SERS active substrate by atmospheric-PLD: a mini review and suggestion for biomedical application

Taj M. Khan[1,2]*

[1]School of Physics and CRANN, Trinity College Dublin, the University of Dublin, Dublin 2, Ireland
[2]National Institute of Lasers and Optronics (NILOP), P.O. Nilore, 45650, Islamabad, Pakistan

Abstract

SERS is an emerging research area which has been under constant investigation from years. Researchers have manufactured a variety of SERS active substrates for multifold applications and today, with SERS substrate, single molecule detection is on fingertip. Several review reports are available, describing the preparation and application of SERS substrates with application in diverse fields of biomedical and engineering sciences. This mini review briefly sheds light on the SERS substrates of plasmonic nanomaterial of silver or gold, by atmospheric-PLD (APLD). This will help in realization the effectiveness of newly introduced APLD method produced SERS substrates and upscale for practical use in biomedical and pharmaceutical industry. This will facilitate the industry by providing a simple and cost effective route to production of SERS active substrates.

Keywords: SERS substrate, APLD method, SPR, Biomedical, Nanosilver

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A brief background

Surface-enhanced Raman spectroscopy (SERS) arises in presence of an active plasmonic nanostructured surface such as silver (Ag) and gold (Ag) [1, 2]. It is will understood that a widely accepted mechanism for the surface-enhanced processes is predominantly electromagnetic in nature [3]. The electric filed of a laser radiation strikes on the surface is confined in presence of a nanostructure and amplified several order in magnitude due to surface plasmon resonance (SPR); thus boosting the Raman signals and enhance detection sensitivity of Raman spectroscopy. The main advantages of using SERS are: it serves as a decent analytical tool for chemical and biomolecular detection; it is a label-free technique with capability to detect multi-components. This technique facilitates normal Raman spectroscopy to measure with sensitivity down to molecular level [4, 5]. There are countless reports on this topic available in the literature [1-6], so rather than to give further touch to these studies, we orient our attention to convey main theme of this short letter. The first atmospheric-pulsed laser deposition (APLD) letter describes diamond-like-coating (DLC) was published in 2003 [7] and paved a platform for further research in this direction. Later on, N. Nedyalkov et. al produced porous nanostructured Au films in air using APLD and directly used in optical application as SERS substrate for detection of Rhodamine 6G (Rh6G) of concentration 10-3 M [8]. This was the first APLD substrate used for sensing purpose. Though the SERS performance was not that much impressive, still this study indicated an alternative easy route to fabrication of designing sensitive elements and sensors for practical application. It was also noticed that both the porous and aggregated nanostructures are not favourable candidates for SERS particularly on silicon (Si). After this report none of the studies devoted to APLD, described SERS fabrication for practical application.

In this mini letter, a brief overview is presented to shed light on recent developments in APLD carried out in the Laser plasma application group, TCD, Ireland, for structuring surfaces with nanoparticulate films and particle aggregates for application in SERS. The various approaches adopted and have been used for the fabrication of SERS substrates is outlined and SERS performance of these substrates is highlighted. Quantitative information of our produced plasmon active SERS substrates will help the readers to incorporate APLD prepared SERS substrates in biomedical and pharmaceutical applications but not limited.

Apld fabrication of sers substrates

The various types of approaches we use for the fabrication of SERS substrates by APLD methods are mainly based on a gas flow or atmospheric flowing plasmas and are described in Ref. 9-11. In all these methods, ablation plume is captured by the gas and forms a nanoparticle (NP) aerosol by collisional condensation. The NP aerosol is effectively entrained in a flow of gas or atmospheric flowing plasma and delivers to the surface for deposition. The surface with nanostructured features is effective to use as SERS substrate. The SERS efficacy of produced substrates is tested for detection a crystal violet or Rh6G of molecular concentration of 10-4 or 10-5 M results are quantified in term of signal to noise ratio (SNR) and apparent enhancement factor (AEF).

