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Surface-Enhanced Raman Spectroscopy with Abrasively Modified Fiber Optic Probes

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INTRODUCTION

Raman spectroscopy is a very attractive technique for in situ monitoring of remote environments with optical fibers. The major advantage of Raman over its vibrational counterpart, IR spectroscopy, is the use of visible radiation. Raman can be excited with visible light, which has a high transmission in optical fibers. Furthermore, an important application of remote, optical fiber sensors is water quality analysis and water

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does not interfere with Raman spectroscopy. The advantage of Raman over other visible spectroscopies (fluorescence and absorbance spectroscopy) is the large amount of structural information about the analyte that can be gleaned from Raman spectra. Normal Raman, resonance Raman, and SERS fiber optic probes have been constructed and shown to provide good sensitivity in special cases (*1, 2*). However, in many situations samples will contain fluorescent impurities or analyte concentrations that are too low to be detected with a probe based on normal or resonance Raman scattering.

We have shown that it is possible to use an indicator molecule to flag the presence of an analyte through characteristic changes in the indicator's Raman spectrum (*3*). In order to improve sensitivity, the indicator molecule was chosen such that resonance Raman was possible. A further improvement in enhancement was achieved by placing the indicator directly on roughened silver substrates and using surface-enhanced Raman spectroscopy (SERS). In our test case of metal ions as the analyte and Eriochrome Black T as the indicator we found a 3-s detection limit on the order of 1×10^{-6} M. The selectivity was found to be superior to absorption spectroscopy. These studies were performed on carefully fabricated 1 in. square SERS substrates.

In this Technical Note we would like to describe a method by which we can obtain strong SERS spectra by using an abrasively modified optical fiber. This represents an important step toward the fabrication of remote, fiber optic probes. Previously described SERS fiber optic probes have focused on the spatially separated triad of excitation fiber, SERS substrate, and collection fiber. The SERS substrates have been either specially prepared roughened surfaces (*2a,b*) or electrode surfaces (*2c*). A particularly interesting study by Bello and Vo Dihn showed that one could excite SERS through relatively thick silver films (*2a*). We have used this to advantage in removing spurious Raman lines that form in the fiber due to excitation of vibrational modes in the fiber material and possible fluorescence excited in the media surrounding the fiber.

EXPERIMENTAL SECTION

The optical fibers and polishing paper were obtained from General Fiber Optics. Our experiments were performed with approximately 1 m of 600-μm core silica fibers. The NA of the fibers was 0.26. The fibers were clad with a UV-enhanced polysiloxane–hexafluorine copolymer, which was not removed for the experiments. The fibers were cleaved and abrasively roughened with polishing papers of decreasing particle sizes. After polishing, the fibers were thoroughly cleaned with distilled water to remove residual polishing grit. The fibers were then rinsed with concentrated ammonium hydroxide to improve adhesion of the silver film. The silver was deposited at an angle of 20° to the fiber axis. Different angles (0–50°) were tested, and no angle dependence was observed. The silver (99.9%, Aldrich) was thermally evaporated from a molybdenum boat at 4×10^{-6} mbar. The silver thickness was monitored with a water-cooled quartz crystal microbalance. The silver-coated fibers were stored under vacuum until the spectroscopic measurements were made. Island films were used as a reference to determine the relative enhancement observed on the abrasively roughened optical fibers. The island film substrates were fabricated from 1 in. square slides. The slides were cleaned with concentrated ammonium hydroxide and plasma cleaned in a Harrick PDC-3XG RF plasma cleaner. The mass thickness of the silver island films was 5 nm. We chose cobalt phthalocyanine (CoPc) (Kodak) as our probe molecule for substrate evaluation. The fibers were coated with CoPc by dip-coating in a 1×10^{-6} M spectral grade pyridine solution. A 50-μL aliquot of the CoPc solution was spun-coat onto the island films under an aspirator-driven vacuum. We used SERS to determine the coverage produced by spin coating and dip coating. We found that the coverages were identical. The intensity ratio of the 683–1540-cm^{-1} peak indicates that the CoPc coverage was on the order of one monolayer (*4*).

