CHAPTER 2

REVIEW OF SERS SUBSTRATE FABRICATION

This chapter illustrates different SERS substrate fabrication methods. SERS substrates can be classified in three categoris according to their fabrication methods. These are SERS substrates where metallic nanoparticles in a dispersion medium, metal nanostructures fabricated directly on solid substrates and metal nanoparticles immobilized on solid substrates.

SERS substrates are basically a metal nanostructured surface that enhances Raman signal of an adsorbed analyte molecule. An efficient SERS substrate should provide a high order of enhancement with a good degree of uniformity and reproducibility characteristics. There are various methods of fabrication of efficient SERS substrates, the most widely used and popular methods have been discussed below.

2.1 Metallic nanoparticles in a dispersion medium

Chemical and physical methods have been employed to prepare metallic nanoparticles for SERS-based sensing method. Through wet chemical synthesis of SERS-active metal nanoparticles, gold and silver salts in a solvent are reduced using the reducing agents like sodium borohydride, citrate, hydroxylamine hydrochloride, or hydrazine [1, 2]. Chemical reduction techniques further include capping agents that attach to the nanoparticle's surface and prevent it from aggregating due to steric or repulsive forces [3, 4]. Sodium citrate, cetrimonium bromide, polyethylene glycol, dodecanethiol, hydroxylamine hydrochloride, and polyvinylpyrrolidone are commonly used capping agents. In the synthesis procedure, the concentration and strength of the reducing agent can regulate the dimension of the nanoparticles. Metal atoms combine to form clusters and eventually crystal nuclei during the nucleation process. In growth step, nanoparticles are formed from these crystal nuclei or seeds. The shape of the metal nanopartices are controlled by adding surfactants during synthesis. A broad spectrum of nanoparticle morphologies, including nanospheres, nanorods, nanocubes, nanotriangles, nanowires, nanoplates, and nanostars have been produced using wet chemical method by changing the surfactant, nanoparticle material, and other experimental parameters [5, 6]. Pulsed laser ablation is one of the physical technique where highly stable plasmonic nanoparticles are prepared in organic solvent or water [7]. Here, the laser pulse is focused on a target material which absorbs the wave and produces plasma plume. In a fraction of second, this hot material cools down and disintegrates in the surrounding medium near the target. After that, the removed atomized material undergo nucleation, growth, and formation of the nanoparticles.

2.2 Lithographic SERS substrates

Most common way to fabricate SERS substrates is by fabricating noble metal nanostructures on a planar substrate. Patterned nanostructures on SERS substrates have the ability to deliver reproducible Raman scattered signals. Sophisticated techniques like electron-beam lithography (EBL), nanosphere lithography (NSL), focused ion beam lithography (FIB), and nanoimprint lithography (NIL) provide patterned nanostuctures. These methods are extensively used to fabricate sensitive and highly reproducible SERS substrates. In the EBL technique, desired patterns are printed on the resist by exposing it with electron beam [8]. The FIB technique enables direct writing and generation of patterned nanostructures. After that, thin metal layer is deposited using sputtering methods [9]. Both the FIB and EBL techniques are costly process and time consuming with the requirement of sophisticated laboratory instrumentation. In the NSL technique, a monolayer of polymer nanospheres are first allowed to assemble on a plane substrate. Using physical vapor deposition, a thin metal film is deposited over the nanosphesres. Triangular shaped metal nanostructure array is formed after etching out the nanospheres [10]. In NIL procedure, desired nanopattern is first developed on a rigid mask. The pattern is then transfered to polymer coated substrate. After that, deposition of metal film and etching are performed to fabricate cost-effective and reproducible SERS substrates. The two primary drawbacks of this technology are the difficulty in transferring the metal film onto a given substrate, and the development of structures with a high aspect ratio [11].

2.3 Metal nanoparticles immobilized on solid substrates

Aggregation is required for spherical particles in order to maximize the SERS effect. Several strategies have been utilized to immobilize the plasmonic nanoparticles on solid substrates which offers a method for bringing them closer together. Silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) have been deposited on the naturally and commercially available, and bio-inspired patterned nanostructured surfaces. These substrates provide high SERS intensity and good degree reproducibility in a very low fabrication cost, and simple fabrication process. Lotus leaf [12], printing-grade papers, filter papers, polymer nanofibers [13], bio-polymers [14], compact discs (CDs) [15], and Blu-ray digital versatile disc (BR-DVD) [16] substrates have been widely used for the fabrication of SERS substrates [17–19].

