Current Applied Science and Technology Vol. 22 No. 2 (March-April 2022)

Research article

Efficiency of Raman Signal Enhancement by Ag and Au/Ag Nanoparticles Decorated on Aluminum Sheet SERS

Nampueng Pangpaiboon[1], Kawinphob Phetnam[1], Sukon Kalasung[2], Chanunthorn Chananonnawathorn[2], Viyapol Patthanasettakul[2], Mati Horprathum[2], Pitak Eiamchai[2], Noppadon Nuntawong[2] and Saksorn Limwichean[2]*

[1]Department of Industrial Physics and Medical Instrumentation, Faculty of Applied Science, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand
[2]Opto-Electrochemical Sensing, National Electronics and Computer Technology Center, Pathumthani, Thailand

Received: 28 January 2021, Revised: 21 May 2021, Accepted: 5 August 2021

DOI: 10.55003/cast.2022.02.22.011

Abstract

Surface Enhance Raman Spectroscopy (SERS) is a well-known technique used to analyze solutions of various substances that are at very low concentration levels. To create plasmonic resonance, many researchers have used Au nanoparticles decorated on SERS. Although Au nanoparticles offer high efficiency and high stability, they are expensive. An inexpensive noble metal with high numbers of free electrons, Ag nanoparticles has become an interesting alternative. However, Ag has a major drawback because it is easily oxidized. Therefore, this research aims to combine the good properties between Au and Ag nanoparticles for Raman signal enhancement. A low-cost laser marking technique was used to engrave aluminum surface. The Au/Ag nanoparticles were co-sputtered on the aluminum template with decorating times ranging from 30-360 s. FE-SEM was used to characterize the nanostructure of the nanoparticles on SERS. Hydrophobic properties of the SERS surface were identified by contact angle measurement. A Raman spectrometer was used to measure the intensity of the enhanced Raman signal. From the results, the decorating time that provided the highest contact angle and highest Raman intensity enhancement was 270 s for both Ag and Au/Ag nanoparticles. The limit of detection of Ag and Au/Ag aluminum SERS was 10^{-8} M for Rhodamine-6 G. The enhancement factor for Ag aluminum SERS was slightly greater than that for Au/Ag aluminum SERS, as expected. After 60 days of shelf-life testing, Ag aluminum SERS presented the highest Raman enhancement. However, the Raman signal from Ag aluminum SERS dramatically decreased, afterwards. On the other hand, Au/Ag aluminum SERS showed a constant ability to enhance the Raman signal for as long as 150 days.

Keywords

Raman scattering;

laser-engrave;

Au/Ag nanoparticle SERS;

3D hybrid SERS;

sputtering

---

*Corresponding author: Tel.: (+66) 830187227
E-mail: saksorn.limwichean@nectec.or.th

1. Introduction

Surface Enhance Raman Spectroscopy (SERS) is an ultra-sensitive surface-based Raman technique. SERS is a well-known surface with powerful detection. Normally, SERS is used for detecting analytes at very low concentrations. There are 3 types of SERS: colloid-based [1, 2], thin film-based [3, 4] and 3D-hybrid structure-based SERS [5-9]. Colloid-based and thin film-based SERS can enhance the Raman signal, but they are non-uniform and non-repeatable devices. These SERS require a high production cost and involve a complex process. On the other hand, 3D-hybrid structure SERS is low cost, easy to fabricate, repeatable and uniform [9]. An important part of SERS is a nanostructure of noble metal that is decorated on the SERS surface. SERS can enhance the Raman signal detected by a Raman spectroscope more than one million times because of plasmonic resonance [10]. This phenomenon occurs by vibration of free-electron clouds at the surface of the noble metal. Distancing between the noble metals, called hot spot, from 50 to 100 nm, causes a high electromagnetic field that induces the Raman spectrum intensity [11].

Nowadays, SERS is used in many applications, for example, in medicine to analyze blood [12] and in forensic science to analyze addictive substances or dietary supplements [13]. Many researchers try to improve the efficiency of SERS in order to enhance the Raman signal. Recently, our research team discovered a new fabrication SERS prepared by a low-cost laser-engraved aluminum substrate. The SERS was built using Au nanoparticles as the decorating noble metal on laser-engraved aluminum substrate [9]. The decorated Au nanoparticles on SERS produces high stability; however, it is expensive.

Many researchers have studied SERS with Ag nanoparticles replacing Au nanoparticles; Ag also has a high degree of free-electron surface. Various techniques have been used to fabricate SERS devices; however, the processes were complex, time-consuming, expensive and left chemical residues [14-17]. Some SERS featured non-uniform Ag distribution, uncontrollable amounts of nanoparticles, and were difficult to handle, such as the paper/filter-based SERS [15, 16]. Kim *et al.* [10] produced a handy SERS with Ag decoration in 2017. The SERS presented a significant Raman enhancement; however, easy oxidation in the air was still a major problem with this noble metal. In the same year, Ju *et al.* [17] introduced a way of protecting the Ag nanoparticles with small nitrogen-doped graphene quantum dots that preserved the SERS performance in a normal indoor environment. Though the SERS showed a good performance after storage for 30 days, there were many chemical reagents used in the preparation process.