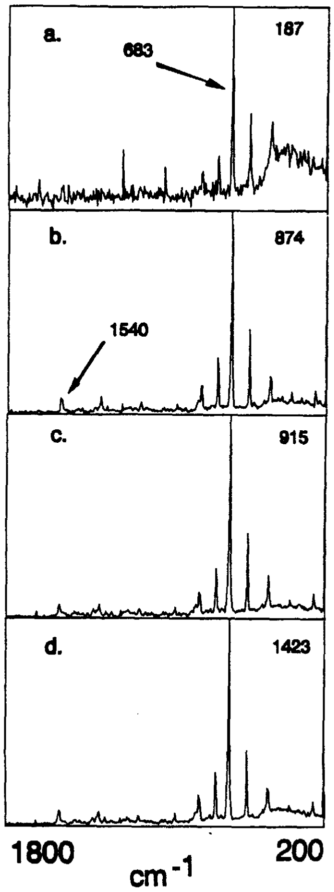

Figure 1. Roughness dependence. The spectra of CoPc were obtained with 2 mW of laser power on fibers roughened with (a) 0.3, (b) 3.0, (c) 15, and (d) 32-μm polishing papers. The roughened fibers were coated with 50 nm of silver. The intensities in the upper right hand corners correspond to counts per second for the 683-cm^{-1} Raman band.

All spectra were obtained with a Spectra Physics 2025 Kr$^+$ ion laser operating at 647 nm. The custom-built Raman instrument has been previously described (*3*). A bandpass of 5 cm^{-1} (860-μm slit width) was used in all spectra. An integration time of 3 s was maintained throughout the series of experiments. Laser powers were determined immediately before the fibers. We did not focus the laser beam onto the fiber tips. Our desire was to test the fibers at low laser powers and this was best achieved by spatially extracting only a small portion of the laser beam. We determined a 1.68 mm, $1/e^2$ diameter for our laser beam. This leads to a 40% coupling of the laser beam into the 600-μm fiber (*5*). The powers reported in Figures 1 and 2 are corrected for losses around the fiber. In our power vs SERS intensity study the powers reported are not corrected for the losses around the fiber. This is due to the need for an additional fixed aperture to maintain constant beam size. Since the size of the beam was fixed in this study the relative powers are meaningful.

The fiber positioning was controlled with Melles Griot XYZ translators. Fibers were held in the translators by using Newport fiber chucks or facsimiles made in house. The immersion experiments were performed with fiber chunks that were drilled out large enough to accommodate a 2.5-mm glass tubing. The fiber was inserted into a glass tube filled with water and positioned in the laser beam. The output cone of Raman light from the fiber was partially collimated with a spherical ball lens (Edmund Scientific), resulting in a narrower cone of light. We empirically adjusted the collection lens to focus this Raman light through the slit (860 μm) and to just fill the *f*/8 mirrors of the Jobin-Yvon Ramanor U 1000 double monochromator. The complete SERS fiber system is illustrated in Figure 3.

RESULTS AND DISCUSSION

Polishing Paper Dependence. The goal of this project was to develop a robust, water resistant fiber coating for in

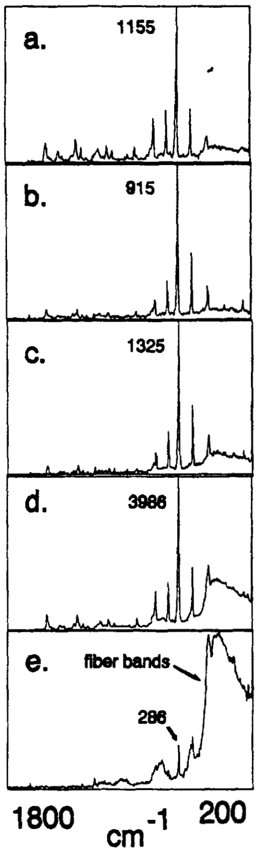

Figure 2. Silver thickness dependence. The spectra of CoPc were obtained with 2 mW of laser power on fibers roughened with 15-μm polishing paper. The silver mass thickness was varied: (a) 60 nm; (b) 50 nm; (c) 30 nm; (d) 20 nm; (e) 15 nm. Most notable are the maximum enhancement at 20-nm mass thickness and the appearance of the fiber Raman bands at low silver thicknesses. Intensities are in counts per second for the 683-cm^{-1} Raman band.

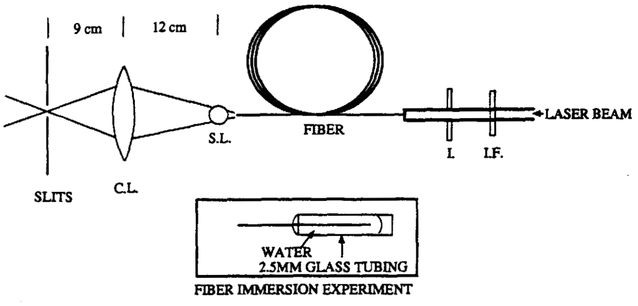

Figure 3. Schematic of the fiber Raman system. The collection lens, CL, is a 50 mm, f/2 Mamiya/Sekor camera lens. The 4-mm spherical ball lens, SL, was purchased from Edmund Scientific. The interference filter, IF, was used to remove laser plasma lines, and the iris, I, was used to maintain a constant laser beam diameter at the fiber tip. The focal distances were empirically determined to provide the largest signals.

