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Surface-enhanced raman scattering (SERS) spectroscopy: a versatile tool in electrochemistry

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ABSTRACT

This review article describes the recent development in field of surface-enhanced Raman scattering research. The first SERS spectra was obtained from an electrochemical system of pyridine molecule adsorbed on roughened silver electrode, which led to the discovery of the SERS effect in the mid-1970s. The various aspects of SERS research which includes various SERS active substrates, mechanism of SERS and the various applications have been described in this review article. Special emphasis is given to the important features of electrochemical SERS (EC-SERS), a special branch of SERS.

KEYWORDS

Surface-enhanced raman scattering;
Scattering cross section;
Roughened silver electrode;
Nanoparticle;
Electrochemical SERS.

INTRODUCTION

The discovery of surface-enhanced Raman scattering spectroscopy (SERS) by Fleischmann and co-workers in 1974 at the University of Southampton, which is intimately connected with the electrochemical systems, has drawn a lot of attention to researchers due to the large enhancement of weak Raman signal and thereby facilitate convenient identification in chemical and biological systems. Later, with the advent of scanning probe microscopy technique (SPM) in the early 1980s, it was revealed that the order of surface roughness is in nanometer dimension. Therefore, SERS and nanoscience/nanotechnology are now intimately related. SERS has now emerged as a powerful technique not only for studying the molecules or ions at trace concentrations down to single molecule detection level but also for helping to understand the surface chemistry especially electrochemistry at the nanometer scale. The rapid development of

nanoscience and nanotechnology in recent years boosted the scientific community and attracted a wide interest of SERS. Thus, SERS has become an important branch of nanoscience and nanotechnology and also a strong analytical tool available both in surface chemistry as well as in electrochemistry. Electrochemical SERS (EC-SERS) is a special branch of SERS. It is a very important yet very complex tool in electrochemistry as evident from the moderate number of publications on various aspects of SERS from electrochemical systems. As the SERS spectra can be recorded by the application of electrode potential, which makes EC-

SERS one of the most complicated systems in SERS.

Although, several review articles (both tutorial and critical) had been written on

various aspects of SERS, none of these articles covers the prospective development of SERS in terms of substrates, methods, theory based on the mechanism as well as its various applications and its correlation with electrochemistry, nanoscience/nanotechnology and surface chemistry. There are few review articles on the development of EC-SERS. The aim of this paper is to provide an updated review on various apects of SERS effect which include historical background and its development, correlation with both electrochemistry and nanoscience, various SERS active substrates, the various theories to explain the mechanism of SERS and its various applications. Due to space limitations, a complete review of all recent work on this important area of research in both electrochemistry/nanoscience is not possible. However, a few representative examples had been summarized to illustrate the recent development in SERS research.

HISTORICAL BACKGROUND

Raman spectroscopy is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It depends on the inelastic scattering, or Raman scattering of monochromatic light, usually from a laser in the visible, near-infrared or near-ultraviolet range of electromagnetic spectra. This effect was discovered by famous Indian physicist Professor C.V. Raman in the year 1928[1]. The shift in wavelength of the inelastically scattered radiation provides the chemical and structural information of the molecule. Raman shifted photons can be of either higher or lower energy, depending upon the vibrational state of the molecule under study. Raman line intensity (I_r) is proportional to $\nu^4 * \sigma * I * \exp(-E_i / kT) * c$, where ν and I are the frequency and intensity of incident radiation, σ is the Raman cross section, $\exp(-E_i / kT)$ is the Boltzmann factor for state i and c is the concentration of the molecule which scattered the radiation to produce Raman line. The weak intensity of Raman signal due to the low scattering cross-section (~ 10^{-30} cm^2 $molecule^{-1}$) is the biggest disadvantage of Raman spectroscopy with low sensitivity, which is the reason why it was not widely used for a long time.