In this work, we sought to create better performance of laser-engraved aluminum substrate SERS than was evident in previous research [9]. The laser marking technique adopted was simple, low-cost, non-toxic, and could be used for mass production. In order to increase cost effectiveness, the decorating Au nanoparticles were replaced by Ag nanoparticles. However, the weakness of Ag, which is easily oxidized, remained a concern. Therefore, an interesting decorative material, which was a combination of Au and Ag nanoparticles, was selected. The SERS with an alloyed Au/Ag enhancing metal was expected to be low cost, highly efficient, and was thought to offer high stability SERS. Ag and Au/Ag nanoparticles were deposited on the laser-engraved aluminum substrate by a sputtering technique which provided a uniform and controllable nanoparticle distribution. The easy-to-handle SERS chip with homogeneous enhancing material required a small amount of testing solution and simple maintenance.

Surface topography of the nanoparticles, hydrophobic properties at the SERS surface, and the Raman signal enhancement from Ag and Au/Ag aluminum SERS were investigated. Moreover, the efficiency of Ag and Au/Ag aluminum SERS was verified by its limit of detection, enhancement factor, and shelf-life. We expected to discover a high-performance SERS fabricated with low-cost materials and by low-cost techniques.

2. Materials and Methods

2.1 Aluminum sheet engraving

A commercial aluminum sheet with thickness of 0.4 mm was used as a template. A rough structure of the template was designed and fabricated by laser mark technique. Firstly, an aluminum sheet was cleaned with strain remover. After nitrogen gas drying, the aluminum sheet was ready for laser marking. Then, the micro-nano structure on the aluminum surface was engraved with a laser markings machine and engraving machine with laser class IV at 1060-1070 nm (Smart mark, Photonics Science Co., Ltd). The laser power, fill spacing, and frequency used in this research were 12 W, 0.02 mm and 30 kHz, respectively [9]. The micro-nano structures of the bare aluminum sheet template, after laser-engraving process, were studied by Field-Emission Scanning Electron Microscope (FE-SEM; Hitachi, SU8030).

2.2 Ag aluminum SERS fabrication

After the engraving process, Ag nanoparticles were decorated on the aluminum sheet template by a magnetron sputtering technique (lab-assembled, single-cathode PVD system). An ultra-high vacuum (UHV) sputtering system with 5×10^{-6} mbar base pressure was used. When the chamber reached the base pressure, Ag nanoparticles were deposited on the aluminum sheet template. The operating pressure was 1.1×10^{-3} mbar. This process was performed under 90 W of AC power and 30 sccm rate of Ar gas. Sputtering times were varied from 30-360 s. Finally, the Ag aluminum sheet template was cut into 5×5 mm^2 piece, which became the Ag aluminum SERS samples.

2.3 Au/Ag aluminum SERS fabrication

Au/Ag nanoparticles were decorated on the aluminum sheet template by magnetron sputtering technique used to make the Ag aluminum SERS. Both Au and Ag were sputtered together at the same time under the same conditions used in our previous work [18]. The base pressure of the co-sputtering in the chamber was 5×10^{-6} mbar as in Ag system. However, the sputtering conditions for Ag and Au/Ag nanoparticles were different. Au and Ag targets were connected with DC power and AC power, respectively. The operating pressure was 4.2×10^{-3} mbar. The co-sputtering process was performed under 50 W of both power supplies with 20 sccm rate of Ar gas. Sputtering times were also varied from 30-360 s. After that, the sample was cut into square piece of 5×5 mm^2. Finally, the alloyed Au/Ag aluminum SERS were completely fabricated.

2.4 Ag and Au/Ag aluminum SERS characterization

After Ag and Au/Ag aluminum SERS were successfully fabricated, the topography of Ag and Au/Ag aluminum SERS were examined using FE-SEM. The diameters and hot spots of the nanoparticles at different decoration times were measured from FE-SEM images. Contact angle measurement was used to analyze the hydrophobic properties of the SERS surface. Droplet of DI water, about 20 µl, was used in this process. Rhomdamine 6G (R6G) solution at 1×10^{-5} M concentration was used as a testing solution. Droplet of R6G, about 2 µl, was used to test the SERS. The efficiency on enhancement of the Raman signal was examined by inVia Raman microscope from Renishaw. The laser wavelength and exposure time used in the Raman test were 785 nm and 30 s, respectively. To study SERS ability to enhance the Raman signal at very low concentrations, limit of detection (LOD) was tested using R6G solution with varied concentrations from 1×10^{-5} to

1×10^{-9} M. The enhancement factor (EF) values of Ag and Au/Ag aluminum SERS were calculated. Finally, shelf-life was assessed by storing the SERS in an ambient environment. For accuracy purposes, the Raman signals from the SERS were tested from the 1st day to the 150th day by selecting different areas on the same SERS.

