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Abstract. Surface enhanced Raman scattering (SERS) is an optical spectroscopy technique with single molecule sensitivity and chemical specificity. The electromagnetic enhancement mechanism of SERS is facilitated by the localized surface plasmons of metallic nanostructures utilized in experiments. The magnitude of the local optical field created by the plasmonic nanostructure depends on parameters such as size, shape, morphology, arrangement, and local environment of the nanostructure. By tuning these parameters, electromagnetic hot spots can be created to facilitate ultra-sensitive, subwavelength SERS detection platforms. In recent years, there have been a number of innovations in nanofabrication and synthesis of plasmonic nanostructures. This has led to a variety of plasmonic nano-architectures that can be harnessed for SERS. Recently investigated plasmonic nanostructures in the context of SERS include nanosphere dimers, individual nanocubes, nanotriangular arrays, nano-pyramid shells, individual and assembly of nanorods, nanowires, and nanotips, and some unconventional nano-architectures. Challenges in fundamental and application aspects of SERS remain for future research. © 2012 Society of Photo-Optical Instrumentation Engineers (SPIE). [DOI: 10.1117/1.JNP.6.064503]

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1 Introduction

One of the most important aspects of nanoscale materials is that many of its physical properties can be dramatically tuned by altering its size, shape, and morphology. In recent years, various new tools and techniques have emerged to fabricate and visualize nanomaterials.1 This has led to better understanding of physical and chemical properties of nanomaterials, and has further motivated research in various directions. The preparation of nanostructures can be broadly classified in to two categories: the top-down approach and the bottom-up approach. In the top-down approach, such as electron beam lithography,2 the starting point is a bulk material which is further processed by the electron beam to create nanoscale entities. In contrast, the bottom-up approach, such as chemical synthesis or self assembly,3 starts with molecular entities and builds up the nanomaterials. Each approach has its advantages and shortcomings, but can also be combined to prepare nanomaterials with unique properties.4,5

Of the many kinds of nanomaterials, metal nanostructures have been extensively studied in the context of their optical properties.6 The interaction of light with noble metals, such as silver, gold, and copper, has been a topic of research for number of years,6,7 but in last couple of decades there is a surge of interest6–10 in understanding how light interacts with metallic nanostructures. One of the main reasons for this is the plasmonic property of metallic nanostructures in and around the visible frequency spectrum. Plasmons are essentially the coupled oscillations of light and free electrons at the metal-dielectric interface. These coupled oscillations facilitate optical fields that can be used for propagation and localization of light beyond the diffraction limit. In the context of plasmons there are two fundamental excitations: surface plasmon polaritons (SPPs) and localized surface plasmons (LSPs). SPPs are propagating plasmons and can be
harnessed for various applications, including nanophotonic waveguides. LSPs facilitate localized optical fields confined to nanoscale volumes, and hence are good candidates for nano-optical sensing.

Various optical processes of molecules such as fluorescence and Raman scattering can be influenced by the localized optical fields created by LSPs. Important aspects of molecular spectroscopy and imaging such as spectral intensity, spatial and temporal resolution can be greatly influenced with the assistance of plasmonic nanomaterials. This has led to the emergence of a variety of optical spectroscopy techniques such as metal enhanced fluorescence, plasmon resonance energy transfer, and surface enhanced Raman scattering (SERS). Among them, SERS has emerged as very promising spectroscopy method with single molecule sensitivity and chemical specificity.

A variety of plasmonic nanostructures can improve the capabilities of SERS towards single molecule detection limits and towards spatial resolution of few nanometres. The motivation behind this article is to review a few recently studied plasmonic nano-architectures in the context of fundamental and application aspects of SERS.

2 Brief Overview of Surface Enhanced Raman Scattering

Raman scattering of molecules is an inelastic scattering process whose cross-section is around $10^{-29} \text{ cm}^2/\text{molecule}$. When compared to cross-section of other optical processes, such as fluorescence ($10^{-19} \text{ cm}^2/\text{molecule}$), Raman scattering is a weak phenomenon. This hindered the usage of Raman scattering in applications where the background fluorescence was eminent. One of the effective ways to overcome this disadvantage is through surface enhanced Raman scattering (SERS). Upon adsorption of molecules on plasmonic nanostructures, the Raman signal intensity can be enhanced by many orders of magnitude. This phenomenon is generally called as surface enhanced Raman scattering and has emerged as one of the most active fields of research in plasmon enhanced optical spectroscopy.