The name surface enhanced Raman spectroscopy implies that it provides the same information that normal Raman spectroscopy does, simply with a greatly enhanced signal. The weak Raman signal can be greatly enhanced by the introduction of surface-enhanced Raman scattering (SERS) spectroscopy in 1974 by Fleischmann, Hendra and Mcquillan of University of Southampton[2]. It was accidentally discovered by them when they tried to do Raman with an adsorbate of very high Raman cross section, such as pyridine (Py) on the roughened silver (Ag) electrode. The initial idea was to generate high surface area on the roughened metal surface. On the basis of their extensive experience in increasing the surface area of a Ag electrode by using an electrochemical roughening method, they applied about 450 potential oxidation and reduction cycles (ORC) to a Ag electrode in an aqueous electrolyte comprised of 0.1 mol L^{-1} KCl + 0.05 mol L^{-1} Py. The Raman spectrum obtained was of unexpectedly high quality and evidently due to the adsorbed Py and the spectra was found to be dependent on the electrode potential. They initially explained the intense surface Raman signal of Py due to increased surface area. This was, in fact, the first SERS measurement and that roughened electrode was the first nanostructure exhibiting the SERS activity, although it was not recognized as such in 1974. Later, Jeanmaire and Van Duyne from Northwestern University, USA, first realized that surface area is not the main point in the above phenomenon in 1977[3]. Albrecht and Creighton of University of Kent, UK, reported a similar result in the same year[4]. These two groups provided strong evidences to demonstrate that the strong surface Raman signal must be generated by a real enhancement of the Raman scattering efficiency (10^5 to 10^6 enhancement). The effect was later named as surface-enhanced Raman scattering and now, it is an universally accepted surface sensitive technique. Although, the first SERS spectra were obtained from an electrochemical system (Py + roughened Ag electrode), all important reactions on surfaces including electrochemical processes can be studied by SERS. The technique is so sensitive that even single molecule can be detected. The exact mechanism of the enhancement effect of SERS is still a matter of controversy in the literature. There are two main mechanisms on the large enhancement effect of weak Raman signal from Py adsorbed on electrochemically roughened Ag. Jeanmaire and Van Duyne proposed an electromagnetic effect on the enhancement[3]. The electromagnetic theory is based on the excitation of localized surface plasmons. Albrecht and Creighton proposed a theory based on the charge transfer effect of the adsorbed molecule on the enhancement efficiency[4]. This chemical enhancement theory relies on the charge transfer complex formation of the adsorbed molecule. However, it is very difficult to separate these two effects experimentally.

The main features of SERS technique are summarized briefly as follows.

1) It is a highly surface sensitive, non-destructive and *in-situ* vibrational spectroscopic technique.
2) SERS occurs when target molecules are brought closer within the few nanometers of the surface of SERS active substrates of different morphologies.
3) The excitation profile (scattering intensity versus excitation frequency) deviates from the fourth power dependence of normal Raman scattering.
4) It has extremely high spatial resolution. The enhancement range is several nanometers, effective for one or several molecular layers close to the SERS active substrate.
5) SERS activity strongly depends on the nature of metal and surface roughness.

The recent advancement in the field of SERS research is mainly focused in the following directions :

- Fabrication of new, novel and efficient SERS active substrates to overcome the substrate generality of SERS.
- Single molecule SERS to improve the molecule generality and enhance the detection limit of various adsorbates/species.
- Understanding the mechanisms involved in the SERS phenomenon.
- Use of SERS for imaging, sensing, diagnostics and further search for new applications.

GENERAL FEATURES OF ELECTROCHEMICAL SERS (EC-SERS)

The electrochemical surface-enhanced Raman scattering (EC-SERS) is a special branch of SERS technique, which generally consists of nanostructured electrodes and electrolyte. Thereby, an electrochemical double layer is formed in between, as the most important and complicated interfacial region. Beyond the analytical aspect, EC-SERS has paid more attention to provide really meaningful information for revealing the adsorption configuration or the reaction mechanism for electrochemistry[5].

Generally, it has been widely accepted that the SERS enhancement effect is contributed by the long range electromagnetic field enhancement (EM) and short range chemical enhancement (CM). The former is the main contribution to SERS signals in most SERS systems. However, in case of electrochemical systems, CM also plays an important role especially in characterization of chemical species as it is closely associated with the chemical property of surface species and substrate. Both chemical and physical or electromagnetic field enhancements can be influenced to some extent by changing the applied electrode potential, i.e., the Fermi level of metal and dielectric constant of interfacial electrolyte, in an EC-SERS system. The chemical enhancement can be strongly tuned by the potential, leading to extreme change of interfacial structure and property. This makes EC-SERS as one of the most complicated systems in SERS. Another important and common feature of EC-SERS is that the SERS intensity strongly depends on the electrode potential. The change of the electrode potential may result in the change of the coverage and/or the adsorption orientation of the molecule, both of which will lead to a change in the SERS intensity.

