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Recent Developments on Metal Nanoparticles for SERS Applications

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Abstract

Surface-enhanced Raman spectroscopy (SERS) is a popular and potential area of investigation in many applications because of its high sensitivity even at mono-molecular level. SERS substrates that typically composed of metal nanostructures can enhance the Raman signal level up to several orders of magnitude, making it a powerful analytical tool in chemical and biomedical applications. The present book chapter is aimed to provide insight about design and latest developments on metal nanoparticles and their application in the field of SERS. The chapter starts with the discussion of basic concept and theories of Raman scattering and SERS based on examples from recent research. It then primarily reviews various potential metallic nanostructures and their geometry as SERS substrates, followed by recent reports and theories on application of bimetallic nanostructures for the purpose. Toward the end, we briefly discuss the research progress in designing hybrid SERS substrates using emerging materials like photonic crystals and graphene.

Keywords: SERS, Raman spectroscopy, plasmonic materials, vibrational spectroscopy, metal nanostructures, electromagnetic enhancement

1. Introduction

Raman spectroscopy is a type of vibrational spectroscopy which is based on inelastic scattering of photons from a chemical or biological molecule, causing changes in the scattered photon frequency that is proportional to the difference in the vibrational energy levels in the molecule. It can therefore give us various information about the target molecule, like chemical composition and structure of the molecule, its surface information including surface or interfacial reactions, impurity identification and so on [1, 2]. The phenomenon of Raman scattering was discovered in 1928 by Sir Chandrasekhara Venkata Raman, for which he received Nobel prize in physics in 1930. In his discovery, he observed that certain molecules scatter a small portion

of incident light at a different frequency, where the scattering is therefore inelastic type and the energy difference between the incident and scattered light is proportional to the vibrational frequency of the molecule [3]. Although he used sunlight to explain his discovery, modern day Raman spectroscopy uses high energy monochromatic laser light to excite samples.

Figure 1 illustrates the Raman effect in terms of an incident laser light and the vibrational energy levels of a sample. Once the incident light hit the sample, the energy can be absorbed, transmitted or scattered by the sample. The major portion of the scattered light from the sample carry same frequency (ω_{inc}), representing the Rayleigh scattering effect. However, about one in every million photons scatter inelastically from the sample with an energy different from the incident energy, representing the Raman scattering effect. This energy difference (ω_{vib}) is associated with the molecular vibrations of the sample and is unique for every molecule resulting in exclusive Raman spectrum for each sample providing precise spectral fingerprint of the samples [2]. Inelastically scattered photons typically carries lower frequencies ($\omega_{inc} - \omega_{vib}$) which are called as '*Stokes scattering*'. However, if the molecular vibrational states are significantly excited with high energy, then the inelastic scattering can occur at higher frequencies ($\omega_{inc} + \omega_{vib}$) than the incident frequency. In that case, the vibrational frequency gets added to the incident frequency and is called as '*anti-Stokes scattering*'.
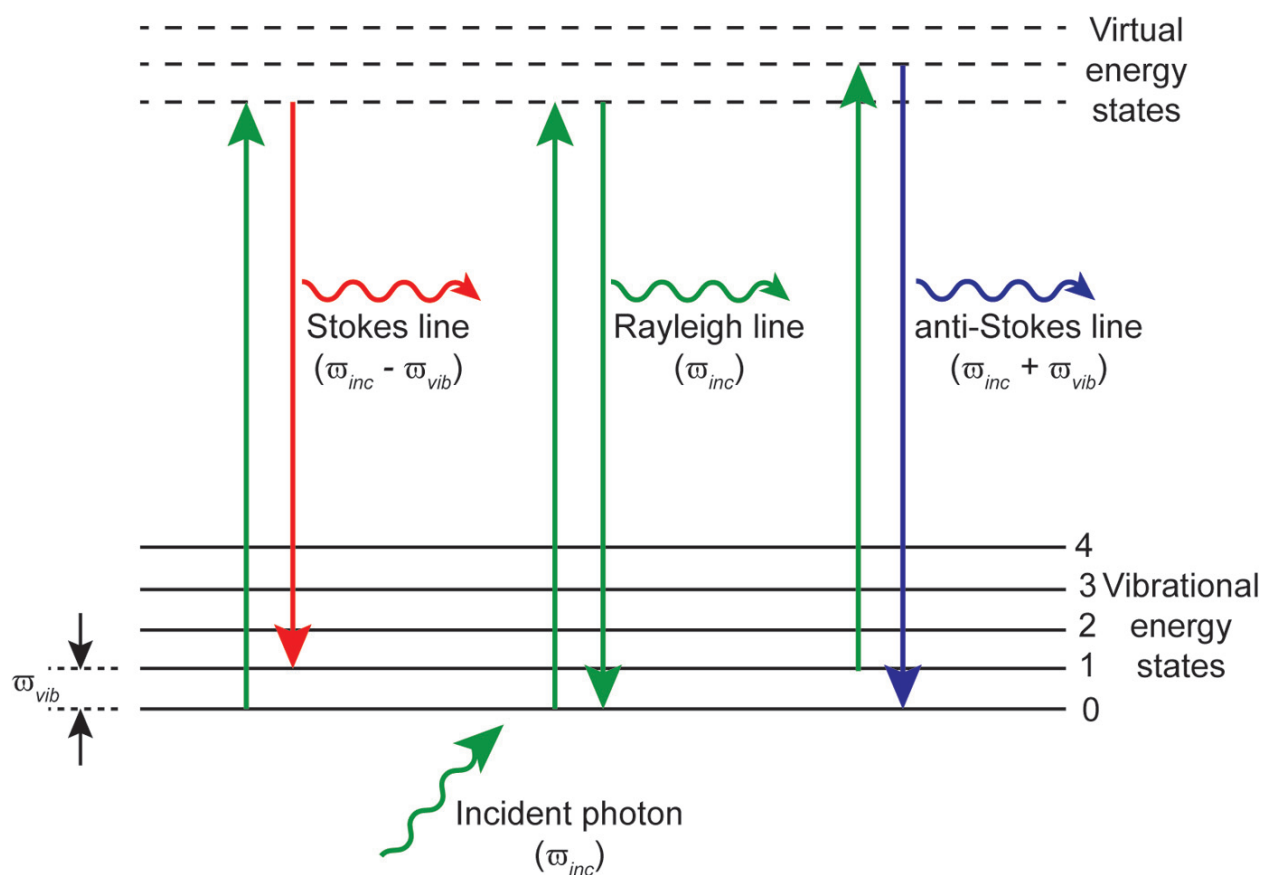