The enhancement in the Raman signal was first observed by Fleischmann et al. in 1974 on roughened silver electrodes, and the increment in the Raman signal was attributed to a large number of molecules on the corrugated surface of the electrode. In 1977, two different reports by Jeanmarie et al. and Albercht et al. showed that an enhancement in the Raman signal was due to a localized electromagnetic field around the metallic nanostructure. Since then, there has been an enormous amount of work in SERS, especially in the context of its applications in molecular detection and sensing. The general consensus is that there are two important mechanisms underlying SERS. First, and the dominant contribution towards enhancement is due to electromagnetic enhancement, where the optical field facilitated by localized plasmon resonance of metallic nanostructure increases the Raman signal intensity. The other contribution towards enhancement in SERS is due to the chemical enhancement mechanism, where the charge transfer mechanism between the adsorbed molecule and metal plays a critical role in enhancing and modifying the modes of molecular vibration.

One of the important parameters to characterize SERS substrates is to calculate the enhancement factor. The total enhancement in SERS is the product of incident electric field intensity enhancement $[(E(\lambda_{\text{inc}}))^{2}$ and radiated field intensity enhancement $[(E(\lambda_{\text{rad}}))^{2}$, where $\lambda_{\text{inc}}$ and $\lambda_{\text{rad}}$ are the incident and radiated wavelengths, respectively. If the wavelength of radiation from the SERS substrate is almost equal to the incident radiation (i.e., small values of Stokes shift) and if the losses are minimal, then the Raman enhancement factor can be approximated to be $[(E(\lambda_{\text{inc}}))^{4}$. A rigorous theoretical justification for the $[(E(\lambda_{\text{inc}}))^{4}$ enhancement can be found in Ref. A good SERS substrate usually has enhancement factors between the values of $10^6$ to $10^{11}$. A comprehensive study of SERS enhancement factors can be found in Ref. 29.

Another important concept is the SERS hot spot, which are locations in vicinity of the plasmonic nanostructures where the local optical field is enhanced tremendously when compared to its surrounding. Any molecule in an SERS hot-spot will exhibit an enormous enhancement in its Raman scattering signal. One of the important aspects of single molecule SERS is to localize molecules in SERS hot-spots leading to high sensitivity.
3 Plasmonic Nano-Architectures for SERS:

To facilitate SERS hot-spots, plasmonic nanostructures used as SERS substrates have to be designed in such a way that their geometrical features and arrangement can lead to maximum optical field, and hence maximum Raman signal enhancement. The focus of this review is to discuss some recent developments on plasmonic nano-architectures that exhibit SERS hot-spots.

3.1 Nanospheres

Chemically synthesized gold and silver nanoparticles of spherical geometry are the one of the oldest and most popular substrate in SERS studies. Their preparation is simple, cost-effective, and have been adapted for various SERS-based applications. The most common strategy to prepare them is to reduce metal salt with a relevant reducing agent and a capping agent. There are two methods of preparation of plasmonic nanoparticles that are extensively employed in SERS: 1. the Lee and Meisel method, which is based on citrate reduction of either \( \text{AgNO}_3 \) or \( \text{HAuCl}_4 \) and the resultant silver or gold nanoparticle has an average size of around 60 nm; or 2. the Creighton method, which uses ice-cold sodium borohydride to reduce \( \text{AgNO}_3 \) or \( \text{HAuCl}_4 \) and leads to nanoparticles of average size around 20 nm. Both these methods give excellent enhancement in Raman signature and have been employed in various SERS experiments.