In a typical EC-SERS study, the electrochemical system is studied while the electrode potential is tuned and the spectral response (including the intensity and frequency change or even the appearance of new bands) is recorded. In most cases, the experimental data will be interpreted by analyzing the intensity or frequency change of some characteristic bands (vibrational modes), which may directly reflect a change in the surface coverage, orientation, structure, composition and morphology, and sometimes may indicate the involvement of a certain kind of surface enhancement. Figure 1 illustrates the schematic of a typical experimental setup used in *in situ* EC-SERS, which includes a Raman spectrometer, a potentiostat or galvanostat, a computer and an EC-

SERS cell. The EC-SERS cell consists of three electrodes configuration : A conductive SERS active working electrode, an inert counter electrode and a reference electrode (usually a saturated calomel electrode (SCE) or Ag/AgCl electrode).The three electrodes should be assembled in a good relative geometric position to allow both efficient Raman signal and accurate electrochemical measurements. Most of the systems which have been investigated by EC-SERS deals with the adsorption and reaction of inorganic species, organic molecules and biomolecules in aqueous solutions. In case of EC-SERS, a collective analysis of the spectral features from the experimental and theoretical aspects is essential to obtain the important information of chemical bonding, orientation and even electrochemical reactions of the molecules at the electrode surfaces, thereafter to understand the overall interfacial structure at the electrode|electrolyte interface. Py was the first molecule which was used to demonstrate the SERS effect in electrochemical system and since then, it has been a very important probe molecule to verify the SERS activity and surface properties of a new SERS active substrate. The relative intensities and frequency shifts of the major bands of Py are very sensitive to the electrode potential and the surface properties of the metal surfaces used as SERS substrates. These phenomena cannot be solely interpreted with the electromagnetic field enhancement (EM) effect, and contribution of CM effect should be taken into account.

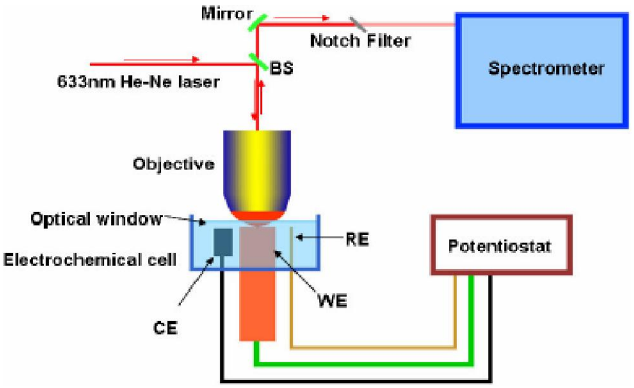

Figure 1 : The schematic of a typical experimental setup used in *in situ* EC-SERS, which includes a Raman spectrometer, a potentiostat or galvanostat, a computer and an EC-SERS cell.

Tian and his group carried out systematic SERS studied of Py on different metal surfaces (both coinage and transition metals) illustrating how EC-SERS can be used to characterize the surface adsorption and molecule–metal interaction[6]. Their study also revealed that the frequencies and the intensities of SERS of Py were correlated to the chemical interaction between Py and the metal surface and the adsorption orientation.

It is highly desirable to apply *in-situ SERS* to obtain molecular-level information about the breaking and formation of bond in the reaction, observe the reaction intermediate on the surface and finally, to distinguish the reaction products. The microscopic structure and dynamics of interfacial water molecules is important in understanding the electrode/electrolyte interface and is still an ongoing issue in electrochemistry as well as surface science. However, the interactions between water molecules and electrolyte ions as well as between water and electrode surface are very complex. Recently, Tian et al. have characterized the surface water on Au core Pt group metal shell nanoparticles coated electrodes[7]. They obtained the potential-dependent SERS spectra of water molecules adsorbed on Pt, Pd and Au electrode surfaces in the potential region of the hydrogen evolution reaction, wherein the band at around1615 cm^{-1} is the bending vibration of water[7]. The broad band at around 2000 cm^{-1} observed only on the Pt surface can be attributed to the Pt–H stretching vibration. Scientists are optimistic that SERS will become an indispensable tool in the study of interfacial structures and various surface processes involving interfacial water molecules without any interference from bulk water.

