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Synthesis, characterization, and experimental investigation of surface activity of SERS substrates using neodymium oxide (Nd$_2$O$_3$)

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Abstract

The activity of two surface-enhanced Raman scattering (SERS) substrates was investigated using neodymium oxide (Nd$_2$O$_3$) molecules. Colloidal silver solution, containing nano-sized silver particles and silver-coated filter papers were used as the SERS substrates. In order to characterize the substrates, ultraviolet–visible spectroscopy, dynamic light scattering, and scanning electron microscopy were used. Subsequently, gain enhancement factors were calculated from the measured spectra to monitor the change in effectiveness of the SERS substrates under prolonged storage time. Experimental results show that for enhancing the Raman signal, the activity of two fabricated substrates is very effective.

Keywords: Surface-enhanced Raman scattering (SERS), Colloidal silver, Silver-coated filter paper, Neodymium oxide (Nd$_2$O$_3$)

Background

Surface-enhanced Raman scattering (SERS) is a sensitive and selective technique in which Raman scattering enhancing is achieved for those adsorbed molecules on metal nano-sized particles. Using this method, not only for the molecule structure analysis but also the information about the direction of molecule absorption and interaction between the molecule and the substrates can be attained [1-3].

SERS was first observed on absorbed pyridine molecules on the surface of roughed silver electrode with chemical method by Fleischmann et al. [4]. At the beginning, an unusual increase in the intensity of Raman signals was attributed to the growth of roughed substrate area. Then in 1977, Jean Marie and his colleagues found that the growth of the Raman scattering's cross section has another reason than the increase of molecules due to being roughed [5]. Nowadays, there are different ideas

to describe this effect, which two major categories are considering the intensity proportion of Raman scattering with the polarization of molecule and electric field shown as follows.

1. Electromagnetic effect: The mechanism is based on the optical properties of the noble metals and their ability to support plasmon resonances at visible wavelengths.
2. Chemical effect or charge transition: In this condition, the molecule is absorbed chemically by the metal nano-sized particles, and Raman enhancing is due to the exchange of electrons from metal to molecule and their return to the metal.

In other words, the molecule's polarization is affected by the interaction between the molecule and metal's surface. This effect is possible only for the first electronic state of the adsorbed molecule. Another important factor is the selection rules. When a molecule is adsorbed 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 [6-8].

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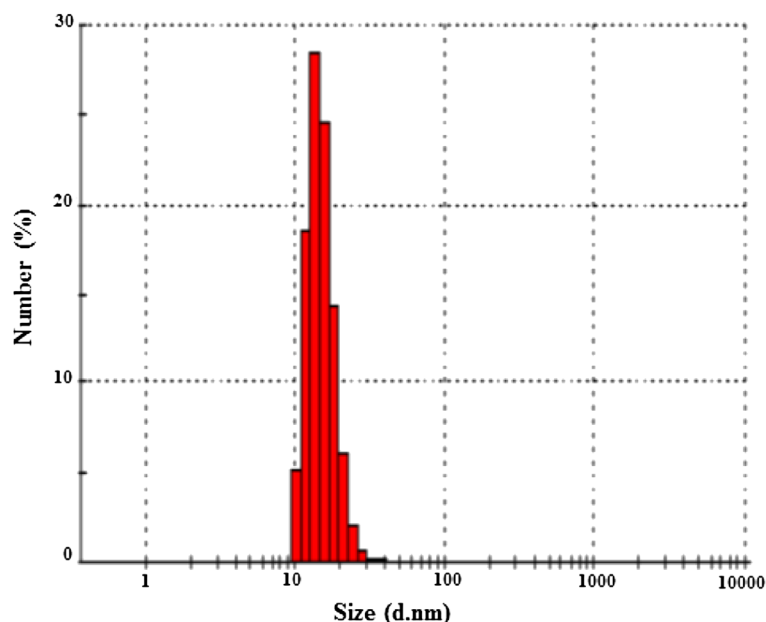
Figure 1 The particle size distribution of a typical prepared sample.

There are different kinds of SERS-active substrates used in the wide range of SERS applications such as metal colloids, coated filter papers with metal nanoparticles, electrochemically roughened metal electrodes, etc. [9-11].

In this study, we report a fabrication of the SERS-active substrate using colloidal silver nanoparticles and then characterized surface activity of SERS substrates by several methods such as scanning electron microscopy (SEM); dynamic light scattering (DLS) was investigated. Also, the plasmon absorption of the formed nano-crystals was monitored by ultraviolet–visible (UV–vis) spectrometry.

