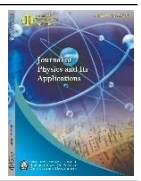
Journal of Physics and Its Applications

Journal homepage :https://ejournal2.undip.ac.id/index.php/jpa/index



Effect of Yield Silver Nanoparticles in Enhancing Raman Signal of SERS Substrate Fabricated on Whatman Filter Paper

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A R T I C L E I N F O

Article history:
Received: 22 December 2021
Accepted: 24 April 2022
Available online: 27 May 2022

Keywords:
Silver nanoparticles
Raman signal
SERS substrate
Whatman filter paper

A B S T R A C T

On Whatman Filter Paper, Surface Enhanced Raman Scattering (SERS) Substrate was created from colloidal silver nanoparticles by drop casting in varied volume colloidal nanoparticles of 3 ml and 6 ml. Using Raman Spectroscopy, SERS substrates were investigated for their ability to enhance 500 ppm of Deltamethrin pesticides Raman Signal. The number of colloidal nanoparticles is related to the volume of colloidal nanoparticles, indicating that high yields nanoparticle synthesis. The results demonstrate that fabricating SERS substrates in 6 ml increased Raman signal more than fabricating nanoparticles in 3 ml.

1. Introduction

In recent years, Surface-enhanced Raman scattering (SERS) has recently emerged as a simple, ultra-sensitive, non-destructive, and promising analytical technique for hazardous chemical detection in a variety of applications, including food contaminant detection, environmental monitoring, drug, biological entity, and explosive trace detection [1-4]. The presence of metallic nanostructure embedded in the surface amplifies the weak Raman signal that the molecules will be adsorbed and increased by SERS [5-6]. The main key to enhancing electromagnetic field in the SERS enhancement mechanism is the plasmonic characteristics of metallic nanoparticles.

Surface plasmons is a collective of surface conductive electrons excited when electromagnetic radiation interacts with metal-dielectric interface such as noble metal thin films or nanoparticles surface. There are two types of SPs : propagating SPs generated on noble metallic thin film are called surface plasmon polaritons (SPPs) and non propagating SPs generated on the surface of NPs are called localized surface plasmon resonances (LSPRs) [7-8]. The electromagnetics fields generated by SPs and localizes SPs at surface of metal nanoparticles will interacts with Raman emitted photons to provide significant enhancement of the Raman scattered photons (electromagnetic enhancement) these processes are forming the basis of SERS [9].

Metallic nanoparticles such as Au, Ag, Cu, and Bi are often utilized as SERS substrates [10-11]. Due to its narrower and sharper plasmonic width, Ag has better plasmonic than the others. Ag is also distinct from gold and platinum because of its high electrical and thermal conductivity, high primitive character, and low cost [12]. The size, shape, and properties of the nanoparticles placed into the substrate have an impact on the SERS enhancement factor [13].

Generally, SERS substrates are often prepared using conventional substrates such as silicon wafers, glass, and metal, which have limitations such as fragility, rigidity, high cost, and difficulty in solid sample collecting and manipulation efficiency [14]. As a result, alternative materials as SERS substrates must be sought. Filter paper is another option because of its versatility, low cost, and biodegradability [15].

The quality of the nanoparticles incorporated in the SERS substrate determines its performance. We fabricate silver nanoparticles in various yields in our experiment. Silver nanoparticles with a high yield embedded in Whatman filter paper are expected to improve the analyte's Raman signal more than nanoparticles with a lower yield.

Metal nanoparticles yield is metal nanoparticles concentrations assumed amount of metal atoms in the colloidal suspension. The number of nanoparticles in a colloidal suspension can determine total quantities of nanoparticle suspensions and the unit quantity of one nanoparticles which is represented from volume of colloidal suspension [16].

2. Methods

Based Using a simple and easy drop-casting method, we fabricated SERS substrate on Whatman filter paper using various volume colloidal nanoparticles of 3 ml and 6 ml.

Silver nanoparticles were synthesized by dissolving silver salt (silver nitrate (AgNO3, 99.9% purity, Sigma Aldrich) in 100 ml of water, adding 100µlof ammonia, and mixing 0.01 wt percent polyvinylpyrrolidone (PVP, 99.9% quality, Sigma Aldrich, Molecular Weight 40,00) in 4.22 x 10-4 M.The solution was placed in a quartz cuvette and exposed to laser femtosecond irradiation for 5 minutes.

A femtosecond laser (Mai Tai, Spectra Physics) has an 800 nm wavelength, a 1 kHz repetition rate, and a 2 Watt laser output. After the nanoparticles were manufactured, the sample was examined using a home-built UV-Vis spectrophotometry from a Halogen Lamp (Ocean Optics) and spectrophotometry (MayaPro 2000, Ocean Optics) that depicted absorption spectra in the 300-800 nm range as Localized Surface Plasmon Resonance (LSPR).

When silver ion metallic Ag+ cations in solution contact with Laser Femtosecond, hydrogen radicals function as a strong reducing agent, reducing and converting silver ion metallic Ag+ cations in solution to Ag0 atoms, resulting in AgNPs [17].