2.3.1 Using plant-based components

Yao et al. have developed a sensitive and reproducible SERS sensor using natural lotus leaf. [12] Utilizing the hydrophobicity-induced concentrating effect, AgNPs have been assembled in closely packed arrays on the surface which generates large number of hot-spot regions. Qauntitative detection of Paraquat has been performed using the SERS sensor for a wide range of concentraion from 5 μgL^{-1} to 50 mgL^{-1}, and a detection limit of as low a s 1.2 μgL^{-1}. Sarma et al. have developed a sensitive SERS substrate by depositing AuNPs on microscopically roughned SERS substrate of *aegle marmelos* leaf [20]. Limit of detection was found to be 0.88 nM for rhodamine 6G, and the substrates have been employed to detect two antibiotics samples in cow milk samples.

2.3.2 Paper-based SERS substrates

Paper-based SERS substrates have been fabricated following three techniques:(a) drop-casting cooloidal nanoparticles on paper surfaces, (b) dip-coating paper into metal colloids and (c) spray-coating colloids into paper surfaces.

Chamuah et al. have explored different printing grade papers to fabricate cost-effective and reliable SERS substrates by drop-casting AgNPs. The AgNPs have been adsorbed into the micropores on the paper surface. The performance of the SERS substrates have been evaluated using malachite green (MG), rhodamine6G (R6G) and 1,2-bis(4-pyridyl)ethylene (BPE) [21]. Siebe et al. have developed a unique way to increase the uniformity of the plasmonic nannoparticles and prevent from air-oxidation [23]. Martins et al. have developed a hydrophobic SERS substrate by inkjet printing of aqueous emulsions containing polystyrene (PS) and Ag colloidal nanoparticles. The substrates have been used to detect the pesticide thiram in mineral water sample and apple juice with a LoD of 0.024 ppm [22].

2.3.3 Flexible SERS substrates

The rigid supports for the nanoparticle assembly generally do not contribute to SERS enhancement. Flexible SERS substrtaes have a great potential for the in-situ and rapid SERS sensing applications. Zheng et al. have fabricated AgNP assembly method based on vortex evaporation method to batch assemble multiple silver ring SERS substrate array on a parafilm [24].

Graphene-mediated SERS substrates have been fabricated by directly decorating AgNPs on CVD graphene/copper foil under ultrasonic condition [25]. Ultrasensitive detection of rhodamine 6G with a LOD of 1×10^{-14} and and a high EF of 8.85 $\times 10^{8}$ have been obeserved with these substrates.

2.4 Semiconductor-based SERS substrates

Most of the SERS-based substrates have been developed using silver and gold noble metals that provide very high signal enhancement and enables the detection of analyte upto single molecule level. In the year 1982, Yamada et al. first reported a significant enhancement of the Raman signal of pyridine upon adsorption on NiO, a semiconducting material [26]. After that discovery, many semiconductor-based SERS substrates have been developed which provide high enhancement factor, signal reproducibility and stability.

2.4.1 Inorganic semiconductor-based SERS substrates

Metal oxides have been known for their robust nature and diverse electronic properties and have emerged as promising inorganic semiconductor materials for SERS applications. Among inorganic semiconductor-based SERS-active substrates, TiO_2 has been used widely due to it's nontoxicity, chemically stability, and controlled band gap energy [27]. ZnO-based substrates have been fabricated for the sensitive detection and analysis of chemicals [28].

2.4.2 Metal-semiconductor composite SERS substrates

Noble metals have been compounded with traditional semiconductor materials and have become a hotspot in SERS research due to their relatively simple recovery and excellent performance. Silver-coated flower-like ZnO nanorod arrays have been fabricated for sensitive detection of analyte molecules. These substrates have enabled ultra-low concentration detection of R6G and exhibited a long-term optical stability with a shelf life longer than two years [29].

2.4.3 Organic semiconductor-based SERS substrates

The most prominent example of a pure organic semiconductor is graphene. In 2010, Ling et al. discovered Raman enhancement on graphene by using pure graphene as a SERS-active substrate and adsorbing common probe molecules on the graphene substrate via vacuum evaporation and solution immersion [30]. The SERS enhancement of organic semiconductors mainly comes from the molecular resonance of organic semiconductors and the CT between organic semiconductors and probe molecules. Due the unique SERS enhancement mechanism of organic semiconductors, they are also widely used in the fields of biological detection, device performance, medical research, and sensing.