Figure 1. Schematic representation of the concept of Rayleigh, Stokes and anti-Stokes scattering when an incident photon with frequency ω_{inc} interacts with a sample molecule with vibrational frequency ω_{vib}. In the case of Stokes scattering, the molecule absorbs energy resulting in the reduction in the scattered energy, while for anti-Stokes scattering, the molecule loses energy resulting in an increased in the scattered energy.

Since only a small fraction of incident photons show inelastic scattering, the Raman signal is therefore a very weak signal which sometimes can be very difficult to detect even by using latest detector technologies available till date. Therefore, a new technique was developed in 1973 by Martin Fleischmann, Patrick J. Hendra and A. James McQuillan at the University of Southampton, UK to enhance the Raman signal of a molecule by adsorbing it onto a rough metallic surface. Since the technique is surface sensitive, it was termed as '*surface-enhanced Raman scattering*' or '*surface-enhanced Raman spectroscopy*' (SERS). However, the mechanism behind SERS was explained independently by two research groups later in 1977. Van Duyne and coworkers linked the Raman signal enhancement to an electromagnetic effect, while Creighton and coworkers proposed a charge transfer mechanism for the enhancement [4].

At the beginning, this chapter will briefly discuss the SERS mechanism based on both the proposed routes, followed by discussions on some recent developments in applications of noble metal nanostructures in terms of SERS signal enhancement. Toward the end, the chapter will also briefly touch upon some emerging nonmetallic materials which have potential SERS applications.

2. Principle of SERS

The mechanism behind SERS enhancement is always an area of interest for several researchers to understand and explain the phenomena. There are two commonly accepted theories which were proposed and demonstrated by various groups [4, 5]. The first one is the electromagnetic (EM) enhancement and the second one is chemical enhancement. In any cases, samples are typically placed on or at a proximity of a nanostructured metallic substrate, known as SERS substrate, where the enhancement occurs as a result of the interaction among the incoming light, the target sample molecule and the metallic surface. Nanostructures of noble metals, such as silver and gold, are common examples for SERS substrates since they do not have any Raman active modes for themselves.

The EM enhancement occurs when excitation of localized surface plasmon resonance (LSPR) modes of the metallic nanostructures occur at the resonance frequency of the incoming light, which can be considered as an EM wave [6]. At this condition, localized dipoles are created resulting in an enhancement in the localized electric field around the metal nanostructure (**Figure 2a**). The magnitude of such induced dipoles is dependent on the incident electric field strength (E_{inc}) and the polarizability of the metal structure (α_{metal}) [7]. The enhanced localized electric field around the metal nanostructure then interacts with the sample molecule placed near the metallic surface and results in another induced dipole in the target molecule. The induced dipole in the target molecule has three possible dipole components: a dipole with similar angular frequency (ω_{inc}) as the incident EM radiation, a second component with slightly lower angular frequency ($\omega_{inc} - \omega_{vib}$) than the incident EM radiation, and a third component with slightly higher angular frequency ($\omega_{inc} + \omega_{vib}$) than the incident EM radiation, where the difference in the angular frequencies in the last two components are proportional to the vibrational energy of the molecule. These three components therefore correspond to the Rayleigh, Stokes, and anti-Stokes scattering, respectively.
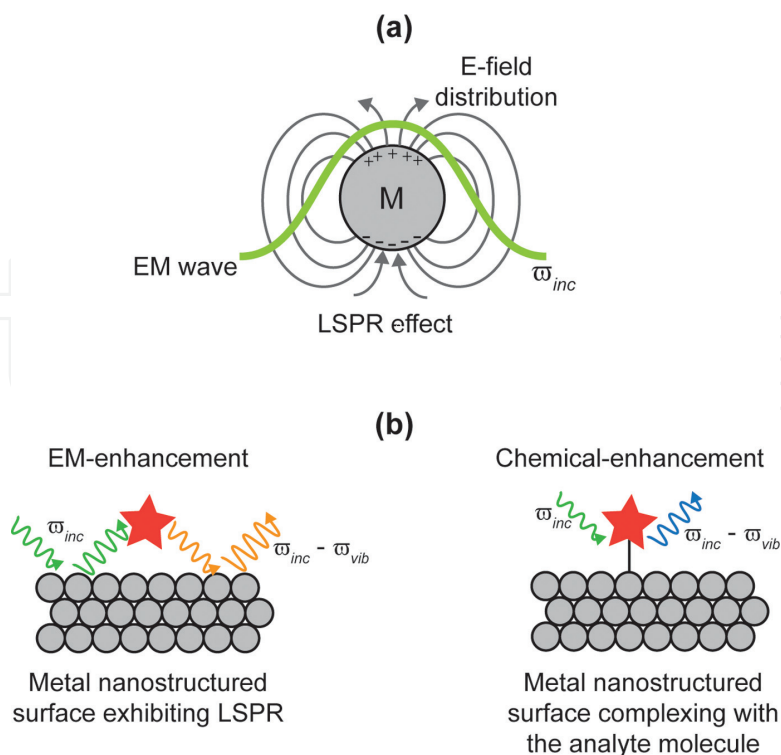
Figure 2. (a) Localized surface plasmon resonance (LSPR) effect exhibited by a metal nanoparticle (M) in the presence of an electromagnetic wave (EM wave) with frequency ω_{inc} resonating with the plasmon frequency. (b) SERS enhancement mechanism showing both electromagnetic (left) and chemical (right) enhancement of the scattering signal. In chemical enhancement, formation of substrate-analyte complex takes place leading to a change in the polarizability of the analyte molecule.