Although individual nanoparticle themselves facilitate Raman enhancement, it is the junction of these nanoparticles which provide enhanced optical fields that makes single molecule SERS based detection a possibility. This has motivated various researchers to systematically study the dimer and metal junction nano-lens structures of plasmonic nanoparticles. The gap junction between the nanoparticles is essentially an SERS hot-spot. Any molecule in this junction is subjected to an enormous electric field, and hence their Raman scattering signals are enhanced by many orders of magnitude. In recent years, many innovative methods have been employed to produce plasmonic nano-dimers. For example, Li et al., have introduced a simple chemical synthesis method that can generate dimers of silver nanospheres (Fig. 1(a)). Their design yielded dimers of single crystal silver nanosphere (~30 nm in diameter) and with a gap of around 2 nm. Such controlled and repeatable procedures provide well-defined systems to study SERS hot spots. The authors recorded SERS spectra of isolated nanoparticles, well-separated nanoparticles, and closely interacting dimer structures, as shown in Fig. 1(b). They observed that the molecular signature was evident only in the dimer configuration indicating that the contribution of the gap junction facilitates enhanced optical field leading to SERS signature of the molecule.

To facilitate SERS hot spots on individual nanoparticles, sharp metallic features can be incorporated on the surface of nanospheres. Recently, such nanostructure, usually called as spiked nanoparticle or nanostars, have been utilized to obtain large electric field enhancements.

![Fig. 1](https://www.spiedigitallibrary.org/journals/Journal-of-Nanophotonics on 13 Jun 2020 Terms of Use: https://www.spiedigitallibrary.org/terms-of-use)
Another important category of nanoparticles are the core-shell nanostructures, or the nanoshells. One of the major advantages of the shell-based nanoparticle is the ability to tune the plasmon resonance by tuning the physical and chemical parameters of both the shell and the core substance. Such nanoshell geometries have now found applications as tunable SERS substrates. An added advantage of this configuration is that two different kinds of nanomaterials can be incorporated as core and shell. For example, one can synthesize a nanoparticle with magnetic core and a plasmonic shell, thereby making the nanoparticle not only sensitive to light but also an external magnetic field. Such magnetic core metallic nanostructures can be utilized as probes for magnetic resonance imaging (MRI), which is an important diagnostic tool. Due to their versatile optical properties, nanoshells also have good potential as probes for photothermal treatment of cancer, as revealed recently.

3.2 Nanocubes

Precisely shaped plasmonic nanocubes have been recently synthesized and studied in the context of SERS. One of the advantages of nanocubes is their equidistant sharp edges that facilitate highly localized optical fields, which can be harnessed to enhance Raman scattering signatures. In order to test the effect of edge sharpness, Xia and co-workers prepared isolated Ag nanocubes with sharp and truncated edges as shown in SEM images of Fig. 2. A thin layer of 1,4-benzenedithiol (1,4 BDT) was adsorbed on these nanocubes and a linearly polarized Raman excitation laser of 514 nm was incident on these individual nanocubes and the polarization was varied as shown in the Fig. 2. The Raman spectra in Fig. 2(a)–2(c) represent the polarization dependent SERS signatures from sharply-edged Ag nanocubes corresponding to the directions indicated on the SEM images. The data indicated that when the polarization is aligned along one of the edges of the nanocube, the Raman signal intensity is enhanced. In contrast, Fig. 2(d)–2(f) shows that when the edges are truncated, the SERS signature is independent of the polarization of Raman excitation. This observation was also supported by polarization dependent discrete dipole approximation calculation of near-fields, which indicated that field enhancement along the diagonal of the sharp-edged nanocubes was greater for the aligned electric field.

![Fig. 2](https://www.spiedigitallibrary.org/journals/Journal-of-Nanophotonics) Normalized SERS spectra of 1,4-BDT adsorbed on a Ag nanocube with sharp corners [left panel, (a)–(c)] and a highly truncated Ag nanocube [right panel, (d)–(f)], at various angles relative to the polarization of the excitation laser. Each SEM image shows the nanocube used and the arrows indicate the polarization directions of the incident laser corresponding to the spectra. The scale bar applies to both images. Reproduced with permission from Ref. 68.
Camargo et al.\textsuperscript{74} have further extrapolated this work to show that SERS hot-spots can be isolated and probed by bringing two silver nanocubes close to each other. By employing a technique based on plasma etching of molecules, they isolated the molecules from all parts of the nanocube dimer except for the gap between them, thereby exclusively measuring the SERS signal between the coupled nanocubes. Such innovation can be further harnessed and applied to other plasmonic dimer nanostructures, where the SERS contribution from the gap junction is to be probed exclusively. Recently, Rycenga et al.,\textsuperscript{78} have also shown that single silver nanocubes placed on metallic substrates can facilitate single molecule SERS sensitivity. Their strategy was to use coupling between the sharp edges of the nanocube with metallic layer underneath it. This coupling effectively provides a reproducible hot-spot with large field enhancement, thereby leading to ultrasensitive SERS effect on a consistent basis. Plasmon coupling effects have also been observed\textsuperscript{75} in two-dimensionally (2-D) ordered gold nanocubes on indium tin oxide substrates indicating that nanocube geometries are good substrates to study certain fundamental aspects of plasmonics and SERS.