3. Results and Discussion

Aluminum sheet templates were successfully prepared using the laser-engraved technique as in literature [9]. The FE-SEM image illustrated the micro-nano structure on the aluminum surface; those images are not shown here. A homogeneous rough surface was used as the SERS template. Ag and Au/Ag nanoparticles were sputtered on the template with varying sputtering times at 30, 90, 180, 270, and 360 s. Topography images of the decorated Ag and Au/Ag nanoparticles on the aluminum sheet were investigated by FE-SEM. The structures of Ag nanoparticles on the aluminum sheet SERS are presented in Figure 1 a)- e). The FE-SEM images show that the Ag nanoparticles were widely spread on the rough surface of the aluminum sheet template. The diameters of the Ag nanoparticles increased with increasing decoration time. Figure 2 a) shows the relationship between diameter and decoration time of the Ag nanoparticles, which were 78.31±4.03, 95.64±5.03, 105.91±7.44, 116.11±10.25, and 125.30±11.12 nm, when the sputtering times were 30, 90, 180, 270, and 360 s, respectively.

As was the case for the Ag aluminum sheet SERS, the Au/Ag aluminum sheet SERS was also prepared by sputtering Au/Ag nanoparticles on the engraved aluminum template. Topography images of Au/Ag aluminum sheet SERS were presented by FE-SEM, as shown in Figure 3 a) - e). After increasing sputtering time, the diameters of the nanoparticles also increased. At 30, 90, 180, 270, and 360 s of decorating, the diameters of Au/Ag nanoparticles were 37.63±2.03, 51.92±3.89, 60.14±4.52, 64.20±6.85, and 72.09±7.61 nm, respectively. The diameters of the alloyed Au/Ag nanoparticles increased with increasing decoration time as shown in Figure 2 b).

From the results, both Ag and Au/Ag nanoparticles were revealed to be spherical structure. Increasing sputtering time enlarged the diameters of the nanoparticles. The average diameter of Au/Ag nanoparticles was a little bit smaller than Ag nanoparticles. There were some agglomerates occurring early in the decorating process. However, the nanoparticles fully covered the rough aluminum surface. Uniformity of the nanoparticles increased with increasing decoration time.

Because of nanoparticle aggregation, hot spots could not be measured. Thus, the optimum decoration time which provides a good enhancement of the Raman signal could not be predicted. From literature review, some researchers reported that hydrophobic property of the SERS surface determined the efficiency of the Raman signal enhancement [6, 19-21]. Therefore, in this part, hydrophobic properties of the Ag and Au/Ag aluminum SERS were determined.

For the Ag aluminum SERS, the contact angles of DI water droplets on the surface of the SERS with decoration times at 30, 60, 120, 240, and 360 s were 120±2.25, 121±1.06, 126±0.97, 139±0.52, and 129±0.31 degree, respectively, as shown in Figure 4 a) - e). The results of contact angle measurement of the Au/Ag aluminum sheet SERS are shown in Figure 5 a) - e). The contact angles were 111±3.02, 113±2.42, 120±1.21, 137±0.94, and 131±0.53 degree, when measuring droplets of DI water on Au/Ag surface at sputtering times 30, 60, 120, 240, and 360 s, respectively. From the results, both Ag and Au/Ag aluminum SERS surfaces presented the highest contact angle at 270 s of decoration time. Moreover, over the decoration time range of 30 to 270 s, for both Ag and Au/Ag aluminum SERS, increasing of contact angle depended on decoration time and the highest contact angle presented when the sputtering process was continued to 270 s. However, the contact angle decreased when the decoration time was 360 s, as shown in Figure 6 a) - b).

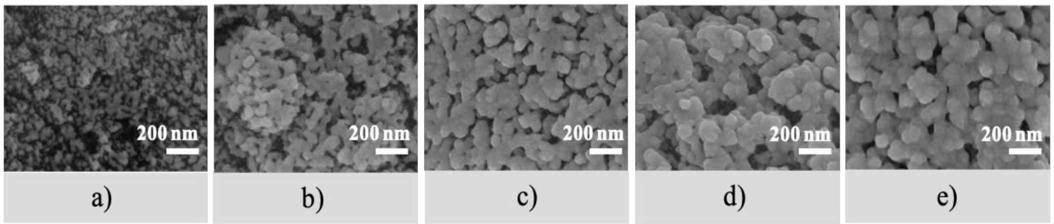


Figure 1. FE-SEM images presenting topography of Ag nanoparticles decorated on aluminum sheet with decoration times: a) 30 s, b) 90 s, c) 180 s, d) 270 s, and e) 360 s

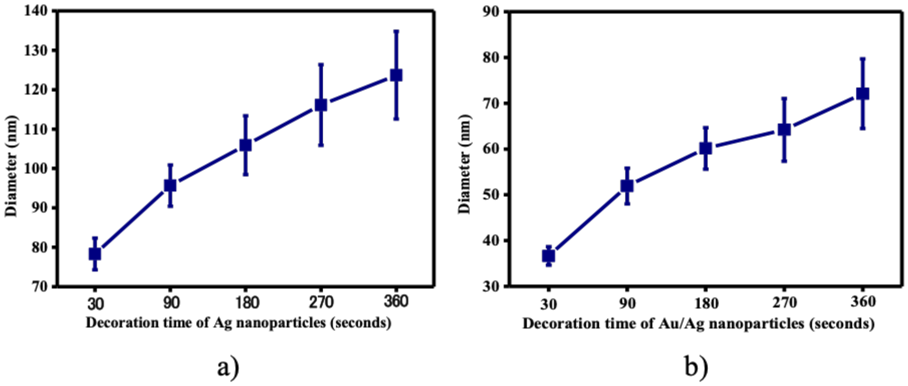


Figure 2. Relationship between decoration time and nanoparticle diameter of a) Ag nanoparticles and b) Au/Ag nanoparticles on aluminum sheet

