Abstract

Raman Spectroscopy is a vibrational spectroscopic technique that provides fingerprint of molecules. Owing to its advantages such as requirement of very less sample preparation steps, in-situ and in-vitro investigations of biological samples, non-destructive and non-invasive investigations of samples etc. [1–3] the technique has been used in different fields spanning from biology, chemistry, medicine to environmental sciences. However, low cross-section of Raman scattering process, limits its applicability in various fields. With the advent of surface enhanced Raman scattering (SERS) this limitation has been overcome. Due to this nanomaterial assisted phenomenon namely localized surface plasmon resonance (LSPR), enhancement in the Raman signal intensity was first observed by Martin Fleischmann [4] in the year 1974. Later this process was confirmed by R P Van Duyne [5], M. G Albrecht and A Creighton [6] in the year 1977. With the SERS technique Raman signal intensity can be enhanced upto the order of 10^{14}, and detection of a single molecule is now possible.

The intrinsic characteristic of Raman process for fingerprinting of molecules with additional advantages of being label free technique, fluorescence quenching ability, detection of trace amount of concentration etc., make it popular for biosensing [7, 8], DNA, RNA detection [9, 10], detection of chemicals [11, 12], food additives [13, 14], explosives [15]etc. Noble metal nanostructures such as gold (Au), silver (Ag), copper (Cu) etc. support strong localized surface plasmon (LSP) field and thus, enhances scattered Raman signal of analyte molecules absorbed on it or when brought to close proximity to the nanostructure. The enhancement in the SERS is obtained from two mechanisms namely electromagnetic (EM) mechanism and chemical mechanism (CE). Being a predominant mechanism, EM mechanism refers to excitation of LSP of the metal nanostructure. The generation of strong electric field due to LSPR is responsible for enhancement of the Raman signal. The region between the two closely spaced nanomaterials confine the coupled EM field very strongly and this region is also termed as hot-spot region. In the CE mechanism the surface-absorbed molecule provides higher Raman scattering cross-sections, which eventually contributes to enhancement of the

Raman signal. However, only one or two orders of magnitude enhancement can be achieved with this mechanism. SERS substrates are generally colloidal nanoparticles, nanostructures on plane surface and roughened electrodes obtained from noble metals like gold, silver and copper. These metals exhibits LSPR at visible region. Metal nanoparticles suspensions is the most studied class of substrate. As surface morphology of nanostructures greatly influence the Raman signal intensities, different nanostructured such as nanorods [16, 17], nanowires [18, 19], nanocube [20, 21], nanostars [22], nanoprisms [23] etc. have been reported for SERS studies. The fabrication of colloidal SERS substrate is however relatively simple. The colloidal nanostructures are used either in solution form or immobilized on planer solid support. With these kind of SERS substrates different groups have demonstrated the detection of pesticides [24], antibiotics [25], melamine [26], toxins [27], food additives and illegal food dyes [13, 14] etc. Detection of single molecule also has been demonstrated using colloidal SERS substrates [28]. Though the metal nanoparticle colloidal SERS substrate yields higher order of magnitude due to random distribution of nanoparticle in the solution produces poor reproducibility. The patterned nanostructures can be obtained from lithographic techniques such as electron beam lithography (EBL) [29, 30], focus ion beam lithography (FIB) [17, 31], nanosphere lithography(NSL) [32, 33], nano imprinting lithography (NIL) [34] etc. which yields highly reproducible SERS substrate. Such substrates has been used for detection of bio-molecules, chemicals, pesticides, proteins, drug quality monitoring etc. Such techniques are in general expensive and thus the fabricated SERS substrate cannot be used for disposable purpose. In recent years, designing of SERS substrates alternative to above techniques such as diatom [35], rose petal [36], inject printed paper [37], DVD [38], blu-ray DVD [39] etc. have been exploited to obtain reliable and reproducible SERS substrate.

While designing a SERS substrate, it is expected that the substrate yields high reproducibility, high enhancement factor, cost effective and has a good life span. This research work focus on development of reproducible SERS substrate with high enhancement factor and good life-span by using different low-cost approaches, and to use these substrates for different real field applications. In this PhD work, design of metal nanostructures for generation of strongly coupled LSP field using simulation tool and fabrication of the optimized structure using EBL technique has been carried out. Further the performance of the designed SERS substrates have been evaluated by measuring Raman signal intensities of different Raman active samples. In the next phase, low-cost SERS substrates with good degree of reproducibility have been proposed, which were obtained from diatom and printing grade papers. By incorporation of Au and Ag nanoparticles in the micropores of these samples SERS substrates have been obtained. Initially the proposed substrates have been characterized using commonly used Raman active samples and upon observing its reliable performance the AuNPs attached diatom SERS substrate has been used for detection and quantification of fluoride in drinking water. The paper based SERS substrate has been used for detection and quantification of glucose and artificial urine. In the third part of the thesis work, low-cost SERS substrates with good degree of reproducibility and relatively longer durability has been proposed using electrospun polyvinylalcohol (PVA) nanofibers. Here also, the initial characterization of the proposed substrate has been carried out using Raman active sample- malachite green. Using thermal evaporation technique gold film has been coated on the PVA nanofibers and used the substrate for detection of harmful pesticides commonly used in agriculture. In the fourth and final part of the thesis work, nano channels of blu-ray DVD (BRDVD) have been exploited for SERS enhancement. Au nanoparticles have been incorporated on BRDVD substrate and use it for detection and quantification of clinically important parameters in urine sample.

Chapter wise organization of the thesis work is given below-

Chapter 1 of the thesis discuss the basic principle of Raman scattering, Raman instrumentation, overview of SERS along with its enhancement mechanisms. The advancement in the development of SERS substrate in last two decades and various applications in different fields have been described in detail. Also, scope of the thesis and statement of the thesis problem is defined.

Chapter 2 deals with designing of metal nanostructures for optimization of structure that would generate maximum LSP field intensity using finite element method (FEM) based simulation tool (COMSOL Multiphysics). The realization of the optimized structure using EBL technique and characterization of developed SERS substrate have been narrated in this chapter.

Chapter 3 presents the development of SERS substrate from diatom frustule through incorporation of Au nanoparticles in to it. The effect on SERS enhancement depending upon size of Au nanoparticles has also been discussed in this chapter. Finally, real field application of proposed SERS substrate has been demonstrated.

Chapter 4 of the thesis deals with the development of SERS substrate from printing grade paper. Performance of the proposed SERS substrate with different gram per square meter (GSM) grade paper has been initially studied. Distribution of nanoparticles on different GSM grade paper has been illustrated. Also this chapter includes how, PVP capped Ag nano ink effects on durability of the substrate. As a proof of concept, the field application of the substrate has been demonstrated for detection of glucose and artificial urine sample.

Chapter 5 of the thesis, discusses the development of SERS substrate from electrospun PVA nanofiber by coating Au film using thermal evaporation process. Detection and quantification of three harmful pesticides largely used in agriculture namely deltamethrin, quinalphos and thiacloprid have been demonstrated. Further, the figure of merits of the proposed SERS substrate are included in this chapter.

Chapter 6 of the thesis presents the development of SERS substrate form BRDVD. The effect of Au nanoparticle attached in the nano-channels of BRDVD to SERS signal enhancement has been discussed in this chapter. Using the designed substrate, detection and quantification of different parameters in urine sample has been demonstrated.

Chapter 7 summarizes the entire work done during the research work along with future prospect of the present thesis work.

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