and ultraviolet-visible (UV-vis) spectrometry were used respectively. The methods that were used to characterize the Al foil were: X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy.

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Experimental

Preparation of colloidal silver

We prepared the colloidal silver solution via Lee's and Meisel method [14]. At first, we dissolved 18 mg of silver nitrate (AgNO_3) in 100 ml distilled water to obtain the AgNO_3 solution. Then we heated up the solution into boiling. Afterwards, we stirred the boiling solution strongly and added 7 ml of 1% tri sodium citrate to it simultaneously. By keeping the obtained mixture to boil for 8 minutes, we obtained the green-gray solution. To prepare TNT using colloidal silver, 0.5 ml of its 0.01 molar solution was mixed by 4 ml colloidal silver solution and 0.5 ml of 0.6 molar NaCl solution. The solution's pH was altered up to 13 [15,16].

Preparation of the silver-coated filter papers

By doing the following process for several times we could obtain a group of filter paper which covered by different sized of silver nanoparticles of layers.

We dropped the colloidal silver solution one by one on the low filtration filter paper (MN 61q de125 mm) and gave it up for 10 minutes to dry in the common temperature. To characterize the sample, three drops of 0.01 molar TNT aqueous solution were dropped on the filter paper and put it aside to dry in room temperature.

Preparation of the film of silver dendrites on the surface of aluminum foil

An aluminum foil was put into acetone and vibrated in an ultrasonic cleaning cell to remove the grease on the surface; then it was polished in perchloric acid. So a clean aluminum foil was obtained. The clean aluminum foil joined the cathode of the regulated power supply, and an aluminum sheet joined the anod. The electrodeposition action occurred in 0.02 molar silver nitrate solutions with a D.C voltage of 12 V about 20 s. [17]. To prepare TNT using the Al substrate, one drop of 0.01 molar TNT aqueous solution was dropped on the surface of the foil and let it to dry in the ordinary temperature.

Characterization

The silver nanoparticles on surfaces of coated substrates were investigated by SEM (JSM-6700F, JEOLLtd., Akishima-shi, Japan). The SERS spectra of the samples were measured By using of a microscopic confocal Raman spectrometer (RM 2000, Renishaw, Wottonunder-Edge, UK), where, the light source was Nd-YAG laser, its operating wavelength was 532 nm, beam diameter was equal to 1 mm and the time of integration was set as 10 s for each spectrum. DLS (NanoZS4700, Malvern Instruments, Worcestershire, UK) was used to measure the hydrodynamic diameter of the nanoparticles. To prevent the effect of viscosity due to existence of impurities, all paper formulations were diluted by using of deionized water.

Result and Discussion

Scanning electron microscopic images of aluminum foil and filter paper substrates that both coated by using freshly prepared nanoparticles of silver are shown in Figure 1a.

By using microstructure measurement to estimate the size distribution of nanoparticles the values about 40 to 240 nm were attained. Larger nanoparticles attributed to existence of salts in colloidal solution. As a matter of fact, it is believed that after drying out the sample the salts are recrystallized. Moreover, according to micrographs it can be deduced that in nanometric rang, there is a

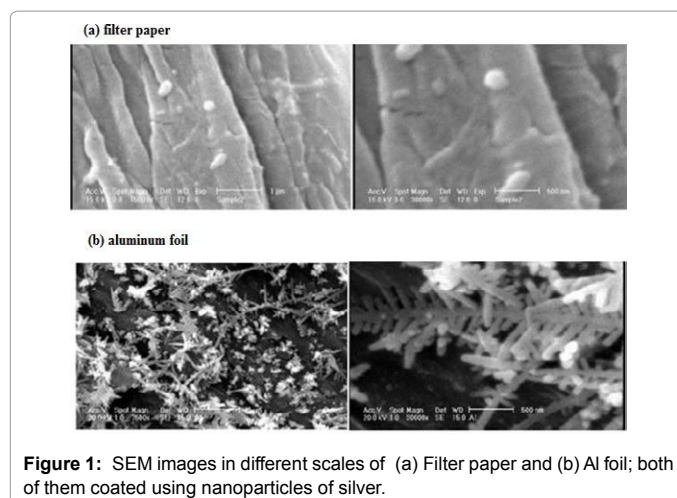


Figure 1: SEM images in different scales of (a) Filter paper and (b) Al foil; both of them coated using nanoparticles of silver.

