



The evolution and recent research trends of Surface Enhanced Raman Scattering sensors using plasmonics: Citation network analysis

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HIGHLIGHTS

- Different types of Plasmonic materials for SERS sensors.
- Citation network analysis of Plasmonic based SERS.
- Global main path of ongoing research in enhancing properties of plasmonic substrates.
- Cluster analysis of the available Web of Science (WoS) data.

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ABSTRACT

The surface enhancement of Raman scattering of molecules in contact with plasmonic substrates revitalized the field of sensors. Since its discovery in the 1970s, many experimental and theoretical studies have been aimed at understanding the effect of different types of plasmonic nanomaterials on surface-enhanced Raman scattering (SERS) and how it can be applied in different forms of ultrasensitive sensing. In this work, the trajectory of global evolution and emerging research trends as well as the different prospects for surface enhanced Raman scattering sensors using plasmonics are systematically examined using citation network analysis. The growth curve, the number of papers published each year indicates that research activities are still in the emerging stage. We obtained the global main path of the on-going research and examined each node to identify major milestones and emerging research fronts. The cluster analysis of the available Web of Science (WoS) data was also done.

1. Introduction

Surface-Enhanced Raman Scattering (SERS) is a spectroscopic technique, combining conventional laser spectroscopy with special optical properties of metallic nanostructures. Martin Fleischmann et al. [1], who first observed SERS in 1974, recorded an extremely strong Raman signal from pyridine adsorbed on a roughened silver electrode. Without much delay, Fleischmann's observations were confirmed by the scientists, Jeanmaire and Van Duyne [2], M. G. Albrecht and J. A. Creighton [3] and M. Moskovits [4]. As our understanding of the interactions between molecules and nanostructures is improving rapidly, a broad range of applications is realized in the field of nanoscale optical spectroscopy, surface-enhanced Raman spectroscopy and surface plasmon resonance sensing. One of the most sensitive and efficient tools for sensors as

compared to other spectroscopic techniques is the SERS, which boasts a million times enhancement in the Raman signals by using the required SERS substrates [5,6]. Two mechanisms are reported to be the reason for the large enhancement of otherwise weak Raman signals of analytes at close proximity with nanoparticle/nanostructure. The first mechanism is the electromagnetic field (EM) enhancement at the metal particle surface due to the phenomenon known as surface plasmon resonance (SPR). Chemical enhancement in which the charge transfer takes place between the adsorbed molecule and the metal surface is the second mechanism responsible for the Raman signal enhancement. In determining the magnitude of the surface-enhanced Raman scattering, it is the electromagnetic enhancement that plays a key role. For the very same reason, we will limit our search for articles that display the major breakthroughs in plasmonics based SERS research.

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Traditionally, SERS substrates are made from coinage materials that support plasmonic resonance, primarily silver (Ag) and gold (Au). When light interacts with these materials having negative real and small positive imaginary dielectric constant, an oscillatory motion of the conduction electrons occurs and is known as the surface plasmon resonance. This provides extreme light confinement and huge local electromagnetic field enhancement in the proximity of nanoparticles. The distinctive features of such oscillations arise from the enclosed spatial distribution of polarization charges over the nanostructure surface. On thin metallic films, propagating surface plasmons are observed, while localised surface plasmons (LSPR) are observed on nanoscale structures.

In the Raman Effect, the inelastic scattering of the incident light by the molecule of interest is generally a weak signal. However, the intensity of Raman signals is proportional to the fourth power of the local electrical field. Any molecule near the nanoparticle surface will experience large fields due to plasmons and this constitutes the foundation for the surface-enhanced Raman spectroscopy. The distribution of field enhancement on the surface of a plasmonic substrate is extremely inhomogeneous and often distributed in very specific local regions called “hot spots”. The enhancement factor (EF) is possibly the most commonly used figure of merit for comparing the efficiency of various SERS substrates. However, there are broad differences in the estimate of the SERS enhancement in literature, primarily due to various interpretations of the enhancement and the way it is experimentally tested. In addition, EF is dependent on other variables such as the molecules used for analysis and the excitation wavelength.

After the detection of SERS phenomenon on silver substrates, as the research domain is advancing rapidly, its evolution, novel research trends and major thrust areas are important factors to be recorded for further fruitful research. In this context, this paper explores the vibrant spectrum of research and core research groups in the field of plasmonics based SERS sensors using the citation network analysis evaluating the bibliographic details of the relevant research papers. The current paper provides a detailed analysis of research articles over these years in order to classify the prominent research topics. Reviewing the bibliometric details of research papers on SERS sensors, the evolution of research groups and the relevant research topics are traced in this study. The latest developments in the global research indicate that a significant number of articles are available in the relevant topic of sensors. In the current scenario the literature review done manually will be challenging and therefore this study adopts a methodology of analytic techniques applied to the bibliometric knowledge of research papers based on SERS sensors employing the tool of plasmonics. Using the aforementioned method, a citation network of the corpus of research articles is constructed. The obtained citations network consists of several nodes and edges with a trajectory showing the evolution of the topic of research. Each node in the path represents the articles while the edges represent the citations that can be joined to illustrate the flow of research in this field. Thus, the main objective of the study is to develop a model that shows the key developments and how the current topic of plasmonics induced surface enhanced Raman spectroscopy is evolving.

2. Methodology

2.1. Analytic technique

The keywords used to obtain the bibliography are Surface Plasmon Resonance, Sensor, Sensitivity, Nanomaterials, and Surface Enhanced Raman Spectroscopy. Bibliometric details of the research corpus of the referred field are analysed using the tool of citation network. A two-step process was executed to obtain the necessary evolution of the research articles on Plasmonics based SERS sensors. The first step to create the citation network is done by collecting citation data from the Web of Science (WoS) search engine. For further analysis, the next step is to obtain the largest component which gives the global main path. Next, to obtain the main path which is a chain of links connecting the most

significant nodes is to assign a weight to each directed link connecting two nodes. Three major measures for estimating the weights of the links are Node Pair Projection Count (NPPC), Search Path Node Pair (SPNP) and Search Path Link Count (SPLC) as suggested by Hummon and Der-eian [7]. The SPLC of a directed link counts all possible search paths within the network originating from the tail node of the link and its ancestral nodes [7,8]. In a citation network, the main path is built from a source node, by adding links with the highest weight and finally a sink node is reached. The nodes in the main path represent the prominent stages in a research field’s evolution. To obtain the global main path, the first step is to identify the link with the highest traversal count originating from all sources. In the main path, the beginning node of this link is the first node. This procedure is repeated and continued until a sink node is reached. In case of ties, all links with the tie are considered. In this work, the software package PAJEK was used to construct the global main path [9].

Considering all possible global main paths, analysis was carried out to trace the various research directions through the articles that are prominent in the evolution of SERS based sensors. The main path algorithm in the citation network consists of two phases with the first phase to create a weighted citation network and allot significant traversal weight to the links. Whereas the second phase is to execute a priority search algorithm for selecting the most significant follower of an article based on the traversal weight of links attached to it. The priority search algorithm selects the next connecting link of a node as the one with the largest traversal weight and iterates the procedure for all the links from source to sinks [10].

To identify the diversity of research domains, clustering of the largest component was also done [11]. The clustering algorithm based on modularity computes the quantity Q given by

$$Q = \sum_1^{N_m} \left[\frac{l_s}{l} - \left(\frac{d_s}{2l} \right)^2 \right] \quad (1)$$

where N_m is the number of clusters, l is the total number of links, l_s is the number of links between the nodes in cluster S and d_s is the sum of degrees of the nodes in the cluster [12,13]. Each term in Eq. (1) corresponding to a cluster is the difference between the fraction of links that fall within the cluster and the expected value of the same quantity if the links are distributed randomly without considering cluster structures. A high value of Q indicates a good division of the network into clusters.

3. Findings

3.1. Topic evolution model

One of the key features of SERS is its interdisciplinary nature; it is included in the frontier of physics, chemistry, colloid science, nanotechnology and biology. Additionally, the proliferation in nanoscience and nanotechnology research has sparked a growing interest in SERS. The evolution of this area of research and its potential in the field of sensing are depicted using the global main path constructed using citation network analysis [Fig. 1]. The rise in the number of papers published over the past two decades indicates that this research field is still in the growth stage and the exploration has not yet reached maturity.