Colloidal silver nanoparticles in various volume nanoparticles of 3 ml and 6 ml were dropped repeatedly using a pipette on Whatman filter paper in the dimensions of a circle with a diameter of 2 cm and dried on a hot plate at 100°C.The morphology and particle size of SERS substrate in varied volume nanoparticles of 3 ml (sample 1) and 6 ml (sample 2) were observed using FE-SEM. The effectiveness of SERS substrate in increasing Deltamethrin pesticides was examined using a Raman spectrometer (HR550, Horiba Jobin Yvon) with a 532 nm laser as the excitation source and a selected grating of 1800 grooves per mm.

3. Results and Discussion

The SERS substrate was fabricated from colloidal silver nanoparticles in two varied volume nanoparticles of 3 ml and 6 ml into Whatman filter paper using drop-casting method. Where colloidal silver nanoparticles were synthesized using photochemical reduction methods have LSPR at 406.27 nm showed in Fig.1.

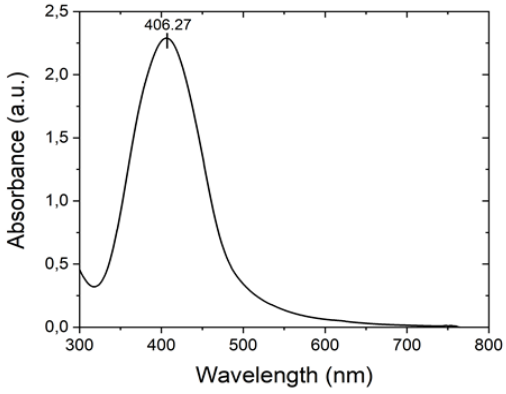

Fig. 1: The LSPR of silver colloidal nanoparticles.

Two different volume nanoparticles of silver colloidal nanoparticles (3 ml and 6 ml, respectively) were placed into a Whatman filter paper and dried on a hot plate. FE-SEM was used to characterize each SERS substrate.

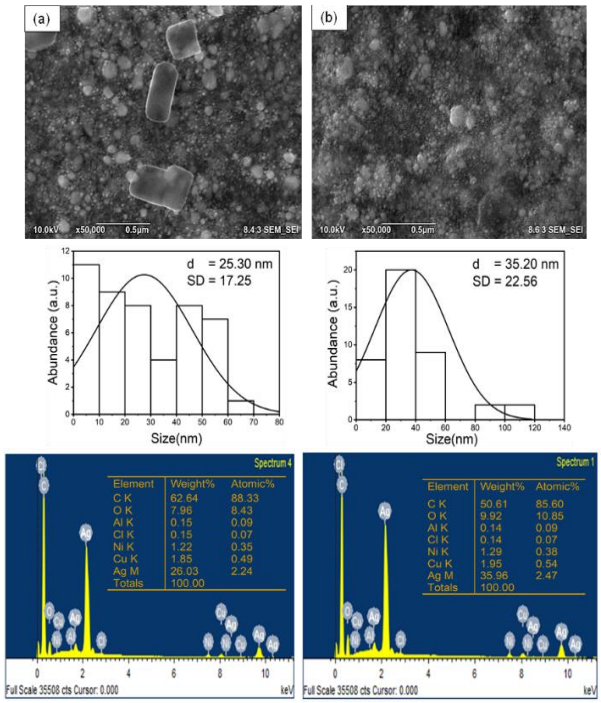

Fig. 2: The result of FE-SEM image of varied volume nanoparticles (a) 3 ml and (b) 6 ml.

In Fig.2, the FE-SEM results for 3 ml of nanoparticles (sample 1) and 6 ml of nanoparticles (sample 2) reveal that sample 2 has larger particles than sample 1.Sample 2 also produces more yield nanoparticles than sample 1, as seen by the greater Ag % in sample 2 when compared to sample 1.

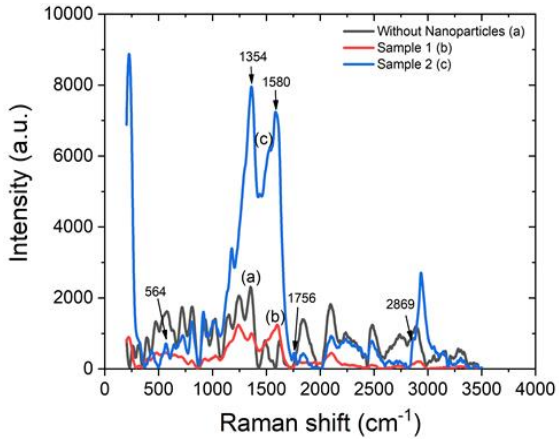

Fig. 3: The result of Raman image of varied volume nanoparticles(a) 3 ml and (b) 6 ml.