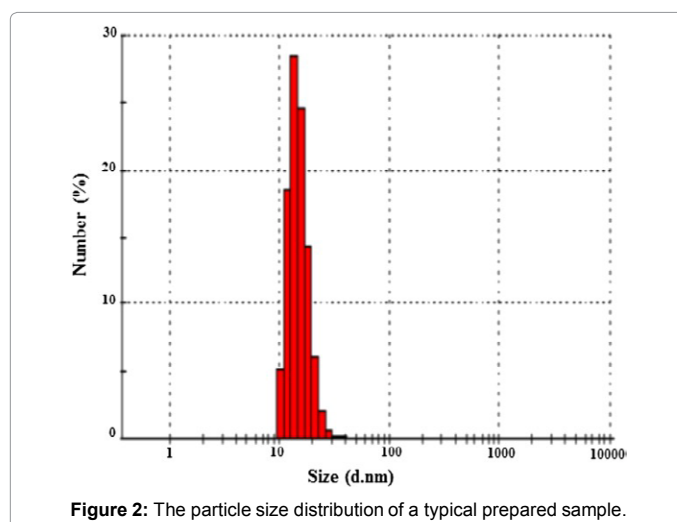


Figure 2: The particle size distribution of a typical prepared sample.

spherical shape and a smooth surface with a particle size. The size of the nano-sized particles was estimated around 10 to 100 nm (Figure 1b). The concentration of AgNO_3 solution and reaction time plays an important role in the formation of Ag dendrites [17,18].

The silver dendrites on the surface of the aluminum foil have the island form. By increasing the concentration of the AgNO_3 solution, the silver dendrites were still deposited in island form but The concentration of them in each island became more. A visible feature in the SEM images of the silver film was clearly the branch pattern. The observation showed that each dendrite has a long central backbone and grows along it.

To define the size of silver nanoparticles We used Zetasizer Nano-Zs by Malvern Instruments (Worcestershire, UK). The colloidal solution was diluted by using of deionized water with proportion of 5:1. The effects of oscillations were vanished at the large scattering number (N) because by increasing N a number of oscillations were decreased [19]. In Figure 2 the size distribution of silver metal was shown. As to be seen it was a narrow distribution and the average size of particle could be obtained about 16.9 nm [20,21].

To achieve the best result in Raman signal enhancement one could be adjust the maximum wavelength of the excitation laser and longitudinal resonance plasmon [22]. We used UV/vis/near-infrared

(NIR) spectrophotometer to characterize the colloidal silver solution. As to be seen in Figure 3, about 430 nm wavelength the maximum absorption of the surface plasmon in colloidal silver was occurred.