Weaver and his group carried out a combined study of EC-SERS and cyclic voltammetry (CV) to investigate the nitrobenzene surface reaction on the SERS active Au surface[8]. It is well known fact that nitrobenzene can be reduced by three two-electron steps to form nitrosobenzene,

$$C_6H_5NO_2 + 2e^- \rightarrow [C_6H_5NO] + 2e^- \rightarrow$$
$$[C_6H_5NHOH] + 2e^- \rightarrow C_6H_5NH_2$$

They acquired the SER spectra during the potential sweep for the reduction of nitrobenzene at the SERS active gold electrode and correlated the voltammetric and SERS results and proved that the peak at -0.11 V potential can be assigned to the reduction of nitrobenzene to nitrosobenzene. Their study based on EC-SERS in combination with CV provides a new dimension in the investigation of electrochemical reaction on the electrode surfaces and identification of the intermediates and products of the reaction.

The non-destructive, highly surface-sensitive and *in-situ* nature of surface SERS can be utilized to detect reaction intermediates such as radical and radical ions on the electrode surface and elucidate the reaction mechanism. Recently, Tian and his group at Xiamen University, China reported the first *in-situ* electrochemical SERS (EC-SERS) study on the electrochemical reduction of $PhCH_2Cl$ in acetonitrile (CH_3CN) on Ag electrode[9]. They detected benzyl radical anion as an intermediate of the above surface reaction. The overall reaction mechanism revealing the adsorption process of $PhCH_2Cl$ on the Ag surface and all other possible interactions including the solvent has been elucidated from the SERS study. The SERS results were confirmed by Density Functional Theory (DFT) calculations, which can provide concrete evidence to identify the reaction intermediate and products.

ENHANCEMENT MECHANISM IN SERS

Despite numerous theoretical and experimental works on SERS and large number of research publications based on these works, the exact nature of the gigantic enhancement in Raman intensity found in SERS is still a matter of controversy. However, it is generally accepted that two enhancement mechanisms, one a long-range electromagnetic (EM) effect and the other a short-range chemical (CM) effect, are operative simultaneously. The EM mechanism is based on the amplification of the electromagnetic field generated due to coupling of the radiation field with the localized surface plasmons (LSP) of the metal nanoparticles. The localized surface plasmon resonanace (LSPR) occurs when a resonance condition between the incident wavelength of light and the electrons in the nanoparticles is achieved. This causes a collective oscillation of the conduction electrons and has two primary consequences. First, the wavelengths of light that cause this collective oscillation are selectively absorbed by the nanoparticles and can be monitored using UV-Vis spectroscopy. The second consequence is the formation of enhanced electromagnetic fields that extend from the nanoparticle surfaces. These fields are responsible for a large portion of the enhancement observed in SERS. The enhancement is roughly proportional to $|E^4|$ and generally in the order of 10^8 or more, where E is the intensity of the electromagnetic field.

Localized surface plasmon resonance (LSPR), the lightning rod effect, and the image field effect have all been considered to contribute to SERS. Among them, LSPR makes the major contribution to the electromagnetic field enhancement and SERS. Anisotropic metal nanoparticles exhibit 'lightning-rod effect'[10], another type of field enhancement refers to an enhanced charge density localization at a tip or vertex of a nanoparticle. When an electromagnetic field (laser light) excites the free electrons of a metallic tip, a highly localized, strong electric field develops at these sharp tip or vertex with large curvatures, leading to large field enhancement in those regions[10]. This is the reason for the high SERS activity of an anisotropic nanoparticle. Anisotropic metal nanoparticles had been used as an efficient SERS active substrate with high SERS activity. The high SERS activity of the anisotropic metal nanoparticles can be explained in terms of their unusual LSPR properties and the sharp edges on the surface of a nanoparticle being able to generate a greater localized electric field in comparison to isotropic (spherical) nanoparticles.

The chemical enhancement mechanism reflects the enhancement as a result of the chemical interaction between the adsorbates and the metal surface. Among the various types of chemical enhancements such as chemical bonding enhancement, resonance enhancement of a surface complex, and photon-induced charge-transfer enhancement (PICT), PICT is the most important one. Therefore, the CM mechanism is also known as the charge transfer (CT) mechanism, involves the photoinduced transfer of an electron from the Fermi level of the metal to an unoccupied molecular orbital of the adsorbate or vice versa depending on the energy of the photon and the electric potential of the interface. The enhancement of CM is usually in the order of 10-10^2. EM is a long-range effect, which requires rough surface as SERS active substrate, while CM is a short-range effect occurring on the molecular scale. The two mechanisms ca EM and CM are not mutually exclusive, but work together in concert to produce the overall SERS effect. It is very difficult to separate CM from EM. Several research groups have tried to overcome this problem. Therefore, it is desirable to evaluate the relative contribution of these two mechanisms to the overall understanding of the SERS phenomenon.