Knowledge on the creative topics added to the domain in the recent past would be beneficial to scientists, research scholars and other common people who are curious to know about nanotechnology. The preliminary findings of the citation network analysis illustrate the topic evolution identifying the key research themes as shown in Table 1. Initially during stage I, researchers were mainly focussing on the fundamental theories on light/complex shaped nanoparticle interaction rather than the usual spherical particles. The inclusion of nanoparticles (mostly silver during the initial years) and the corresponding LSPR it can provide was the centre of research. The dependence of LSPR wavelength

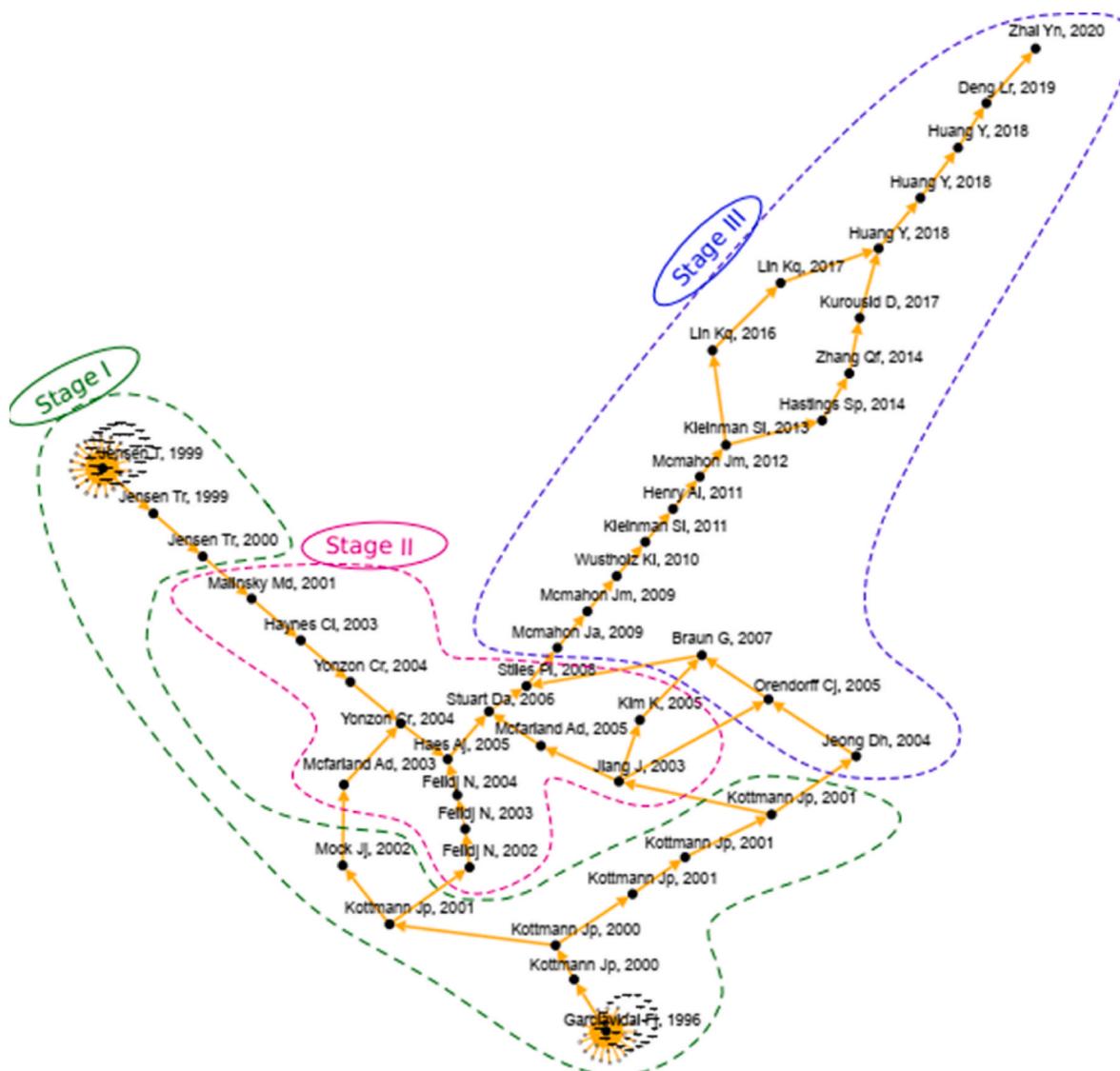


Fig. 1. Global main path of the evolution of SPR based SERS sensor literature.

Table 1

Major research topics related to Stages I, II and III of the maturity model of SERS biosensors.

Stages	Major themes
Start-up Stage I	<ul style="list-style-type: none"> ● Fundamental aspects related to the interaction of electromagnetic waves with metal particles. ● Theoretical formulation for validating observed electromagnetic enhancement using complex nanoparticles. ● The effect of different size/shape of nanoparticles on spectral response of nanoparticles.
Application.level Stage II	<ul style="list-style-type: none"> ● Analysis of molecular dynamics using SERS technique ● Correlation between SERS and the resonance properties of nanoparticles. ● Single molecule detection
Flourishing/Refinement Stage III	<ul style="list-style-type: none"> ● Different architecture/various shapes of nanoparticles or nanoparticle clusters for the enhancement of SERS signal ● Studies on assembly of nanoparticles on different types of surfaces ● Identification of different "hot spots" in an assembly of nanoparticles.

on the refractive index of the surrounding media was clearly

demonstrated and provided a tool for plasmonic based sensors. Single particles as well as arrays of nanoparticles were analysed and there were studies on how the particle size/shape affects the plasmonic resonance tunability.

In the second stage, a group of researchers/scientists across the globe started implementing this concept into the fabrication of chemical or biological sensors in the background of SERS. The vast increase in the publications during these years specifies the success of researchers in implementing the idea. Many chemicals as well as biological samples were analysed through this technique and also obtained appreciable success. Even single molecule detection was reported. Many factors including the role of excitation wavelength, structure of the molecule, its adsorption geometry on the substrate surface and the nature of the surface itself were investigated by many researchers in the subsequent years. This era can be marked as the stage III in the development of SERS optical sensors.

3.2. Main path analysis

In the field of plasmonics based SERS sensors, the design and development of different plasmonic substrates capable of providing large electromagnetic enhancements is a major research topic. An analysis on the topics of articles listed in various nodes in the global

main path can lead to the evolution trajectory in this area. The main path started almost simultaneously from two central nodes and finally merged into a single base path. This consists of two major works done by T. R. Jensen et al. [14] and F. J. Garcia-Vidal et al. [15]. As evident from Fig. 1, it can be seen that the area of research evolved almost simultaneously from these two central nodes. The selection, as well as the fabrication of noble-metal substrates is the most essential part of designing a SERS based sensor. As the intensity of SERS signal is determined by the LSPR's excitation, it's critical to keep track of all aspects that influence the LSPR. Excitation of LSPR results in selective absorption and scattering (extinction) of the resonant electromagnetic radiation, as well as the formation of large electromagnetic fields in close proximity to nanoparticles. The first central node [14] and the successive works in the path [16,17] theoretically explain the influence of size, shape and surrounding dielectric environment on plasmonic properties of nanoparticles. Moreover, they mainly focussed on far field plasmonic properties such as resonance as a function of incident wavelength and how it can be tuned by varying the properties of nanoparticles. Whereas in the second central node F. J. Garcia-Vidal et al. [15], near field properties of metallic nanoparticles such as maximum electric field intensity in the vicinity of the nanoparticle and nanoparticle junctions known as hot spots, was the focus.