situ SERS analysis. We have found that the roughness produced by polishing fibers with large grit paper is sufficient to produce large enhancements. Figure 1 shows the variations in the SERS spectra obtained with optical fibers polished with 0.3-, 3-, 15-, and 32-μm polishing paper and coated with 50 nm of silver. A 7.6-fold intensity increase is observed for fibers polished with 32-μm paper vs 0.3-μm paper. The intensity at 0.3 μm was low enough to allow the weak 200–500-cm^{-1} Raman bands due to the fiber to become apparent. The 32-μm paper left microscopically visible scratches on the fibers. The number and size of visible abrasions decreased as the alumina particle size went from 32 μm down to 0.3 μm. The size dependence appears to contradict the current model of electromagnetic enhancement. The electromagnetic model predicts that enhancements should occur for particle sizes less than the wavelength of light (6). In the visible range of wavelengths this should occur for ellipsoids with a major axis radius of about 100 nm. The increased enhancement for larger grit paper is most likely due to the production of scratches with sharp edges and a grating-like structure on the surface. It is well-known that gratings can be used to couple light into surface plasmons (7). We have observed on thick, unroughened silver films that "hot spots" of Raman intensity occur near visible scratches.

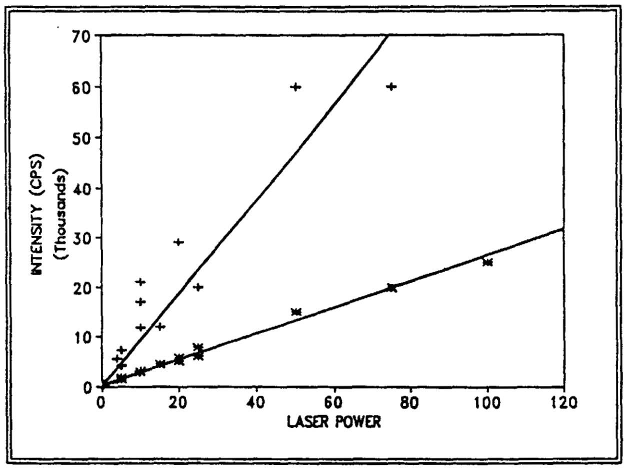

Figure 4. Graphical representation of the laser power dependence. All data were collected from the same fiber. The laser power was varied in a staggered fashion such that irreversible laser-induced damage would be observed. Irreversible laser damage was not found. The better correlation of fiber surrounded by water indicates improved stability when the fibers are immersed in water: (+) = air, (*) = water.

Silver Thickness Dependence. Figure 2 shows the dependence of SERS intensity on silver film thickness. These spectra clearly illustrate the plasmon resonance involved with SERS. The penetration depth of 647-nm light in silver is 12 nm. This was found from (8)

$$y = c/2k\omega$$

where y is the penetration depth, c is the speed of light, ω is the frequency of the light, and k is the imaginary part of the index of refraction. For silver at 647 nm k is 4.3 (9). At 60-nm thickness of silver only 0.67% of the light from the surface would be expected to penetrate the silver film. Figure 2a shows that the signal at 60 nm of silver thickness is equivalent to 30 nm thick films. The apparent penetration of light through the silver is due to the electromagnetic enhancement associated with surface plasmons in the silver film. This effect is fortuitous for fiber optic probes since the thick films effectively remove much of the laser excitation prior to the fiber. This keeps Raman bands due to fiber material vibrations from forming. At 15- and 20-nm film thicknesses the excitation of Raman scattering in the fiber is clearly visible. We established that the maximum enhancement is found at 20 nm and is approximately 4 times larger than for the thicker silver films.

Laser Power Dependence. Figure 4 shows the power dependence of the abrasively roughened fibers. The plot contains data for fibers in air and fibers immersed in water. In both cases the data fit a straight line. The intensities were measured immediately after the power measurement. It was observed that in air the signal decreased rapidly with time when the laser power was above 50 mW. However, when the laser power was decreased the original SERS intensities were recovered. In other words the loss of intensity at high laser powers appears to be reversible. The straight lines indicate that the laser is not immediately damaging the surface or sample at high laser powers. The slow loss of signal may be