Discussion

Here in this mini letter, we firefly discuss and convey our recently reported results on SERS with the aim just to bring to the readers the main findings at the research forefront described elsewhere [9-11]. A brief overview of APLD for SERS has been given in our recently published mini review articles [12-14] In our first report on the preparation and application of SERS

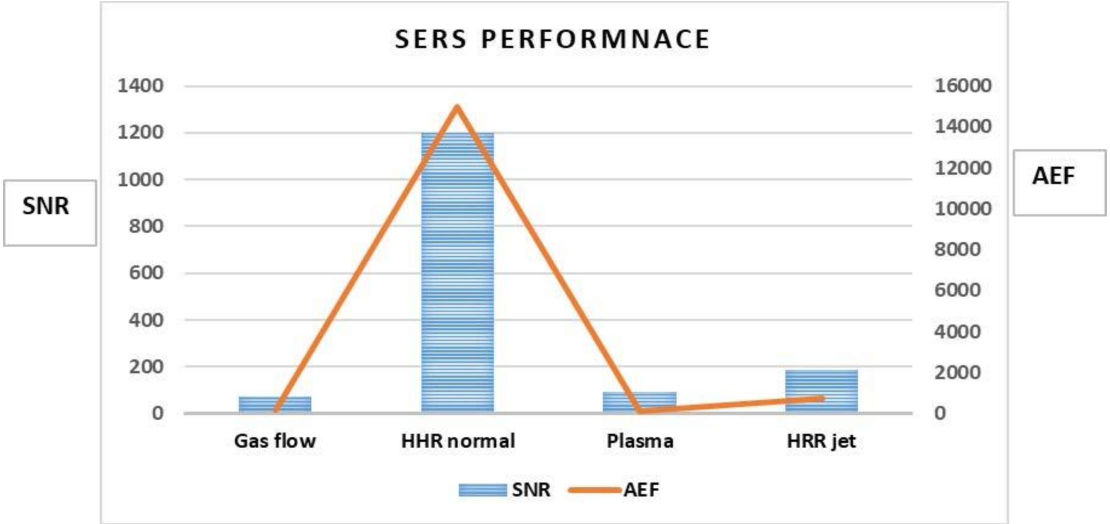

Figure 1. *SERS performance in terms of SNR and AEF of the substrates produced by APLD methods.*

substrate, published in 2017 [9], the SERS substrate produced was presented a particulate surface with the particle mean Feret diameter in the range of 15-25 nm. The surface texture of the substrate changed and showed large round shape particles of mean size of about 50 nm after annealing in air at 400℃ for 30 min. These SERS substrates showed good Raman signals with signal to noise ratio (SNR) 72 for the first film and 220, for the annealed film. The apparent enhancement factor (AEF) for these films were 160 and 960 respectively. The SERS activity of the substrate fabricated with the plasma APLD method was reasonably good with SNR 90 and AEF of 110. With high repetition APLD in gas flow, the SERS substrate of relatively more thickness was obtained. This substrate out performed with SNR and AEF of 1200 and 15000 respectively and proved that this method has strong efficacy for the fabrication of SERS substrates; which are more effective and shows enhanced detection sensitivity. The comparison of these APLD fabricated SRES substrates with commercial substrate showed their outperformance for chemical detection. The different performance of these SERS substrates actually indicated that the surfaces with altered morphological features and texture are capable of producing a different SERS effect and hence detection sensitivity. No doubt, APLD method is a better approach and offers significant scope for the preparation of highly sensitive SERS substrates. Clearly this gives a green signal to work with these methods to make SERS active substrates through easy route for biomedical and pharmaceutical applications. The overall SERS performance of these substrates is shown in **Figure 1** given below.

Conclusion

To summarise, we outlined that the various APLD methods which are passing through intensive investigation at the moment are still available today and presenting an alternative easy route to fabrication of SERS active substrates for application in SERS. There is great possibility to include their application in biomedical and pharmaceutical sectors. The SERS sensitivity of these substrates strong depends on the surface texture and particle size, the surface with large particle size showed better performance. High repetition APLD with the fiber laser is the most suitable fabrication approach available Today. Agglomerates formation did not support SERS activity very well; however, further research is required to establish this fact. This mini report was floated as outlook to motivate researchers to spend more energy to upscale things for multifold applications.

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***Correspondence to:**
Taj M. Khan
The University of Dublin, Dublin 2, Ireland
E-mail: tajakashne@gmail.com