Dual modal plasmonic substrates based on a convective self-assembly technique for enhancement in SERS and LSPR detection

MUNSIK CHOI,1 TAELYOUNG KANG,1 SEUNG HO CHOI,2 AND KYUNG MIN BYUN1,3,*

1Department of Biomedical Engineering, College of Electronics and Information, Kyung Hee University, Yongin 17104, Republic of Korea
2Department of Biomedical Engineering, Yonsei University, I Yonseiade-gil, Wonju, Gangwon-do 26493, Republic of Korea
3Department of Electronics and Information Convergence Engineering, Kyung Hee University, Yongin 17104, Republic of Korea
*kmbyun@khu.ac.kr

Abstract: In this study, surface-enhanced Raman scattering (SERS) scheme is combined with localized surface plasmon resonance (LSPR) detection on a thin gold film with stripe patterns of gold nanoparticles (GNPs) via convective self-assembly (CSA) method. The potential of dual modal plasmonic substrates was evaluated by binding 4-ABT and IgG analytes, respectively. SERS experiments presented not only a high sensitivity with a detection limit of 4.7 nM and an enhancement factor of $1.34 \times 10^5$, but an excellent reproducibility with relative standard deviation of 5.5%. It was found from plasmonic sensing experiments by immobilizing IgG onto GNP-mediated gold film that detection sensitivity was improved by more than 211%, compared with a conventional bare gold film. Our synergistic SERS–LSPR approach based on a simple and cost-effective CSA method could open a route for sensitive, reliable and reproducible dual modal detection to expand the application areas.

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1. Introduction

High sensitivity sensor platform has played an important role in many interdisciplinary research fields from medical diagnostics to biophysics and biochemistry [1]. Researchers have investigated a variety of metallic nanostructures for biosensing applications based on surface-enhanced Raman spectroscopy (SERS) and localized surface plasmon resonance (LSPR) [2,3]. Two detection schemes of SERS and LSPR are commonly associated with an amplification of electromagnetic (EM) fields generated by the excitation of localized surface plasmons (LSPs) [4]. Among various nanostructures, metallic nanoparticles allowing for simple and low cost manipulation have been widely used to provide an enhanced sensing performance [5,6].

For decades, a dominant contributor to SERS processes has been known as EM field enhancement, especially in the nano-sized gaps [7–10] or sharp features [11–14] of plasmonic materials. While aggregation of metallic nanoparticles is efficient for improving the detection performance, irregular distribution of nanoparticles often gives rise to poor reproducibility and repeatability in SERS and LSPR applications [15–18]. In recent years, several strategies of manipulating nanoparticle patterns have been attempted to realize a high reproducibility as well as significantly improved sensitivity.

For example, Si at el. introduced Au nanoparticle monolayer with high density sub 1-nm gaps by taking an advantage of oil-water interfacial self-assembly techniques [19]. Liu el al. reported Ag nanoplate-built hollow microsphere arrays with controllable structural parameters and centimeter-squared dimension based on electrodeposition [20]. More interestingly, Farcau

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et al. demonstrated Au nanoparticle clusters on hydrophilic glass substrate using convective self-assembly (CSA) technique to achieve a notable improvement of reproducibility and sensitivity in plasmonic detection [21]. Despite a few practical constraints related to evaporation and convection occurring at a much larger volume than nanoparticle size, CSA method is advantageous for plasmonic applications due to its versatility and scalability [22,23].

In this study, we proposed dual SERS-LSPR platform with gold nanoparticles monolayer deposited on a thin gold film. Contrary to other approaches on multi-modal biosensing applications based on both LSPR and SERS measurement [24–26], we demonstrated for the first time, to our knowledge, that a nanostructured substrate was developed by employing a CSA-based surface treatment which has been often used for patterning plasmonic nanoparticles in a controllable way. Next, we measured sensitivity and reproducibility characteristics obtained from 4-ABT and IgG experiments after optimizing the density of gold nanoparticles (GNPs). We believe that our CSA-based plasmonic substrate of combing both SERS and LSPR schemes could be useful for biomolecular dual modal detection to expand the range of practical sensor applications.