To obtain a deep insight into surface enhancing properties of metal nanoparticles (LSPR), it is important to comprehend and monitor the resonance properties of nanoparticles. For so long, Classical Mie's theory has remained significant for the theoretical explanation of linear optical properties such as absorption and scattering of spherical particles. However, for complex or non-regular shaped particles, more advanced numerical methods are needed for the complete description of optical properties of nanoparticles which includes resonant wavelength, extinction spectrum (combinations of absorption and scattering) and local field enhancement at NP surface. With the advent of nanosphere lithography (NSL) by 1990, fabrication of nanoparticles with more accurate shape and size was possible and this led many researchers across the globe to investigate the resonance properties of various shapes/sizes of nanoparticles. A theory on electrodynamics of nanoparticles of arbitrary shape and size was well explained by the research article in the first central node (T. R. Jensen et al. [14]). They employed discrete dipole approximation (DDA), a theoretical modelling tool to explain plasmon resonance properties of silver (Ag) nanoparticles of dimension 40–200 nm range. Non-spherical shapes such as truncated tetrahedron and oblate ellipsoid were investigated. They obtained a linear relationship between the refractive index of the surrounding dielectric medium and the extinction maximum (LSPR peak) and demonstrated a sensitivity of 200 nm/RIU (refractive index unit). Also, the particles with the highest aspect ratio showed the greatest sensitivity to the external dielectric environment (T. R. Jensen et al., [16,17]). These research works reveal the scope of employing Ag nanoparticles for the application in sensors. This was possible by monitoring the refractive index variation in the surrounding environment due to the adsorbates of the nanoparticle surface. The effect of molecular adsorption on the nanoparticle spectrum was further studied by M. D. Malinsky et al. [18] in 2001. This was done by chemically modifying the Ag nanoparticles using self-assembled monoayers (SAM). Other than resonance tuning, this technique provides an effective way to get hold of biological samples to be sensed onto the surface of nanoparticles. From these works it is quite clear that the nanoparticle LSPR resonance can be tuned successfully by varying the size, shape and local dielectric environment. A further significant aspect of the LSPR is the strong electromagnetic field at the nanoparticle surface that enables enhancement of Raman scattering of molecules located near the surface, generally referred to as "hotspots".

To successfully employ plasmonic properties of metals in SERS, it is utmost important to find the relationship between nanoparticle resonance wavelength and SERS enhancement factor. C. L. Haynes and co-authors [19] in 2003 had done a correlation between LSPR (Ag nanoparticles) and the corresponding SERS enhancement. Largest EF (10^8)

was achieved when the LSPR wavelength lies between excitation wavelength and Raman shifted wavelength for Benzenethiol solutions with concentration of 1 mM. After all these fundamental studies, C. R. Yonzon et al. [20] illustrated the functioning of an in-vivo glucose sensor (concentration range of 0–25mM) using SAM modified silver film over nanosphere (AgFON) and was more focussed on the stability of the sensors. Along this trajectory, most cited works were mainly focussed on silver nanoparticles and the associated LSPR. The growth from the basic fundamental studies to the realization of plasmonic SERS sensors is quite evident along this path. Along this path, there were successful demonstrations of plasmonic based SERS sensors [21–23].

In the second central node, the main article is "Collective Theory for Surface Enhanced Raman Scattering" by F. J. Garcia-Vidal et al. [17]. They modelled roughened metal surfaces as periodic cylinder gratings and showed that the gaps between nearby particles, usually referred to as hotspots can also provide additional field enhancement leading to SERS enhancement factor. Further along this path nanoparticles other than simple shapes were investigated. However, a precise theoretical solution for the localised electromagnetic field of arbitrary-shaped nanoparticles remained the main challenge in exploring novel shapes. A numerical method to solve the electromagnetic fields of two dimensional plasmon resonant particles was put forward by J.P. Kottmann et al. [24] for particles of dimensions, 10–100nm. As mentioned in the work done by T. R. Jensen et al. [14], they were also in agreement that the shape of the particles influences resultant plasmonic modes, with the triangular particle displaying much more complex behaviour. It was also shown that the field distribution associated with each plasmon resonance can be correlated with the polarization charges at the particle surface [25]. At this node, the path diverges and progresses along two parallel sub paths almost simultaneously before converging to the main path.

In the first sub path, J.P. Kottmann et al. [26] (2001) reported about plasmon resonances of 10–50nm nanowires with a non-elliptical cross-section and it was found that such nanowires can provide enhancement up to hundred times of the incident amplitude. J. J. Mock et al. [27] depicted how subtle changes in the morphology of individual nanoparticles influences resulting plasmon resonances and further contributes to our understanding of how shape characteristics lead to signal improvements in LSPR, thus strongly supporting the realization of a biosensor with zeptomol sensitivity [28]. Alongside this research, there were studies based on an array of gold nanoparticles [29–31] and associated SERS for *trans*-1,2-two-(4-pyridyl) ethylene (BPE) molecule with a concentration down to 5×10^{-5} M, with an enhancement of 10^8 [31].

In the second sub path, J. P. Kottmann et al. [32] discusses the field distribution occurring across the sharp corners of a metallic nanoparticle. They also illustrated theoretically the effect of interaction or coupling between nanoparticles, resulting in hybridization of plasmon modes (J. P. Kottmann et al., [33]). In the same year, they have also studied numerically (P. Kottmann et al., [34]) how the particle cross-section or symmetry influences the resulting resonance spectrum. They considered silver nanowires (20–50) nm and got the largest EM enhancement of the order of 10^{12} for particles less than 50nm range. Other research work along this sub path is by J. Jiang et al. [35] and A. D. McFarland et al. [36]. Single-molecule detection using SERS (SM-SERS) reported in 1997 with an EF of 10^{11} to 10^{12} by Nie and Emory [37] and Kneipp et al. [38] opened new possibilities toward obtaining the vibrational fingerprint of a single molecule. The first article deals with single molecule detection using Raman scattering analysis with electromagnetic hot spots at gap junctions of nanoparticle aggregates (30–70nm) and the second work showed the relationship between the LSPR maximum and the SERS excitation wavelength with maximum enhancement ($\sim 10^8$) obtained, when the excitation wavelength is blue shifted to LSPR resonance wavelength such that both incident and Raman scattered wavelength are enhanced.

Fabrication of different architecture that provides a high

enhancement factor always remains a challenge and a side-line of research emerges which deals with these topics. D. H. Jeong et al. [39] fabricated flat arrays (rafts) of aligned silver nanowires and studied the sensitivity of rhodamine 6G molecule adsorbed onto the rafts. They also illustrated the dependence between SERS spectra and the polarization with respect to nanowire axes. Next series of works concentrated on different architecture for the sensors and also employed gold (Au) in addition to silver. C. J. Orendorff et al. [40], K. Kim et al. (4-aminobenzenethiol (4-ABT) monolayer) [41] and G. Braun et al. (single-stranded DNA) [42] demonstrated a sandwich architecture in which a biological sample was sandwiched between Au substrates and Ag/Au nanoparticles. Enhancement factor of 10^7 – 10^9 for 4-mercaptobenzoic acid (4-MBA) SAMs was reported [40] and the increase in its value is likely due to the plasmon coupling between nanoparticle and metal substrate.

The sensitivity of plasmon modes to the local dielectric environment, such as the substrate, is one of the characteristics of LSPRs that is especially important for sensing devices [43,44]. In the main path, the work done by J. A. McMahon et al. [45] in 2009, reported the need to identify the relationship between optical responses of nanoparticles deposited on a dielectric substrate. Here hybridization of plasmon modes was observed due to the strong coupling between the metallic nanocube and a dielectric substrate nearby. In addition to size, shape and external environment of the nanoparticles, SERS behaviour is also strongly dependent on inter-particle distance. When two particles are in close contact with one another (dimer), the gap between the particles can serve as hot spots with large enhancement for SERS. Using Au aggregates (dimers), J. A. McMahon et al. [46] demonstrated a shift of resonance wavelength to NIR range. Also, with an inter particle distance less than 0.5nm, EF up to 10^{10} can be achieved. As a further step, in the article by K. L. Wustholz et al. [47], Au nanoparticle dimers and trimers encapsulated in SiO₂ shells, referred to as "nanoantennas" were analysed. It was shown that the inter-gap between nanoparticles influences the SERS intensity and there is not any correlation between the states of aggregation on the same. S. L. Kleinman et al. [48] demonstrated SM-SERS of isotopically edited crystal violet (CV) molecules (isotopologue approach) and thus expanding its generality. Further, J. M. McMahon et al. [49] in 2012 demonstrated that electromagnetic SERS enhancement factor is indeed inversely proportional to the inter-gap between the particles with an approximate of $1/\text{gap}^2$. In simple nanostructures, SERS enhancement was shown to be well correlated with far-field plasmon resonances [19,36]. Whereas, an entirely different result was obtained for nanostructures with hotspots at the junction between the particles. S. L. Kleinman et al. [50] performed surface-enhanced Raman excitation spectroscopy (SERES) experiments to investigate the wave-length dependence of silica-enclosed nanoantennas with target molecules attached. They confirmed that the maximum value of EF is not dependent on the LSPR wavelength as well as on the number of cores in the aggregate and obtained an EF of 10^8 for an excitation wavelength of >750nm. Even though SERS based on hotspots at nanoparticle junctions is found to be promising, there are certain drawbacks such as the difficulty in the nanostructure fabrication and positioning of the analyte exactly at the hotspot.