Results and discussions

Zetasizer Nano-Zs by Malvern Instruments (Worcestershire, UK) was used to define the size of the silver nano-sized particles. In this experiment, we dilute the collide solution with proportion of 5:1 using deionized water. Since, by increasing the average of scattering numbers of N, the number of oscillations is declined, and their effects are vanished in the large N [12]. The distribution of particles size of Ag metal that was shown in Figure 1 is relatively narrow, and the average particle size is about 16.9 nm.

In order to obtain a scanning electron microscopic image, we used freshly prepared nano-particles and micrographs of the samples (Figure 2). The size of the
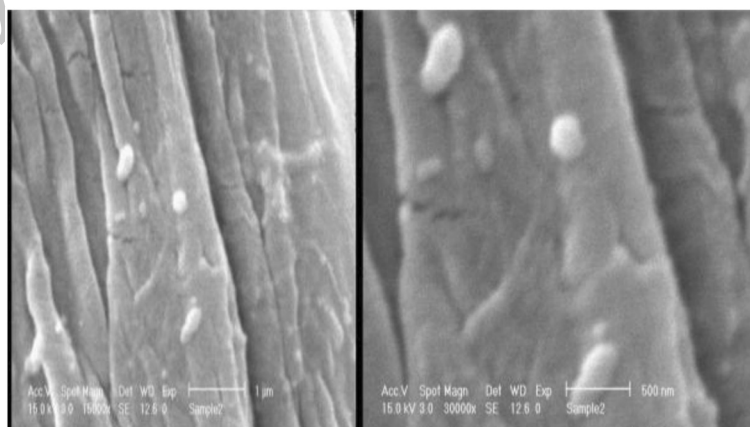
Figure 2 SEM of filter paper coated using nano-particles of silver.

Figure 3 UV/vis spectrum of the prepared Ag colloidal sample.
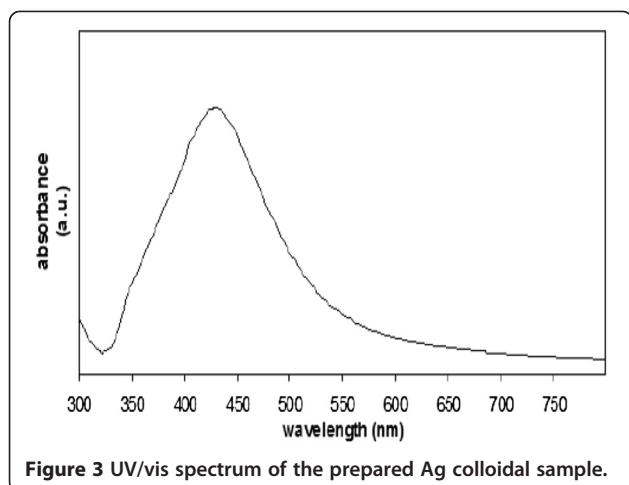
nano-sized particles is estimated around 40 to 240 nm by microstructure measurement. In fact, it is supposed that the larger nano-sized particles are not, silver, perhaps they are salts existing in colloidal silver solution that are recrystallized after drying. Moreover, the micrographs demonstrated a spherical shape and a smooth surface, with a particle size in the nano-metric range [13,14].

Excitation of the localized surface plasmon resonance (LSPR) is characterized by strong, wavelength-selective absorption and enhanced electromagnetic fields at the nano-particle surface. This provides the opportunity to simply follow the optical properties of the nanostructures utilizing UV–vis spectrometry and the tremendous enhancement of the weak Raman signal, respectively.

The maximum SERS enhancement is expected to take place when the max of LSPR is slightly longer than the laser (excitation) wavelength such that both the Raman scattered photon and the incident photon are strongly enhanced [11,15].

Hence, it is possible to adjust the wavelength maximum of the longitudinal resonance plasmon according to the excitation laser wavelength to obtain the largest Raman enhancement [16]. Colloidal silver solution was characterized using UV/vis/near-infrared (NIR) spectrophotometer. Figure 3 showed that the surface plasmon absorption band of colloidal silver was around 430 nm.

In Figure 4, we showed the Raman spectra and SERS of Nd_2O_3 molecules using colloidal silver: Figure 4a shows Raman spectrum in 1 M Nd_2O_3 solution without using SERS substrates. In Figure 4b, Raman spectrum in 0.01 M Nd_2O_3 solutions is shown which has lower density. According to Figure 4b, the peaks of Nd_2O_3 do not appear in this concentration. But in Figure 4c, the SERS spectrum for 0.01 M of Nd_2O_3 that was calculated using the colloidal silver shows the peaks of Nd_2O_3 even better than in 1 M solution.

