

Fiber-optic SERS sensor with optimized geometry

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Abstract

A novel surface enhanced Raman scattering (SERS) sensor has been developed and built. This sensor uses an "optrode" configuration in which a single optical fiber transmits both the exciting laser radiation and the SERS signal from the molecules adsorbed onto the SERS active substrate. The main advantage of this sensor is its unique geometry which can be obtained by means of a double static etching process achieved with a 40% hydrofluoric acid aqueous solution covered with an organic solvent over-layer. The SERS active substrate is prepared by a standard process of immobilizing silver nanoparticles with 3-aminopropyltrimethoxysilane. The optimized geometry permits attainment of the best limit of detection (LOD) value ever reported in the literature for a fiber-optic SERS sensor. In particular, we are able to record SERS spectra from a 10^{-9} M (0.018 ppb) solution of crystal violet in distilled water both with measurements performed in solution and with a "dip and dry" technique. Moreover, the capability to detect molecules such as crystal violet at such very low concentrations make this SERS sensor very promising for monitoring the diffuse illicit use of this molecule in aquaculture industry.

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1. Introduction

With the present technology the main advantage of Raman spectroscopy is its capability to provide abundant information regarding molecular vibrations and molecular structure without any sample pretreatment. Raman spectroscopy has become an attractive analytical spectroscopic technique that provides a "fingerprint" of the molecular structure. Unfortunately the relatively low Raman scattering cross-section and superposition of a fluorescence signal (intrinsically stronger) limits the potential applications.

However, since its discovery in 1974 (and confirmation 1977), an effect named surface enhanced Raman scattering (SERS) has been exploited [1,2]; it is able to dramatically enhance the Raman scattering signal from molecules adsorbed or near metal nanostructures especially for metals such as silver, gold and copper. Many SERS active substrates have been

used including electrochemically roughened electrodes, silver films obtained by evaporation or sputtering, acid-etched silver foils and colloidal metal nanoparticles. Kneipp and other authors have shown that at present it is possible to obtain SERS spectra of single molecules in extremely diluted solutions by means of colloidal silver nanoparticles [3,4]. An interesting application of Raman spectroscopy outside of standard laboratory applications consists of the use of a portable Raman spectrometer equipped with measurement heads connected to the spectrometer by means of fiber-optic cables. The use of fiber-optic connections makes it possible to record Raman spectra from samples located far from the spectrometer and/or in hazardous environments. An exciting development has combined both the advantages of remote optical fiber-based detection and the advantages imparted by the SERS-effect, namely high sensitivity. One of the first fiber-optic SERS sensors was realized with two fibers: one for carrying the laser excitation radiation to the sample and the other to collect and transport the scattered light from the SERS active substrate to the spectrometer. A simpler, and alignment free, configuration was soon discovered [5–7]; this configuration named "optrode configuration" includes a single optical fiber which transports both the laser

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radiation to the sample and the resulting SERS signal to the spectrometer and a SERS active substrate formed on the end of the optical fiber (Fig. 1a). Many geometries, SERS active substrates and roughening procedures have been explored in order to achieve the highest SERS signal. A series of geometry optimization studies, beginning with the normally cleaved fiber [7], continuing with angled cleaved tips [8], and concluding with conically etched tips [9], has produced an increased sensitivity of the sensor. A literature search of SERS active substrates with optimized characteristics has prompted the consideration of two different types of SERS active substrates in this study. The first one is obtained by metal evaporation or sputtering [7–9] and the second one is obtained through immobilization of silver or gold nanoparticles on the optical fiber tip [23].

The main purpose of this work is to find a useful geometry of the fiber tip, which increases both the surface of the SERS active substrate and the number of internal reflections at the silica–silver interface. To demonstrate the functionality of the fiber tip SERS sensor in the analysis of dangerous molecules in water below the ppb detection limit we have used crystal violet molecules (Fig. 5b). The choice is justified since crystal violet, together with malachite green and other similar molecules, belongs to the class of triphenylmethane dyes that are anti-microbial [10–13], toxic to mammalian cells and mutagenic [14–17]. Although crystal violet and malachite green are not approved by the FDA (Food and Drug Administration) for use in the aquaculture industry, they have been diffusely used to fight ectoparasites and fungi on fish and fish eggs because of their anti-parasitic and anti-microbial properties. For this reason there is a need of a very sensitive analytical method for monitoring the illicit use of crystal violet and malachite green in fish-farms.

