CHAPTER 7

CONCLUSIONS AND FUTURE PROSPECTS OF THE THESIS WORK

The overall findings of the thesis work has been summarized in the final chapter. The limitations of the proposed SERS-based sensing systems have been discussed. At the end of the chapter, the potential applications and future prospects of the present thesis work in various fields of sensing has been elaborated.

7.1 Conclusions

The present thesis has demonstrated the design of different sensitive SERS-based platforms through various low-cost routes. The SERS substrates have been fabricated utilizing the micro and nanostructures of commercially available plastics and printing-grade paper. The usability of SERS substrates have been demonstrated through detecting dye molecules, pesticides, and biological samples such as rotavirus RNA, rotavirus particles in stool sample. The outcomes of the present research work are summarized as follows:

1. The dimension and pattern of nanostructure are critical to understand the insight of coupled electromagnetic field at the site of the hot-spot regions of SERS substrate. Simulation studies have been perform to understand the generation and distrbution of localized surface plasmon field by the gold and silver nanoparticles upon irradiation of suitable laser source. Finite element method (FEM)-based COMSOL Multiphysics software (Wave Optics Module) has been used to perform this work. The parameters like nannoparticles' size, shape, material, environment, separation between two nanoparticles, etc. affect the intensity and the distribution of the local electic field. This simulation model have been utilized to study the distributions of LSPR field for complex distribution of metal nanoparticles and to design new SERS substrates.

2. Flexible and transparent SERS substrates have been used to detect and analyse toxic chemicals like pesticides in rapid and in-field conditions. A SERS sensing platform has been proposed using commercially available PET sheet, and drop-casting AgNPs on the PET sheet. Significant Raman signal enhancement has been observed when Raman signals were collected from the rear side of the MG treated transparent SERS substrates. These fabricated SERS substrates have been used for sensitive detection and identification of insecticides in water.

3. To improve the reproducibility characteristics, a BR-DVD-based SERS substrate has been proposed. AuNPs of diameter 23 nm were drop-cased on the BR-DVD substrate surface which contain the periodic nanochannels. The developed substrates were then treated with MG and BPE, and sensitivity and reproducibility characteristics were evaluated. The substrates provide an enhancement factor of 3.2×10^6 for 1172 cm^{-1} of MG and a good degree of signal reproducibility as 94%. The usability of the designed SERS substrate was further investigated by detecting Raman spectra of rotavirus RNA in the laboratory environment. The cost involved in fabricating the substrate is very low, INR 16 ($\sim$ \$0.2) per substrate, and can be used as a disposable SERS substrate. The proposed SERS substrate could emerge as a highly reproducible platform for other SERS-based sensing studied in the laboratory environment.

4. A simple and rapid SERS substrate fabrication technique has been proposed to detect rotavirus in clinical stool samples. The designed substrates have been obtained by drop-casting of AgNPs on two different 85 and 100 GSM-grade papers. The performance of the substrates was initially evaluated by detecting and analyzing Raman active molecules, MG and R6G. With 85 GSM paper as a platform, the proposed SERS substrates exhibits an enhancement factor of 5×10^6 and signal reproducibility is 90%. The experimental data obtained from the paper-based SERS substrate has been compared with the data from a commercial-grade counterpart and a fairly accurate results yielded by the proposed scheme has been noticed. Owing to its low-fabrication cost INR 5 ($\sim$ \$0.06) per substrate, the fabricated substrates can be used as disposable and for large-scale sensing of rotavirus particles.

In this thesis, fabrication, testing and application of three SERS substrates have been demonstrated. Average enhancement factor (EF_{avg}), reproducibility and fabrication-cost (considering only the consumables) of these substrates have been summarized in the Table 7.1.

Table 7.1: Comparison of various parameters of the developed SERS substrates

Sl. No.	SERS substrtae	EF_{avg}	Reproducibility	Fabrication cost
1	PET-based SERS substrate	3×10^5	85%	INR 6 (∼ $0.08)
2	BR-DVD-based SERS substrate	3.2×10^6	94%	INR 16 (∼ $0.2)
3	Paper-based SERS substrate	5×10^6	90%	INR 5 (∼ $0.06)

7.2 Limitations

Present thesis primarily focused on the development of three different low-cost approaches to fabricate SERS substrates. Depending on the nature of the substrates several limitations have been encountered during the fabrication processes and sensing applications. In the case of PET-based SERS substrate, when collecting Raman spectrum from the bare substrates, characteristic peaks of PET were also present. This will hinder the detection of ultra-low concentration of analyte molecule. For paper-based SERS substrates, the distribution of the nanoparticles on the micropores depends on the morphology of the paper. The paper substrates should be selected and handled carefully during sensing study. Otherwise, the distribution of the nanoparticles on the SERS substrates, and consequently Raman signal intensity from different batches could vary exceeding the acceptable limit. The BR-DVD nanochannel being extreamly narrow, trapping larger nanoparticles, nanorods and nanostars would be difficult. The region of the BR-DVD substrate from where the SERS substrate has been fabricated determines the property of the substrate. For instance, SERS substrate fabricated from the internal region of the BR-DVD will have different EF and reproducibility characteristics than the substrate fabricated from the outer region of the BR-DVD. It is anticipated that the later type of SERS substrate would yield a higher EF and better reproducibility characteristic than the former type SERS substrate.

7.3 Future prospects

The cost-effective SERS substrates have been developed by depositing laboratory synthesized AgNPs and AuNPs on different supports. The nanoparticles are not highly monodispersed which is desirable for a reproducible SERS substrate. In the future, the metal nanoparticle synthesis procedure would be optimized to develop stable and highly monodispersed naoparticles for reliable SERS sensing. The SERS EF could be improved further by optimizing the concentration of the nanoparticles in the sensing region of the substrate. With a hand-held Raman spectrometer, on-field detection and identification of pesticide samples, and other harmful chemicals like heavy metals, food preservatives and colours can be performed. In addition, the SERS substrates have huge potential in diagnostic and analytical applications, and could be used for the sensing of biomarkers, bacteria and viral proteins, etc. These highly sensitive SERS substrates with high enhancement could be marketed for commercial applications.