Figure 5 depicted the SERS spectrum of Nd_2O_3 molecules using filter paper coated with nano-silvers. Figure 5b shows that filter paper possesses high enhancing power than colloidal silver although the filter paper does not show some weak peaks. Comparison between the location of the main flow peak and their intensities is shown for both substrates in Table 1. To quantify the degradation in the SERS effectiveness of the silver nano-rods affected by the storage time, we calculated the Raman enhancement factor from the SERS spectra as previously
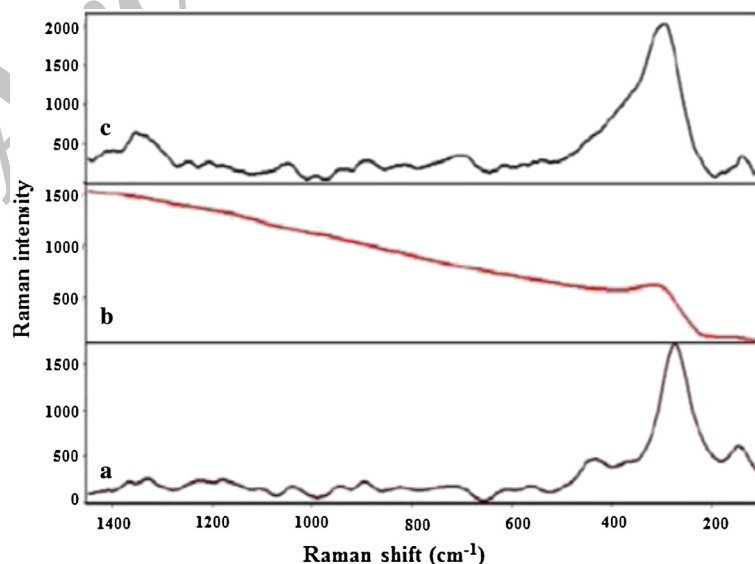
Figure 4 Raman spectra and SERS of Nd_2O_3 molecules using colloidal silver. The Raman spectrum of 1M Nd_2O_3 solution (**a**). The Raman spectrum of 0.01 M Nd_2O_3 solution (**b**). The SERS spectrum of 0.01 M Nd_2O_3 by silver colloid (**c**).
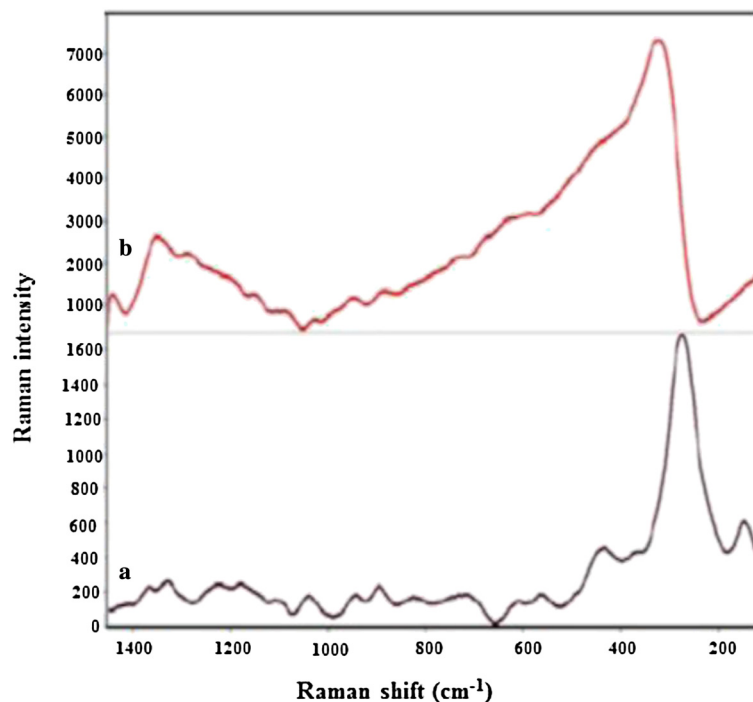
Figure 5 The Raman spectrum and SERS of Nd$_2$O$_3$ molecules using filter paper. (**a**) The Raman spectrum of 1 M Nd$_2$O$_3$ solution and (**b**) the SERS spectrum of 0.01 M of it using filter paper.

shown. The enhancement factor was defined as the ratio of inelastic scattering intensity per molecule between the presence and absence of the SERS structure. The Raman enhancement factor was calculated by following formula [17]:

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{C_{Raman}}{C_{SERS}} \qquad (1)$$

In which, I is the intensity of the peak and C is the concentration or molarity of the solution. We use the selected solution molarity of C_{SERS}. The EF values were shown in Table 1. According to the relatively high enhancement factor (428 for filter paper and 127 for sliver colloidal, the method is practical to detect the molecules with a low concentration and even single molecules.