Another efficient technique for improving EF, without the need of nanoparticle aggregation is to produce a number of sharp tips on its surface. The research article by S. P. Hastings et al. [51] deals with the modelling (FDTD) of spiky nanoshells with quadrupole resonances that can efficiently enhance the electromagnetic field and thereby increase Raman scattering intensities (4-mercaptobenzoic acid). Considerably, it has been shown that the EF of such a spiky nanoshell is sensitive to slight changes in surface morphology. Thus, due to the strong localization of the EM fields at their sharp corners or tips, the particles such as concave nanocubes, nanotrisoctahedra, and nanostars are extensively exploited and obtained an enhancement factor of 10^7 (Q. F. Zhang et al. [52]). They demonstrate that large SERS enhancements do not usually require intraparticle gap geometries and it can also be achieved using single

particle SERS (sp-SERS). The morphology of nanostructures and spatial distribution may have a strong effect on the spectral alignment of far and near field responses. This was demonstrated by D. Kurosu et al. [53].

Precise correlations between surface enhanced Raman scattering and LSPR is required for the realization of nano-optic devices and is still a challenge. The next article along this path is "Detailed correlations between SERS enhancement and plasmon resonances in sub-wavelength closely spaced Au nanorod arrays" by Y. Huang et al. [54] in 2018. They have also extended their work (Y. Huang et al. [55]) in the demonstration of enhancement of SERS in the visible and near-infrared wavelength range by nanoparticle dimers of exceptionally large size. They showed that particles with diameter ~200nm are the optimal size rather than the usually reported 100nm size for both Au and Ag. Also, various mechanisms, such as the shape, size, and surrounding dielectric properties, were shown to effectively amplify the peak resonance and field-enhancement efficiency of such dimers. By manipulating surface morphologies, alteration of the near- and far-field plasmonic properties has been also illustrated (Y. Huang et al. [56]).

The shell-isolated nanoparticle-enhanced Raman spectroscopy-SHINERS, is an interesting form of SERS spectroscopy developed in 2010 [57]. Plasmonic nanoparticles are covered with a very thin protective layer in this process, and the obtained core-shell structures are deposited on the surface under analysis. The main advantage of this method is that it prevents agglomeration of the nanoparticles and direct contact with the molecule to be tested. Here, an increase in the thickness of the deposited protective layer, slightly dampens the enhancement of the electromagnetic field which thereby affects the Raman efficiency [58]. Towards the last nodes in the main path, L. R. Deng et al. [59] and Y. N. Zhai et al. [60], showed an increase in the enhancement of the local electric field rather than being weakened, using an appropriate high refractive index dielectric coating. In applications of surface enhanced spectroscopies and other plasmonic devices, these results should be of major importance.

Recently, there have been reports of employing sputtering other than commonly used fabrication methods such as nanosphere lithography, electron beam lithography and chemical synthesis, for the development of SERS substrates. This is simple as well as economical compared to other methods and can be a viable method for the fabrication of highly efficient SERS substrates [61–64]. It can be seen that earlier research was much concentrated on plasmonic properties of different types (shape/size) of silver and gold nanoparticles, though the most cited literature discussing silver nanoparticles and inclusion of gold nanoparticles took place gradually in the following years. Also, from the research works, it is well documented that LSPR and the resulting SERS is dependent on the size, shape, inter-particle spacing, excitation wavelength and any changes in the surrounding medium including solvent, adsorbates etc. of the nanoparticles. Even though there are research articles that reported EF ~ 10^{12} , the most reproducible value of EF attained is, EF > 10^8 . The design of highly efficient and dependable SERS substrates having a number of hot spots is extremely fascinating since it permits the detection of a wide range of biological as well as chemical species. As for any sensor, other than the enhancement factor, one of the most important characterization tools is its limit of detection (LOD) or sensitivity. Throughout these years, scientists across the globe are concentrating on fundamental aspects related to various factors for the electromagnetic enhancement as well as for the realization of SERS sensors with high sensitivity. The prominent research trends obtained along the main path in all these years are summarized in Fig. 2.

3.3. Cluster analysis

Clustering of the giant component resulted in many clusters with cluster #0 being the largest cluster [Fig. 3]. Cluster #0 includes 61.12% of research articles with slightly varying research topics. Since it was the largest cluster with various subdomains, it was further sub-clustered and obtained four main sub-clusters (Table 2).

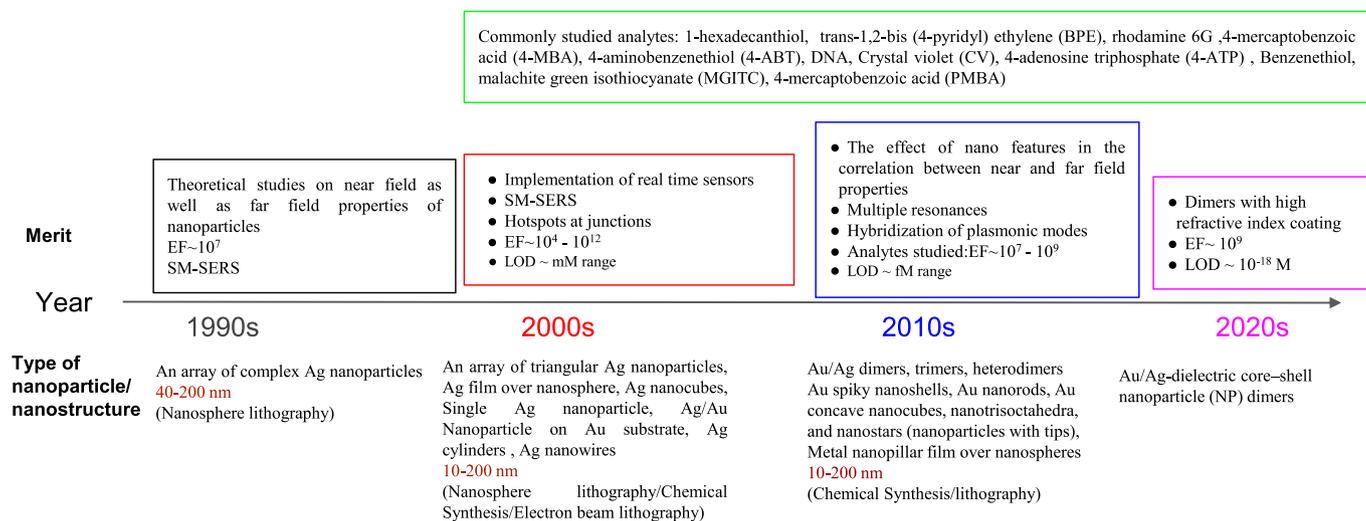


Fig. 2. The prominent research trends deduced from the main path.

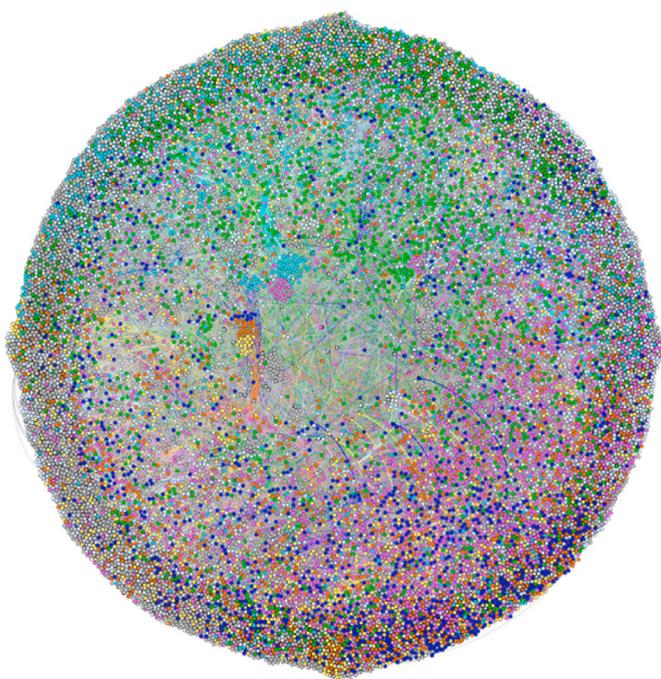


Fig. 3. Sub-clusters of the largest cluster of the citation network.