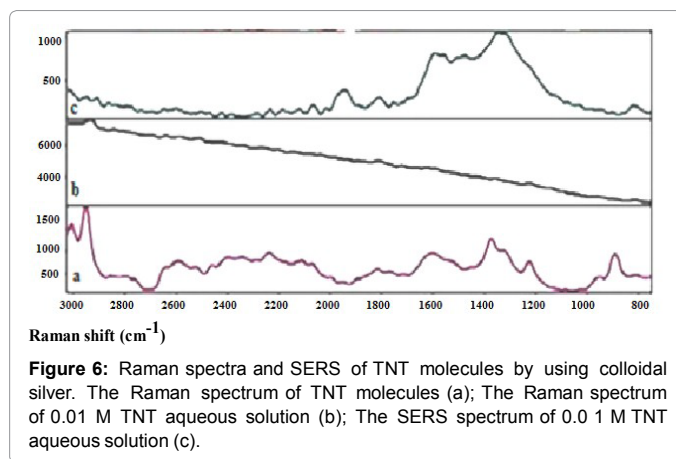
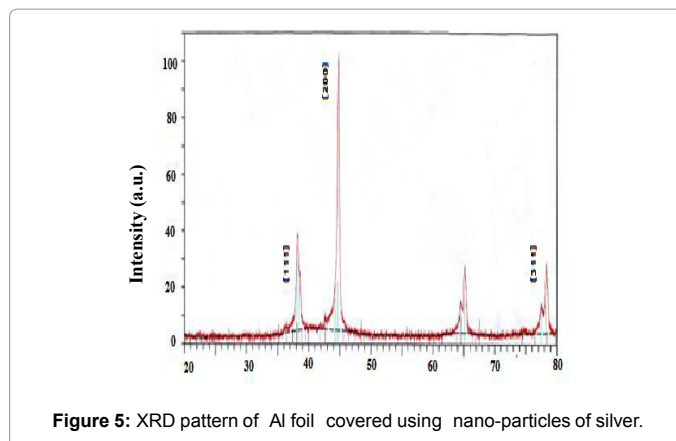
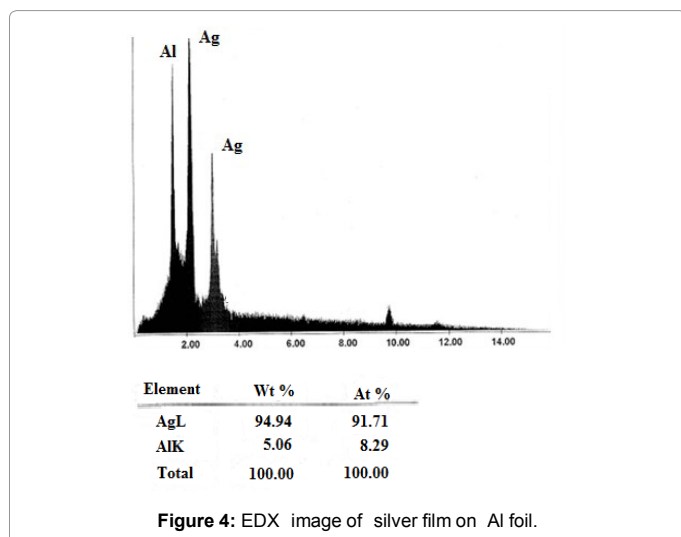
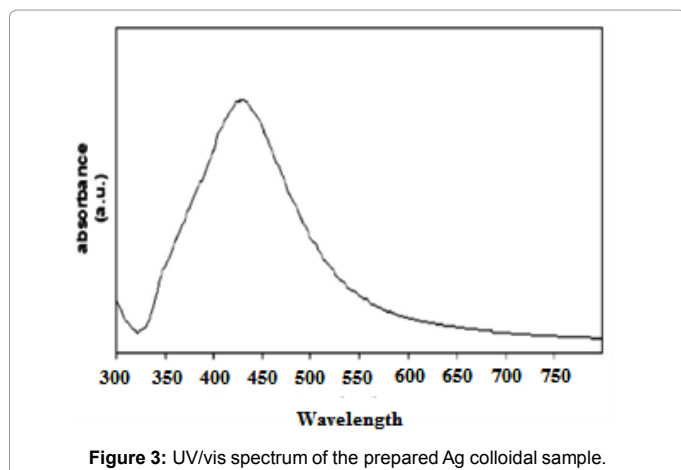
To confirm the existence of silver dendrite film on the surface of Al foil and the crystal structure of the sample the EDX spectroscopy and XRD were used. As shown in Figure 4, Ag appeared. Because the substrate was the aluminum foil, the signal of Al appeared too. Appearance of signal of Ag indicated that the flocs have been composed of silver.

Figure 5 shows a XRD pattern of the sample after the silver dendrites formed on it. We can see that the long central branches clearly point to the preferred growth direction along the (200) axis and each dendrite has very sharp secondary branches that have some small secondary branches.

There are two factors at the nanoparticle's surface which play in an important role to characterize the excitation of the LSPR goes as following:

- I. Intense absorption that is wavelength-selective.
- II. Electromagnetic fields that are enhanced.

Silver and gold mainly used as primary materials for SERS applications, owing to their optical response in the visible region of the



electromagnetic (EM) spectrum. In particular, silver particles provide a larger SERS enhancement in a wider spectral range, from near-UV to near-IR [23,24]. The optimum size which is preferable for the SERS enhancement can be found in a range from about 50 to 100 nm and from the near-UV to the near-IR range [25]. According to previous discussion and Figures, the structures are propitious for enhancing the SERS effect.

In Figure 6, Raman spectra and SERS of TNT molecules using colloidal silver are shown. Figure 4a shows Raman spectrum of TNT molecules. In Figure 4b Raman spectrum in 0.01 molar TNT aqueous solution without using SERS substrate is shown. According to Figure 4b, the peaks of TNT did not appear in this concentration. The SERS spectra for 0.01 molar TNT aqueous solution by using colloidal silver are shown in Figures 4c. Despite of very lower density in Figure 4c the SERS substrate enhanced the Raman signal effectively.

Figure 7 depicted the SERS spectrum of TNT molecules by using filter paper coated with silver nanoparticles. Figure 5b showed that filter paper possesses high enhancing power than colloidal silver.

The SERS spectrum of TNT molecules by using Al foil coated with silver nanoparticles is shown in Figure 8. Figure 8b showed that Al foil possesses higher enhancing power than colloidal silver and filter paper.