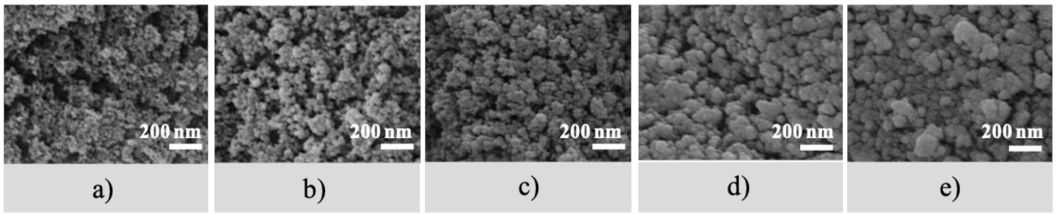


Figure 3. FE-SEM images presenting topography of Au/Ag nanoparticles decorated on aluminum sheet with decoration times: a) 30 s, b) 90 s, c) 180 s, d) 270 s, and e) 360 s

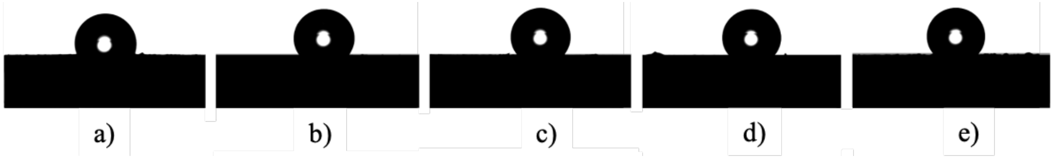


Figure 4. Contact angles of DI water droplet on Ag aluminum SERS with decoration times at a) 30 s, b) 90 s, c) 180 s, d) 270 s, and e) 360 s

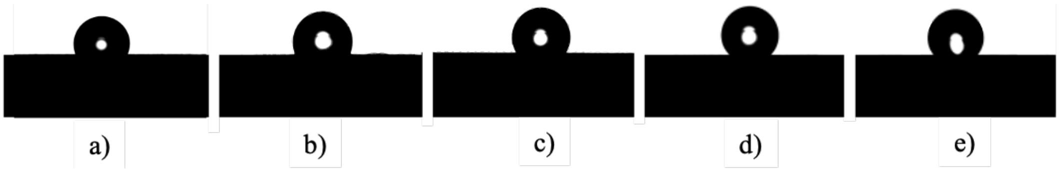


Figure 5. Contact angles of DI water droplet on Au/Ag aluminum SERS with decoration times at a) 30 s, b) 90 s, c) 180 s, d) 270 s, and e) 360 s

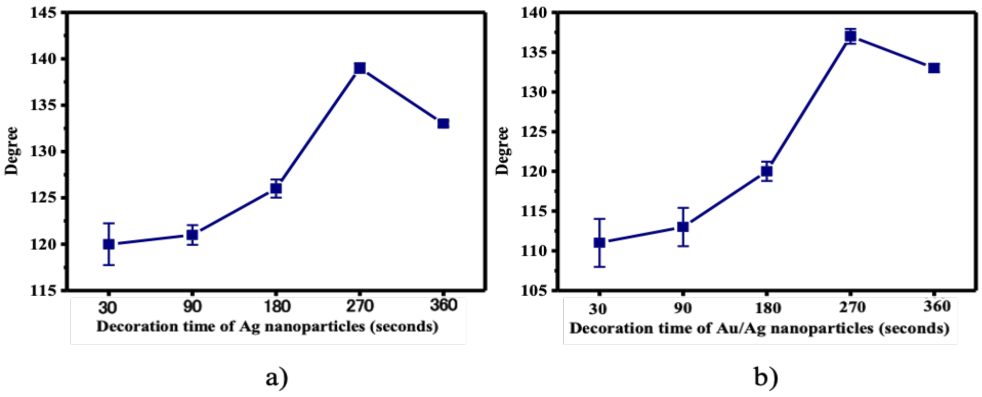


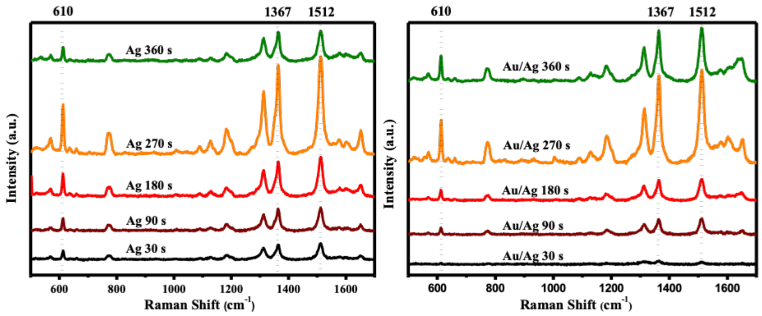
Figure 6. Relationship between decoration time and contact angle of DI water on a) Ag aluminum SERS and b) Au/Ag aluminum SERS