Bibliography

[1] Asapu, R., Ciocarlan, R.-G., Claes, N., Blommaerts, N., Minjauw, M., Ahmad, T., Dendooven, J., Cool, P., Bals, S., Denys, S., et al. Plasmonic near-field localization of silver core–shell nanoparticle assemblies via wet chemistry nanogap engineering. *ACS applied materials & interfaces*, 9(47):41577–41585, 2017.

[2] Lee, C.-W., Chia, Z. C., Hsieh, Y.-T., Tsai, H.-C., Tai, Y., Yu, T.-T., and Huang, C.-C. A facile wet-chemistry approach to engineer an au-based sers substrate and enhance sensitivity down to ppb-level detection. *Nanoscale*, 13(7):3991–3999, 2021.

[3] Shrestha, S., Wang, B., and Dutta, P. Nanoparticle processing: Understanding and controlling aggregation. *Advances in colloid and interface science*, 279:102162, 2020.

[4] Israelsen, N. D., Hanson, C., and Vargis, E. Nanoparticle properties and synthesis effects on surface-enhanced raman scattering enhancement factor: an introduction. *The Scientific World Journal*, 2015(1):124582, 2015.

[5] Burrows, N. D., Vartanian, A. M., Abadeer, N. S., Grzincic, E. M., Jacob, L. M., Lin, W., Li, J., Dennison, J. M., Hinman, J. G., and Murphy, C. J. Anisotropic nanoparticles and anisotropic surface chemistry. *The journal of physical chemistry letters*, 7(4):632–641, 2016.

[6] Ortiz-Castillo, J. E., Gallo-Villanueva, R. C., Madou, M. J., and Perez-Gonzalez, V. H. Anisotropic gold nanoparticles: A survey of recent synthetic methodologies. *Coordination Chemistry Reviews*, 425:213489, 2020.

[7] Jing, Y., Wang, R., Wang, Q., Xiang, Z., Li, Z., Gu, H., and Wang, X. An overview of surface-enhanced raman scattering substrates by pulsed laser deposition technique: fundamentals and applications. *Advanced Composites and Hybrid Materials*, 4(4):885–905, 2021.

[8] Petti, L., Capasso, R., Rippa, M., Pannico, M., La Manna, P., Peluso, G., Calarco, A., Bobeico, E., and Musto, P. A plasmonic nanostructure fabricated by electron beam lithography as a sensitive and highly homogeneous sers substrate for biosensing applications. *Vibrational Spectroscopy*, 82:22–30, 2016.

[9] Yang, J.-Y., Park, S.-G., Jung, S., Byeon, E.-Y., Kim, D.-g., Jung, H. S., Kim, H. J., and Lee, S. Sers substrates based on self-organized dimple nanostructures on polyethylene naphthalate films produced via oxygen ion beam sputtering. *Applied Surface Science*, 572:151452, 2022.

[10] Fang, X., Zheng, C., Yin, Z., Wang, Z., Wang, J., Liu, J., Luo, D., and Liu, Y. J. Hierarchically ordered silicon metastructures from improved self-assembly-based nanosphere lithography. *ACS applied materials & interfaces*, 12(10):12345–12352, 2020.

[11] Cai, J., Liu, R., Jia, S., Feng, Z., Lin, L., Zheng, Z., Wu, S., and Wang, Z. Sers hotspots distribution of the highly ordered noble metal arrays on flexible substrates. *Optical Materials*, 122:111779, 2021.

[12] Yao, L., Dai, P., Ouyang, L., and Zhu, L. A sensitive and reproducible sers sensor based on natural lotus leaf for paraquat detection. *Microchemical Journal*, 160: 105728, 2021.

[13] Chamuah, N., Bhuyan, N., Das, P. P., Ojah, N., Choudhary, A. J., Medhi, T., and Nath, P. Gold-coated electrospun pva nanofibers as sers substrate for detection of pesticides. *Sensors and Actuators B: Chemical*, 273:710–717, 2018.

[14] Wang, C., Wong, K. W., Wang, Q., Zhou, Y., Tang, C., Fan, M., Mei, J., and Lau, W.-M. Silver-nanoparticles-loaded chitosan foam as a flexible sers substrate for active collecting analytes from both solid surface and solution. *Talanta*, 191: 241–247, 2019.