The chemical enhancement, on the other hand, involves enhancement through charge transfer mechanism between the substrate and the target molecule (**Figure 2b**) [8, 9]. Upon chemisorption of target molecules on the metallic substrate, new electronic states are formed having possible intermediate energies resonating with the resonance frequency of the metal. Under resonance, exchange of charges occurs between the substrate and the molecule resulting an enhancement in the Raman signal. However, chemical enhancement mechanism is molecule specific and typically shows lower enhancement factor (in the order of 10^3–10^5) compared to the EM enhancement, where the enhancement can be in the order of 10^8–10^{12} [10].

The SERS enhancement factor (EF_{SERS}) is therefore one of the major aspect to characterize SERS effect or a SERS substrate. The total enhancement factor is normally contributed by both the EM and chemical enhancements. The most widely used mathematical form for EF_{SERS} is given as:

$$EF_{SERS} = \frac{I_{SERS}/N_s}{I_{RS}/N_V} \qquad (1)$$

In Eq. (1), I_{SERS} denotes the intensity of the specific Raman band of the target molecule adsorbed on a SERS substrate, I_{RS} is the intensity of the same Raman band of the target molecule without any SERS effect, and N_S and N_V represents the average number of molecules in the scattering volume for the SERS and non-SERS Raman measurements, respectively. An

in-depth comprehensive study about the SERS enhancement factors considering several overlooked issues was reported by Ru et al. [10].

3. Preparation of SERS substrates

It is now clear that SERS enhancement is dependent on the interaction between the target molecule and SERS substrate. Therefore, preparation of the SERS substrate is crucial for the success of the SERS enhancement. The SERS enhancement is mainly contributed by EM enhancement, which is highly dependent on the size, shape and structure of the material used to prepare the substrate. Typically, nanostructured plasmonic materials, like gold (Au), silver (Ag) and copper (Cu), are used for the preparation of SERS substrates. However, application of Cu is limited since the material show oxidation problem in air. Gold and silver are, on the other hand, most widely used due to their high stability compared to copper and most importantly they have LSPR frequencies in the visible to NIR range where most of the Raman scattering occurs. In this part, we will therefore briefly describe the application of some of the promising plasmonic noble metals for SERS substrates.

3.1. Nanoparticles of plasmonic metals

Nanoparticles of noble metals are most commonly used materials for the preparation of SERS substrates, because of their LSPR properties. These properties are useful only when the materials are in nanoscale, that is, less than 100 nm in dimensions. Several papers are now available reporting the synthesis and development of noble metal nanostructures focusing on their tailored shapes and sizes for SERS applications. Colloidal monodisperse metal nanoparticles show high SERS enhancement due to the controlled size and shape of the nanoparticles. A systematic study on colloidal Ag nanostructures with sizes ranging from 60 to 100 nm showed dependency of the SERS enhancement on the shape and size of the nanoparticles [11]. It was found that EF_{SERS} improves with the increasing size of the nanoparticles from 60 to 100 nm, while cubical nanoparticles with sharp edges produced EF_{SERS} in the order of 10^5 when compared to the EF_{SERS} of almost spherical Ag nanoparticle (in the order of 10^4). The shape dependency of the EF_{SERS} is mainly due to the concentrated nonuniform electric field density (hot spots) near the sharp edges of the cubical Ag nanoparticle, whereas in case of the spherical nanoparticles the field spreads over the surface uniformly. For example, it has been shown that the strength of the hot spots can be altered by varying the shape of the colloidal nanoparticles from spherical to anisotropic shapes [12]. It was found that a spherical nanoparticle exhibits weak hot spot compared to an anisotropic particle resulting in improved EF_{SERS} from 10^4 to 10^7 making the anisotropic particles suitable for single molecule detection. The authors have also demonstrated that more anisotropy or higher aspect ratio of such colloidal metal nanoparticles can further improve the EF_{SERS} [13]. An enhancement factor as high as 10^{14} was also reported by using aggregated colloidal Ag nanoclusters [14, 15]. SERS application of colloidal gold (Au) nanoparticles was also explored by many researchers. The cost of gold is on the higher side compared to Ag, and gold typically results in moderate EF_{SERS} compared to Ag nanoparticles. However, Au has excellent biocompatible properties, which makes it a