The superhydrophobic surface SERS can enhance the Raman signal greatly because the contact area between molecules of solution and SERS surface is small. After the solution dries, the solution molecules settle at the bottom. Hence, this small contact area is full of the tested molecule which increases the intensity of the Raman signal [6]. Therefore, from the contact angle results, we concluded that a decoration time of 270 s, which provided the highest contact angle, offered the optimal efficiency to enhance the Raman signal for both Ag and Au/Ag aluminum SERS.

The Raman spectra of R6G solution for the Ag aluminum SERS with decoration time from 30-360 s are shown in Figure 7 a). The individual Raman shifts of R6G Raman spectrum, which are 610, 1367, and 1512 cm^{-1}, are presented. Intensities of R6G spectrum increased with continuing nanoparticle sputtering process from 0 to 270 s and reached the highest intensity at 270 s. The intensities obviously dropped when decoration time went past 360 s.

For Au/Ag aluminum SERS, the intensities of the R6G solution Raman signal are shown in Figure 7 b). The intensities increased with increasing decoration time until 270 s. After that, the intensity decreased, and at 360 s sputtering, the intensity of the signal was the same as that of the Ag aluminum SERS at the same sputtering time.

From the Raman spectroscopy analysis, Ag and Au/Ag aluminum SERS were able to enhance the Raman signal. The optimum time to sputter the nanoparticles was 270 s for both the Ag and Au/Ag systems. At this condition, the SERS revealed the best efficiency to enhance the Raman signal according to their hydrophobic properties.



a)

b)

Figure 7. The Raman spectrum of R6G solution enhanced by a) Ag aluminum SERS and b) Au/Ag aluminum SERS at different nanoparticle sputtering times

The best enhancing SERS with 270 s sputtering time were selected to compare their efficiency of enhancement of Raman signal by calculating the Enhancement Factor (EF). EF is a number used to express the ability of SERS to enhance the Raman signal at any solution concentration. This factor is internationally accepted and widely used to clarify SERS performance [22]. The EF values of Ag and Au/Ag aluminum SERS were calculated using the equation 1 [23].

$$\mathrm{EF} = \left(\frac{\mathrm{I\ surf}}{\mathrm{I\ bulk}}\right) \times \left(\frac{\mathrm{N\ bulk}}{\mathrm{N\ surf}}\right) \tag{1}$$

where I_{surf} is an intensity of the vibration modes in SERS and I_{bulk} is the vibration mode in the Raman spectrum. N_{bulk} is the number of a probed molecules on the Raman spectrum, and N_{surf} is the number of a probed molecules on the SERS.

The substrate used for I_{bulk} was a glass slide. The enhancement factors of the SERS were calculated from the reference peak of the Raman spectrum at 1367 cm^{-1}. We found that EF values of Ag and Au/Ag aluminum SERS were 3.19 x 10^{9} and 4.85 x 10^{8}, respectively. Ag aluminum SERS showed higher EF value than Au/Ag aluminum SERS, as expected. Both Ag and Au/Ag aluminum SERS, in our work, demonstrated an impressive ability to enhance the Raman signal. From the literature, the EF values of SERS fabricated with Ag nanoparticles are in the range of about 4.5 x 10^{5} to 4.20 x 10^{7} [15, 17, 22, 24-26]. For practical purposes, SERS should enhance the Raman signal for analytes even at very low concentrations. Therefore, to confirm the efficiency of our SERS, limit of detection and shelf-life were examined.

One of the important properties of SERS is it can enhance the Raman signal even at a very low concentration of solution. Therefore, the lowest solution concentrations at which the Ag and Au/Ag aluminum SERS could enhance the Raman signal, or the limit of detection (LOD), were studied. The Ag and Au/Ag aluminum SERS with 270 s sputtering time were selected to be tested with R6G solution at various concentrations from 1 x 10^{-6} to 1 x 10^{-9} M. Figure 8 a) - b) shows the Raman shift of R6G Raman spectrum for Ag and Au/Ag aluminum SERS. At 1 x 10^{-8} M concentration, R6G Raman spectrum enhancement could be observed for both Ag and Au/Ag SERS. However, when the concentration was decreased to 1 × 10^{-9} M, both Ag and Au/Ag aluminum SERS did not show any R6G Raman spectrum. From the LOD testing, although the EF value of the Ag aluminum SERS was higher than that of the Au/Ag aluminum SERS, the efficiencies of enhancement of the Raman signal for both Ag and Au/Ag aluminum SERS were of the same level. We found that addition of Au nanoparticles in Ag system did not significantly reduce the enhancement of the Raman intensity of Ag nanoparticles.

