Development of a Solid Substrate for Surface Enhanced Raman Spectroscopy

Felipe Hornung, Marcia Muller and José Luís Fabris
Federal University of Technology-Paraná, 3165 Av. Sete de Setembro, Curitiba, Brazil, 80230-901
felipehornung@alunos.utfpr.edu.br, mmuller@utfpr.edu.br, fabris@utfpr.edu.br

Abstract: In this work, a solid substrate for Surface Enhanced Raman Spectroscopy was developed and characterized. The interaction of silver nanoparticles with the probe molecule rhodamine 6G was compared for both liquid and solid substrates. Parameters of the solid substrate were optimized for use with an optical fiber Raman spectrometer.

1. Introduction

Surface Enhanced Raman Spectroscopy (SERS) is a powerful technique that extends the applications of traditional Raman spectroscopy, normally impaired by a poor signal-to-noise ratio. The enhancement is observed when an analyte is adsorbed on or is close to a specially designed metal surface. This kind of spectroscopy has shown prospective applications in the fields of biochemistry, forensics, food and beverage safety, environmental control and medical diagnosis [1]. Under appropriate circumstances, enhancements of 14 magnitude orders can be reached, making possible the identification of organic compounds in sub-micromolar concentrations or even single molecules [2].

The development of active SERS substrates with nanoparticles of noble metals is a key step for the detection and characterization of substances at the molecular level [3]. Nanostructures deposited on solid substrates present increased enhancement factors when compared with colloidal substrates due to the facility of the former in producing the so-called hot spots, well-defined regions where the electromagnetic fields are maximized. However, there are technological challenges for producing reproducible and uniform solid SERS substrates with large number of such hot spots [4].

In this work, a solid substrate for SERS was developed using silver nanoparticles produced by laser ablation in liquid as enhancement medium. As probe molecule, rhodamine 6G was chosen owing to its high efficiency for Raman scattering [5].

2. Materials and Methods

Silver nanoparticles (AgNPs) were produced by laser ablation of a silver plate in liquid solution. The light of a Nd:YAG (New Wave, Tempest 20, 532 nm, 3-5 ns pulse width) was focused by a 15 cm focal length lens onto a silver plate (Sigma Aldrich®, 99,9% CAS: 6440-22) submersed in 10 mL of a 0.1 mM dihydrate sodium citrate solution (Biotec®, 99%) in a glass beaker. Ablation was carried out at 17 mJ laser pulse energy, 10 Hz pulse rate along 20 minutes at a room temperature of approximately 22 ºC. A polytetrafluoroethylene (PTFE) membrane filter (22 μm pore diameter) presenting one rough and one smooth side was used as base for the solid substrate for SERS. Samples for SERS measurements in liquid substrate (R6G-AgNPs) were prepared using 1.95 mL of the AgNPs colloid and 50 μL of rhodamine 6G (R6G, Sigma Aldrich®, solution @ 10^{-3} mM concentration). For the solid substrate, drops (7 μL) of the R6G-AgNPs colloid were transferred to the PTFE membrane and allowed to dry.

UV-Vis extinction/absorption spectra of samples were measured with an optical fiber spectrometer (Ocean Optics, HR4000, 6.6 nm resolution) and a tungsten halogen lamp (Ocean Optics, LS-01), connected by optical fibers to a cuvette holder (Ocean Optics, CUV-ALL-UV). Raman spectra were measured by an optical fiber spectrometer (StellarNet, HR-TEC-X2, 200 - 3900 cm^{-1}, 4 cm^{-1} resolution) excited by a 638 nm, 50 mW spectrum stabilized single-mode semiconductor laser (StellarNet, Lab-LS-638), plus an optical fiber Raman probe (StellarNet, Raman-Probe-638). For liquid samples it was used a vial & probe holder (StellarNet, RPH4) and for solid samples an Olympus CX31 microscope (4x, 10x and 40x objectives).

The produced solid substrates were tested by individually analyzing the hole of the following parameters: roughness versus smoothness of PTFE membrane side; microscope objective lens magnification (4x, 10x, 40x); PTFE drying time and colloid pH. Changes in the pH of AgNPs colloids were accomplished by adding minute amounts of H_2SO_4 or NaOH. When not otherwise specified, colloids present pH = 7. SERS intensities for liquid and solid substrates were compared.