suitable SERS candidate for biological samples. SERS properties of Au nanoparticles with different sizes (10–200 nm) and shapes (spherical, triangles, hexagons and pentagons) has been studied by Quester et al. [16]. Similarly, Liu et al. [17] has reported a laser irradiation rapid synthesis route of various shaped colloidal gold nanoparticles for SERS applications (**Figure 3**). Using the nanospheres of Au nanoparticles, they have successfully demonstrated detection of Rhodamine 6G (R6G) dyes at concentration levels as low as 10^{-11} M.
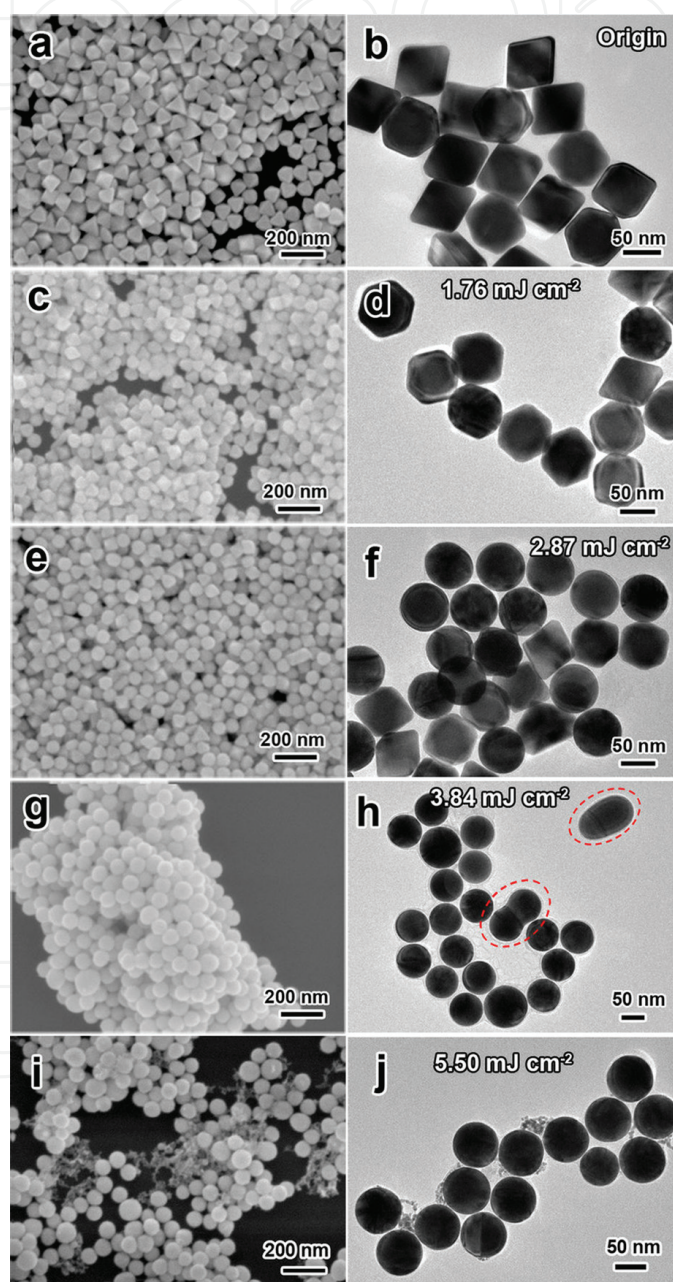
Figure 3. SEM and TEM micrographs of laser irradiated various shaped colloidal SERS Au nanoparticles. Au nanoparticles were prepared by a polyol route at 195 °C. (a, b) original octahedral nanoparticles and nanoparticles in (c, d), (e, f), (g, h) and (i, j) were irradiated with a Nd: YAG laser (532 nm, pulse duration: 10 s) operated at 20 Hz with laser fluences equal to 1.76, 2.87, 3.84 and 5.50 mJ.cm^{-2} respectively. Reprinted by permission from Macmillan Publishers Ltd.: Scientific Reports [17], copyright 2015.

The size of the metal nanoparticles also is another crucial factor contributing to the SERS enhancement. It is well known that for LSPR effect, the size of the metal nanoparticles should be comparable to or smaller than the wavelength of the incident light. However, at very small size the nanoparticles start to show poor polarization resulting in loss of LSPR properties, making them inoperable for SERS applications [18]. A recent study on the size effect of Ag nanoparticles on SERS showed reduction (in the order of 10^2) in the signal EF_{SERS} when particle size was reduced from about 65 to 35 nm [19]. Earlier, similar observations were reported for gold nanoparticles as well [20].

3.2. Bimetallic nanoparticles

As the name suggests, the bimetallic nanoparticles are composed of two types of metals atoms in various configurations. These bimetallic nanoparticles are not only interesting for SERS point of view, but also for their other tunable properties like catalytic, optical, and magnetic properties. There are two common configurations of bimetallic nanoparticles used for SERS applications, namely alloyed and core-shell nanoparticles. In the alloyed configuration, the two types of metals are mixed homogeneously at their atomic level and hence the surface of the nanoparticle contains both the metal atoms. The EF_{SERS}, in case of bimetallic nanoparticles, is dependent on both the composition and ratio of the bimetallic nanoparticle [21–24]. Alloyed Ag-Au hollow nanocubes have been reported by Li et al. [25] for SERS applications with EF_{SERS} in the order of 10^7, which was found to vary with varying configuration of the alloyed nanostructure (**Figure 4**). Sun et al. [26] has reported significant enhancement in the SERS signal for Au-Pd bimetallic flower shaped nanoparticles compared to the similar sized spherical Au-Pd nanoparticles. Application of Au-Pd alloyed nanoparticles for SERS with high EF_{SERS} was also reported. Lee et al. [27] has reported synthesis of hexagonal shaped Au-Pd alloyed nanoparticles with {110} facets exposed at the surface and demonstrated SERS enhancement at least twice than the regular spherical Au-Pd alloyed nanoparticles. It was proposed that the {110} facets of the hexagonal Au-Pd nanoparticles provide higher SERS activity through preferential adsorption of certain molecules at the {110} facets. On the other hand, Liu et al. [28] has reported nanoporous Au-Pd nanoparticles with enhanced SERS activity compared to the traditional Au based SERS substrates.