2. Experimental

SERS measurements were carried out using a triple monochromator Raman spectrometer (DILOR XY) with subtractive configuration of the first two stages. The spectrometer was equipped with a liquid nitrogen-cooled 256×1024 pixel CCD detector. The excitation source was an Ar⁺ laser operating at a wavelength of about 514.5 nm. The laser radiation selected by an appropriate prism inserted in the resonant cavity was filtered by an interference filter and was focused through a microscope objective (Olympus, Mplan 10 \times /NA=0.25) in the core of the optical fiber. The integrated optical system produced a four-fold enlarged image of the backscattered light in the plane of the entrance slit of the Raman spectrometer. The optical fiber chosen for the experiments was a silica fiber with an inner core diameter of about 200 μm and a numerical aperture of about 0.22. An adaptive fiber-optic holder was built in order to suitably couple the laser radiation to the fiber core (Fig. 1b).

2.1. Reagents

AgNO₃ (99.8%), 3-aminopropyltrimethoxysilane (APTMS) (97%), crystal violet (Basic Violet 4) (90%), Rhodamine 6G (95%), HF (40%), trisodium citrate (99%), decanoic acid (99%) were all purchased from Aldrich chemicals and used without further purification. Methanol (99%), toluene (99%) and H₂O₂ (30%) were of analytical grade and were supplied by Fluka. Ethanol (99.9%), sodium hydroxide (99%), xylene (98.5%) and H₂SO₄ (95–97%) were supplied by J.T. Baker.

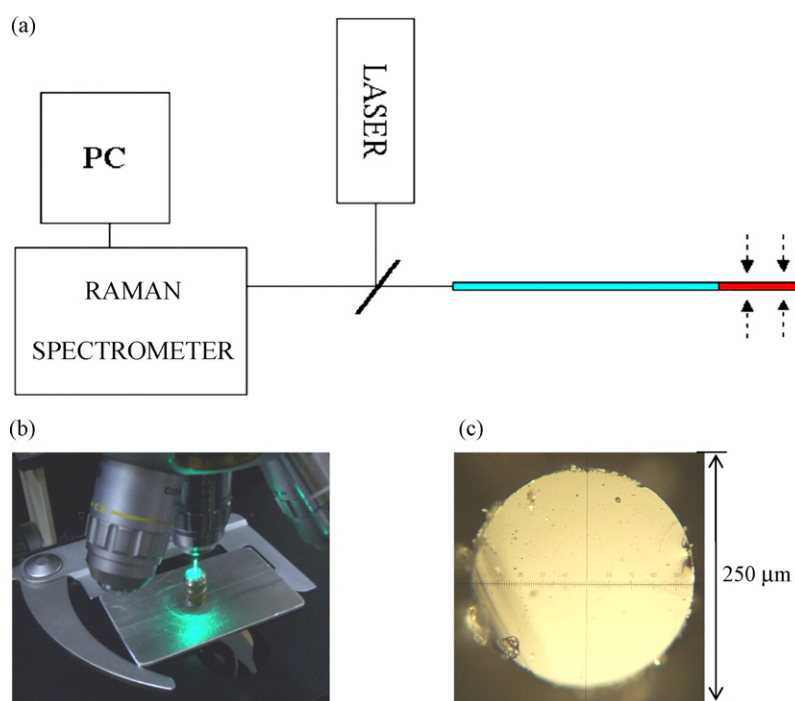


Fig. 1. (a) Schematic diagram of the measurement setup for a fiber-optic SERS sensor in optrode configuration (the arrows show the sensitive zone of the optical fiber); (b) photos of the homemade fiber-optic holder used to align the fiber-optic core with the microscope optics; and (c) normally cleaved optical fiber.

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