3.3 Nanotriangle

Another important category of plasmonic nanostructure that has been studied in the context of SERS is nano-triangular patterns.\textsuperscript{79–81} Nanotriangles have sharp edges at their vertex which facilitate localized optical fields, and hence can be harnessed for SERS applications. One of the effective ways to produce patterns of nanotriangle pioneered by Van Dyne and co-workers\textsuperscript{82,83,84} is to employ nanosphere lithography (NSL), which is an inexpensive, versatile, and inherently parallel lithography method. Briefly, the procedure of NSL is as follows. First, size-monodisperse nanospheres are self assembled on a substrate such as glass to form a 2-D colloidal crystal deposition mask [see Fig. 3(a)]. Second, upon solvent evaporation, the desired metal is deposited either by thermal evaporation or electron beam deposition, or pulsed laser deposition through the nanosphere mask. Next, the nanosphere mask is removed by sonication of the sample in a solvent, thereby leaving behind the metal deposited in the interstitials of the nanosphere mask. A typical sample prepared using NSL is shown in Fig. 3(b). One of the major advantages of this technique is that it can be modified to vary the size, shape and arrangement of

![Image of nanotriangles and AFM image](https://www.spiedigitallibrary.org/journals/Journal-of-Nanophotonics)

**Fig. 3** Schematic illustration of a colloidal crystal mask (a) and representative AFM image (b) of Ag nanotriangular structures. Reproduced with permission from Ref. 82. (c) SERS enhancement achieved from R6G adsorbed on ordered 200 nm Ag nanocluster regions (gray trace) in comparison with amorphous Ag “film” regions (black trace) within the same sample. The signal increase is \(	imes 3\). Reproduced with permission from Ref. 90.
the plasmonic nanostructures. Schmidt et al. employed NSL to study SERS properties of triangular shaped silver nanocluster arrays. They made direct comparison of rhodamine 6G SERS signals between ordered nanocluster region and amorphous Ag regions in the same sample [Fig. 3(c)]. The authors found that for the case of nanotriangles, the SERS signal intensity was enhanced by a factor of 3 compared to amorphous Ag regions, indicating large electromagnetic fields facilitated by the edges of the nanotriangles.

Another category similar to triangular geometry is the plasmonic nanopyramids. Stoerzinger et al. have recently screened individual gold nanopyramid shells and their assembly in a systematic way. The authors employed fabrication methods involving phase-shifting photolithography, etching, E-beam, and lift off (PEEL) procedures to create plasmonic nanopyramids, and by controlling the evaporation rates of the solvent of nanopyramids, they could assemble them in three different categories: isolated single pyramids, lower order assembly, and higher order assembly (Fig. 4). They observed that as the order of assembly increased, the Raman signal intensity increased. They supported their experimental data with numerical simulations that indicated enhanced electromagnetic field between adjacent particle faces in the higher order structure. Such hierarchical nanostructures are useful to produce few-particle localized electromagnetic fields in a controlled fashion.

