Periodically nanostructured substrates for surface enhanced Raman spectroscopy

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HIGHLIGHTS

- A brief introduction to surface enhanced Raman spectroscopy is given.
- Localized and propagating surface plasmons in SERS electromagnetic mechanism.
- Several types of periodically nanostructured surfaces are described.

GRAPHICAL ABSTRACT
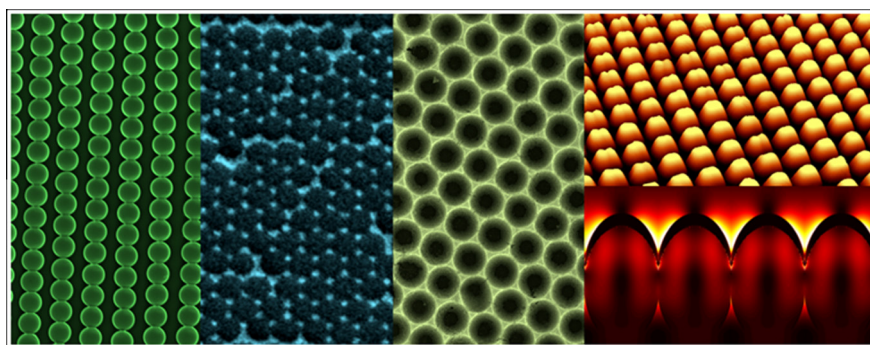
ABSTRACT

Surface Enhanced Raman Spectroscopy (SERS) is a technique capable of specifically detecting trace amounts of a given substance, based on the vibrational molecular signature. Developing cutting-edge applications and furthering a detailed understanding of SERS relies strongly on controling the nano- and micro-scale morphology of metal nanostructured SERS substrates. In this review, we present the most widespread classes of SERS substrates comprising periodic surface features, and the corresponding nanofabrication methods. A brief discussion on surface plasmon polaritons, in the context of the electro-magnetic enhancement mechanism, explains the need for SERS substrates of controlled morphology.

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Introduction

Raman spectroscopy is one of few optical spectroscopy methods that are able to provide fingerprint-like molecular information, by analyzing molecular vibrations. It is therefore well-suited for chemical analysis, and has a wide field of applications, ranging from pharmaceutical and biomedical studies to environmental studies, art and archaeology [1,2]. The technique is based on the

property of molecules to inelastically scatter light; the difference in energy between incident photons and inelastically scattered ones is directly related to the energy of molecular vibrations, from here originating the method's fingerprinting capability. Very often it is desirable to detect/analyze very small amounts of a given substance (e.g. toxins, drugs, bio-markers). In such situations the capabilities of classical Raman spectroscopy are outperformed, due to the very low efficiency of the Raman scattering process, i.e. roughly only one from one million incident photons is inelastically scattered. To overcome this drawback, several tools/strategies are available: (a) one such tool is resonance Raman spectroscopy,

which is the same as normal/classical Raman, with the condition that the excitation laser energy matches a molecular electronic transition; this increases the scattering rate probability, and thus also the efficiency of the process. (b) Surface Enhanced Raman Spectroscopy (SERS), which relies on amplifying, mainly by electromagnetic mechanisms, the Raman signals of molecules adsorbed on nanostructured metal surfaces.

Surface enhanced Raman spectroscopy provides the means for improving the capabilities of the Raman technique by amplifying the original Raman scattering intensity for several (∼3 to 10) orders of magnitude. The first enhanced Raman signals were observed from molecules adsorbed at roughened silver electrode surfaces, more than thirty-five years ago [3,4]. Since then a huge amount of work is being done in order to understand its physico-chemical mechanisms, and develop SERS applications. Although very important fundamental aspects of the technique have been elucidated in the 1980s, important contributions to the current understanding and developments have been achieved in recent years; these came in conjunction with the rising field of Plasmonics, which contributed to the development of SERS. Further, these were facilitated by the rapid overall evolution of nanotechnology, which provided nanofabrication and characterization methods of continuously increasing performance.

The main mechanism for increasing the Raman intensity is now known as the electromagnetic enhancement mechanism, and involves enhancements of the electric field (light component) intensity, resulting from the excitation of surface plasmon resonances. A complementary, less efficient mechanism in SERS, relies on polarizability enhancement, attributed to chemical effects such as charge-transfer excited states. The efficiency of a SERS substrate is described by its enhancement factor (EF), which is quantitatively related to the ratio between the enhanced electric fields at the metallic surface where the Raman scatterer molecule is located and the incident field away from the surface. Current challenges addressed in the last years, and ongoing, are both on the fabrication of SERS substrates with nanoscale precision, aiming at controlling electric field amplification, and on furthering the current understanding of the details of SERS effects.

