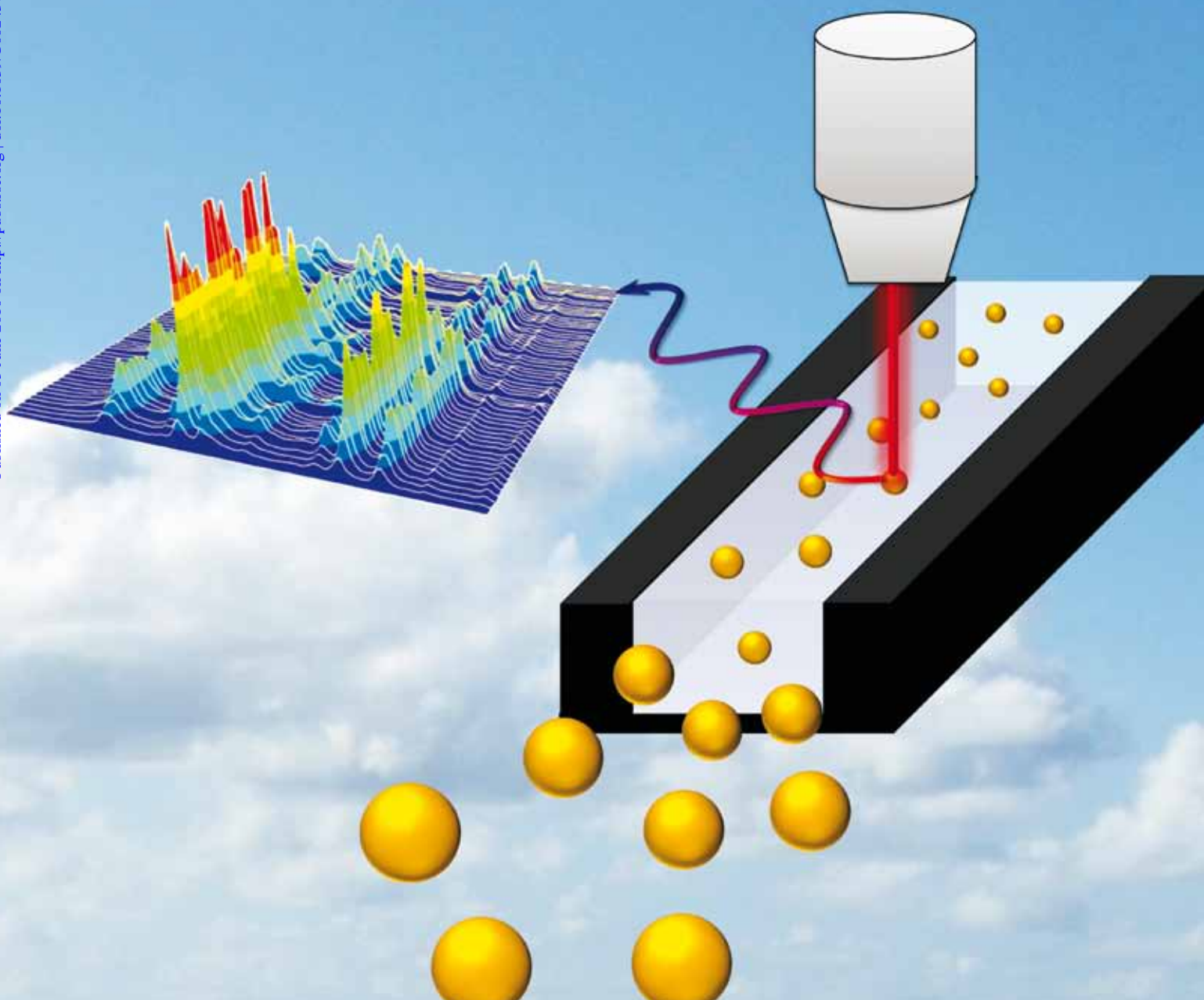


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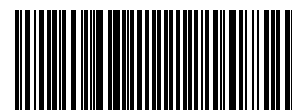
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REVIEW

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Environmental applications of plasmon assisted Raman scattering

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We present in this review article an overview of the capabilities of surface enhanced Raman scattering (SERS) spectroscopy as a technique for applications related to environmental analysis and monitoring, ranging from the structural characterization of soils, through ultrasensitive detection of pollutants and heavy metal ions, to the analysis of plants, tissues and microorganisms, with a critical approach in which the drawbacks and difficulties associated to the various experimental configurations and enhancing substrates are introduced, as well as perspectives in the different fields.