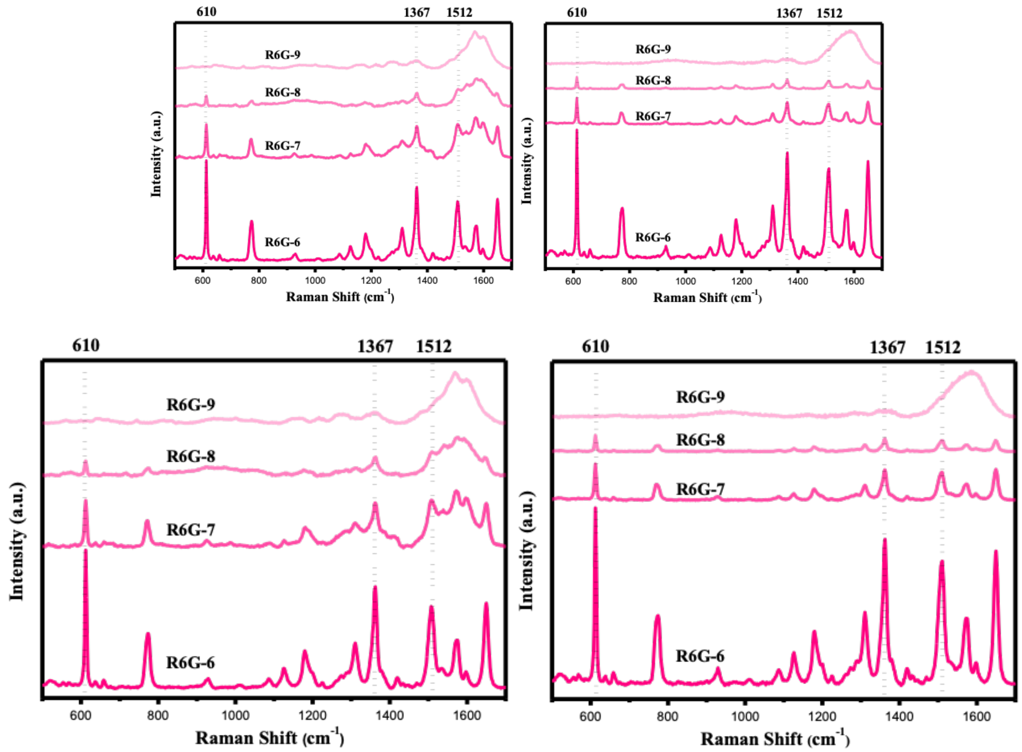


Figure 8. Limit of detection of R6G solution from a) Ag aluminum SERS and b) Au/Ag aluminum SERS

Shelf-life, which is an expression of SERS ability, is measured when the SERS is kept in an ambient environment for a long time and the Raman enhancement signal is checked over the period. There are a lot of factors to make SERS de-grade, for example, humidity, temperature, and pressure. In this experiment, the shelf-life of Ag aluminum SERS, Au/Ag aluminum SERS, and a commercial SERS chip were observed and compared. The commercial SERS chip, invented by ONSPEC Lite NECTEC, was made by decorating Au nanoparticles on an aluminum sheet [9]. R6G solution with 1 x 10^{-5} M concentration was used as a testing solution. The Raman spectrum data of the SERS were collected for 150 days and the results are shown in Figure 9. The raw data received from each SERS were calculated by averaging the intensities of R6G Raman spectrum at peak positions of 610, 1367, and 1512 cm^{-1}. Before testing, the Ag aluminum SERS showed the highest enhancement intensity of the Raman signal, followed by Au/Ag aluminum SERS and Onspec Lite NECTEC SERS chips, and this trend remained for 60 days. Though the enhancement ability of the Ag aluminum SERS rapidly decreased after first 7 days of the period, it still provided the highest Raman signal intensity. After that, the signal detected from the Ag aluminum SERS decreased and eventually, demonstrated the lowest ability to enhance the Raman signal after 90 days, due to oxidation.

On the other hand, the Au/Ag aluminum SERS demonstrated a constant ability to enhance the Raman signal. Over first 90 days, Au/Ag aluminum SERS showed a greater intensity effect than the commercial one, and slightly decreased after that. The alloyed Au/Ag nanoparticles improved the stability of Ag aluminum SERS, maintaining an effective ability to enhance the Raman signal.

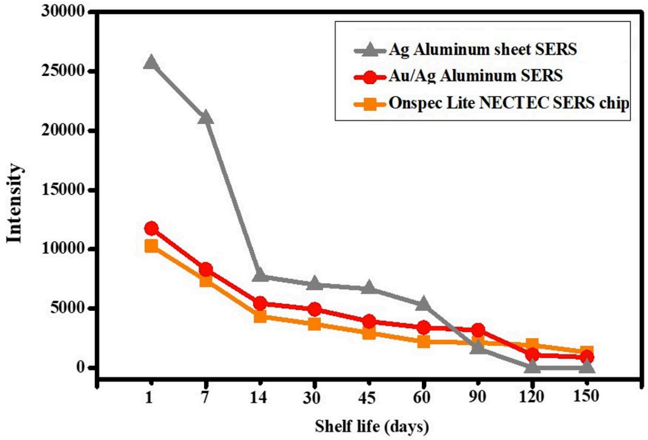


Figure 9. Relationship between shelf-life and intensity of R6G Raman spectrum of Ag aluminum SERS, Au/Ag aluminum SERS, and Onspec Lite NECTEC SERS chip