2. Experimental details

2.1. Materials

Distilled water (H\textsubscript{2}O), acetone (C\textsubscript{3}H\textsubscript{6}O) and ethyl alcohol (C\textsubscript{2}H\textsubscript{5}OH) were obtained from DaeJung Chemicals & Metals Co., LTD. (Siheung, Korea). Human immunoglobulin G (IgG), glutaraldehyde (C\textsubscript{5}H\textsubscript{8}O\textsubscript{2}), cysteamine (C\textsubscript{2}H\textsubscript{7}NS) and 4-aminobenzenethiol (4-ABT, C\textsubscript{6}H\textsubscript{7}NS) were purchased from Sigma-Aldrich (St. Louis, MO, USA). NSF10 glass substrate was obtained from Schott AG (Mainz, Germany). Gold nanoparticle with an average diameter of 30 nm, polydispersity index (PDI) of 4% was purchased from Nanopartz (Loveland, CO, USA).

2.2. Preparation of GNP dispersion

Since GNP adsorption on the substrate surface was found to be dependent on a concentration of GNPs, we optimized the concentration of GNP dispersion by using solvent evaporation method. When the concentration was as small as 1 optical density (OD), GNPs were not adsorbed onto the substrate efficiently. On the other hand, when the concentration was larger than 10 OD, aggregated GNPs formed multiple layers on the substrate [27]. The solvent of GNP dispersion was evaporated on a hot plate at 40 °C and an optimal concentration of 5 OD was determined.

2.3. Fabrication of GNP stripe-patterned substrates using the CSA technique

NSF10 glass substrate was employed for multi-functional optical biosensing platform. An organic cleaning was performed to remove any organic residues on a glass surface. The glass substrate was cleaned by sonication in acetone and ethyl alcohol sequentially for 10 min, and rinsed with distilled water and ethyl alcohol for 5 min, and then dried with nitrogen gas. 5 nm-thick titanium adhesion layer and 45 nm-thick gold layer were deposited onto the glass substrate at a deposition rate of 0.1 nm/s via electron beam evaporator, respectively. Before applying CSA technique, the substrate was immersed in 1 mM cysteamine with thiol [-SH] and amine [-NH\textsubscript{2}] groups, for 24 h to convert surface characteristics from hydrophobic to hydrophilic.

Figure 1 displays fabrication processes for GNP stripe-patterned plasmonic substrates. First, hydrophilic cysteamine-treated gold substrate was vertically immersed into GNP suspension whose temperature was maintained at 40 °C. To avoid an adsorption of GNPs onto the side of glass substrate, Kapton tape was used as a protection layer. We could observe a specific CSA feature of meniscus tip at the interface between substrate surface and GNP suspension. GNPs were deposited at the meniscus tip region via evaporation, which is associated with evaporation-induced upward convection [28,29]. During the evaporation process, liquid level was manipulated by use of syringe pump to control the distribution and density of GNPs deposited.
onto a gold surface. Withdrawal rate for liquid level manipulation was set to be 15.12 µm/h (Sample A), 7.56 µm/h (Sample B) and 5.04 µm/h (Sample C), respectively. Then, vertical position of the substrate was adjusted via motorized z-axis stage at regular intervals. Finally, the two processes were sequentially repeated for achieving a stripe pattern, which was designed to confirm the possibility of controlling a particle distribution effectively. Note that attached GNPs were strongly bound to a gold surface and any destruction or damage of the stripe pattern was not found during or after washing, cleaning and binding processes.