Introduction

Environmental monitoring often requires the determination of extremely low amounts of pollutants in rivers, lakes, soil, or simply in the atmosphere. The application of nanostructured materials toward the development of novel detection techniques with improved sensitivity or simplified and faster applicability has rapidly become an appealing perspective and a large number of examples are currently available. We shall concentrate in this review article on the application of plasmon assisted Raman scattering (more commonly known as surface enhanced Raman scattering, SERS) as a powerful analytical technique, with potential detection limits down to the single molecule.¹ The interest of SERS is, however, not only dictated by such low detection limits, but also by the complete information that it can provide, since the spectra contain all the vibrational information of the molecular analytes, and its simple application, which can be carried out at environmental conditions of pressure and temperature, in solution, and with no need of sophisticated analytical preparations.² The advances in laser technology, detection devices (*i.e.* CCDs) and nanoscale synthesis have brought about a revival of this technique, especially in biomedical applications because it has the potential to draw a rapid and sensitive picture about the health condition of an individual or even an entire community, or to prevent pandemics and bioterrorism threats.³ However, the promising results obtained in bioapplications have cast a shadow over other interesting applications such as environmental detection and monitoring of

pollutants in soil, air and water or the structural characterization of environmentally relevant organic phases. Thus, in this review article, rather than a discussion of the physical phenomena involved in SERS, which can be found in other excellent reviews,^{1a,4} we focus on environmental applications, including characterization of macromolecules, determination of the fate of pollutants and their ultrasensitive detection, and the relation of these applications with the design of new plasmonic materials and sensor devices.

The SERS effect originates from the coupling of the electromagnetic field that originates from a suitable metallic nanostructure upon excitation by light of the appropriate energy with the vibrational modes of the molecule under study, and requires a close contact between molecule and metallic surface.⁵ This close contact is not only essential for the target molecule to feel the electromagnetic field of the nanoparticle, which lies at the basis of SERS, but also for the chemical effects (*i.e.* charge transfer and resonance at the surface) to take place and further increase the signal. Therefore, the plasmonic material used as optical enhancer and its surface chemistry (which will ultimately determine the affinity of the analyte toward chemisorption onto the plasmonic material) play key roles in the detection process. A wide variety of optically enhancing materials have been explored, including Cu, Rh, Pd, Ru or In, but Au and Ag still remain the most commonly used platforms, mainly due to their higher efficiency and chemical stability. Regarding the optical enhancer, two different types of substrates are usually distinguished: colloidal dispersions of metal nanoparticles with various shapes and sizes, prepared by chemical methods,^{2,6} or nanostructured thin films prepared by controlled nanoparticle assembly or by physical methods such as physical vapour deposition, sputtering, electrochemical roughening or electron

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Broader context

This review article summarizes the capabilities of surface enhanced Raman scattering (SERS) spectroscopy as a tool of choice for accurate and fast characterization, detection and monitoring a range of environmental problems, not limited to detection of pollutants in air, but also including changes in the structure of soil, soil phases, or composition, including the incorporation of organic pollutants, heavy metal ions or inorganic anions, which are commonly released during energy production industrial processes. SERS is also a suitable technique for the monitoring of changes in plants and environmental microorganisms, which are closely related to changes in their surrounding media.

beam lithography.⁷ Both types of substrates have their own advantages and drawbacks in relation to each particular application.