[15] Li, L., Yang, S., Duan, J., Huang, L., and Xiao, G. Fabrication and sers performance of silver nanoarrays by inkjet printing silver nanoparticles ink on the

gratings of compact disc recordable. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 225:117598, 2020.

[16] Chamuah, N., Saikia, A., Joseph, A. M., and Nath, P. Blu-ray dvd as sers substrate for reliable detection of albumin, creatinine and urea in urine. *Sensors and Actuators B: Chemical*, 285:108–115, 2019.

[17] Li, Z., Huang, X., and Lu, G. Recent developments of flexible and transparent sers substrates. *Journal of Materials Chemistry C*, 8(12):3956–3969, 2020.

[18] Bharati, M. S. S. and Soma, V. R. Flexible sers substrates for hazardous materials detection: recent advances. *Opto-Electronic Advances*, 4(11):210048, 2021.

[19] Rebollar, E., Pérez, S., Hernández, M., Domingo, C., Martín, M., Ezquerra, T. A., García-Ruiz, J. P., and Castillejo, M. Physicochemical modifications accompanying uv laser induced surface structures on poly (ethylene terephthalate) and their effect on adhesion of mesenchymal cells. *Physical Chemistry Chemical Physics*, 16 (33):17551–17559, 2014.

[20] Sarma, D., Marak, M. R., Chetia, I., Badwaik, L. S., and Nath, P. Aunp decorated aegle marmelos leaf as sers substrate for trace detection of antibiotics and machine learning based classification. *Physica Scripta*, 99(2):026006, 2024.

[21] Chamuah, N., Hazarika, A., Hatiboruah, D., and Nath, P. Sers on paper: an extremely low cost technique to measure raman signal. *Journal of Physics D: Applied Physics*, 50(48):485601, 2017.

[22] Martins, N. C., Fateixa, S., Fernandes, T., Nogueira, H. I., and Trindade, T. Inkjet printing of ag and polystyrene nanoparticle emulsions for the one-step fabrication of hydrophobic paper-based surface-enhanced raman scattering substrates. *ACS Applied Nano Materials*, 4(5):4484–4495, 2021.

[23] Siebe, H. S., Chen, Q., Li, X., Xu, Y., Browne, W. R., and Bell, S. E. Filter paper based sers substrate for the direct detection of analytes in complex matrices. *Analyst*, 146(4):1281–1288, 2021.

[24] Zheng, X., Huang, Z., Guo, P., Zhou, W., Wu, P., Zhao, Y., Xu, J., Sun, J., and Lei, Y. Flexible silver ring sers substrate array fabrication by vortex evaporation method and its application for high sensitive detection of sulfonamides residues in water. *Microchemical Journal*, 196:109559, 2024.

[25] Zhang, Z., Mei, L., Niu, Y., Deng, W., and Shao, Y. A new highly sensitive flexible sers substrate: Cvd graphene/copper foil decorated by ag nps. *Materials Letters*, 375:137224, 2024.

[26] Yamada, H. and Yamamoto, Y. Surface enhanced raman scattering (sers) of chemisorbed species on various kinds of metals and semiconductors. *Surface science*, 134(1):71–90, 1983.

[27] Samriti, Shukla, K., Gupta, R., Gupta, R. K., and Prakash, J. Highly efficient visible light active doped metal oxide photocatalyst and sers substrate for water treatment. *Environmental Science and Pollution Research*, 30(12):34054–34068, 2023.

[28] Yang, S., Yao, J., Quan, Y., Hu, M., Su, R., Gao, M., Han, D., and Yang, J. Monitoring the charge-transfer process in a nd-doped semiconductor based on photoluminescence and sers technology. *Light: Science & Applications*, 9(1):117, 2020.

[29] Sun, Q., Zhang, Q., Zhou, N., Zhang, L., Hu, Q., Ma, C., Zhang, C., and Yi, Z. Silver-coated flower-like zno nanorod arrays: Ultrastable sers substrates and the mechanisms of optical stability. *Applied Surface Science*, 526:146565, 2020.

[30] Ling, X., Xie, L., Fang, Y., Xu, H., Zhang, H., Kong, J., Dresselhaus, M. S., Zhang, J., and Liu, Z. Can graphene be used as a substrate for raman enhancement? *Nano letters*, 10(2):553–561, 2010.