In this Review we describe some of the nanofabrication techniques that are employed for the preparation of SERS substrates of controlled morphology. The aim is to present a large palette of periodically ordered SERS substrates available nowadays, but also to highlight those kinds of SERS substrates that, in authors view, made seminal contributions to the recent advancements in the understanding of the SERS phenomenon. Authors' contributions from Nanobiophotonics and Laser Microspectroscopy Centre at the Interdisciplinary Research Institute on Bio-Nano-Sciences in Cluj-Napoca are also included. Before describing SERS substrates, an introduction to surface plasmons, playing a major role in the SERS enhancement is given. The number of SERS publications in the last years is overwhelming, with more than 2000 article-type publications containing 'surface enhanced Raman' in the title, found on the Web of Science database, only from 2009 to present. Considerably broad is also the palette of noble metal nano-architectures demonstrated to be efficient as SERS-active substrates. That is why this review does not aim at being exhaustive, but rather at giving an overview to the molecular spectroscopist, by introducing her/him to some of the most representative periodically ordered nanostructures to be used as SERS substrates.

Surface plasmons and SERS

About 10 years ago a spectacular phenomenon was discovered by Ebbesen and co-workers and has been dubbed Extraordinary Optical Transmission [5]. The authors observed that a thick metallic film pierced with subwavelength sized holes arranged in a regular array can transmit much more light than would give the summation of transmittances of the same number of individual holes. There has been much debate on the physical origin of the phenomenon, and even nowadays there is not a completely unified view. However, in many experiments the role of surface plasmon excitations has been evidenced. This discovery marked an important boom of the field of Plasmonics, dealing with the design, fabrication and investigation of the optical properties of metal nanostructures supporting surface plasmon polaritons. SERS has also drawn important benefits from this field, i.e. the ability to fabricate nanostructures possessing a well-defined optical response allowed to observe correlations between these optical properties and the SERS efficiency. This brief introduction into the physics of surface plasmons aims at motivating why SERS needs nanostructured surfaces, either as nanoparticle arrangements, or continuous films with periodic topographical patterns. As discussed in the following, surface plasmon polaritons can be either propagating on extended surfaces, or localized at isolated nanoscale features.

Localized surface plasmons

It has been known for a long time that very fine particles of noble metals appear brightly colored. Noble metal colloids have actually been used, by craftsmen from the Middle Ages, as dyes to color church windows. Although they probably did not realize it, they were the first to develop applications of localized surface plasmons (LSP). The colors of these minuscule noble metal particles are a result of electromagnetic interaction between incident light and conduction electrons in the metal particle.

Consider a spherical particle much smaller than the wavelength (few to tens of nanometres), with its diameter on the order of the penetration depth of electromagnetic waves in metals [6]. If exposed to light, this excitation incident light field is able to penetrate the particle. The electric field inside the particle produces a displacement of the conduction electrons relative to the fixed positively charged ionic lattice. These displaced electrons cause charge accumulation on the surface at one side of the particle. The attraction between this negative charge and the positive charge of the fixed lattice ions on the opposite side results in a restoring force. If the frequency of the incident light field is in resonance with the eigenfrequency of this collective oscillation, even a small exciting field can lead to a strong oscillation. The magnitude of the oscillation depends mainly on the damping involved, which can be both radiative and nonradiative [7]. The strength of the restoring force is the main parameter determining the resonance frequency. This force depends on the separation of the surface charges, i.e. the particle size, the polarizability of the core electrons of the metal particle, and that of the surrounding medium. The alternating surface charges effectively form an oscillating dipole, which radiates electromagnetic waves. Localized surface plasmons are thus non-propagating excitations of the conduction electrons in metallic nanostructures coupled to an electromagnetic field. The consequences of the resonant excitation are to significantly increase the absorption and scattering cross sections for electromagnetic waves, as well as to strongly enhance the near fields in the immediate vicinity of the particle surface [8]. It is this resonantly enhanced near field that is exploited in most of the promising applications of metal nanoparticles. By considering a spherical particle of diameter d, much smaller than the wavelength of incident light $d \ll \lambda$, its interaction with the electromagnetic field can be analyzed using a quasi-static electrostatic approximation (i.e. the harmonically oscillating electromagnetic field can be approximated as constant over the particle volume, so the problem can be equivalent to the simplified problem of a particle in an elec-