![Diagram](image)

**Fig. 1.** Scheme of CSA techniques for GNP stripe-patterned plasmonic substrate. (Step 1: Hydrophilic cysteamine-treated gold substrate immersion in GNP solution, Step 2: Evaporation and liquid level manipulation for GNP deposition onto gold surface, Step 3: Lifting the substrate up using a motorized z-axis stage, Step 4: Repetition of steps 2 and 3 for stripe pattern formation)

### 2.4. Sample preparation for SERS and LSPR measurement

For SERS detection, we measured sensitivity, reproducibility and linearity performance using 4-ABT analytes as Raman probe molecules and compared the results with those of a conventional bare gold film. Substrates were immersed in various concentrations of 4-ABT solution in the range of $10^{-8}$ to $10^{-4}$ M for 30 min. After 4-ABT immobilization, the substrates were rinsed with ethyl alcohol and distilled water for 5 min to remove non-immobilized 4-ABT analytes. Raman signals of 4-ABT were measured at 10 different points with acquisition of 10s with 100× objective lens. Raman spectroscopic system consists of a microscope (BX43, Olympus), a continuous-wave laser (785 nm, 350 mW, I0785MM0350MF, Innovative Photonic Solutions), a spectrometer (SR-303i-A, Andor Technology) and a low dark current deep-depletion CCD detector (iVac, Andor Technology).

For LSPR detection, each substrate was immersed in 1 mM cysteamine solution for 24 h, and then immersed in glutaraldehyde solution for 30 min. After 500 nM IgG was immobilized onto the substrate surface, the substrates were rinsed with ethyl alcohol and distilled water for 10 min. SPR signals were scanned before and after IgG binding interaction using an angle interrogation setup based on the Kretschmann configuration. Experimental set-up was based on dual concentric motorized rotation stages (URS75PP, Newport, Irvine, CA) for angle scanning measurement with a nominal angular resolution at 0.002°. The LSPR detection scheme employed a polarized 10 mW He–Ne laser ($\lambda = 632.8$ nm, 25-LHP-991, Melles-Griot, Carlsbad, CA) as a light source and a calibrated photodiode (818-UV, Newport, Irvine, CA) as a photodetector. Multiple (typically five) sites in a given sample were measured by translating the sample spatially to ensure consistency and thereby to reduce the standard variation.
3. Results and discussion

First, we measured a change of surface characteristics via contact angle. Contact angle test has been often used to evaluate the wettability of substrate surface [30]. To measure a contact angle, water droplet was applied onto the substrate surface, and then the angle difference between substrate surface and droplet was calculated via a contact angle analyzer (Phoenix 300, S-EO Korea). Figure 2 shows that contact angles, 29.03° for cysteamine-treated gold substrate and 33.67° for NSF10 glass substrate are much smaller than 63.19° for a bare gold substrate. The hydrophilic feature for cysteamine-treated gold substrate is attributed to adhesive force by hydrogen bond, which was induced by hydrogen atom of amine group of cysteamine [31–33].

![Fig. 2. Contact angle test results for (a) bare gold substrate (average contact angle = 63.19°), (b) NSF10 glass substrate (average contact angle = 33.67°) and (c) cysteamine-treated gold substrate (average contact angle = 29.03°).](image)

Figure 3 presents the field-emission scanning electron microscope (FE-SEM) images for three GNP stripe-patterned substrates. The stripe patterns of individual substrates indicate that the distribution of GNP can be effectively controlled through CSA techniques combined with liquid level manipulation. For periodic pattern, bright lines mean the places where GNPs were adsorbed, while dark lines imply the empty spaces where no GNPs were found. By using the motorized z-axis linear stage and syringe pump, we could change the period and width of the stripe pattern in a controllable manner.

![Fig. 3. FE-SEM images of GNP stripe-patterned plasmonic substrates. (a, d) Sample A (withdrawal rate: 15.12 µm/h), (b, e) Sample B (withdrawal rate: 7.56 µm/h) and (c, f) Sample C (withdrawal rate: 5.04 µm/h).](image)

Figures 3(d)-(f) show that the number of GNPs per unit area was increased as withdrawal rate was decreased from 15.12 µm/h to 5.04 µm/h. In particular, when the withdrawal speed became very slow, multilayered GNP structure was observed as shown in Fig. 3(f). While the results
are not shown, multiple GNP layers thicker than 30 nm produced complex interactions between SPR and LSPR modes and finally lead to a significant distortion in SPR characteristics. For that reason, we could not find any resonance signal in Sample C and thus, we chose Samples A and B for investigation of dual modal detection. Such trend is consistent with our previous theoretical and experimental results that ordered or non-ordered gold nanostructures with a thickness larger than 30 nm produced highly broad and shallow SPR curves [34–36].