Each SERS substrate will be tested in enhancing the Raman signal of the analyte deltamethrin pesticides. Pesticides with a concentration of 500 parts per million (ppm) were made from dilute commercial pesticides containing 25 mg/L deltamethrin. Pesticides were sprayed on the SERS

substrates, and Raman Spectroscopy was used to measure the results.

At both sample 1 and 2, the Raman peak of deltamethrin pesticides was successfully detected. The results demonstrate that five Deltamethrin pesticides Raman peaks of 564, 1354, 1580, 1756, and 2869 cm-1 in sample 2 that represent stretching vibration of (C-Br) ip+(C-C), (C-H) ip, (C=C) ip, and (CH2), whereas only two Raman peaks of 1354 and 1580 cm-1 in sample 1 were definitely observed. The Raman peaks of delta methrin pesticides in sample 2 have higher intensity than sample 1.

Because the SERS substrate in sample 2 had higher yield of nanoparticles than sample 1. As demonstrated in Fig. 2b, the higher yield of nanoparticles substituted into the substrate, the more hot spot areas will be performed. If several nanoparticles have been successfully replaced to substrate, a hot spot is a gap between two or more nanoparticles where the area will be more created. This hotspot is where the most enhancements are made.

Furthermore, as indicated in eq 3, a higher yield of nanoparticles increases the surface density of individual nanoparticles, which increases the Enhancement Factor (EF) value and the Enhancement Raman signal.

EF (Enhancement Factor) where the most widely used definition for the average SERS EF is eq 1:

$$\mathrm{EF} = \frac{I_{\mathrm{SERS}}/N_{\mathrm{Surf}}}{I_{\mathrm{RS}}/N_{\mathrm{Vol}}} \qquad (1)$$

where I_{SERS} is intensity for SERS measurement, I_{RS} is intensity for Raman (non-SERS) measurement, $N_{Vol} = C_{RSV}$ is the average number of molecules in the scattering volume (V) for the Raman (non-SERS) measurement, and N_{Surf} is the average number of adsorbed molecules in the scattering volume for SERS experiment. This definition of EF is not rigorous enough, therefore EF formally defines the SERS substrate Enhancement Factor (SSEF) which is the following eq 2 and 3.

$$\mathrm{SSEF} = \frac{1}{A_M}\int_{A_M} \mathrm{OASMEF(r)d}S \qquad (2)$$

Where A_M represents the surface area of the substrate. The SSEF can be expressed in terms of the experimentally measured signal as eq 3:

$$SSEF = \frac{I_{SERS}/(\mu_M \mu_S A_M)}{I_{RS}/(c_{RS} H_{eff})} \qquad (3)$$

where c_{RS} is the concentration of the solution in non-SERS measurement, Heff is the effective height of the scattering volume, $\mu_M[m^{-2}]$ is the surface density of the individual nanostructures producing the enhancement, and $\mu_S[m^{-2}]$ is the surface density of molecules on the metal [18].

The Electromagnetic Enhancement Factor (EM) and the Chemical Enhancement Factor (CM) are thought to contribute the most to enhancement factors [19]. Due to the coupling Raman signal as a result of light localization at the substrate's surface, EM is assumed to be the main source. Localized plasmon nanoparticles on the substrate are thought to influence EM. While CM will be increased as a result of a change in the polarizability of molecules caused by the Raman cross-section of their vibrational modes, and will vary depending on the type of molecule [20].

Due to the vibration mode between the Raman source and the deltamethrin molecule, CM only contributes to the Raman shift of the Deltamethrin Pesticide peak. High yield nanoparticles are contributed as EM factor and increase the Raman signal higher than sample 1. High yield nanoparticles also increase the process of coupling Raman signal as a result there are many localized plasmon when light interacts with the surface of SERS substrate.

Due to the vibration mode between the Raman source and the deltamethrin molecule, CM only contributes to the Raman shift of the Deltamethrin Pesticide peak. As a result of the high yield nanoparticles contributing as an EM factor, sample 2 will enhanced the Raman signal more than sample 1. When light interacts with the surface of the SERS substrate, high yield nanoparticles increase the process of coupling Raman signal, resulting in a large number of localized plasmons.

4. Conclusion

Using the drop-casting method, a SERS substrate was successfully fabricated on Whatman filter paper with two different volume nanoparticles of 3 ml and 6 ml of silver colloidal nanoparticles. The SERS substrate was examined for its ability to enhance the Raman signal of the deltamethrin pesticide as an analyte. In comparison to the SERS substrate with a lower yield of nanoparticles (Sample 1), the findings of enhancing the Raman signal demonstrated that the SERS substrate with higher yield nanoparticle (Sample 2) could increase the Raman signal (Sample 1).In sample 2, five Deltamethrin pesticide Raman peaks of 564, 1354, 1580, 1756, and 2869 cm-1 were found, but only two Raman peaks of 1354 and 1580 cm^{-1} were clearly observed in sample 1.As a result of the high yield nanoparticles contributing as an EM factor, sample 2 will enhance the Raman signal more than sample 1.

5. Conflict of Interest

The authors declare that they have no conflict of interest.

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