Structural characterization of organic phases from soils and waters

Humic substances (HS) are natural macromolecules that can be found ubiquitously in nature, comprising up to 80% of soil organic matter and up to 60% of dissolved organic carbon. They are products derived from the humification of organic material from plants, animals, microorganisms, and their metabolic products. HS affect soil fertility, mineral weathering, and water acidity. They are also involved in the transport, sequestration, and mitigation of contaminants, thereby affecting atmospheric chemistry through the carbon cycle, in which carbon is constantly recycled within plants, animals, soil, air, and water. Systematic studies of the composition and structure of HS contribute to the understanding of the role of their interactions with other elements and compounds. Such knowledge is necessary to predict and control the impact of chemical and biological changes in the environment. Regarding composition, many techniques have been applied, such as mass spectrometry, solid-state NMR or FTIR,⁸ whereas their structure has been studied by means of SEM, light scattering or gas adsorption.⁹ Each of these techniques provides important but partial information about the system. First of all, they only give information on either composition or structure. Second, most of them can only be used under special conditions, far away from those of the environment. In this scenario, SERS arises as a versatile tool that can provide information on both composition and structure, under environmental conditions, either in solution or in the solid state. After the first report regarding the application of SERS on colloidal silver to sort organic matter in natural waters,¹⁰ many others were published dealing with the determination of HS molecular composition.¹¹ In fact, by measuring SERS on silver

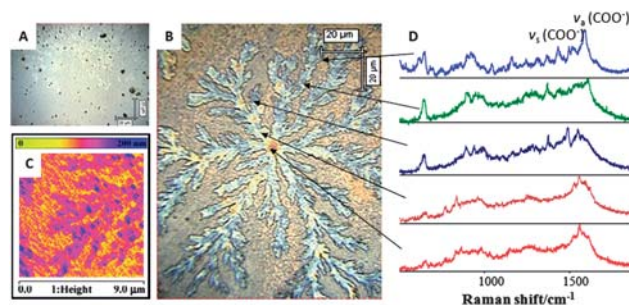


Fig. 1 Optical images of a humic substance deposited on a silver island film at acidic (A) and alkaline pH (B). Topographic AFM micrograph of the fractal structure of the HS in alkaline conditions (C). SERS spectra of the HS film acquired from different regions, showing the localization of the charged species in the edge of the structure (D). Adapted with permission from ref. 15. Copyright 2004 American Chemical Society.

colloids it was possible to elucidate the critical building blocks that integrate the molecular structure of these substances.¹² SERS has also been applied to study the adsorption behaviour of HS onto different natural colloids, which is essential to understand the fate of these substances in the environment, as well as the structure of soils. To this aim, different pure metallic (Ag, Au or Cu)¹³ or modified¹⁴ (Fe–C–Cr–Ni) nanostructured surfaces were used, under different pH and ionic strength conditions. As an example, Fig. 1 shows the adsorption of purified HS on silver island films, under different pH conditions. It was found that, at acidic pH, the protonated groups in HS, mainly carboxylic acids, phenols and alcohols, tend to form inter- and intra-molecular H-bonds, giving rise to globular structures (Fig. 1a). However, when they ionize (deprotonate), the structure expands because of its internal negative charge. Thanks to the spectral and spatial resolution of SERS (below 500 nm), it was possible to characterize the position of the different building blocks on the fractal structure. As shown in Fig. 1d, highly polar charged species characterized by strong symmetric and antisymmetric stretching



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of several chemistry and materials science journals. His current interests include the synthesis and assembly of nanoparticles, nanophotonics, and the development of nanoparticle-based biosensors.

modes of COO^- , at ~ 1350 and ~ 1620 cm^{-1} (top three spectra in Fig. 1d), rearrange at the interface while highly aromatic non-polar groups characterized by a strong resonance due to sp^2 carbon hybridization, the so-called cathedral bands from 1300 to 1600 cm^{-1} (bottom two spectra in Fig. 1d), tend to stay at the centre of the HS structure.¹⁵

Ultrasensitive detection of molecular pollutants in soil, air and water

Probably one of the most obvious applications of SERS toward environmental science is the direct ultradetection of pollutants from natural and waste waters, which can be readily achieved by simply adding a small volume (10 mL) of the sample to the optical enhancer (the metallic nanostructure), which can be either in suspension (0.5–1 mL of colloid) or supported onto an active film, with no need of any complex preparation protocol. Due to the simplicity of this method and the availability of portable Raman spectrometers,¹⁶ SERS may become a simple method for accurate and sensitive field analysis. As an example, SERS has been used for the direct determination, down to the atto/femtomolar regime, of molecular contaminants, such as pesticides, industrial derivatives, and other molecular species of relevance, present in natural waters.^{10,17}