Table 2

Topics related to the sub-clusters of the largest cluster of the citation network.

Sub-cluster	Size	Topic
#1 (Pink)	11.49%	SERS using complex particles (non-regular particles)
#2 (Green)	9.21%	SERS in anisotropic particles (rod and star shaped nanoparticles)
#3 (Blue)	7.39%	Chemical enhancement of SERS
#4 (Yellow)	5.24%	Catalytic action of Plasmons

The sub-cluster #1 was found to be the biggest with 11.49% of the total articles. The majority of the research papers dealt with the enhancement of Raman signals using complex particles other than simple shapes. Particle size of 10–100nm range was mainly considered. The main reasons were experimental capabilities to synthesize these complex particles of the above-mentioned dimension and high

enhancement observed for similar sized spherical particles. For detailed analysis, the main path of evolution of research articles was also done for subcluster #1 [Fig. 4]. In this sub-cluster, plasmon resonances of individual particles as well as the resonance arising from the coupling between the particles were also discussed and it was seen that the additional resonances depend on the suitable combination of size and separation. An important aspect of plasmon resonance studies of complex nanoparticles is that lower the particle symmetry, the more resonances it exhibits [34]. Symmetry breaking occurring in these types of nanostructures enables higher-order multipolar modes to be excited, resulting in greater electromagnetic field enhancements. Resonance tuning using nanoshells and the strong resonance obtained at the junction of nanoshells, (nanoshell dimers and nanoshell arrays) were also investigated [65,66]. Even for non-resonant molecules on gold nanoshells, SERS enhancement factors of around 10^{10} were achieved. The advantage with nanoshells is that other than the size of the particle, it provides additional tunability by changing the core and shell properties. SERS enhancement due to the coupling between nanoshell dimers was reported using computational simulations (FDTD) by C. Oubre et al. [66]. Afterwards in this sub-cluster, researchers were focused on different types of SERS substrates ranging from metallic nanoparticle/film system, metallic ring/disk nano-cavities. One of the key focuses of these studies was on the hybridization of plasmonic modes as well as the dependence of the coupling strength on the spacing between nanoparticles. This aspect in addition to the material properties of nanoparticles allows systematic tuning of optical resonance, as well as near-field enhancement, enabling improved field-enhanced spectroscopy such as SERS sensors [67–70]. The LSPR spectrum of a pair of coupled nanoparticles can also be used to identify the inter-particle distance, as a "plasmonic ruler" since the strength of the plasmon coupling (and the LSPR shift induced by it) depends on the distance between the particles [71].

An unusual pattern in the SERS enhancement of aggregated 80-nm gold nano-frame assemblies was recently observed by Mahmoud et al., in 2009 [72]. As the aggregation increases or the separation between the nanoframes decreases, the intensity of Raman signals from adsorbed thiophenol molecule is found to decrease. It was shown that the electromagnetic enhancement occurred non uniformly across the junction and within the nanoframes. As the gap between the nanoframes was decreased, the field within the nanoframes where the molecules get absorbed was decreased. This result indeed shows that to get the maximum SERS using complex nanoparticles, it is utmost important to know the hot spot formation with respect to the adsorption of the molecule of interest. SERS of single-DNA-tethered nanoparticle dimers

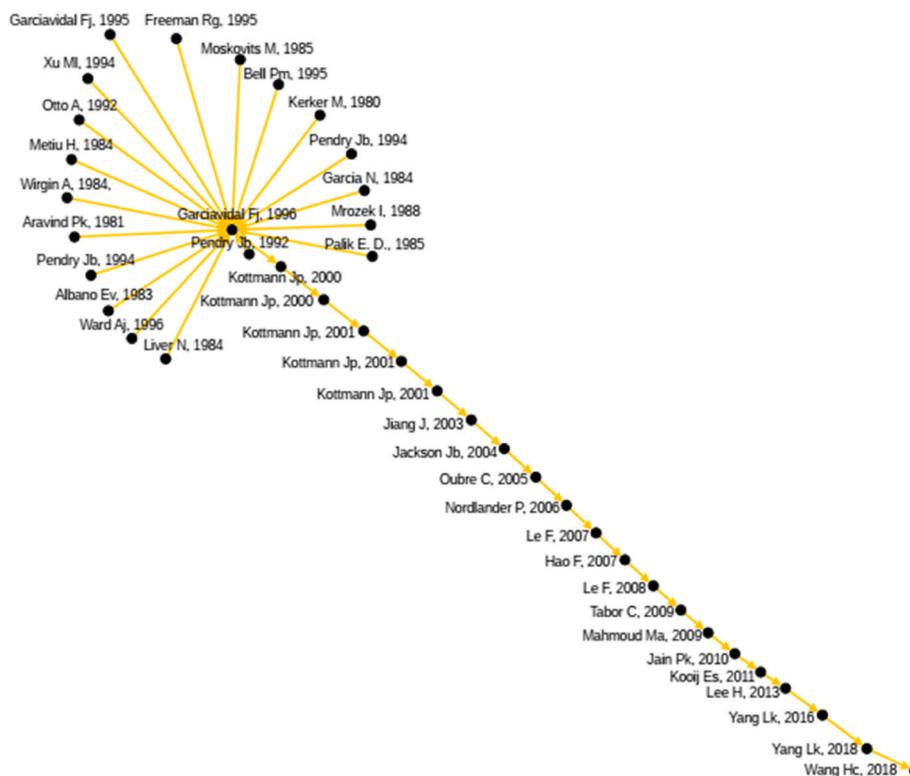


Fig. 4. Main path of evolution of sub-cluster #1.

with small gaps, < 2nm, were reported with large enhancement at the junctions [73].

The polarization states of scattering for different gap distances between dimers was investigated and it was also shown that as the gap size approaches ~ 1 nm, quantum effects become more prevalent and exhibit drastically different resonance characteristics [74–76].

The second largest, sub-cluster #2 contains 9.21% of articles and it mainly deals with the plasmon resonances occurring across anisotropic nanoparticles, specifically on gold nanorods and gold nanostars. When considering plasmonics for in-vivo as well as in-vitro applications, it is very desirable to have the resonance wavelength in the near Infra-red (NIR) window. The plasmon resonance wavelength is reported to vary up to NIR range by changing the aspect ratio of the nanoparticle [77]. Another type of anisotropic nanomaterial which was widely studied in this sub-cluster #2 was nanostars consisting of a central core and several protruding tips. F. Hao et al. [78] in 2007 studied the plasmon hybridization, across the nanostar core and tips using finite-difference time-domain method. It was demonstrated that plasmon resonance tuning can be done by varying the geometry of nanostars. For the very same reason, several research groups focussed on the synthesise of Au nanostars with controlled geometry such as T. K. Sau et al. [79], P. S. Kumar et al. [80], C. G. Khoury et al. [81], J. Xie et al. [82] and S. Barbosa et al. [83]. A seed-mediated growth approach was generally employed for the synthesis of these anisotropic particles. Most of the processes involved the presence of surfactant which makes them less biocompatible. Surfactant free synthesis as well as wide tuning range up to near infra-red window which is much suitable for in vivo imaging was reported by H. Yuan et al. [84] in 2012. The localised surface plasmon resonance (LSPR) wavelength can be tuned widely from the visible to near-infrared (NIR) region by modifying the core size, tip length and tip angle. The sea urchin or star shaped nanoparticles leads to an even longer wavelength than gold nanorods in the LSPR band. But the mechanism of growth and optical properties has still not been fully understood. Recent works in this sub cluster #1 include nanoshells and nanocrevices of the inter-particle junction [85,86], as well as more innovative anisotropic shapes

such as nanoflowers [82,87–89] and sprouted potato shaped nanoparticles with a LOD of 1 femtomolar (fM) for methylene blue molecules [90]. Recently, in 2021 using Ag nanostructures on paper-based substrates, attomole sensitivity for Rhodamine 6G was reported (LOD of 1.54 aM) [91].

Sub-cluster #3 includes 7.99% of research articles. Most of the SERS substrates are composed of metals such as Au and Ag nanomaterials and the scope of SERS has been greatly restricted by a lack of substrate generality. However, as further study was carried out, it became apparent that not all the findings could be interpreted by the plasmon theory alone. It was observed that for some molecules such as pyridine, thiols and carboxylic acids with the potential to get adsorbed on the metal surface displayed the largest enhancement. In sub-cluster #3, research articles dealing with molecule-to-metal and metal-to-molecule charge transfer resulting in the additional SERS enhancement was obtained. In sub-cluster #4, the research activities were mainly focused on plasmon driven catalytic reactions.