![Fig. 4](image-url)

**Fig. 4** (a) (top) SEM and (bottom) corresponding Raman images of the 1624 cm$^{-1}$ MB vibrational mode intensity from a single tip-down pyramid (TD), a low-order dimer of pyramidal nanoshells (L2), and a high-order dimer of pyramidal nanoshells (H2). The scale bar applies to all images. (b) Dark-field scattering spectra of TD, L2, and H2. (c) Raman spectra corresponding to the most intense point of the Raman image in (a). Reproduced with permission from Ref. 91.
3.4 Nano-Rods

Nanorods are one of the extensively studied anisotropic plasmonic geometries. Various research groups have studied optical properties of gold nanorods and have utilized them for a variety of applications. Owing to their anisotropic geometry, nanorods exhibit two plasmon modes: transverse and longitudinal. The transverse plasmon mode is at lower wavelength and the longitudinal mode is at higher wavelength. The longitudinal plasmon mode is sensitive to the aspect ratio of the nanorod, and hence can be utilized in wavelength dependent studies. One of the important issues in plasmonics is to understand how plasmons in individual nanostructures can be coupled to obtain enhanced electromagnetic interactions. In this context, gold nanorods have been employed to study the plasmon coupling in anisotropic nanostructures. Kumar and Thomas recently investigated the SERS properties of individual nanorods and their assembly. The authors chemically couple the 111 plane at the edges of Au nanorods with linker molecules and show that the SERS signature is enhanced when the rods are in dimer geometry (Fig. 5). They further show that end-to-end coupling can be extended to form a linear chain of Au nanorods leading to an enhanced signature in Raman intensity. Such linear chains of anisotropic nanorods are good candidates to study sub-diffraction plasmonic coupling and electromagnetic transport.

Since Au nanorods are anisotropic in their geometry, they are sensitive to linear polarization of incident radiation. El-Sayed and co-workers have utilized this polarization dependence to show that Au nanorods conjugated with antibodies can be aligned and assembled on the surface of cancer cells. They further show that such aligned assembly of nanorods can be used as cancer diagnostic markers. Such innovations have opened up avenues for biological applications of nanorod based SERS.

3.5 Nano-Wires

Plasmonic nanowires are unique substrates as they support propagating plasmon polaritons. They sustain plasmon modes with wavelengths shorter than the incident light. Interestingly, chemically synthesized plasmonic nanowires, such as Ag nanowires, show minimal plasmon damping due to well-defined crystal structure, and hence have been employed in studies of plasmon polariton based waveguiding. In the context of SERS, coupling of an individual nanowire to another plasmonic nanostructure creates a spatially confined SERS hot spot at the junctions. One of the recent innovations in nanowire-based SERS is the remote excitation of Raman scattering. The authors have shown that the propagating plasmon property of the plasmonic nanowires can be used to perform Raman scattering at a remote location (see Fig. 6). By exciting the plasmon polariton at one end of the nanowire, a source of light can be created at the distal end of the nanowire, which further can be utilized as a Raman excitation source. The advantage of this technique is that the Raman

![Fig. 5 TEM images of gold nanorods (a)–(c) in isolated, dimer, and chain configurations; and Raman spectrum of molecule bipy-DT (d)–(f) at various stages of plasmon coupling. Reproduced with permission from Ref. 104.](https://www.spiedigitallibrary.org/journals/Journal-of-Nanophotonics on 13 Jun 2020 Terms of Use: https://www.spiedigitallibrary.org/terms-of-use)
excitation source is confined to the apex of the nanowire, and is devoid of background radiation of incident laser excitation (Fig. 6). Thus by separating the channels of excitation source and Raman scattering source, molecules in the vicinity of the distal end of the nanowire can be probed at high spatial resolution. Nanowires have also been utilized to create SERS hot-spots. Recently, Chikkaraddy et al. have shown that by coupling two plasmonic nanowires in an end-to-end configuration, SERS hot-spots can be created at the nanowire junction. The advantage of this method is that the end-to-end coupling configuration not only facilitates SERS hot-spot, but also provides SPP based light propagation capability from one end of the nanowire pair to other distal end.

3.6 Nanotips

Although SERS microscopy facilitates large scale enhancement factors, it is constrained by the diffraction limit, and hence cannot spatially resolve entities smaller than the Raman excitation wavelength. Tip enhanced Raman scattering (TERS) has recently emerged as method to perform vibrational spectroscopy beyond diffraction limit. The technique employed in TERS is essentially borrowed from apertureless near-field optical microscopy, where a sharp metallic tip is brought into close proximity of the sample deposited on the surface. The tip facilitates the localized optical field which interacts with molecules beneath it, thus enhancing the Raman signal intensity. One of the important components in TERS is the morphology and composition of the tip. The radius of curvature of the apex of the tip determines the spatial resolution, and hence it is necessary to fabricate high quality plasmonic nano-tip. The most popular configuration of the tip used in TERS is a gold or silver nano-tip. This is usually prepared by chemical etching of wire. Another method to perform TERS is to employ a plasmonic nanoparticle attached to dielectric tip.