More challenging is the direct determination of contaminants in atmospheric air. The nature of the matrix, a gas with suspended particles rather than a liquid, hinders the contact between sample and optical enhancer. Several approaches have been developed to overcome this difficulty. For example, the air sample has been allowed to naturally adsorb onto freshly

prepared films, either produced from colloids¹⁸ or by nanosphere lithography.¹⁹ This approach, however, only works properly when the target analytes display functional groups with high chemical affinity for gold or silver surfaces. Unfortunately, most pollutants do not contain such functional groups and thus cannot be directly detected *via* SERS. In this respect, several hybrid materials have been devised with the ability to retain “non-adsorbing” molecules. This strategy has been widely demonstrated specially with polycyclic aromatic hydrocarbons (PAHs), which are known to be human carcinogens and are widely present, either as vapours or adsorbed onto the particulate matter suspended in the air. Since PAHs are highly non-polar, plasmonic materials with hydrophobic interfaces, such as self-assembled monolayers of aliphatic chains,²⁰ calixarenes,²¹ or dicarbamates,²² can be used to promote the adsorption of these analytes. This trapping concept can also be applied to fluid samples and, in fact, has been extended to other types of interaction, such as electrostatic attraction,²³ or mechanical trapping,²⁴ for direct ultrasensitive detection of dioxins or naphthol in aqueous solutions. A recent example of special interest is the *in situ* production of plasmonic nanoparticles inside a porous polymer matrix like agarose^{24a} (Fig. 2). Agarose swells in contact with water, reaching up to 12 fold its dry volume, so that it can be filled with the probe fluid. Upon subsequent drying, the polymer collapses, trapping whatever analytes are present in the fluid and bringing them in contact with the plasmonic hot spots created by silver nanoparticles in close contact. Proof of concept of this strategy has been provided for non-adsorbing contaminants as dichlorodiphenyltrichloroethane (DDT), even allowing recycling of the substrate upon washing with water.

By far the most demanding matrix for chemical analysis in the environment is soil. Soil is composed of a mixture of inorganic and organic components such as clays, inorganic oxides and humic substances. All of them have high surface areas and, especially the HS, high affinity for the adsorption pollutants. Unlike inorganic species, molecular organic compounds are usually destroyed using digestion methods. Moreover, due to the high complexity and natural fluorescence of HS, direct detection of pollutants in the soil matrix is impossible using mass spectrometry or optical spectroscopy. Therefore, to gain knowledge about the nature and amount of contaminants in a soil area, extensive and time consuming extraction methods are required. However, soil lixiviates can be directly analyzed by SERS, and this technique has been applied, for example, to the trace detection of organophosphorous agents.²⁵ Additionally, one can take advantage of some of the properties of the HS for the direct analysis of pollutants in soil. Humic substances typically contain several functional groups which are capable of reducing gold salts into nanoparticles (*e.g.* hydroquinone and phenol groups). In fact, when no sulfur is present in nature, gold forms metallic colloids in the presence of HS.²⁶ This property has been exploited for the synthesis of environmentally friendly gold nanoparticles,²⁷ and since the HS remain in close contact with the nanoparticles, the native fluorescence of HS is quenched. In addition, because of the low SERS cross section of HS, these natural macromolecules can be used to trap and analyze pollutants, thus becoming excellent and clean substrates for SERS analysis.²⁸ More importantly, by producing gold nanoparticles *in situ*, previously contaminated HS can be directly

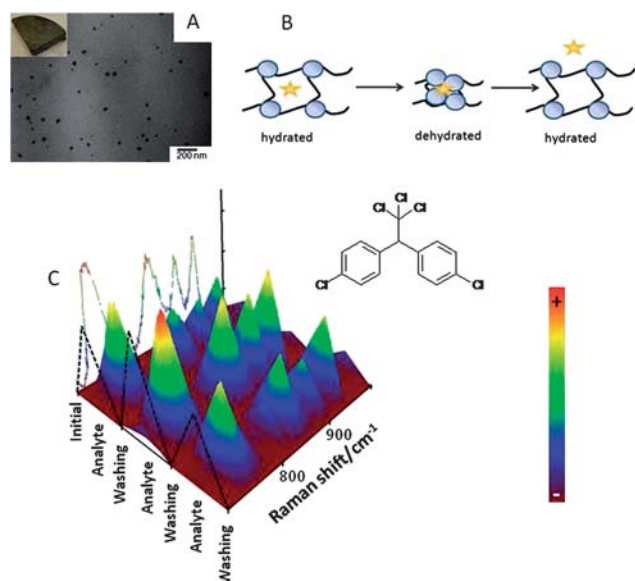


Fig. 2 (A) Cross-sectional TEM image of an Ag-Agarose gel (inset shows a picture of the bulk polymer). (B) Scheme of the trapping and washing processes for an analyte in solution: the analyte diffuses into the polymer matrix when in contact with the sample solution, and becomes trapped after drying. Reusability is achieved upon washing with water. (C) SERS spectra of DDT in the gel, before and after contact with the sample solution, along several washing cycles. Adapted with permission from ref. 24a. Copyright 2009 American Chemical Society.