FABRICATION OF ORDERED SERS SUBSTRATE

Although, nanoparticles and nanoparticle film electrodes show very good surface uniformity, it is difficult to control the spacing of the nanoparticles to optimize the SERS activity. Template methods can provide highly ordered SERS substrates with controlled inter-particle spacing. Among various templates, nanosphere lithography (NSL) and anodic aluminum oxide (AAO) films have been most widely used for the fabrication of SERS-active substrates. In addition to these, Langmuir-Blodgett technique can be used to fabricate highly-ordered SERS active substrates.

Nanosphere lithography

NSL technique has been well developed by the groups of Van Duyne and Bartlett[11,12]. In this technique, monodispersed polystyrene or SiO_2 nanospheres of the desired diameter are self-assembled on clean conductive substrate such as indium tin oxide (ITO) or evaporated metal substrate over glass to form a very ordered single or multi-layer colloidal crystal template or mask for metal deposition. Afterwards, a metal layer is deposited by physical vapour deposition or electrochemical deposition on the substrate with a controlled thickness. It will then result in three types of structured SERS substrate: a) physical vapour deposition on the nanosphere template leads to the formation of Ag metal "film over nanosphere" (FON) surface; b) the removal of nanospheres of the FON surface by sonicating in a solvent results in surface confined nanoparticles with a triangular footprint; c) electrochemical deposition followed by removal of spheres leaves a thin nanostructured films containing a regular hexagonal array of uniform segment sphere voids.

Ag/AAO systems for chemical and bio-sensing

Wang et al. had utilized porous AAO film as template to electrochemically deposit arrays of silver (Ag) nanoparticles with a precisely controlled gap upto 5 nm[13]. This Ag/AAO system with tunable sub-10 nm interparticle gap can be used as a uniform SERS active substrate with large enhancement factor (~ 10^8). The "hot junction" present at the interparticle gap of this nanostructure-based SERS substrates can increase the SERS sensitivity (a key factor for large electromagnetic field enhancement and increased SERS sensitivity). This Ag/AAO based SERS substrate with highly uniform and reproducible SERS signals can be used as bio/chemical sensor and concentration upto picomolar level had been detected. This excellent SERS substrate can be further extended into single molecular regime increasing the detection limit and SERS sensitivity.

Recently, Liu et al. used these SERS-active Ag/AAO system to monitor antibiotic induced chemical changes in bacteria cell wall[14]. The SERS profiles recorded by them are sensitive and stable and the 'chemical features' obtained from SERS spectrum of bacterial cell wall enables rapid identification of drug resistant bacteria within an hour. The SERS based novel technique was applied to a single bacterium. This high speed SERS detection makes possible direct analysis of clinical specimen instead of pure cultured bacteria.

Langmuir-blodgett technique

Chemical assembly of metal nanoparticles on solid substrates like glass, silicon ,ITO can be used as ordered SERS substrates through electrostatic or chemical interaction to form an ordered layer of nanoparticles. However, this method still can not provide totally defect free SERS substrate over a large area of few hundred of cm^2.

The Langmuir-Blodgett (LB) technique can potentially solve this problem. The LB method was originally used to prepare a large-area surface film of amphiphilic molecules on solid substrates. In this method, the amphiphilic molecule dissolved in a volatile solvent immiscible with water, and dispersing the solution on the surface of the water phase, a monolayer of the amphiphilic molecule will form at the air/water interface after the evaporation of the volatile solvent. By changing the position of the movable barrier in the LB trough, one can change the density of the monolayer film. The film can then be deposited on the substrate by the dipping and pulling method. Similarly, a nanoparticle film can be fabricated by LB method. At first, the nanoparticles should be modified with hydrophobic molecules and dispersed into highly volatile solvent, which is immiscible with water. By dispersion of the solution into the water phase, a layer of randomly distributed nanoparticles will be left at the interface after the evaporation of the solvent. As a result of compression of the layer through moving the barrier, an ordered layer of nanoparticles will be formed on the surface. The LB technique has been shown to be a high-throughput, low-cost, rapid and easily integrated method for the controlled assembly and patterning of nanoparticles and nanowires.