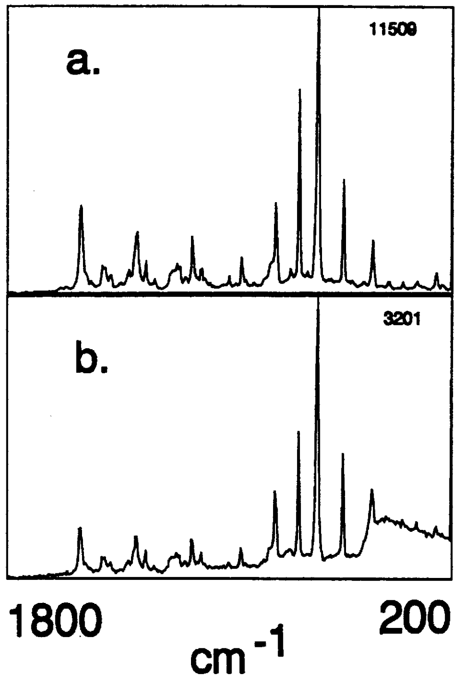

Figure 5. (a) Enhancement determination shown by a Raman spectrum of CoPc on an island film. Comparing this spectrum with our fiber spectra, we find an enhancement of 1.2 × 10^5 for abrasively roughened fibers. Enhancement determination is described in the text. (b) CoPc spectrum from a fiber immersed in water. The fiber was roughened with 32-μm paper and coated with 50 nm of silver. The fiber was placed in a thin glass tube filled with water and excited with 20 mW of 647-nm laser light. The losses due to reflections at the water-air interface were not measured. The intensity in the upper right hand corner is for the 683-cm^{-1} band.

due to localized heating of the sample. This will cause a shift in the dielectric constant of the metal through a shift in the Fermi velocity of the electrons (*10*). In particular, the increased Fermi velocity will increase the imaginary part of ϵ through increased lattice collisions. Subsequently, the surface plasmon resonance will be dampened. It will also cause a Boltzmann redistribution of intensities away from the Stokes Raman. We attempted to measure the temperature of CoPc through the Stokes/anti-Stokes ratio. However, since the Raman signal is resonantly enhanced, we found a quite different anti-Stokes spectrum. This led to inconstant temperatures for CoPc. In water the signal is about a factor of 2 lower than in air. The lower signal may be due to shifting of the plasmon resonance due to the dielectric constant of the wter or beam aberrations due to the focusing affect at the water–air interface in the capillary tube. We found that the much higher laser powers could be used for fibers immersed in water. At 100 mW the signal was observed to be more stable than the same sample in air at 50 mW. This justifies our conclusion that the loss of signal is due to localized heating. The fibers in water can disperse the heat much faster than in air.

Enhancement Determination. Figure 5a shows a SERS spectrum of CoPc on a 5-nm mass thickness island film. The intensity of the 683-cm^{-1} Raman band is 11 509 counts/s. When the size of the laser beam in comparison to the fiber tip is accounted for, the intensity observed with our best fiber is 87% that of silver island films and a conventional backscattering collection system. Using Meier et al. comparisons of island films with other substrates (*11a*) and Carron's reported enhancement for CoPc on CaF_2-roughened silver (*11b*), we find an enhancement of 1.2 × 10^5 for our abrasively roughened fibers.

Surrounding Media Effects. Figure 5b shows a spectrum of CoPc on an abrasively roughened fiber that is immersed in water. Since one important application of Raman fiber probes will be in situ monitoring of groundwater, we tested the durability of abrasively modified fibers in water. We did not observe any deleterious effects on the surface due to immersion. We checked the signal after 2 days of immersion. A loss of approximately half the signal was observed. The original signal was recovered after this probe was coated again with CoPc. This indicates that the silver surface is not degrading and the signal loss is due to loss of CoPc off the surface. However, an earlier attempt at using CaF_2 to produce roughened substrates on fibers failed due to serious degradation in an aqueous environment and rapid peeling of the silver from the CaF_2 layer.

CONCLUSIONS

We have demonstrated that it is possible to obtain high-quality SERS spectra through direct deposition of Ag onto abrasively roughened optical fibers. The large signals observed appear in part to be due to high collection efficiencies and Raman enhancements from surface plasmon coupling at scratches on the fiber tips (*7*). The collection efficiency is related to the NA of the fibers and the distance between the fiber tip and the Raman scatterer. The distance between the fiber and scatterer is effectively zero, by placing the silver directly on the fiber tip. The NA of a smooth fiber would be greatly reduced by coating it with silver. The NA of a silver-coated smooth fiber would be reduced to 0.26 × 0.05 or 0.013 (*12*). Where 0.05 is the index of refraction for silver at 647 nm (*9*). However, the unique optical properties of surface plasmons allow them to couple efficiently into the fiber. We tested the fibers in aqueous environments and found them to be stable. We tested silver island films and CaF_2-roughened films at the fiber tips but found the SERS intensities were inferior to those for silver-coated abrasively roughened fibers.

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