In Fig. 4, SERS spectra of 4-ABT for GNP stripe-patterned substrates were measured at concentrations varied in the range of 10 nM to 100 µM. 4-ABT analyte is one of the most commonly used molecules because of its strong adsorption on a gold surface by gold-thiol bonds [37]. Even at the concentration as small as 10 nM, the characteristic Raman peak at 1076 cm\(^{-1}\), which is associated with the \(a_1\)-type vibrational mode, was distinguishable. Also, we performed linear regression analysis between SERS intensities and concentration of 4-ABT to analyze both limit of detection (LOD) and limit of quantification (LOQ) using the relations of LOD = 3\(S_b/a\) and LOQ = 10\(S_b/a\), where \(S_b\) and \(a\) are the standard deviation of intercept and the slope of linear fitting curve [38].

![Fig. 4.](image)

**Fig. 4.** Experimental results of sensitivity and linearity performance for Sample A (a, b) and sample B (c, d); SERS spectra of 4-ABT at various concentrations (a, c) and linear regression analysis of SERS intensities of 4-ABT at 1076 cm\(^{-1}\) at various concentrations (b, d)

For Sample A, the LOD and LOQ values were determined to be 8.4 and 28.1 nM, respectively. On the other hand, LOD of 4.7 and LOQ of 15.7 nM were measured for Sample B, implying that the performance of Sample B is about 2 times better than that of Sample A. Since the slope and coefficient of determination (R\(^2\)) are highly associated with sensor sensitivity and linearity, it is interesting to note that the slope of 6508.9 for Sample B was almost twice as large as that of 3244.5 for Sample A. Such enhancement in LOD, LOQ and sensitivity can be explained by...
an increase in the numbers of GNPs and hot-spots between adjacent GNPs [39,40]. In general, hot-spots occur between nanoparticles or in the crevice of nanoparticles that supports intense and highly localized electromagnetic fields. When target molecules are positioned near the regions of hot-spots, Raman scattering signals could be boosted prominently at the nano-featured plasmonic substrates.

In order to estimate the sensitivity improvement more quantitatively, we calculated SERS enhancement factor (EF) for 4-ABT as follows

\[
EF = \frac{I_{\text{SERS}}/N_{\text{SERS}}}{I_{\text{Raman}}/N_{\text{Raman}}}
\]

where \(I_{\text{SERS}}\) and \(I_{\text{Raman}}\) are the SERS and normal Raman intensities of 4-ABT peak at 1076 cm\(^{-1}\) and \(N_{\text{SERS}}\) and \(N_{\text{Raman}}\) are the numbers of 4-ABT molecules on the SERS substrates and 4-ABT powders [41]. In our experiments, normal Raman intensity of 4-ABT peak at 1076 cm\(^{-1}\) for 4-ABT powders was measured to be 918.1 and SERS Raman intensities of 4-ABT peak at 1076 cm\(^{-1}\) for Samples A and B were measured to be 12511.3 and 24152.0, respectively. Using the beam spot size of \(\sim 10 \mu m\) and 4-ABT molecule size of \(\sim 0.2\) nm [42], the EF values were obtained to be \(7.27 \times 10^4\) for Sample A and \(1.34 \times 10^5\) for Sample B, respectively. Sample B was still favorable and SERS EF characteristics were in good agreement with previous results obtained from aggregated nanoparticles [43,44].