In addition to Raman enhancing and detecting the molecules with low concentration, we can obtain information about molecule structure of Nd$_2$O$_3$ and its absorption trait

using SERS effect. The location of Raman and SERS peaks of Nd$_2$O$_3$ molecules is investigated in Table 2.

Conclusions

In this study, SERS was used to characterize colloidal silver solution, containing nano-sized silver particles. The solution was used to make filter paper covered using nano-sized silver. Absorption spectrum of colloidal silver showed the plasmon resonance in 430-nm wavelength

Table 1 Comparison of the intensities of the main peaks of Nd$_2$O$_3$ for two substrates

Substrate	Location of the peak (cm^{-1})	Intensity of the peak	Enhancement factor
Filter paper	322	7,327	458
Silver colloid	294	2,026	127
Nd$_2$O$_3$ molecule, 1 M solution	279	1,599	

Table 2 The location of Raman and SERS peaks

1 M solution of Nd$_2$O$_3$ (cm^{-1})	0.01 M solution of Nd$_2$O$_3$ in silver colloid (cm^{-1})	0.01 M solution of Nd$_2$O$_3$ on filter paper (cm^{-1})	Band
147	140		
274	294	322	Stretching vibration Nd-O
434			Stretching vibration Nd$_2$O$_2$
592		588	
721	701	722	
896	815	948	
1,180	1,209	1,154	Stretching vibration O-O
1,330	1,355	1,352	

using UV/vis/NIR. The DLS method also showed that the average size for nano-sized particles in colloid is 16.9 nm. To be certain about the existence of nano-sized silver particles on the filter paper, we used SEM imaging. SEM imaging proves the existence of the nano-sized silver particles on the filter papers, and their size is estimated about 40 to 240 nm. Moreover, the micrographs demonstrated a spherical shape and a smooth surface for particles. SERS spectrum for Nd_2O_3 was investigated for both substrates, and a satisfactory enhancement was observed.

Methods
Preparation of colloidal silver
Colloidal silver nano-particles were prepared according to Lee and Meisel's method [18]. Briefly, 18 mg of $AgNO_3$ was dissolved in 100-ml distilled water, and the solution was heated to boiling. Then, 7 ml of 1% trisodium citrate aqueous solution was added into the boiling silver nitrate solution at once, under vigorous stirring. The mixed solution was kept boiling for a further 8 min. Finally, the green-gray solution was obtained which was stable for several days or weeks.

In order to investigate rang of colloidal silver activity, we used Nd_2O_3. Nd_2O_3 is used to cover the glass for example in sunglasses, solid-state laser, and colored glasses [19]. To prepare Nd_2O_3 using colloidal silver, its molar solution with the proportion of 1:2 was mixed by colloidal silver, and the solution's pH was altered 8 up to 13 [20,21]. The peaks existing in 1 M solution were observed more clearly in pH = 12.

Preparation of the silver-coated filter papers
The filter paper used in this method has a very low filtration speed (MN 61q de 125 mm). We dropped the colloidal silver solution one by one on the filter paper, then let it to dry in the room temperature for about 10 min, and did this action several times. In this way, a group of filter papers covered using different nano-sized silver layers were achieved [22]. Finally, we drop the 0.01 M Nd_2O_3 solution drops one by one on the papers and let it to dry in the ordinary temperature.

Structural characterization and SERS detection
For characterization, the morphology of Ag-NPA-coated substrate was examined by a SEM (JSM-6700F, JEOL Ltd., Akishima-shi, Japan). The surface-enhanced Raman spectra were measured using a microscopic confocal Raman spectrometer (RM 2000, Renishaw, Wotton-under-Edge, UK), employing a Nd-YAG laser as the light source (_ = 532 nm). The beam diameter was 1 _m, and the integration time for each spectrum was set as 10 s.

Measurement of the hydrodynamic diameter of the nano-particles was accomplished using DLS (Nano ZS4700, Malvern Instruments, Worcestershire, UK). For size measurement, all paper formulations were diluted using deionized water to eliminate the effect of viscosity caused by the ingredients.

Authors' contributions
AHA and YM conceived of the study, participated in its design and coordination, and worked on the preparation of nanoparticles, the silver-coated filter papers, and characterization with Zetasizer. FS and FK participated in the design of the study and performed the statistical analysis. ZSM drafted the manuscript, and AN rechecked the whole manuscript. All the authors read and approved the final manuscript.

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