In recent times, an alternative method based on adiabatic focusing of plasmons at the apex of the tip has been introduced to perform TERS by Raschke and co-workers. The advantage of this method is the non-local generation of nanoscale Raman excitation source which facilitates intrinsic background suppression of Raman pump beam. This was achieved by cutting a grating on a chemically etched plasmon nano-tip (Fig. 7) and exciting it with Raman pump beam. Propagating plasmons are generated due to this coupling, and further propagate towards the apex of the tip, thus creating a nanoscale light source at the discontinuity. This light source

![Fig. 6 Transmission (a), wide-field illumination (b), and focused laser excitation (c) images of a NPs-pATP-nanowire exhibiting seven SERS hot-spots. Focused excitation was at the left end of the wire in panel (c). (d) 3-D view of the image in panel (c). Reproduced with permission from Ref. 122.](https://www.spiedigitallibrary.org/journals/Journal-of-Nanophotonics)
can be harnessed to perform Raman spectroscopy as shown in Fig. 7(c). Adiabatic nano-focusing is an efficient method of converting far-field optical signal into near-field localized light source, and has immense potential to perform background-free nanoscale chemical spectroscopy and imaging.

Recently, Capasso and co-workers have also shown that optical antenna arrays can be fabricated on an optical fiber and can be utilized as SERS micro-probes, thus expanding the prospects of in situ SERS detection.

4 Unconventional Nano-Architectures for SERS

Until now we have discussed plasmonic substrates that are conventionally used for SERS applications. In recent times, there have been innovations on plasmonic nanostructures designed either to probe specific issues in SERS or integrate SERS with other experimental modules. Below we briefly discuss a few cases:

- **Electrostatic force based SERS**—Lacharmoise et al. have come up with an electro-chemistry based approach to guide charged molecules in a solution towards SERS active nanostructures. The authors show the possibility to selectively enhance SERS signal of various types of dye molecules according to their charge. They prepared an electrolytic cell in which charged species were selectively attracted towards SERS substrate by applying a direct current (DC) electric field. Such attracted species give rise to enhanced Raman signatures. The authors envisage their method to be useful in single molecule SERS situations where precise placement of molecules in hot-spot is a necessity.

- **Shell-Isolated Nanoparticle based SERS**—Although SERS is a powerful analytical technique with single molecule sensitivity, it critically depends on interaction of molecules with metallic nanostructures. Gaining control over this interaction is one of the challenges in SERS, and one of the methods towards this goal is the shell-isolated nanoparticle approach innovated by Tian and co-workers. In this method, the Raman signal is...
enhanced by gold nanoparticles with an ultrathin silica or alumina shell. In order to probe the surface of interest, a thin layer of such core-shell nanoparticle is spread as ‘smart dust’. The advantages of this method are: 1. the aggregation of nanoparticles is avoided due to thin protective shell, and 2. the metallic probe is not in direct contact with the probed material. The proof of concept of this SERS technique has been shown to enhance signatures of molecules on yeast cells and citrus fruits with pesticide residues.152

• **Double resonance based SERS**—There are three important spectral regions in Raman spectroscopy: first is the Raman excitation region, second is the Stokes intensity region, and third is the anti-Stokes intensity region. In order to enhance the Raman intensity signatures via SERS, it would be beneficial to have plasmon resonances that overlap with these regions. By tuning the geometrical arrangement of plasmonic nanostructures, Cohen and co-workers154–157 have developed double-resonance SERS substrates. One of the methods154 to prepare double resonance substrate is to deposit gold nanodisk on SiO₂ coated gold film. The gold nanodisk facilitates localized surface plasmon, and the dielectric-metal interface facilitates surface plasmon polaritons. By varying the experimental parameters, such as the geometrical arrangement of gold nanodisk and the angle of incident light, one could fabricate plasmonic substrates with double resonances. Another method155 is to use a pair of different shaped plasmonic nanostructures which inherently show plasmon resonances at different locations of the spectra. Such double resonance SERS substrates have shown to have better enhancement capabilities154,155 compared to single resonance substrates.