This type of nanoparticles assembled on a substrate can be potentially used as highly ordered SERS substrate. During the compression process, the interparticle spacing will decrease, leading to strong electromagnetic coupling between nanoparticles and a significant shift of the LSPR band.

The LB method is the method that is capable of achieving the most uniform SERS substrate based on the nanoparticle assembly method. This LB technique will provide a rapid, low cost and high throughput complementary protocol to fabricate highly ordered SERS active substrates over large area around 20 cm^2 without using any complicated, costly and specialized instrument or tedious steps of fabricating templates for template based synthesis. Yang and his group had carried out systematic SERS studies using SERS substrate fabricated by LB technique[15]. At present, the LB technique has been successfully utilized to fabricate most uniform SERS substrates of films of nanorods, nanowires, and spherical, cubic, cuboctahedral, and octahedral Ag nanoparticles[15]. Among them, the Ag nanocube exhibits the lowest enhancement, and the octahedral nanoparticle shows the highest enhancement, up to 10^7–10^8. With use of the latter as a SERS substrate, a detection limit as low as 1 ppb has been achieved for the detection of arsenate and arsenite in solution[16].

APPLICATIONS OF SERS

Nie and Emory[17] carried out one of the earliest experiment on single-molecule SERS by combining SERS with the transmission electron microscopy (TEM) and scanning tunneling microscopy (STM) techniques. This study enabled them to study the relationship between the morphology of the SERS active nanoparticles and SERS effect. They observed Raman enhancement as high as 10^{14} to 10^{15} for single rhodamine 6G (R6G) molecule adsorbed on selected Ag nanoparticles. In case of single-molecule SERS, they observed a single event rather than an ensemble averaged value generally obtained for conventional SERS measurements. Introduction of single molecule SERS technique has brought a new dimension in biomedical research as a versatile probing tool to study various biological molecules like virus, bacteria, protein, DNA and RNA.

SERS is among the most sensitive techniques available to surface science. This technique can be coupled with a wide range of other surface techniques to study various fundamental and applied research areas such as, corrosion, catalysis, advanced materials, biology and sensors. In a recent development, a new approach has been introduced to enhance the Raman scattering intensity by combining Raman spectroscopy with scanning probe microscopy such as atomic force microscopy (AFM) or STM. Its central element consists of an illuminated AFM or STM tip placed in a close vicinity of a substrate. The tip is operated in contact or tunneling mode. Upon illumination with a laser beam, a localized surface plasmons are excited in the tip-substrate gap, producing a large, local enhancement of electromagnetic field compared to the incident radiation. In this way, Raman spectroscopy and scanning probe technique can be combined and this new technique is known as tip-enhanced Raman spectroscopy (TERS). The technique was invented by Pettinger et al. in 2004 to probe malachite green isothiocyanate adsorbed on Au (111) surface[18]. TERS has been used to study surface reactions on single crystal and smooth surfaces, as surface roughness of the substrate does not play any role in this enhancement. The *in-situ* and non-destructive nature of SERS has been utilized to study various physiological and biochemical processes *in-vivo* in a living cell.

SERS technique can be used in environmental analysis. The target molecules analyzed by SERS included pesticides; herbicides; pharmaceutical chemicals in water; banned food dyes; aromatic chemicals in regular aqueous solutions and in sea water; chlorophenol derivatives and amino acids; chemical warfare species; explosives; and various organic pollutants.

Metal nanoparticles immobilized as SERS substrates can be used in biomedical diagnostics. For example, the SERS substrate can be used as glucose sensor to detect glucose in blood. Although, glucose is most commonly monitored by electrochemical-based sensors, an alternative protocol using SERS substrates prepared by NSL has been devised for the detection of glucose in blood[19]. The key to detection of glucose by SERS was the surface chemistry. The SERS substrate was modified with an alkanethiol partition layer to facilitate the glucose adsorption to the metal surface.

CONCLUSION

Although, the theory to quantify the exact mechanism of SERS effect is yet to be developed, the 30 years of this versatile technique has reached a new height due to the increased efficiency of the modern Raman instrumentation and recent advancement in nanotechnology. Thus, SERS offers a mean to overcome the obstacles of sensitivity and surface/substrate selectivity, allowing the obtainment of surface vibrational data *in situ* in diversed environments such as air, ultrahigh vacuum and electrochemical environments.

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