The core-shell bimetallic nanoparticles, on the other hand, have inhomogeneous distribution of the two metals, where one metal termed as *core* is completely surrounded by another metal termed as *shell*. Hence, only the shell metal is exposed at the surface of the core-shell nanoparticle. Both single and bimetallic core-shell nanoparticles have been reported for SERS applications [29]. In case of the single metallic core-shell nanoparticles, the core is primarily a plasmonic metal nanoparticle, such as Ag or Au, coated with a thin shell layer of non-plasmonic materials, such as silica. In such configuration, the plasmonic core is protected from degradation by the non-plasmonic shell which normally exhibits high chemical stability. Although the single metallic core-shell nanoparticles are not bimetallic system, they are still core-shell type nanoparticles exhibiting excellent SERS properties. An ultrathin silica or alumina shell coating on Au nanoparticles were reported to show significant improvement in the Raman signal [30]. Authors have demonstrated both contact and non-contact SERS modes for these core-shell nanoparticles, and showed that the thin shell layer isolates the plasmonic metal nanoparticle from the probed molecules preventing any unwanted
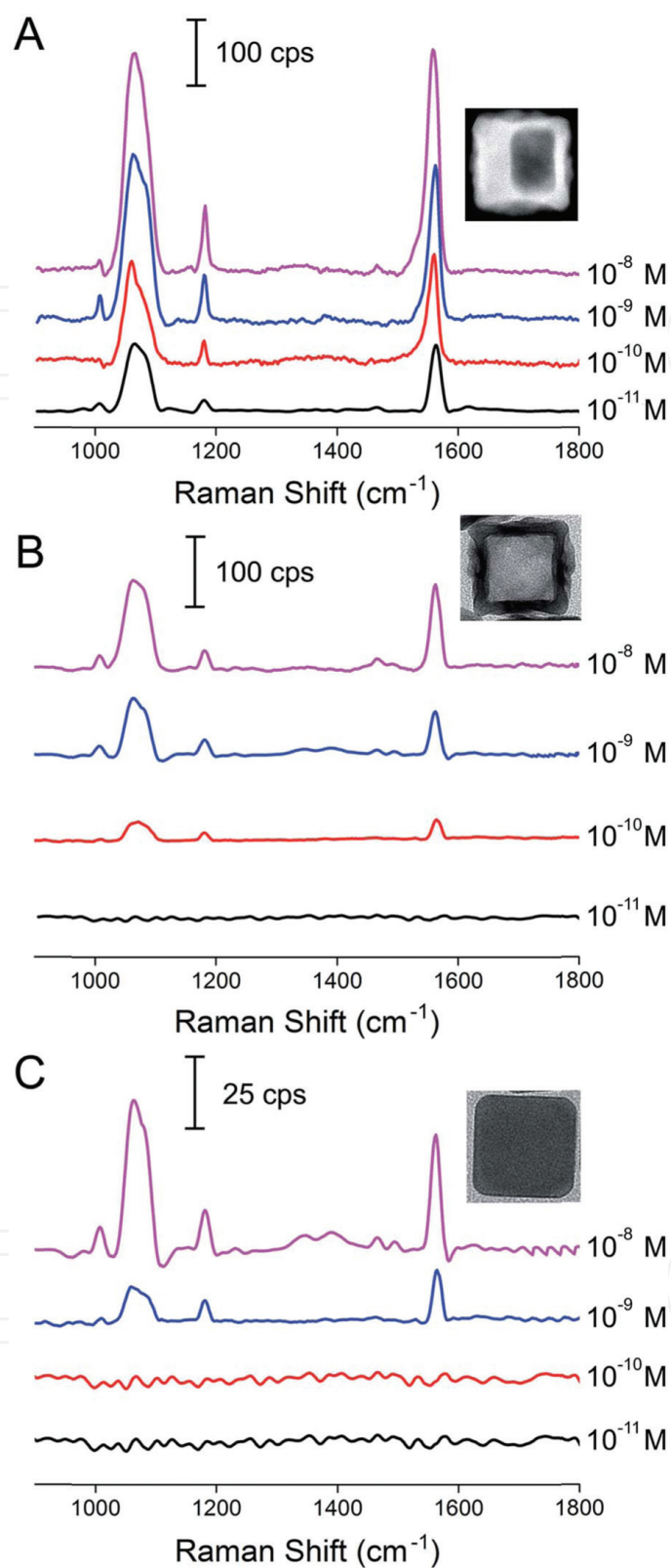
Figure 4. SERS spectra of 1,4-benzenedithiol in ethanol at various concentrations. (A) Hollow nanobox, (B) hollow nanocubes and (C) solid nanocubes of alloyed Ag-Au bimetallic nanoparticles are used as SERS substrate where hollow alloyed nanostructures exhibited improved EF_{SERS} compared to the solid alloyed particles. Reproduced and adapted from Ref. [25] with permission of The Royal Society of Chemistry.

interaction between the molecules and the nanoparticles. The mechanism of these shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) modes is shown in **Figure 5**. They have also shown successful detection of pesticides on fruits by using these SHINERS core-shell nanoparticles. Bimetallic Au-Ag core-shell nanoparticles are also widely studied for SERS applications. Non-spherical nanoparticles, such as core-shell Au-Ag cuboids and dumbbells were reported by Khlebtsov et al. [31] with EF_{SERS} in the order of 10^6. SERS application of Au-Ag core-shell nanoparticles for DNA and RNA detection was also reported by Cao et al. [32] with detection limit as low as 20 fM. Au-SiO$_2$ core-shell nanoparticles were used by Zavaleta et al. [33] as SERS tags for bioimaging applications. Transition metal coated Au cores (Au@TM; TM = Pt, Pd, Rh, Ru, Co, Ni) are reported for determining the structure of interfacial water adsorbed on transition metal surface [34]. The use of Au-SiO$_2$, Ag-C, Au-Ag type core-shell nanoparticles as SERS substrates for food safety applications have been reported as well [35–37].