4. Conclusions and contributions

1. The paper conducted a preliminary analysis to track the rise in research publications on various aspects of plasmonics based SERS using citation network analysis. The analysis listed the most cited papers in chronological order and divided the main research topics suggested by the growth curve into different stages of evolution.
2. As part of the study three stages in the development of SERS biosensors were identified. Identifications of different SERS substrates with properties such as high enhancement, uniform nature, reproducibility, stability, simple fabrication steps/low cost, easily cleanable etc. were carried out during the initial years. Single nanostructures, most commonly Ag nanoparticles, with irregular shape and sharp corners were considered first for the effective enhancement of SERS. Later hot spots formed in the nano-gaps between nano-structure aggregates were the topic of interest. Recently, researchers are more concentrating on the additional plasmonic

coupling arising due to the presence of high refractive index dielectric coating on nanoparticles. As seen from the reported works till date, manufacture of high-enhancement substrates with good uniformity/reproducibility and flexible methods suitable for mass production still remains a challenge. Another important route not yet thoroughly explored is the production of alternative materials other than conventional gold and silver.

- The ultimate detection limit down to the single molecule level, has sparked a surge of new research possibilities and thus the expansion of SERS. In earlier years, the detection limit of SERS sensors was in millimolar range and recently high sensitivity with LOD even upto attomolar (aM) was reported.
- Accessing Web of Science data, a citation network is constructed. The information collected from Scopus is comprehensive, including 56098 records of academic papers in journals and conference proceedings. The giant component, which is the largest section, has been extracted from the obtained citation network and further analysed.
- Identifying current and emerging research priorities is valuable for future research in the area. Pinpointing the key research groups, leading research patterns and conceptualization of the research topic model using theme evolution models can help to explain the context of SERS biosensor technologies and emerging research topics. This aspect of introducing tunability in resonance wavelength was a great achievement and can have immense applications in surface-enhanced spectroscopy, single-molecule spectroscopy, near-field optical microscopy, chemical/biological sensing, information processing, data storage and energy transport in integrated optical devices.

CRediT authorship contribution statement

Ranjini Radhakrishnan: Writing, Formal analysis, Data curation.
Manoj Parameswaran: Supervision, Editing, Reviewing. **K. Satheesh Kumar:** Software, Supervision, Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- M. Fleischmann, P. J Hendra, A.J. McQuillan, Raman spectra of pyridine adsorbed at a silver electrode, *Chem. Phys.* 26 (1974) 163–166.
- D. L Jeanmaire, R.P. VanDuyne, Surface Raman spectroelectro chemistry Part I. Heterocyclic, aromatic, and aliphatic amines adsorbed on the anodized silver electrode, *J. Electroanal. Chem. Interfacial Electrochem.* 84 (1977) 1–20.
- M.G. Albrecht, J.A. Creighton, Anomalous intense Raman spectra of pyridine at a silver electrode, *J. Am. Chem. Soc.* 99 (1977) 5215–5217.
- M. Moskovits, Surface roughness and the enhanced intensity of Raman scattering by molecules adsorbed on metals, *J. Chem. Phys.* 69 (1978) 4159.
- Marta Lafuente, Sarah De Marchi, Miguel Urbiztondo, Isabel Pastoriza, Ignacio Santos, Juste Pérez, Jesús Santamaría, Mallada Reyes, María Pina, Plasmonic MOF thin films with Raman internal standard for fast and ultrasensitive SERS detection of chemical warfare agents in ambient air, *ACS Sens.* 6 (2021) 2241–2251.
- Zhang Yuan, Esteban Ruben, Boto Roberto A, Urbieta Mattin, Arrieta Xabier, Shan ChongXin, Li Shuzhou, J. Jeremy, Javier Aizpurua Baumberg, Addressing molecular optomechanical effects in nanocavity-enhanced Raman scattering beyond the single plasmonic mode, *Nanoscale* 13 (2021) 1938–1954.
- N.P. Hummon, P. Dereian, Connectivity in a citation network: the development of dna theory, *Soc. Network.* 11 (1989) 39–63.
- V. Batagelj, Efficient Algorithms for Citation Network Analysis, 2003 arXiv preprint [cs/0309023](https://arxiv.org/abs/cs/0309023).
- V. Batagelj, A. Mrvar, Pajek-program for large network analysis, *Connections* 21 (1998) 47–57.
- J.S. Liu, L.Y. Lu, An integrated approach for main path analysis: development of the hirsch index as an example, *J. Assoc. Inf. Sci. Technol.* 63 (2012) 528–542.
- M.E. Newman, Fast algorithm for detecting community structure in networks, *Phys. Rev. E* 69 (2004), 066133.
- V.D. Blondel, J.-L. Guillaume, R. Lambiotte, E. Lefebvre, Fast unfolding of communities in large networks, *J. Stat. Mech. Theor. Exp.* 10 (2008), P10008.

