Abstract

In recent times, mainly because of the progress achieved in the field of nanoscience and nanotechnology, surface-enhanced Raman spectroscopy (SERS) experienced perhaps its greatest development stage. In these years, the number of SERS publications is overwhelming, and similarly is also the variety of noble metal nano-architectures proved to be SERS-active substrates. Currently, there is an outstanding research interest concerning how to control, manipulate, and amplify light on the nanometer length scale using the surface plasmons properties. Moreover, the experimental data gathered in the last years has confirmed SERS to be an acceptably sensitive spectroscopic method for a large variety of domains such as biomedicine, biophysics, biochemistry, and surface science, analytical and environmental applications.

The Habilitation thesis is focused on a main topic, specifically the use of SERS in combination with other spectroscopic methods for various applications, and is divided in two main parts that illustrate the scientific and professional results acquired in the period after obtaining a research doctorate and also describe the development directions of my future academic career.

Firstly, a few examples are given describing how SERS can be applied in combination with other molecular spectroscopic methods and theoretical simulations to elucidate the structure and adsorption behavior of some pharmaceutical relevant molecules. Pharmacological studies reveal that each drug is specific to a certain human organ on which it is adsorbed, particularly on some special centers. The adsorption of the molecules on a metal surface (silver or gold) can be considered as a mimic of this adsorption process, the metal surface playing the role of an artificial biological interface. Furthermore, for a complete understanding of the action of various drugs, such as the derivatives under discussion, it is very important to find out if the structure of the adsorbed molecules is the same as that of the free species and also to establish whether or not the molecule-substrate interaction may be dependent on the pH value of the environmental solution.

In the next sections, the assessment of the SERS efficiency of a few new-designed SERS active substrate is described. Prior evaluating their SERS enhancement capability the substrates morphology and optical properties were analyzed with the aim of correlating them with the SERS response. Two kinds of solid substrates, ordered and disordered ones, were studied and were proved to be SERS active for a great variety of laser excitation lines from visible to near infrared range. Additionally, all of the investigated substrates were found to be highly efficient, the enhancement factor of the Raman signal of adsorbed probe molecules being in the range of 10^5-10^7. The opportunity of obtaining good SERS spectra with near infrared excitations could open promising perspectives for the investigations of biological samples.

Finally, the capacity of some porous materials containing Au and Ag colloidal particles, respectively to detect by SERS various organic pollutants from water was evaluated and is presented in the following subchapters of the thesis. The detection limits of a few probe pollutant molecules were established and found to be of around 10^{-2} M for thioacetamide and 10^{-5} M and 10^{-7} M for rhodamine 6G and crystal violet molecules, off and under resonant excitation, respectively, when the composites containing Au nanoparticles were employed. In the case of the composites containing Ag nanoparticles, the probe pollutants detection limits were found to be in the range of 10^{-1}-10^{-4} M for acrylamide and around 10^{-5} M for crystal violet. The obtained results showed the real potential of the investigated porous composites to be used to the development of new SERS-based sensors.

Based on the scientific experience accumulated in the last years and taking into account the current progress of the SERS technique, the development directions of my future academic career will be also connected to the SERS technique. Briefly, they will be related to the following topics: a) SERS detection of biological relevant molecules on highly efficient SERS substrates, b) assessment of the potential of new highly porous nanocomposites containing Ag/Au nanostructures of various dimensions and shapes to detect by SERS pollutant species from water solutions, c) exploration of the light irradiation effect on the SERS response of different probe molecules adsorbed on noble metal nanoparticles in contact with other nanoparticles (e.g. Au-TiO_2, Ag-TiO_2, Au-SiO_2, Ag-SiO_2, etc).

All of these development directions will be permanently correlated to the teaching activities that I will perform and will certainly help the students to better understand the usefulness of the SERS technique in combination with other vibrational spectroscopic methods for a large variety of applications.