Next, it is necessary to present Raman mapping data to prove the uniformity of SERS substrates. Reproducibility in SERS detection was evaluated by 2D SERS mapping of 4-ABT in a square area of \(100 \times 100\) \(\mu m^2\). Figure 5 shows the SERS mapping results and SERS intensities of 100 data points. For Sample A with a relatively sparse GNP distribution, relative standard deviation (RSD) was determined to be 8.6\%. On the other hand, for Sample B, RSD was significantly decreased to be 5.5\%. It is likely for Sample A that sparse and irregular GNP distribution with non-uniform nanogap formation contributed to an increase of RSD [45], while closely packed GNPs in Sample B was advantageous for realizing better spatial uniformity. Also note that no Raman signal was obtained for bare gold substrate.

Finally, as for another detection scheme, SPR characteristics were measured by scanning reflection angles before and after IgG binding reaction. Figure 6 presents SPR curves before and after 500 nM IgG binding reaction. The overall enhancement of GNP-based LSPR substrate relative to a conventional SPR substrate was evaluated by the sensitivity enhancement factor (SEF), defined as the ratio of resonance angle shift by the IgG target on a GNP-based LSPR sample (\(\Delta \theta_{\text{LSPR}}\)) to that on a control sample with no nanoparticles (\(\Delta \theta_{\text{control}}\)), i.e. \(\text{SEF} = \Delta \theta_{\text{LSPR}}/\Delta \theta_{\text{control}}\). Using average value of \(\Delta \theta_{\text{control}} = 0.28^\circ\) and two \(\Delta \theta_{\text{LSPR}}\) data of Samples A and B, maximum sensitivity enhancement of 211\% was obtained for Sample B [46].

The plasmonic interpretation based on a surface-limited increase of interaction area and excitation of LSPs could be adopted to explain the enhanced sensitivity. An increment of interaction area, induced by GNPs on a gold film, resulted in an additional resonance shift in response to the changes in local environments that surrounded the substrate surface. Moreover, enhanced fields from excited LSP modes were attributed to the sensitivity enhancement [35,47]. An incident beam and propagating surface plasmons could directly interact through metallic nanoparticles, which produced LSPs and hot-spots. The existence of plasmonic nanostructures near a gold film lead to a perturbation of the dispersion relation dictated by a conventional SPR structure and contributed to the sensitivity improvement by means of LSPs, although the LSP modes often accompanied broad SPR curves.
4. Conclusion

In this study, we presented SERS-LSPR detection platform by depositing gold nanoparticle monolayer on a thin gold film with the aim of improving both sensitivity and reproducibility performance. Using simple and cost-effective CSA technique, we successfully realized a stripe patterns onto a hydrophobic gold surface. We found that distribution of GNP of stripe patterns could be adjusted reliably through liquid level manipulation based on withdrawal rate control. In both SERS and LSPR experiments, the proposed plasmonic substrates presented an enhanced detection performance in sensitivity and reproducibility as well as in LOD and LOQ. We strongly believe that our approach has a potential of contributing to the development of multifunctional...
biosensing platform with high sensitivity, reliability and reproducibility for expanding the range of practical applications.