3.3. Anisotropic plasmonic nanostructures

As described in Section 3.1, anisotropic metal nanostructures enhance the localized electric field resulting in improved SERS signal enhancement. Especially, nanorods or nanowire-shaped metal nanostructures are mostly preferred since they also exhibit surface plasmon polariton (SPP) propagation along the metal-surrounding interface. Template assisted bundled Ag nanowires were reported for SERS detection by Lee et al. [38] and demonstrated ~50-fold increase in the signal intensity for benzenethiol (BT) used as a Raman probe. The enhancement was attributed to the hot spots created at the tips of the Ag nanowires, where most of the probe
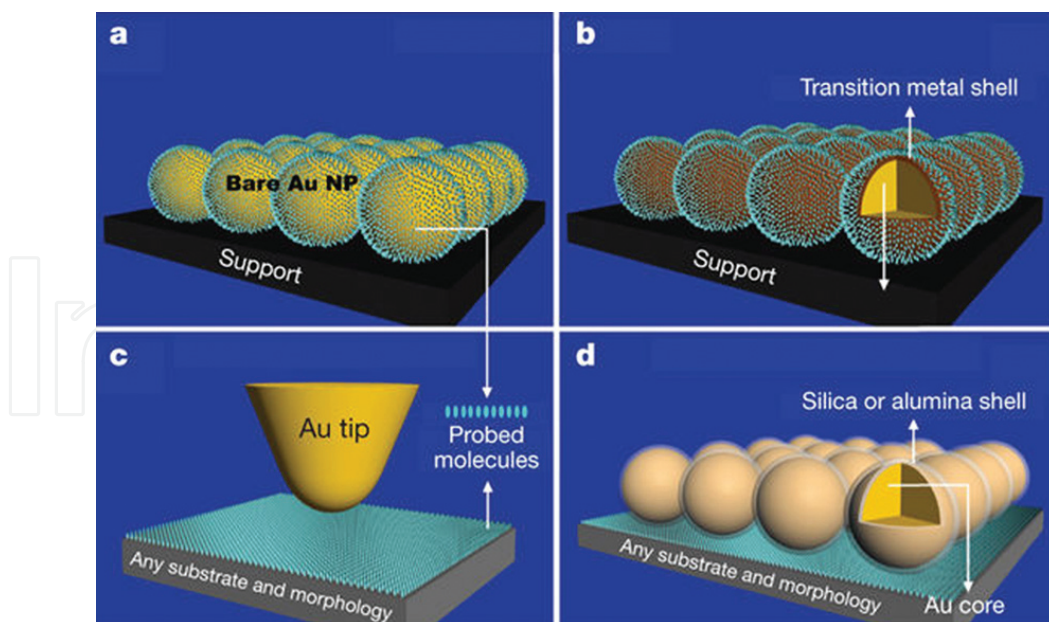

Figure 5. Working mechanism of four types of SERS substrates where small dots represent the probed molecules. (a) Bare Au nanoparticles with probed molecules directly adsorbed to their surfaces, (b) Au core and transition metal shell nanoparticles with probed molecules directly adsorbed to the shell surface, (c) Au tip enhanced Raman probe in non-contact mode and (d) SHINERS: shell-isolated mode preventing the direct contact of the plasmonic core with the probed molecules. Reprinted by permission from Macmillan Publishers Ltd.: Nature Letters [30], copyright 2010.

molecules were adsorbed. Another strategy for preparing monolayers of Ag nanowires using Langmuir-Blodgett (L-B) technique was reported by Tao et al. [39]. In both the cases, the goal was to obtain closely packed Ag nanowires and form hot spots in the region of close contact. The template-assisted method resulted in almost vertically standing Ag nanowires, while L-B method, which is a relatively less complex method, provided a bed of horizontally aligned monolayer of Ag nanowires. The EF_{SERS} for these robust solid substrates was in the order of 10^9 against R6G as probe molecules, which was mainly due to the strong coupling of EM fields among the monolayered Ag nanowires. Another well-ordered assembly of Ag nanowires was reported by Liu et al. [40] by flowing the nanowires through a glass capillary tube, which then demonstrated as a robust, portable and reusable SERS substrate with significant signal enhancement (**Figure 6**). Au nanorods with various aspect ratio were also reported for SERS applications, mostly in the biosensing areas, such as SERS imaging of tumor cells and photothermal heating therapy [41].

Other types of anisotropic nanostructures, such as nanoprism, nanostar, nanosheets of plasmonic metals have also been investigated as SERS substrate by several researchers [42–45]. Due to the presence of corners, edges or branches, such nanostructures always exhibit strong EM enhancement. Highly branched concave nanostructures of bimetallic Au-Pd were reported for their improved catalytic and SERS properties [46]. SERS application of Ag nanoprism and factors affecting its enhancement factors were investigated by Ciou et al. [47]. They presented three possibilities that contribute to the total SERS enhancement in case of the Ag nanorpism. They were namely higher target molecule adsorption, improved SPR resonance in the nanoprism with the excitation laser compared to the regular spherical Ag nanoparticles and presence of Ag nanoclusters along with the nanoprisms.
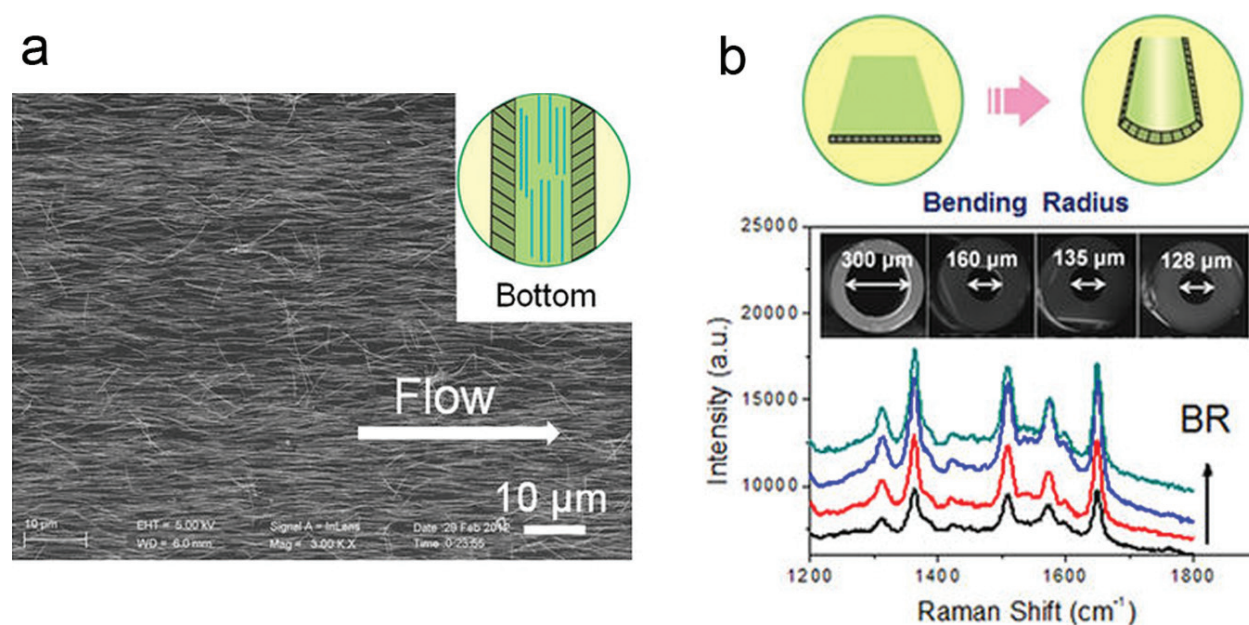