• **SERS in optofluidic chip**—Performing Raman scattering in lab-on-chip configuration has various advantages such as minimal sample requirement, compactness, and cost-effectiveness. Integration of SERS with optofluidic configurations is an active area of research.158–166 Most of the techniques either use nanoparticle-based microfluidic systems167–171 or embedded plasmonic substrates172,173 in fluidic channels to attain high sensitivity and chemical specificity. The envisaged application includes environmental monitoring, clinical diagnostics, forensic investigations, and homeland security.

5 **Future Directions and Conclusion**

SERS is now a matured research field that requires a multidisciplinary approach and fosters the combination of ideas from physics, chemistry, biology, and engineering. Although SERS is now routinely used as analytical tool for characterization of plasmonic substrates, there are some issues that require greater attention, such as:

1. Design and execution of a plasmonic substrates with consistent Raman enhancement factors.
2. Better understanding of the physics behind the SERS hot-spot mechanism.
3. Understanding the mechanism behind the chemical enhancement factor and how it can be harnessed for applications.
4. Plasmon-assisted vibrational pumping mechanism and how it can be used to get deeper insight into molecular structure and function.

Recently, there are a few developments in other research areas where SERS may play an important role. Following are a few examples:

1. There is an active search for new and better plasmonic materials.174 It has been postulated174,175 that nanomaterials made of metal oxides, noble-transition alloys, alkali-noble inter-metallic compounds, semiconductors, and graphene can exhibit plasmonic properties. Sol-gel based photonic structures176 have also been explored and shown to exhibit light management capabilities that can be adapted to perform SERS. Such materials will expand the avenues for SERS substrates and can be utilized for specific applications.
2. There has been tremendous progress made in the field of ultra-fast optics which has led to laser sources that can provide very high temporal resolutions (femto-seconds to atto-seconds). Concomitantly, there has been great progress made in scanning probe techniques that can provide spatial resolution up to a single atom. Combining both
techniques\textsuperscript{177,178} can greatly influence the spatial and temporal resolution of chemical imaging methods, such as SERS. Non-linear Raman scattering techniques, such as coherent anti-Stokes Raman scattering (CARS) and stimulated Raman scattering can also be combined with the concepts of plasmonics. Recently, there have been a few reports\textsuperscript{177,179–183} that show plenty of promise in this direction.

3. Gaining new insight into the light-matter interaction has been one of the important issues in physics, and the question is how SERS can contribute to this. In recent times, SERS has been able contribute towards the understanding of ultrafast non-radiative decay rates of single molecules on metallic surfaces.\textsuperscript{184} Galloway et al. have quantified the total decay rate of single emitters close to the metallic surface, which is difficult to estimate using conventional approaches.\textsuperscript{184} In a different study, Rao et al.\textsuperscript{185} have experimentally measured mechanical forces induced by SERS on an optically trapped dielectric sphere. The authors revealed a correlation between the enhancement of the Raman signal and the average position of the trapped bead indicating momentum transfer of the emitted Raman photons on to the trapped bead.

4. Single molecule junction is one of the important components of molecular electronics that is being studied. A few research groups\textsuperscript{186,187} have employed SERS as an effective method to probe the structure of molecular junctions. Recent developments by Liu et al.\textsuperscript{187} includes a technique called as ‘fishing-mode’ tip enhanced Raman spectroscopy that can measure electrical conductance and Raman spectroscopy signals of a single molecule in a junction. Ward et al.\textsuperscript{186} have used SERS to determine the effective temperature of a biased metallic nano-junction decorated with molecules, which leads to the better understanding of nanoscale heating mechanisms.

Thus, we see how interaction of molecules with plasmonic nanomaterials has opened up new research avenues. Techniques such as SERS contribute to our understanding of both the plasmonic nanomaterial and the molecule interacting with it, thus making them an extremely useful tool in nano-optics and spectroscopy. In the context of nano-science and -technology, Richard Feynman had prophetically predicted that, ‘There’s plenty of room at the bottom’.\textsuperscript{188} Plasmonic nanomaterials combined with nano-optical techniques have shown how insightful his prediction was.

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