Calculating the Raman enhancement factor (EF) is necessary to determine the degradation in the efficiency of the SERS effect. Thus, we would calculate the EF values from the obtained spectra of the

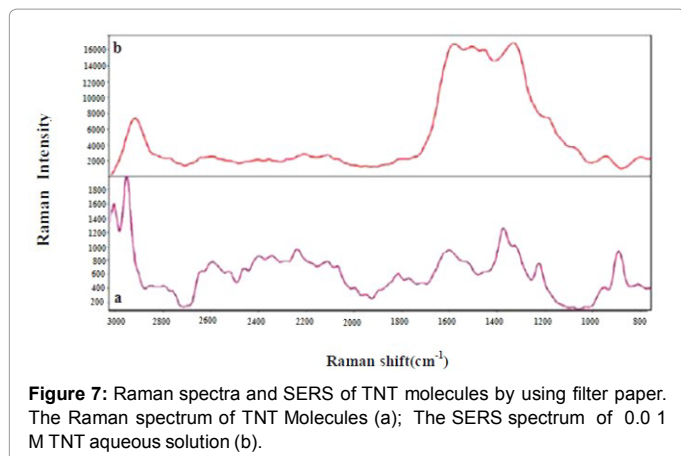


Figure 7: Raman spectra and SERS of TNT molecules by using filter paper. The Raman spectrum of TNT Molecules (a); The SERS spectrum of 0.01 M TNT aqueous solution (b).

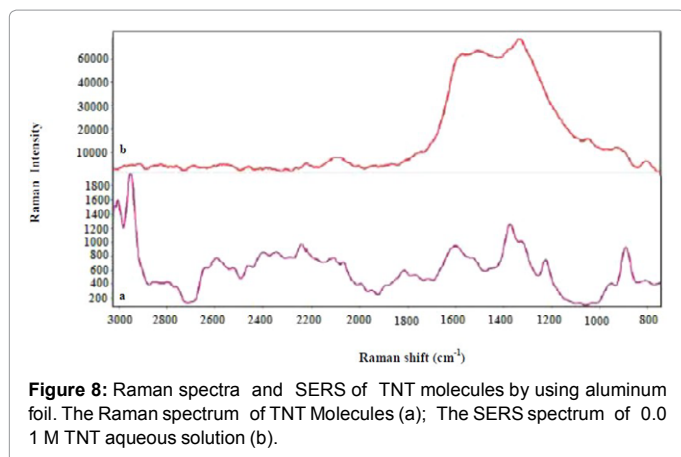


Figure 8: Raman spectra and SERS of TNT molecules by using aluminum foil. The Raman spectrum of TNT Molecules (a); The SERS spectrum of 0.01 M TNT aqueous solution (b).

Substrate	Location of the peak (cm ⁻¹)	Intensity of pick	Enhancement factor
Filter Paper	1332	16833	1329
Silver colloid	1344	1044	824
Aluminum foil	1336	58843	4719
TNT molecules	1375	1276	

Table 1: Comparison of the intensities of the main peaks of TNT for two substrates.

substrates. According to definition, the enhancement factor is attained by ratio of Raman intensity per molecule at presence of SERS structure and its absence. We used the following formula to calculate the EF from spectra [25].

$$EF = (I_{SERS}/I_{Raman}) (C_{Raman}/C_{SERS}) \quad (1)$$

Where, I_{SERS} and I_{Raman} are the intensities and the C_{SERS} and C_{Raman} are the molarities or concentrations of the solution in presence and absence of SERS structure respectively. Table 1 shows the EF values for substrates. The high amount of evaluated enhancement factors ensure the ability and practicality of the method for detecting the very low concentration and even single molecules.

Conclusion

In this paper, three different substrates were characterized by SERS effect. Colloidal silver solution containing silver nanoparticles, filter paper and aluminum foil which both coated by silver nanoparticles separately were used as the substrates. Resonance in absorption of the

surface plasmon in colloidal silver was obtained about 430 nm wave length and the average size of particle was attained as 16.9 nm by UV/VIS/NIR and DLS measurements respectively. Existence of silver nanoparticles and their size (40 to 240 nm) on surfaces of aluminum foil and filter paper would have been proven by using SEM imaging. EDX spectroscopy confirmed the crystallinity of dendrite film on the surface of Al foil. Finally, by using TNT molecules the relevant SERS spectra were investigated and high values of enhancement in Raman signal were obtained.

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