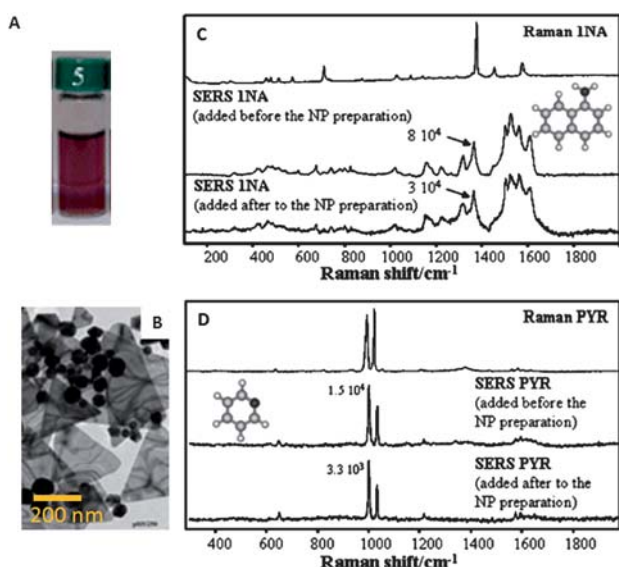


Fig. 3 (A) Photograph of a humic substance suspension after addition of HAuCl_4 . The burgundy colour is due to formation of gold nanoparticles and nanoplates by reduction with the HS (B). (C) Raman and average SERS spectra of 1-naphthylamine, added before and after nanoparticle synthesis. The numbers indicate the relative intensity of the band at 1364 cm^{-1} upon excitation with a 633 nm laser line. (D) Raman and SERS spectra of pyridine added before and after nanoparticle synthesis. The numbers indicate the relative intensity of the band at 1007 cm^{-1} upon excitation with a 633 nm laser line. Adapted from ref. 27 and 29. Copyright Royal Society of Chemistry. SERS spectra for both analytes, INA and PYR, are the same, independent of the method used for sample preparation. However, for samples where the analyte was added before the formation of the nanoparticles, the observed enhancements were around 2.6 (INA) and 4.6 (PYR) fold larger than those of samples prepared with the conventional procedure.

analyzed with no additional treatment.²⁹ Fig. 3A shows the appearance of a gold-HS composite suspension with a burgundy colour resulting from the produced mixture of gold nanoplates and nanospheres (Fig. 3B). Shown in Fig. 3C and D are the SERS spectra from trace analysis of two usual pollutants, 1-naphthylamine and pyridine, both when the humic substance was contaminated prior to the analysis and when the pollutant analyte was added after gold reduction. Thus, this method illustrates a sensitive, accurate and direct analysis of exogenous molecules in soil with no need for sample preparation.

We have limited our discussion so far to methods employed for single-probe analysis. However, and in particular when dealing with environmental pollution, continuous monitoring of certain areas is highly desirable. Recent developments in microfluidic technology, together with the transparency of glass or quartz to visible lasers, which allows focusing of the beam within the flow channel while recording the inelastic radiation in a backscattering configuration, pave the way to the design of a new generation of on-line systems for continuous and remote monitoring of the presence of undesired substances in natural environments and in real time.³⁰ The most common devices employ two microfluidic channels with continuous liquid flows carrying the sample and a colloidal suspension of the optical enhancer (silver or gold nanoparticles). The channels intercept each other