Figure 6. (a) SEM micrographs of highly ordered Ag nanowires assembly in a capillary tube and (b) SERS enhancement of Rhodamine 6G as probed molecule and the ordered Ag nanowires as substrates with respect to the bending radius of the capillary tube. The EF_{SERS} was observed to improve with increasing bending radius of the tubes. Reprinted by permission from Macmillan Publishers Ltd.: Scientific Reports [40], copyright 2012.

3.4. Patterned SERS substrates

While a significant development is taking place in the areas of solution processed SERS substrate preparations, reports on preparation of SERS substrates using non-solution processed techniques to directly transfer patterns on a surface are also surfacing. For example, lithographic techniques are widely used these days to produce highly sensitive, stable and reproducible SERS substrates [48–50]. One of the major advantages for lithographic techniques is the precise control over the geometry and arrangement of the nanostructured substrates, which is crucial for enhanced SERS signal. In this regard, electron beam (E-beam) lithography was employed to produce Au nanostructures showing the highly dependency of the SERS enhancement factors on the geometry and arrangement of the nanostructures [51]. Van Duyne and coworkers [52–54] have invented a novel nanosphere lithography (NSL) technique to produce metallic nano-triangle patterns (**Figure 7**). In their technique, a self-assembled monolayer of similar sized metal nanospheres on a substrate was used a mask and then a thin layer of metal film (such as Au or Ag) was deposited in the gaps using evaporation or vapor phase techniques. The mask layer was then removed by simply applying ultrasonic vibration resulting in regularly spaced triangular shaped metallic patterns which showed EF_{SERS} up to single molecule detection level. In a separate study, Dinish and coworkers [55] compared the performance of SERS substrates fabricated by NSL and deep UV lithography techniques and reported superior SERS enhancement for the NSL fabricated SERS substrates. Combining electroless plating with island lithography technique, Green and Liu [56] has fabricated nanopillars of silver on Si substrate with EF_{SERS} in 10^7 orders. They have also observed dependency of the SERS signal on the surface coverage of the nanopillars, and concluded that the SERS sites must be larger than the area occupied by the adsorbed molecules. Nanolithography was also employed to fabricate silver-based SERS substrates for single molecule detection applications [57].

Periodic metallic structures and plasmonic gratings are also reported to exhibit SERS enhancement. A two-dimensional finite array of Au nanopatches was investigated by Grande et al. [58] reporting EF_{SERS} near 10^5. A narrow groove (sub 15 nm) plasmonic nano-grating was also proposed for SERS applications [59]. However, application of such SERS substrate is limited due to their low EF_{SERS} which is in the range of 10^4–10^5.
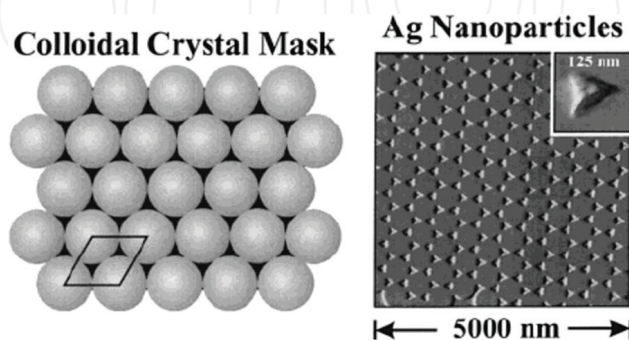

Figure 7. Schematic representation (left) and real AFM image (right) of highly ordered Ag nanotriangles as SERS substrates fabricated by using nanosphere lithography (NSL) technique. Reprinted and adapted with permission from Ref. [52]. Copyright (2001) American Chemical Society.

4. Nontraditional SERS substrates

When traditional plasmonic materials are widely used for SERS substrates, few researchers also started to explore other possible nontraditional materials to prepare SERS substrates. Photonic crystal fibers with embedded metal nanoparticles as a potential SERS substrate were reported [60, 61]. The coverage density of the plasmonic metal nanoparticle in these fibers is the key for the successful SERS applications of such configurations. Zhao et al. [62] has reported significant increasing of the electromagnetic field in amorphous Si photonic crystals embedded in multiple metallo-dielectric units. Sensitivity level of such systems is found to be up to picomolar concentration levels of probe molecules. Another photonic crystal SERS substrate composed of plasmonic SiO_2 nanotubes deposited on silicon nitride substrates was demonstrated by Xu et al. [63], exhibiting almost 10 times higher Raman signal intensities (see **Figure 8**).