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**References**

1. H. Xu, “Nanophotonics: Manipulating Light with Plasmons,” (CRC Press, 2017).
2. A. Campion and P. Kamblampati, “Surface-enhanced Raman scattering,” Chem. Soc. Rev. 27(4), 241–250 (1998).
3. E. Hutter and J. H. Fendler, “Exploitation of localized surface plasmon resonance,” Adv. Mater. 16(19), 1685–1706 (2004).
4. R. Monreal and S. P. Apell, “Electromagnetic-field-enhanced desorption of atoms,” Phys. Rev. B 41(11), 7852–7855 (1990).
5. K. Wolfgang, “Surface enhanced Raman spectroscopy: analytical, biophysical and life science applications,” (John Wiley & Sons, 2011).
6. C. Niu, B. Zou, Y. Wang, L. Cheng, H. Zheng, and S. Zhou, “Highly sensitive and reproducible SERS performance from uniform film assembled by magnetic noble metal composite microspheres,” Langmuir 32(3), 858–863 (2016).
7. Y. Liberman, C. Yilmaz, T. M. Bloomstein, S. Somu, Y. Echegoyen, A. Busnaina, S. G. Cann, K. E. Krohn, M. F. Marchant, and M. Rothschild, “A nanoparticle convective directed assembly process for the fabrication of periodic surface-enhanced Raman scattering substrates,” Adv. Mater. 22(38), 4298–4302 (2010).
8. J. Perumal, T. Gong, U. S. Dinish, K. D. Buddharaju, P. Lo Guo-Qiang, and M. Olivo, “Development of optimized nanogap plasmonic substrate for improved SERS enhancement,” AIP Adv. 7(5), 055017 (2017).
9. Z. Lu, H. Si, Z. Li, J. Yu, Y. Liu, D. Feng, C. Zhang, W. Yang, B. Man, and S. Jiang, “Sensitive, reproducible, and stable 3D plasmonic hybrids with bilayer WS2 as nanospacer for SERS analysis,” Opt. Express 26(17), 21626–21641 (2018).
10. C. Zhang, C. Li, J. Yu, S. Jiang, S. Xu, C. Yang, Y. J. Liu, X. Gao, A. Liu, and B. Man, “SERS activated platform with three-dimensional hot spots and tunable nanometer gap,” Sens. Actuators, B 258, 163–171 (2018).
11. C. G. Artur, T. Womack, F. Zhao, J. L. Eriksen, D. Mayerich, and W. C. Shih, “Plasmonic nanoparticle-based expansion microscopy with surface-enhanced Raman and dark-field spectroscopic imaging,” Biomed. Opt. Express 9(2), 603–615 (2018).
12. T. H. Wood, D. A. Zwemer, C. V. Shank, and J. E. Rowe, “The dependence of surface-enhanced Raman scattering on surface preparation: evidence for an electromagnetic mechanism,” Chem. Phys. Lett. 82(1), 5–8 (1981).
13. W. Yang, Z. Li, Z. Lu, J. Yu, Y. Huo, B. Man, J. Pan, H. Si, S. Jiang, and C. Zhang, “Graphene-Ag nanoparticles-cicada wings hybrid system for obvious SERS performance and DNA molecular detection,” Opt. Express 27(3), 3000–3013 (2019).
14. C. Li, S. Xu, J. Yu, Z. Li, W. Li, J. Wang, A. Liu, B. Man, S. Yang, and C. Zhang, “Local hot charge density regulation: Vibration-free pyroelectric nanogenerator for effectively enhancing catalysis and in-situ surface enhanced Raman scattering monitoring,” Nano Energy 81, 105585 (2021).
15. A. M. Fales and T. Vo-Dinh, “Silver embedded nanostars for SERS with internal reference (SENSIR),” J. Mater. Chem. C 3(28), 7319–7324 (2015).
16. Y. Zhang, B. Walkenfort, J. H. Yoon, S. Schlücker, and W. Xie, “Gold and silver nanoparticle monomers are non-SERS-active: a negative experimental study with silica-encapsulated Raman-reporter-coated metal colloids,” Phys. Chem. Chem. Phys. 17(33), 21120–21126 (2015).