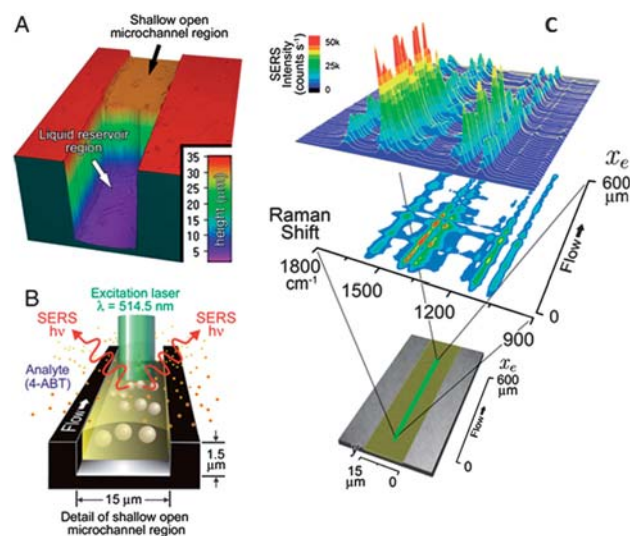


Fig. 4 (A) Scheme of a microfluidic/SERS sensing device. The device is designed for free-surface fluidics and is easily coupled with SERS detection. The 3D profile of the microfluidic device shows the transition from the $30\text{ }\mu\text{m}$ deep fluid reservoir to the open $1.5\text{ }\mu\text{m}$ deep microchannel section. The channels are $15\text{ }\mu\text{m}$ wide. (B) Schematic view of a microfluidic sensor for analysis of gas-phase species. The liquid/atmosphere interface allows analyte adsorption and subsequent optical stimulation with a visible laser for SERS detection. (C) Typical series of SERS spectra, obtained by the stepwise registration of Raman scattering along the microchannel in $10\text{ }\mu\text{m}$ increments, shown as a function of position down the stream direction of the microchannel. The SERS interrogation path down the central region of the microchannel is shown as a green line. Reproduced with permission from ref. 31. Copyright 2007 Proceedings of the National Academy of Sciences of The United States of America.

allowing the mixture of the two fluids. To ensure the complete adsorption of the analyte onto the optical enhancers, a serpentine channel of variable length is usually placed between the interception, where the mixing takes place, and the glass or quartz window through which the laser beam is focused into the microchannel. When the sample is a liquid, the system is straightforward, whereas for gas samples a special design of the mixing chamber is required to avoid the formation of bubbles within the flow. Fig. 4A shows the design of a microfluidic device for the continuous monitoring of airborne pollutants.³¹ In this device, the air sample is bubbled into a silver nanoparticle suspension that continuously flows through a glass channel. The SERS spectra can then be collected from any spot of the channel (Fig. 4B), with the result that the intensity steadily increases as the sample travels farther through the channel (Fig. 4C), due to the aggregation (and hot spot formation) of the colloidal nanoparticles as analyte is adsorbed onto their surface.^{23b} However, even though this uncontrolled aggregation increases the SERS signal leading to lower detection limits, it poses some drawbacks, such as the impossibility of quantitative determination, since the intensity strongly depends on the degree of aggregation, which in turn is determined not only by the analyte but also by other solution components, such as pH or ionic strength. Additionally, such aggregation often leads to formation of deposits inside the microchannels and their optical blocking after some time. These problems can be resolved by using appropriate hybrid materials

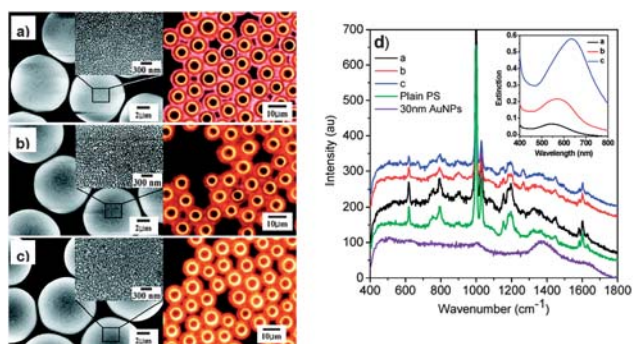


Fig. 5 SEM (left) and dark field (right) images (a–c), and surface-enhanced Raman and UV-vis spectra (d) of 10 μm PS beads covered with 30 nm Au nanoparticles with different levels of metal coverage. Reproduced with permission from ref. 32a. Copyright 2009 American Chemical Society.

instead of nanoparticle colloids. The most usual procedure comprises the design of micron- or submicron-sized hybrid particles containing optically inert platforms, such as silica, a polymer, or even carbon (nanotubes), which are coated with the plasmonic material, *i.e.* silver or gold nanoparticles³² (Fig. 5). Such composite particles present long-term optical and colloidal stability (the support often carries a high surface charge), while supporting an optically active surface, which is densely populated with hot spots.