- M.E. Newman, M. Girvan, Finding and evaluating community structure in networks, *Phys. Rev. E* 69 (2004), 026113.
- T. Jensen, L. Kelly, A. Lazarides, G.C. Schatz, Electrostatics of noble metal nanoparticles and nanoparticle clusters, *J. Cluster Sci.* 10 (1999), 295–31.
- F.J. Garcia Vidal, J.B. Pendry, Collective theory for surface enhanced Raman scattering, *Phys. Rev. Lett.* 77 (1996) 1163–1166.
- T.R. Jensen, M.L. Duval, K.L. Kelly, A.A. Lazarides, G.C. Schatz, R.P. Van Duyne, Nanosphere lithography: effect of the external dielectric medium on the surface plasmon resonance spectrum of a periodic array of silver nanoparticle, *J. Phys. Chem. B* 103 (1999) 9846–9853.
- T.R. Jensen, M.D. Malinsky, C.L. Haynes, R.P. Van Duyne, Nanosphere lithography: tunable localized surface plasmon resonance spectra of silver nanoparticles, *J. Phys. Chem. B* 104 (2000) 10549–10556.
- M.D. Malinsky, K.L. Kelly, G.C. Schatz, R.P. Van Duyne, Chain length dependence and sensing capabilities of the localized surface plasmon resonance of silver nanoparticles chemically modified with alkanethiol self-assembled monolayers, *J. Am. Chem. Soc.* 123 (2001) 1471–1482.
- C.L. Haynes, R.P. Van Duyne, Plasmon-sampled surface-enhanced Raman excitation spectroscopy, *J. Phys. Chem. B* 107 (2003) 7426–7433.
- C.R. Yonzon, C.L. Haynes, X.Y. Zhang, J.T. Walsh, R.P. Van Duyne, A glucose biosensor based on surface-enhanced Raman scattering: improved partition layer, temporal stability, reversibility, and resistance to serum protein interference, *Anal. Chem.* 76 (2004) 78–85.
- C.R. Yonzon, J. Eunhee, Z. Shengli, C.S. George, M.R.P. Milan, A. Van Duyne, Comparative analysis of localized and propagating surface plasmon resonance sensors: the binding of concanavalin A to a monosaccharide functionalized self-assembled monolayer, *J. Am. Chem. Soc.* 126 (2004) 12669–12676.
- A. Haes, C. Haynes, A. McFarland, G. Schatz, R. Van Duyne, S. Zou, Plasmonic materials for surface-enhanced sensing and spectroscopy, 2005, *MRS Bull.* 30 (2005) 368–375.
- D.A. Stuart, K.B. Biggs, R.P. Van Duyne, Surface-enhanced Raman spectroscopy of half-mustard agent, *Analyst* 131 (2006) 568–572.
- J.P. Kottmann, O.J.F. Martin, D.R. Smith, S. Schultz, Spectral response of plasmon resonant nanoparticles with a non-regular shape, *Opt Express* 6 (2000) 213–219.
- P. Kottmann, O.J.F. Martin, D.R. Smith, S. Schultz, Field polarization and polarization charge distributions in plasmon resonant nanoparticles, 27, *New J. Phys.* 2 (2000) 1–27, 9.
- J.P. Kottmann, O.J.F. Martin, D.R. Smith, S. Schultz, Dramatic localized electromagnetic enhancement in plasmon resonant nanowires, *Chem. Phys. Lett.* 341 (2001) 1–6.
- J.J. Mock, M. Barbic, D.R. Smith, D.A. Schultz, S. Schultz, Shape effects in plasmon resonance of individual colloidal silver nanoparticles, *J. Chem. Phys.* 116 (2002) 6755–6759.
- A.D. McFarland, R.P. Van Duyne, Single silver nanoparticles as real-time optical sensors with zeptomole sensitivity, *Nano Lett.* 3 (2003) 1057–1062.
- N. Féridj, J. Aubard, G. Lévi, J.R. Krenn, M. Salerno, G. Schider, B. Lamprecht, A. Leitner, F.R. Aussenegg, Controlling the optical response of regular arrays of gold particles for surface-enhanced Raman scattering, *Phys. Rev. B* 65 (2002), 075419.
- N. Féridj, J. Aubard, G. Lévi, Optimized surface-enhanced Raman scattering on gold nanoparticle arrays, *Appl. Phys. Lett.* 82 (2003) 3095–3097.
- N. Féridj, S. Lau Truong, J. Aubard, G. Lévi, Gold particle interaction in regular arrays probed by surface enhanced Raman scattering, *J. Chem. Phys.* 120 (2004) 7141–7146.
- J.P. Kottmann, O.J.F. Martin, D.R. Smith, S. Schultz, Non-regularly shaped plasmon resonant nanoparticle as localized light source for near-field microscopy, *J. Microsc.* 202 (2001) 60–65.
- J.P. Kottmann, O.J.F. Martin, Retardation-induced plasmon resonances in coupled nanoparticles, *Opt. Lett.* 26 (2001) 1096–1098.
- J. P Kottmann, O.J. F Martin, D.R. Smith, S. Schultz, Plasmon resonances of silver nanowires with a non-regular cross section, *Phys. Rev. B* 64 (2001), 235402.
- J. Jiang, K. Bosnick, M. Maillard, L. Brus, Single molecule Raman spectroscopy at the junctions of large Ag nanocrystals, *J. Phys. Chem. B* 107 (2003) 9964–9972.
- A.D. McFarland, M.A. Young, J.A. Dieringer, R.P. Van Duyne, Wavelength-scanned surface-enhanced Raman excitation spectroscopy, *J. Phys. Chem. B* 109 (2005) 11279–11285.
- S. Nie, S.R. Emory, Probing single molecules and single nanoparticles by surface-enhanced Raman scattering, *Science* 275 (1997) 1102–1106.
- K. Katrin, W. Yang, K. Harald, L.T. Perelman, I. Irving, R.D. Ramachandra, S. Michael Feld, Single molecule detection using surface-enhanced Raman scattering (SERS), *Phys. Rev. Lett.* 78 (1997) 1667–1670.
- D.H. Jeong, Y.X. Zhang, M. Moskovits, Polarized surface enhanced Raman scattering from aligned silver nanowire rafts, *J. Phys. Chem. B* 108 (2004) 12724–12728.
- C.J. Orendorff, A. Gole, T.K. Sau, C.J. Murphy, Surface-enhanced Raman spectroscopy of self-assembled monolayers: sandwich architecture and nanoparticle shape dependence, *Anal. Chem.* 77 (2005) 3261–3266.
- K. Kim, J.K. Yoon, Raman scattering of 4-aminobenzenethiol sandwiched between Ag/Au nanoparticle and macroscopically smooth Au substrate, *J. Phys. Chem. B* 109 (2005) 20731–20736.
- G. Braun, S.J. Lee, M. Dante, T.-Q. Nguyen, M. Moskovits, N. Reich, Surface-enhanced Raman spectroscopy for DNA detection by nanoparticle assembly onto smooth metal films, *J. Am. Chem. Soc.* 129 (2007) 6378–6379.
- A. Douglas, B. Stuart, Kevin, , Biggs and Richard P. Duyne Van, Surface-enhanced Raman spectroscopy of half-mustard agent, *Analyst* 131 (2006) 568–572.

