Chapter 7

Conclusions, limitations and future prospects

This chapter summarizes the major findings achieved in this thesis work. The future scope of the present research work in different fields of sensing applications has been discussed.

7.1 Conclusions

The thesis work mainly focuses on development of low-cost SERS substrates through adopting techniques that require minimum sophisticated instruments. The outcomes of the present thesis work are summarized as follows:

I. Using simulation tool detail study on LSPR field in two newly proposed structures namely periodically varying height Au nanopillar and DASAuNP have been presented. Use of simulation tool enables an user to obtain the optimum condition for LSPR field condition for metal nanostructure at minimum cost and time. For a periodically varying height Au nanopillar structure, the effective coupling cross section for interaction of the incident electromagnetic field is found to be increased. The simulation study reveals that due to increase coupling cross section, the LSPR field magnitude enhances significantly as compared to uniform height Au nanopillar structure. The coupled LSPR filed magnitude in the proposed structure eventually enhances the scattered Raman signal intensity from the structure when an analyte molecule is trapped in the structure. In the DASAuNP structure the squared nanopillars are aligned in such a way that sharp corner edges of squared nanopilars are aligned diagonally with nearby pillars. Due to lightening rod effect, an enhanced LSPR field magnitude would be generated in the gap between the sharp edges. This structure has been fabricated using EBL technique and studied experimentally for SERS application.

II. Fabrication of DASAuNP SERS substrate using EBL technique is discussed in chapter 2. The substrate has been used for detection and quantification of RhB. The study reveals that the proposed SERS substrate is highly reproducible and provide high EF with increased hot spot density. Although the performance of the proposed SERS substrate is found to be at par, the overall cost involvement is significantly high and thus it does not fulfill the objective of this thesis work.

III. Design of SERS substrate by incorporating AuNPs in the micropores of diatom frustule is presented. The substrate yields a good degree of reproducibility. With the proposed SERS substrate fluoride level concentration in water sample far below the danger limit (1.5 mgL^{-1}) has been detected reliably. Owing to the simplicity and relatively low-cost approach for obtaining of SERS substrates with naturally available diatom frustules, it is believed that the proposed technique could emerge as an alternative to sophisticated lithographic techniques for obtaining SERS substrates. It is also envisioned that the designed substrate would be suitable for studying Raman signals of other important and toxic chemicals found in our environment at an affordable cost.

IV. To minimize the fabrication cost further, generation of SERS substrate from printing grade paper has also been studied. The proposed fabrication process is simple, and substrate can be obtained at an extremely low-cost within a very short period of time (approx 30 min). Larger active area substrate can be obtained with this technique. The substrate performance has been evaluated by recording Raman signal of MG, R6G and BPE and upon observing its reliability the same has been used for detection of glucose and artificial urine sample. The developed SERS substrate yields a good degree of reproducibility and provides a good spectral uniformity over an area of 1 cm$\times$1 cm. Due to presence of capping agent, the substrate produces consistent result upto seven days. It is envisioned that the proposed SERS substrate could be used as an ultra-low-cost disposable SERS substrate for detection and quantification of Raman signals from of different Raman active samples.

V. In the third phase of the thesis work, another low-cost, fairly reproducible and sensitive SERS substrate from gold coated PVA nanofibers using electrospinning technique has been demonstrated. The detection and quantification of MG and study of spectral uniformity of the substrate have been performed successfully. Upon observing its reliable performance, the substrate has been used for detection and quantification of three pesticides namely deltamethrin, quinalphos and thiacloprid. The SERS substrate can be fabricated without the requirement of sophisticated instruments and laboratory facility. Owing to biocompatibility nature of PVA, it is envisioned that the designed SERS substrate could emerge as an alternative platform for reliable detection and quantification of other chemicals and biological samples without affecting the nature of the samples.

VI. In the final part of the thesis work, a technique to obtain SERS substrate from BRDVD has been demonstrated. The enhancement in Raman signal due to GMR of the trapped AuNPs in the channels of BRDVD has been studied. The performance of the designed SERS substrate has been initially evaluated both for fluorescent and non-fluorescent Raman active samples. The applicability of the proposed SERS substrate for detection, quantification and specification of three clinically important chemicals namely albumin, creatinine and urea in urine sample have been demonstrated. With the involvement of readily available low-cost nanostructured template it is believed that the designed substrate can be used as an alternative platform where SERS based sensing studies can be performed reliably.