17. Y. Pan, X. Guo, J. Zhu, X. Wang, H. Zhang, Y. Kang, T. Wu, and Y. Du, “A new SERS substrate based on silver nanoparticle functionalized polymethacrylate monoliths in a capillary, and it application to the trace determination of pesticides,” Microchim. Acta 182(9–10), 1775–1782 (2015).
18. V. Dugandžić, I. J. Hidi, K. Weber, D. Cialla-May, and J. Popp, “In situ hydrazine reduced silver colloid synthesis—Enhancing SERS reproducibility,” Anal. Chim. Acta 946, 73–79 (2016).
19. S. Si, W. Liang, Y. Sun, J. Huang, W. Ma, Z. Liang, Q. Bao, and L. Jiang, “Facile fabrication of high-density sub-1-nm gaps from Au nanoparticle monolayers as reproducible SERS substrates,” Adv. Funct. Mater. 26(44), 8137–8145 (2016).
20. G. Liu, W. Cai, L. Kong, G. Duan, Y. Li, J. Wang, G. Zuo, and Z. Cheng, “Standing Ag nanoplate-built hollow microsphere arrays: Controllable structural parameters and strong SERS performances,” J. Mater. Chem. 22(7), 3177–3184 (2012).
21. C. Farcau, N. M. Sangeetha, N. Decorde, S. Astilean, and L. Ressier, “Microarrays of gold nanoparticle clusters fabricated by Stop&Go convective self-assembly for SERS-based sensor chips,” Nanoscale 4(24), 7870–7877 (2012).
22. Y. Minlo, S. Watanabe, and M. T. Miyahara, “Colloidal stripe pattern with controlled periodicity by convective self-assembly with liquid-level manipulation,” ACS Appl. Mater. Interfaces 4(6), 3184–3190 (2012).
23. S. Watanabe and M. T. Miyahara, “Particulate pattern formation and its morphology control by convective self-assembly,” Adv. Powder Technol. 24(6), 897–907 (2013).
24. M. Dustov, D. I. Golovina, A. Y. Polyakov, A. E. Goldt, A. A. Eliseev, E. A. Kolesnikov, I. V. Sukhorukova, D. V. Shitansky, W. Grünert, and A. V. Grigorieva, “Silver eco-solvent ink for reactive printing of polychromatic SERS and SPR substrates,” Sensors 18(2), 521 (2018).
25. F. Toderas, M. Baia, L. Baia, and S. Astilean, “Controlling gold nanoparticle assemblies for efficient surface-enhanced Raman scattering and localized surface plasmon resonance sensors,” Nanotechnology 18(25), 255702 (2007).
26. J. N. Yih, S. J. Chen, K. T. Huang, Y. T. Su, and G. Y. Lin, “A compact surface plasmon resonance and surface-enhanced Raman scattering sensing device,” Proc. SPIE 5327 (2004).
27. S. Watanabe, K. Imakai, S. Mizuta, and M. T. Miyahara, “Mechanism for stripe pattern formation on hydrophilic surfaces by using convective self-assembly,” Langmuir 25(13), 7287–7295 (2009).
28. T. Hanafusa, Y. Mino, S. Watanabe, and M. T. Miyahara, “Controlling self-assembled structure of Au nanoparticles by convective self-assembly with liquid-level manipulation,” Adv. Powder Technol. 25(2), 811–815 (2014).
29. S. Watanabe, Y. Mino, Y. Ichikawa, and M. T. Miyahara, “Spontaneous formation of cluster array of gold particles by convective self-assembly,” Langmuir 28(36), 12982–12988 (2012).
30. X. Zhao, C. Liu, J. Yu, Z. Li, L. Liu, C. Li, S. Xu, W. Li, B. Man, and C. Zhang, “Hydrophobic multiscale cavities for high-performance and self-cleaning surface-enhanced Raman spectroscopy (SERS) sensing,” Nanophotonics 9(16), 4761–4773 (2020).
31. M. F. Chaplin, “Water’s hydrogen bond strength,” Water and Life: The unique properties of H2O (CRC Press, 2010), pp. 69–86.
32. S. Y. Yoo, W. J. Chung, T. H. Kim, M. Le, and S. W. Lee, “Facile patterning of genetically engineered M13 bacteriophage for directional growth of human fibroblast cells,” Soft Matter 7(2), 363–368 (2011).