Even though the Ag aluminum SERS presented an excellent capability to enhance the Raman signal, because of its oxidation, the SERS proved to be an irregular device. Otherwise, the alloyed Au/Ag nanoparticle proved to be a good combination material used as an enhancing noble metal for a low-cost SERS. The Au/Ag aluminum SERS exhibited high efficiency and consistent Raman signal enhancing performance. In this research, we successfully created the mass-produced and highly efficient SERS chip that required a small amount of testing solution, simple maintenance, and was stable over long-time storage.

4. Conclusions

The mass-produced and high efficiency Ag and Au/Ag aluminum SERS were successfully fabricated using a low-cost laser-engraved technique. From topography images studied with FE-SEM, the nanoparticles fully covered the aluminum surface and the diameters of the nanoparticles increased with increasing decoration time. The hydrophobic properties of the SERS were related to the Raman signal enhancement. The optimum sputtering time for both Ag and Au/Ag nanoparticles was 270 s, which provided the greatest contact angle and the Raman intensity. The performance of Ag and Au/Ag aluminum SERS were investigated by measuring enhancement intensity, calculating EF values, testing LOD and observing shelf-life. The Raman intensities and EF values from Ag and Au/Ag aluminum SERS were of the same level. The LOD of both SERS was 1×10^{-8} M measured with R6G solution. Because of oxidation problems, Ag aluminum SERS provided the lowest intensity after 90 days of shelf-life testing. We found that the combination of Au and Ag nanoparticles improved the stability of SERS device over the long term.

5. Acknowledgements

For our success in this research, we would like to thank National Electronics and Computer Technology Center (NECTEC), National Science and Technology Development Agency. This research was funded by Faculty of Applied Science, King Mongkut's University of Technology North Bangkok, Thailand (No.643051).

References

[1] Mou, M., Chen, D., Wang, X., Zhang B., He, T., Xin, H. and Liu, F.-C., 1991. SERS and UV spectra of meso-tetrakis (4-sulfonatophenyl)-porphine adsorbed on Ag2O colloids. *Chemical Physics Letters*, 179(3), 237-242.

[2] Cyrankiewicz, M., Wybranowski, T. and Kruszewski, S., 2007. Study of SERS efficiency of metallic colloidal systems. *Journal of Physics*, 79, https://doi.org/10.1088/1742-6596/79/1/012013.

[3] Kavitha, C., Bramhaiah, K., John, N.S. and Ramachandran, B.E., 2015. Low cost, ultra-thin films of reduced graphene oxide–Ag nanoparticle hybrids as SERS based excellent dye sensors. *Chemical Physics Letters*, 629, 81-86.

[4] Weng, G., Yang, Y., Zhao, J., Li, J., Zhu, J. and Zhao, J., 2020. Improving the SERS enhancement and reproducibility of inkjet-printed Au NP paper substrates by second growth of Ag nanoparticles. *Materials Chemistry and Physics*, 253, https://doi.org/10.1016/j.matchemphys.2020.123416.

[5] Li, R., Lei, J., Zhou, Y. and Li, H., 2020. Hybrid 3D SERS substrate for Raman spectroscopy. *Chemical Physics Letters*, 754, https://doi.org/10.1016/j.cplett.2020.137733.

[6] Pal, A.K., Pagal, S., Prashanth, K., Chandra, G.K., Umapathy, S. and Mohan, B.D., 2019. Ag/ZnO/Au 3D hybrid structured reusable SERS substrate as highly sensitive platform for DNA detection. *Sensors and Actuators B: Chemical*, 279, 157-169.

[7] Zhao, X.Y., Wang, G. and Hong, M., 2018. Hybrid structures of Fe3O4 and Ag nanoparticles on Si nanopillar arrays substrate for SERS applications. *Materials Chemistry and Physics*, 214, 377-382.

[8] Qiu, H., Wang, M., Li, L., Li, J., Yang, Z. and Cao, M., 2018. Hierarchical MoS2-microspheres decorated with 3D AuNPs arrays for high-efficiency SERS sensing. *Sensors and Actuators B: Chemical*, 255, 1407-1414.

[9] Botta, R., Eiamchai, P., Horprathum, P., Limwichean, S., Chananonnawathorn, C., Patthanasettakul, V., Maezono, R., Jomphoak, A. and Nuntawong, N., 2020. 3D structured laser engraves decorated with gold nanoparticle SERS chips for paraquat herbicide detection in environments. *Sensors and Actuators B: Chemical*, 304, https://doi.org/10.1016/j.snb.2019.127327.

[10] Kim, Y.-T., Schilling, J., Schweizer, S.L. and Wehrspohn, R.B., 2017. High density Ag nanobranches decorated with sputtered Au nanoparticles for surface-enhanced Raman spectroscopy. *Applied Surface Science*, 410(C), 525-529.