Ultrasensitive detection of inorganic anions and metallic ions

SERS has been successfully employed in the detection of inorganic oxoanions in natural waters such as perchlorate, sulfate, nitrate, cyanide or sulfocyanide.³³ Determination is either based

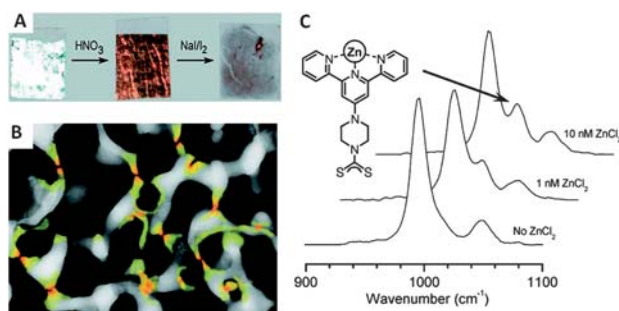


Fig. 6 Optical characterization of nanoporous Au (NPG) films before and after etching. (A) Image of a white-gold leaf mounted onto an 18 mm glass coverslip (prior to dealloying), NPG after 10 min of HNO₃ treatment, and NIR-absorbing NPG after 20 min of immersion in 10 mM triiodide. (B) Partial passivation model for site-selective adsorption on nanostructured substrates, with the SERS-active hot spots shown in colour. (C) Sensitivity of receptor-saturated NPGs toward divalent Zn ions. NPG substrate passivated with pztpy-DTC (0.5 mM); the peak shift in the ring-breathing mode is induced by complexation with Zn²⁺ ions at nanomolar concentrations. Peak intensities at 1020 cm⁻¹ after exposure to 1 nM and 10 nM ZnCl₂ were 3900 and 5000 counts, respectively. Adapted with permission from ref. 37. Copyright 2009 American Chemical Society.

on electrostatic affinity by adjusting the surface charge or by chemical affinity of the cyanide group. Until recently, SERS analysis was considered restricted to molecular entities, and identification of heavy metal ions was restricted to those that form stable oxides or oxyanions in solution, such as Nb₂O₅, CrO₄²⁻, MoO₄²⁻, WO₄²⁻, TeO₄⁻ or UO₂⁺ and NpO₂⁺.³⁴ In such cases, SERS does not only provide information regarding the presence of the chemical element but also of its chemical form, oxidation state or complexation,³⁵ which is a critical aspect in the toxicological issues of heavy metals. Recent progress has been made regarding the ultradetection of heavy metals in their zero-valent or cationic states. Since neither zero-valent metals nor metal cations display signals in vibrational spectroscopy, the analytical approaches are usually based on the complexation of the metallic moieties to an organic ligand with high affinity for the metal. In this way, detection of copper, mercury and cadmium have been reported.³⁶ The method recently developed for Zn²⁺ determination is worth special consideration (Fig. 6),³⁷ because it is based on the interesting idea of fabricating a porous gold structure, partially passivated with dimethyldithiocarbamate while leaving the most accessible “hot spots” available for SERS enhancement. The partially passivated porous gold films were functionalized with supramolecular receptors for chemoselective Zn²⁺ capture (4'-(*N*-piperazinyl)terpyridine-dithiocarbamate, pztpy-DTC), thus enabling the detection of divalent metal ions at trace levels, through measurable shifts of a characteristic Raman peak of the metal ion receptor, upon complexation with the ion. This approach paves the way for future development of sensors for direct and simple determination of heavy metals in fluids. Still, and in contrast with the determination of molecular systems, ultrasensitive SERS detection of metallic cations is still in its infancy and further research needs to be carried out before actual implementation as a spectroscopic tool for field measurements.