33. W. B. Ying, S. Kim, M. W. Lee, N. Y. Go, H. Jung, S. G. Ryu, B. Lee, and K. J. Lee, “Toward a detoxification fabric against nerve gas agents: guanidine-functionalized poly [2-(3-butenyl)-2-oxazoline]/Nylon-6, 6 nanofibers,” RSC Adv. 7(25), 15246–15254 (2017).
34. N. H. Kim, M. Choi, J. W. Leem, J. S. Yu, T. W. Kim, T. S. Kim, and K. M. Byun, “Improved biomolecular detection based on a plasmonic nanoporous gold film fabricated by oblique angle deposition,” Opt. Express 23(14), 18777–18785 (2015).
35. S. M. Jung, D. Kim, S. H. Choi, K. M. Byun, and S. J. Kim, “Enhancement of localized surface plasmon resonance detection by incorporating metal-dielectric double-layered subwavelength gratings,” Appl. Opt. 50(18), 2846–2854 (2011).
36. L. Litti and M. Meneghetti, “Predictions on the SERS enhancement factor of gold nanosphere aggregate samples,” Phys. Chem. Chem. Phys. 21(28), 15515–15522 (2019).
37. D. Y. Wu, X. M. Liu, Y. F. Huang, B. Ren, X. Xu, and Z. Q. Tian, “Surface catalytic coupling reaction of p-mercaptoaniline linking to silver nanostructures responsible for abnormal SERS enhancement: a DFT study,” J. Phys. Chem. C 113(42), 18212–18222 (2009).
38. K. V. Harisha, B. K. Swamy, and E. E. Ebenso, “Poly (glycine) modified carbon paste electrode for simultaneous determination of catechol and hydroquinone: a voltammetric study,” J. Electroanal. Chem. 823, 730–736 (2018).
39. J. Yu, M. Yang, Z. Li, C. Liu, Y. Wei, C. Zhang, B. Man, and F. Lei, “Hierarchical particle-in-quasicavity architecture for ultratrace in situ Raman sensing and its application in real-time monitoring of toxic pollutants,” Anal. Chem. 92(21), 14754–14761 (2020).
40. J. L. Yang, R. P. Li, J. H. Han, and M. J. Huang, “FDTD simulation study of size/gap and substrate-dependent SERS activity study of Au@SiO2 nanoparticles,” Chin. Phys. B 25(8), 083301 (2016).
41. P. Lovera, N. Creedon, H. Alatawi, M. Mitchell, M. Burke, A. J. Quinn, and A. O’Riordan, “Low-cost silver capped polystyrene nanotube arrays as super-hydrophobic substrates for SERS applications,” Nanotechnology 25(17), 175502 (2014).
42. K. Kim and J. K. Yoon, “Raman scattering of 4-aminobenzenethiol sandwiched between Ag/Au nanoparticle and macroscopically smooth Au substrate,” J. Phys. Chem. B 109(44), 20731–20736 (2005).
43. L. Litti and M. Meneghetti, “Predictions on the SERS enhancement factor of gold nanosphere aggregate samples,” Phys. Chem. Chem. Phys. 21(28), 15515–15522 (2019).
44. B. Fazio, C. D’Andrea, A. Foti, E. Messina, A. Ierera, M. G. Donato, V. Villari, N. Micali, O. M. Maragò, and P. G. Gucciardi, “SERS detection of Biomolecules at Physiological pH via aggregation of Gold Nanorods mediated by Optical Forces and Plasmonic Heating,” Sci. Rep. 6(1), 26952 (2016).
45. Y. Lai, S. Sun, T. He, S. Schlucker, and Y. Wang, “Raman-encoded microbeads for spectral multiplexing with SERS detection,” RSC Adv. 5(18), 13762–13767 (2015).
46. K. M. Byun, S. J. Kim, and D. Kim, “Design study of highly sensitive nanowire-enhanced surface plasmon resonance biosensors using rigorous coupled wave analysis,” Opt. Express 13(10), 3737–3742 (2005).
47. N. H. Kim, W. K. Jung, and K. M. Byun, “Correlation analysis between plasmon field distribution and sensitivity enhancement in reflection- and transmission-type localized surface plasmon resonance biosensors,” Appl. Opt. 50(25), 4982–4988 (2011).