In this thesis work five different SERS substrates have been demonstrated. Figure of merits of the developed substrates are summarized in table 7.1 below.

Table 7.1: Comparison of different parameters of the developed SERS substrates.

Substrate type	Minimum detectable sample concentration	EF	Reproducibility	Life span	Fabrication cost (INR)
DASAuNP substrate	1 nM (RhB)	3.27×10^8	87%	-	$\sim 10,000.00$
Diatom based SERS substrate	1nM (MG)	1.66×10^7	92.43%	14 days	< 50.00
Paper based SERS substrate	0.1nM (MG), 1nM (R6G)	$\sim 10^7$	91.24%	7 days	< 5.00
Au coated PVA nanofiber substrate	10nM (MG)	1.48×10^6	92.62%	30 days	< 50.00
BRDVD substrate	0.2nM (MG), 2 nM (BPE)	6.96×10^7	87.95%	45 days	< 10.00

7.2 Limitations

Though four different low-cost approaches have been adopted to obtain SERS substrate at an affordable cost, depending on nature of the substrate several limitations have been encountered while considering it for sensing applications. The AuNPs attached diatom frustule SERS substrate yields a good degree of reproducibility and enhancement factor but depending on its size the pores of the diatom varies, which leads to variation in AuNPs attachment and this would cause fluctuations in Raman signal intensity. Similarly, for paper based SERS substrate the arrangement of attached nanoparticles depend on surface morphology of the paper and it is difficult to obtain same morphology paper all the time, this will again lead to fluctuations in the Raman signal intensity. In case of PVA nanofiber based SERS substrate, the nanofibers are oriented in random manner. With electrospinning technique, it is difficult to control the thickness and orientation of PVA nanofibers deposited on the glass substrate and this would cause fluctuations in Raman signal intensity. For a laser source with relatively larger spot size (few micrometer), an average Raman signal intensity scattered from the SERS substrate is considered and thus the role of surface morphology of the substrate on the fluctuations of Raman signal is not so vital. In the last part of this thesis work, realization of SERS substrates from BRDVD through incorporation of AuNPs into the nanochannels of BRDVD. The trapping of AuNPs in the channel of BRDVD is critical. As the width of the nanochannels are 100 nm, trapping of other nanostructures such as nanorod, nanofiber, nanostar etc. into it would be difficult.

7.3 Future prospect

The present thesis work discusses primarily different approaches by which low-cost SERS substrate can be obtained. The designed substrates are found to be reliable and yields a good EF while measuring Raman signal from different Raman active samples. The present thesis work can be extended to develop SERS substrate from other naturally available patterned structure such as from peacock feather, butterfly wings etc. Also, mass scale production of SERS substrate on low-cost platform using replica molding technique can be adopted in future course of work. Upon observing the reliable performance with the standard sample the substrate can be used for sensing of important chemicals and biological samples. All the proposed SERS substrates yields reasonably good degree of EF and reproducibility. Apart from the DASAuNP SERS substrates, the other substrates can be obtained at an affordable cost. These substrates also have longer durability from 7 days to 45 days and lower detectable concentration limits. The proposed low-cost SERS substrates can be considered as an alternative to the substrates, obtained by using sophisticated instruments such as EBL, FIB and other techniques such as NSL, NIL etc. for detection of chemicals, biomolecules, and other environmental parameters. In future, the designed SERS substrates can be utilized for detection and quantification of water pollutant chemicals such as arsenic, mercury, lead, sulfate, phosphate etc. These substrates can also be utilized for detection of toxic food preservatives and fruits ripen chemicals such as formalin, carbide, nitrite, nitrate etc. It is well known that different pharmaceutical companies manufactures different medicines for same purpose but with different compositions. A comparative study of such drugs for monitoring of their relative compositions can be possible using the proposed SERS substrates. All the proposed low-cost SERS substrates are developed by using laboratory synthesized metal nanoparticles which is not highly monodispersed. By using commercially available highly monodisperse and stable metal nanoparticles, the performance of the SERS substrates can be improved further. Such study would be exploited in the future course of work.