- [44] Paul L. Stiles, Jon A. Dieringer, Nilam C. Shah, Richard P. Van Duyne, Surface-enhanced Raman spectroscopy, *Annu. Rev. Anal. Chem.* 1 (2008) 601–626.
- [45] J.A. McMahon, Y. M Wang, L. J Sherry, R.P. Van Duyne, L. D Marks, S. K Gray, G. C. Schatz, Correlating the structure, optical spectra, and electrostatics of single silver nanocubes, *J. Phys. Chem. C* 11 (2009) 2731–2735.
- [46] J.A. McMahon, I. Henry, K. Wustholz, M. Natan, R. Freeman, R. Van Duyne, G. Schatz, Gold nanoparticle dimer plasmonics: finite element method calculations of the electromagnetic enhancement to surface-enhanced Raman spectroscopy, *Anal. Bioanal. Chem.* 394 (2009) 1819–1825.
- [47] K.L. Wustholz, A.-I. Henry, J.M. McMahon, R.G. Freeman, N. Valley, M.E. Piotti, M. J. Natan, G.C. Schatz, R.P. Van Duyne, Structure-activity relationships in gold nanoparticle dimers and trimers for surface-enhanced Raman spectroscopy, *J. Am. Chem. Soc.* 132 (2010) 10903–10910.
- [48] S.L. Kleinman, E. Ringe, N. Valley, K.L. Wustholz, E. Phillips, K.A. Scheidt, G. C. Schatz, R.P. Van Duyne, Single-molecule surface-enhanced Raman spectroscopy of crystal violet isotopologues: theory and experiment, *J. Am. Chem. Soc.* 133 (2011) 4115–4122.
- [49] J.M. McMahon, S. Li, L.K. Ausman, G.C. Schatz, Modelling the effect of small gaps in surface-enhanced Raman spectroscopy, *J. Phys. Chem. C* 116 (2012) 1627–1637.
- [50] S.L. Kleinman, B. Sharma, M.G. Blaber, A.-I. Henry, N. Valley, R.G. Freeman, M. J. Natan, G.C. Schatz, R.P. Van Duyne, Structure enhancement factor relationships in single gold nanoantennas by surface-enhanced Raman excitation spectroscopy, *J. Am. Chem. Soc.* 135 (2013) 301–308.
- [51] S.P. Hastings, P. Swanglap, Z. Qian, Y. Fang, S.-J. Park, S. Link, N. Engheta, Z. Fakhraei, Quadrupole-enhanced Raman scattering (QERS), *ACS Nano* 8 (2014) 9025–9034.
- [52] Q. Zhang, N. Large, H. Wang, Gold nanoparticles with tipped surface structures as substrates for single-particle surface-enhanced Raman spectroscopy: concave nanocubes, nanotrisoctahedra, and nanostars, *ACS Appl. Mater. Interfaces* 6 (2014) 17255–17267.
- [53] D. Krouslid, N. Large, N. Chiang, A.-I. Henry, T. Seideman, G.C. Schatz, R.P. Van Duyne, Unraveling the near- and far-field relationship of 2D surface-enhanced Raman spectroscopy substrates using wavelength-scan surface-enhanced Raman excitation spectroscopy, *J. Phys. Chem. C* 121 (2017) 14737–14744.
- [54] Y. Huang, X. Zhang, E. Ringe, L. Ma, X. Zhai, L. Wang, Z. Zhang, Detailed correlations between SERS enhancement and plasmon resonances in subwavelength closely spaced Au nanorod arrays, *Nanoscale* 10 (2018) 4267–4275.
- [55] Y. Huang, Y. Chen, X. Xue, Y. Zhai, L. Wang, Z. Zhang, Unexpected large nanoparticle size of single dimer hotspot systems for broadband SERS enhancement, *Opt. Lett.* 43 (2018) 2332–2335.
- [56] Y. Huang, Y. Chen, L.L. Wang, E. Ringe, Small morphology variations effects on plasmonic nanoparticle dimer hotspots, *J. Mater. Chem. C* 6 (2018) 9607–9614.
- [57] J. Li, Y. Huang, Y. Ding, et al., Shell-isolated nanoparticle-enhanced Raman spectroscopy, *Nature* 464 (2010) 392–395.
- [58] Jian-Feng Li, Yue-Jiao Zhang, Song-Yuan Ding, Rajapandiyam panneerselvam, and zhong-qun tian core-shell nanoparticle-enhanced Raman spectroscopy, *Chem. Rev.* 117 (2017) 5002–5069.
- [59] L.R. Deng, Y. Zhai, Y. Chen, N. Wang, Y. Huang, Enhancing the plasmonic fields by a high refractive index dielectric coating for surface enhanced spectroscopies, *J. Phys. D Appl. Phys.* 52 (2019) 43LT01.
- [60] Y. Zhai, L. Deng, Y. Chen, N. Wang, Y. Huang, Reducing the loss of electric field enhancement for plasmonic Core-Shell nanoparticle dimers by high refractive index dielectric coating, *J. Phys. Condens. Matter* 32 (2020), 105001.
- [61] Yu Meidong, Huang Zhenping, Liu Zhengqi, Chen Jian, Liu Yi, Tang Li, Liu Guiqiang, Annealed gold nanoshells with highly-dense hotspots for large-area efficient Raman scattering substrates, *Sensor. Actuator. B Chem.* 262 (2018) 845–851.
- [62] Guiqiang Liu, Yi Liu, Li Tang, Xiaoshan Liu, Guolan Fu, Zhengqi Liu, Semiconductor-enhanced Raman scattering sensors via quasi-three-dimensional Au/Si/Au structures, *Nanophotonics* 8 (2019) 1095–1107.
- [63] Jian Chen, Peng Tang, Guiqiang Liu, Zao Yi, Xiaoshan Liu, Pingping Pan, Zhengqi Liu, *Nanotechnology* 30 (2019), 465204.
- [64] L. Tang, Y. Liu, G. Liu, et al., A novel SERS substrate platform: spatially stacking plasmonic hotspots films, *Nanoscale Res. Lett.* 14 (2019) 94.
- [65] J.B. Jackson, N.J. Halas, Surface-enhanced Raman scattering on tunable plasmonic nanoparticle substrates, *Proc. Natl. Acad. Sci. U. S. A* 101 (2004) 17930–17935.
- [66] C. Oubre, P. Nordlander, Finite-difference time-domain studies of the optical properties of nanoshell dimers, *J. Phys. Chem. B* 109 (2005) 10042–10051.
- [67] P. Nordlander, F. Le, Plasmonic structure and electromagnetic field enhancements in the metallic nanoparticle-film system, *J. Appl. Phys.* B 84 (2006) 35–41.
- [68] F. Le, N.Z. Lwin, N.J. Halas, P. Nordlander, Plasmonic interactions between a metallic nanoshell and a thin metallic film, *Phys. Rev. B* 76 (2007), 165410.
- [69] F. Le, D.W. Brandl, Y.A. Urzhumov, H. Wang, J. Kundu, N.J. Halas, J. Aizpurua, P. Nordlander, Metallic nanoparticle arrays: a common substrate for both surface-enhanced Raman scattering and surface-enhanced infrared absorption, *ACS Nano* 2 (2008) 707–718.
- [70] F. Hao, F.P. Nordlander, M.T. Burnett, S. A Maier, Enhanced tunability and linewidth sharpening of plasmon resonances in hybridized metallic ring/disk nanocavities, *Phys. Rev. B* 76 (2007), 245417.
- [71] C. Tabor, R. Murali, M.A. Mahmoud, M.A. El-Sayed, On the use of plasmonic nanoparticle pairs as a plasmon ruler: the dependence of the near-field dipole plasmon coupling on nanoparticle size and shape, *J. Phys. Chem. A* 113 (2009) 1946–1953.
- [72] M.A. Mahmoud, M.A. El-Sayed, Aggregation of gold nanoframes reduces, rather than enhances, SERS efficiency due to the trade-off of the inter- and intraparticle plasmonic fields, *Nano Lett.* 9 (2009) 3025–3031.
- [73] H. Lee, J.-H. Lee, S.M. Jin, Y.D. Suh, J.M. Nam, J.-M. Nam, Single-molecule and single-particle-based correlation studies between localized surface plasmons of dimeric nanostructures with ~1 nm gap and surface-enhanced Raman scattering, *Nano Lett.* 13 (2013) 6113–6121.
- [74] L. Yang, H. Wang, Y. Fang, Z. Li, Polarization state of light scattered from quantum plasmonic dimer antennas, *ACS Nano* 10 (2016) 1580–1588.
- [75] L. Yang, P. Li, Z. Li, Emitting-polarization of surface plasmons coupling in metallic nanoantennas, *J. Optics-UK* 20 (2018), 014002.
- [76] H. Wang, Plasmonic refractive index sensing using strongly coupled metal nanoantennas: nonlocal limitations, *Sci. Rep.* 8 (2018) 9589.
- [77] X. Huang, I.H. El-Sayed, W. Qian, M.A. El-Sayed, Cancer cell imaging and photothermal therapy in the near-infrared region by using gold nanorods, *J. Am. Chem. Soc.* 128 (2006) 2115–2120.
- [78] F. Hao, C.L. Nehl, J.H. Hafner, Nordlander, plasmon resonances of a gold nanostar, *Nano Lett.* 7 (2007) 729–732.
- [79] T.K. Sau, C. Murphy, Room temperature, high-yield synthesis of multiple shapes of gold nanoparticles in aqueous solution, *J. Am. Chem. Soc.* 126 (2004) 8648–8649.
- [80] P.S. Kumar, I. Pastoriza-Santos, B. Rodríguez-González, F.J. García, de Abajo, L. M. Liz-Marza, High-yield synthesis and optical response of gold nanostars, *Nanotechnology* 19 (2008), 015606.
- [81] C.G. Khoury, T. Vo-Dinh, Gold nanostars for surface-enhanced Raman scattering: synthesis, characterization and optimization, *Phys. Chem. C* 112 (2008) 18849–18859.
- [82] J. Xie, Q. Zhang, J.Y. Lee, D.I. Wang, The synthesis of SERS-active gold nano flower tags for in vivo applications, *ACS Nano* 2 (2008) 2473–2480.
- [83] S. Barbosa, A. Agrawal, L. Rodríguez-Lorenzo, I. Pastoriza-Santos, R.A. Alvarez-Puebla, A. Kornowski, H. Weller, L.M. Liz-Marzán, Tuning size and sensing properties in colloidal gold nanostars, *Langmuir* 26 (2010) 14943–14950.
- [84] H. Yuan, C.G. Khoury, H. Hwang, C.M. Wilson, G.A. Grant, T. Vo-Dinh, Gold nanostars: surfactant-free synthesis, 3D Modelling, and two-photon photoluminescence imaging, *Nanotechnology* 23 (2012), 075102.
- [85] D.K. Lim, K.S. Jeon, J.H. Hwang, H. Kim, S. Kwon, Highly uniform and reproducible surface-enhanced Raman scattering from DNA-tailorable nanoparticles with 1-nm interior gap, *Nat. Nanotechnol.* 6 (2011) 452–460.
- [86] S. Jeong, M.-W. Kim, Y.-R. Jo, N.-Y. Kim, D. Kang, S.Y. Lee, J. H Kim, Hollow porous gold nanoshells with controlled nanojunctions for highly tunable plasmon resonances and intense field enhancements for surface-enhanced Raman scattering, *ACS Appl. Mater. Interfaces* 11 (2019) 44458–44465.
- [87] H.Y. Liang, Z.P. Li, W.Z. Wang, Y.S. Wu, H. Xu, Highly surface-roughened “flower-like” silver nanoparticles for extremely sensitive substrates of surface-enhanced Raman scattering, *Adv. Mater.* 21 (2009) 4614–4618.
- [88] M. Pacaud, K. Hervé-Aubert, M. Soucé, A.A. Makki, F. Bonnier, A. Fahmi, A. Feofanov, I. Chourpa, One-step synthesis of gold nanoflowers of tunable size and absorption wavelength in the red & deep red range for SERS spectroscopy, *Spectrochim. Acta* 225 (2020), 117502.
- [89] H. Ikhtiar Khan, G. Ali Khan, S. Mehmood, A. Daud Khan, W. Ahmed, Gold nanoworms: optical properties and simultaneous SERS and fluorescence enhancement, *Spectrochim. Acta* 220 (2019), 117111.
- [90] R.V. William, G.M. Das, V.R. Dantham, R. Laha, Enhancement of single molecule Raman scattering using sprouted potato shaped bimetallic nanoparticles, *Sci. Rep.* 9 (2019), 10771.
- [91] M. Verma, T.K. Naqvi, S.K. Tripathi, M.M. Kulkarni, N. Eswara Prasad, P. K. Dwivedi, Plasmonic paper based flexible SERS biosensor for highly sensitive detection of lactic and uric acid, *IEEE Trans. NanoBioscience* 21 (2021) 294–300.