Single sheet of carbon atoms, known as graphene was also explored as a potential SERS substrate [64, 65]. For graphene no evidence of EM enhancement is reported, and SERS enhancement is
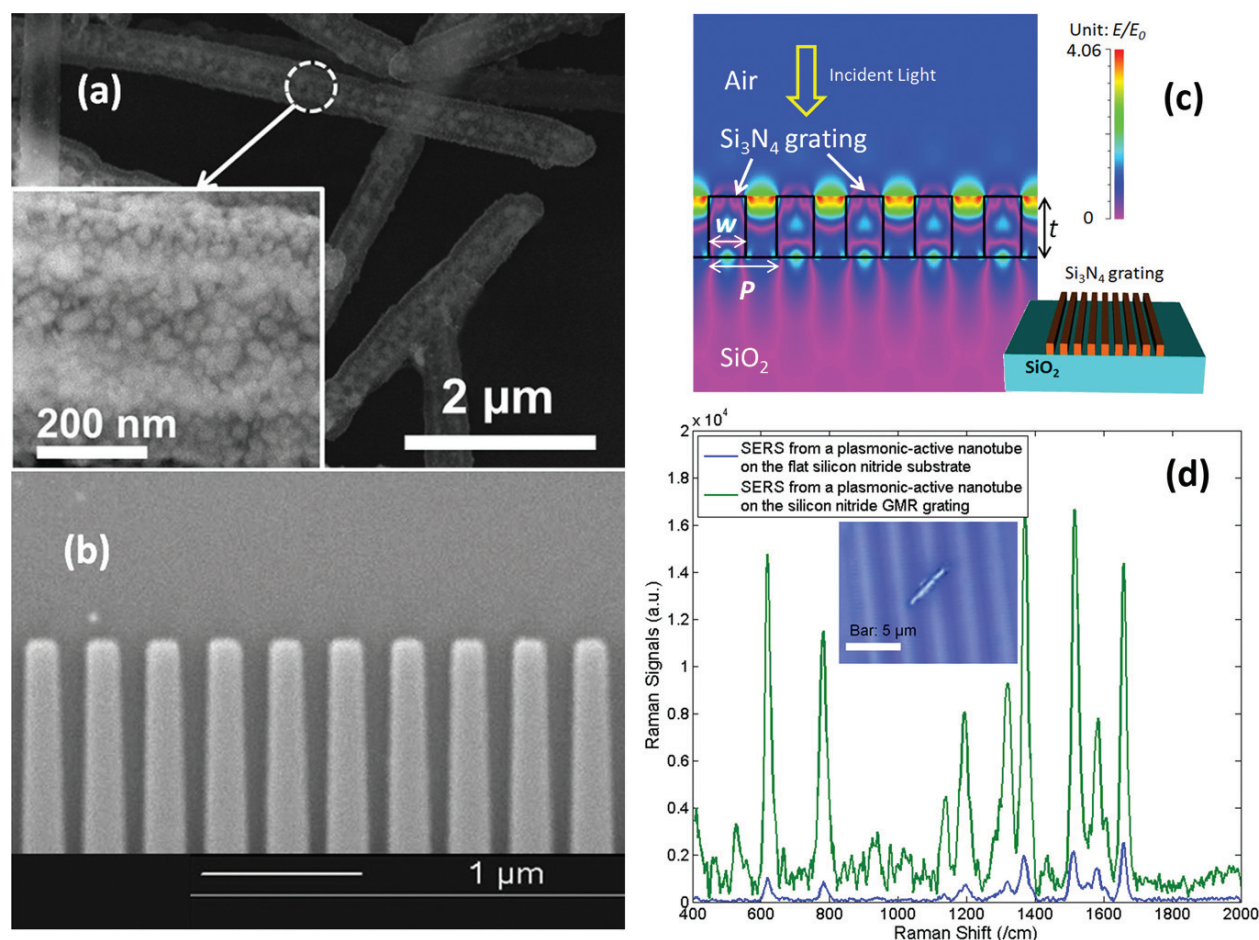

Figure 8. SEM micrographs of (a) plasmonic SiO_2 nanotubes and (b) Si_3N_4 GMR grating used to fabricate the hybrid photonic crystal-based SERS substrates with high sensitivity. (c) TM mode E-field distribution in the GMR grating showing the hot spots at 532 nm excitation and (d) Raman signal from Rhodamine 6G with (high intensity signal) and without (low intensity signal) the Si_3N_4 GMR gratings. Reprinted and adapted from Ref. [63], with the permission of AIP Publishing.

therefore mainly contributed by the chemical enhancement route exhibiting EF_{SERS} in the order of 10^3. To further improve the EF_{SERS}, Wang et al. [66] prepared a composite of Au and graphene by depositing Au nanoparticles on graphene sheets. A strong resonance energy transfer from gold to graphene was evidenced suggesting their potential use for SERS at low concentrations of probed molecules.

Chemically enhanced SERS using semiconductor TiO_2 nanoparticles was also explored by Musumeci et al. [67] reporting an EF_{SERS} in 10^3 range. A slightly improved EF_{SERS} (in the range of 10^4–10^5) was reported for CdSe/ZnBeSe semiconductor quantum dots [68]. InAs/GaAs based SERS substrates were first reported by Quagliano [69] with an EF_{SERS} of 10^3. EF_{SERS} in the order of 10^4 was also reported for 3 nm CdTe nanoparticles [70]. However, in all these cases the overall EF_{SERS} was low due to the lack of EM enhancement in the SERS substrates, and contribution only from the chemical enhancement mechanism. Further work is therefore underway to improve the EF_{SERS} of these nontraditional SERS materials mainly due to advantage of their low preparation cost.

5. Conclusions

Without any doubt, SERS is a very powerful technique in various fields such as biomedical, material science, pharmaceutical, and even sensor application. With the emergence of nanotechnology as an enabling technology, applications of noble metal nanostructures with remarkable optoelectrical properties for SERS applications becomes a major area of R&D, which is not only limited to the synthesis of plasmonic nanostructures for SERS substrates, but also includes patterning of surfaces at nanoscale to enhance the effect. Challenges are there in terms of producing highly sensitive, large area robust and reusable SERS substrates with low-cost fabrication techniques. This chapter highlighted some of the numerous developments happening in this area, exhibiting wide range of SERS substrates available to date.

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