SERS analysis of relevant plant structures, tissues and microorganisms

Environmental applications of SERS are not restricted to the analysis of soil and water or to the ultradetection of pollutants, as it can also be applied to the determination, characterization or sorting of natural products in their natural environment. For example, SERS has been used for the detection and sorting of polysaccharides (celluloses or glucose)³⁸ and natural pigments (flavonoids and carotenoids).³⁹ One interesting additional application is the *in vivo* chemical mapping of plants and seeds, which is extremely helpful to monitor plant growth and to make decisions about the optimal time for crop harvesting.⁴⁰ Further, this analysis is also useful for the taxonomic classification of plants.⁴¹ In this direction, SERS has been used for fast and direct multiplex characterization of pollen grain.⁴²

On the other hand, the most common identification methods for microorganisms, mostly viruses and bacteria, are very time consuming (sometimes taking weeks) since it requires isolation of pure single strains and their recognition relies on a combination of morphological evaluation with specific tests for the microorganisms' ability to grow in various culture media. SERS has been proven to serve for the identification of microorganisms in complex mixtures (so isolation of single strains is not required)

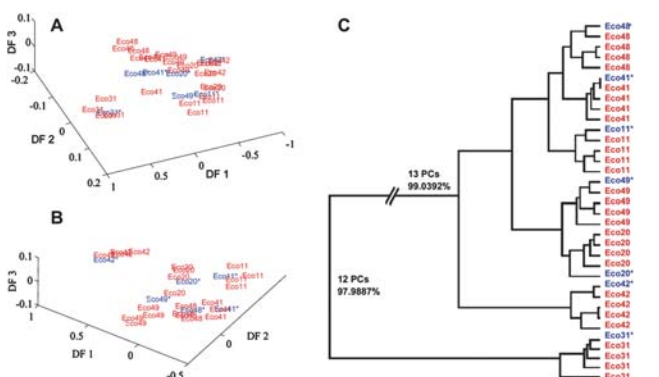


Fig. 7 (A) Ordination plot characterizing seven isolates of *E. coli*. The entries in red represent the training data and those marked with an asterisk in blue, the validation data. The analysis was performed and validated as described in the text. Isolate Eco31 can be seen to form a cluster that is apart from the rest of the isolates. Therefore, Eco31 was extracted and the remaining isolates analyzed again. This result (B) clearly demonstrates that SERS can be applied to discrimination of microorganisms at the strain level. (C) A composite dendrogram generated by HCA using PC space from the training and validation replicates used to generate the ordination plots in (A) and (B). This representation of the results shows how the validation replicates fall tightly within the clusters formed from the training data. Reproduced with permission from ref. 44b. Copyright 2004 American Chemical Society.

and within a few seconds.⁴³ This is due to the powerful combination of confocal optical microscopy, and the unique vibrational fingerprints registered in SERS measurements. As a consequence, the spatial resolution can go down to 500 nm, allowing for direct microorganism identification, including large viruses, as well as all bacteria and their resistance forms and eukaryotic cells, such as yeast or protozoa. This method, for example, can be used to assess the quality of natural waters in rivers, where contamination from improperly treated wastewater usually imposes critical health problems.⁴⁴ Direct SERS discrimination of cells usually relies on the interaction of plasmonic nanoparticles with the membrane of the microorganism, so that the obtained SERS spectra represent the chemical composition of the membrane. However, the chemical composition of the membranes can be very similar, in particular between different strains of the same species. However, this drawback has been readily solved by coupling the SERS output (the vibrational spectra) with pattern recognition statistical methods as principal component (PC) analysis and hierarchical cluster analysis (HCA). The use of these methods in conjunction with SERS can become a powerful identification approach to discriminate bacteria at the strain level (Fig. 7).^{44b}

Conclusions and outlook

SERS has been shown to have sufficiently matured as an analytical technique in a wide range of fields and applications, including environmental characterization and monitoring. The extremely sensitive capabilities of SERS and the flexibility in the design of enhancing substrates, both in solution and on solid substrates have opened new avenues toward generalized use of this technique, not only in the laboratory but also in field assays

through the availability of portable Raman spectrometers. However, real implementation in the market place and routine analysis still requires validation for quantification and reproducibility of the large number of systems that have been reported in the scientific literature and which can be adapted for identification of molecular and ionic species, regardless of their size, composition and aggregation state. The recent progress in the synthesis of metal nanoparticles with tailored size and shape, as well as in their controlled assembly and surface modification is expected to overcome the present limitations and advance the application of the technique.

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