[11] Nuntawong, N., Horprathum, M., Eiamchai, P., Wong-ek, K., Patthanasettakul, V. and Chindaudom, P., 2010. Surface-enhanced Raman scattering substrate of silver nanoparticles depositing on AAO template fabricated by magnetron sputtering. *Vacuum*, 84(12), 1415-1418.

[12] Tang, H., Meng, G., Huang, Q., Zhang, Z., Huang, Z. and Zhu, C., 2011. Array of cone shaped ZnO nanorods decorated with Ag nanoparticles as 3D surface-enhanced Raman scattering substrate for rapid detection of trace poly-chlorinated biphenyls. *Advanced Functional Materials*, 22(1), 218-224.

[13] Xue, L., Yan, B., Li, Y., Tan, Y., Luo, X. and Wang, M., 2018. Surface-enhanced Raman spectroscopy of blood serum based on gold nanoparticles for tumor stages detection and histologic grades classification of oral squamous cell carcinoma. *International Journal of Nanomedicine*, 13, 4977-4986.

[14] Lu, G., Li, H., Liusman, C., Yin, Z., Wu, S. and Zhang, H., 2011. Surface enhanced Raman scattering of Ag or Au nanoparticle-decorated reduced graphene oxide for detection of aromatic molecules. *Chemical Science*, 2(9), 1817-1821.

[15] Moram, S.S.B., Byram, C., Shibu, S.N., Chilukamarri, B.M. and Som, V.R., 2018. Ag/Au nanoparticle-loaded paper-based versatile surface- enhanced Raman spectroscopy substrates for multiple explosives detection. *ACS Omega*, 3, 8190-8201.

[16] Xu, F., Xuan, M., Ben, Z., Shang, W., and Ma, G., 2021. Surface enhanced Raman scattering analysis with filter-based enhancement substrates: A mini review. *Reviews in Analytical Chemistry*, 40, 75-92.

[17] Ju, J., Liu, W., Perlaki, C., Chen, K., Feng, C., and Liu, Q., 2017. Sustained and cost effective silver substrate for surface enhanced Raman spectroscopy based biosensing. Scientific Reports, 7, 6917, https://doi.org/10.1038/s41598-017-07186-9.

[18] Eiamchai, P., Chananonnawathorn, C., Horprathum, M., Patthanasettakul, V., Limwichean, S. and Nuntawong, N., 2020. Spatial elemental investigations in nanostructured alloyed Ag/Au SERS substrates by magnetron sputtering oblique-angle co-deposition towards increased performance and shelf life. *Applied Surface Science*, 513, https://doi.org/10.1016/j.apsusc.2020.145748.

[19] Ruan, S., Li, X. and Jiang, T., 2020. Hydrophilic-hydrophobic poly(dimethyl siloxane)-based SERS substrate with internal Raman signaling. *Materials Chemistry and Physics*, 255, https://doi.org/10.1016/j.matchemphys.2020.123582.

[20] Sakir, M., Yilmaz, E. and Onses, M.S., 2020. SERS-active hydrophobic substrates fabricated by surface growth of Cu nanostructures. *Microchemical Journal*, 154, https://doi.org/10.1016/j.microc.2020.104628.

[21] Li, Z., Zhu, K., Zhao, Q. and Meng, A., 2016. The enhanced SERS effect of Ag/ZnO nanoparticles through surface hydrophobic modification. *Applied Surface Science*, 377, 23-29.

[22] Lv, K., Si, H., Liu, j., Zhu, T., Xia, Y., Chen, S., Zhao, Y. and Yang, C., 2020. Plasmonic filters based on MoS2@Au/Ag hybrids: Controllable separation, preconcentration, and sensitive SERS detection. *Journal of Alloys and Compounds*, 846, https://doi.org/10.1016/j.jallcom.2020.156438

[23] He, S., Chua, J., Tan, E.K.M. and Kah, J.C.Y., 2017. Optimizing the SERS enhancement of a facile gold nanostar immobilized paper-based SERS substrate. *RSC Advances*, 7(27), 16264-16272.

[24] Kundu, S., Dai, W., Chen, Y., Ma, L., Yue, Y., Sinyukov, A.M. and Liang, H., 2017. Shape-selective catalysis and surface enhanced Raman scattering studies using Ag nanocubes, nanospheres and aggregated anisotropic nanostructures. *Journal of Colloid and Interface Science*, 498, 248-262.

[25] Wu, L., Zhang, W., Liu, C., Foda, M.F. and Zhu, Y., 2020. Strawberry-like SiO2/Ag nanocomposites immersed filter paper as SERS substrate for acrylamide detection. *Food Chemistry*, 328, https://doi.org/10.1016/j.foodchem.2020.127106.

[26] Li, Q., Gong, S., Zhang, H., Huang, F., Zhang, L. and Li, S., 2019. Tailored necklace-like Ag@ZIF-8 core/shell heterostructure nanowires for high-performance plasmonic SERS detection. *Chemical Engineering Journal*, 371, 26-33.