A Single Fiber Surface Enhanced Raman Scattering (SERS) Probe

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Raman spectroscopy is a time honored technique for identifying molecular structures. In Surface Enhanced Raman Scattering (SERS) close proximity of the sample to so-called "hot spots" in a rough metallic surface enhances the Raman signal strength enormously. In a typical *in-vitro* arrangement the sample is in a transparent liquid in contact with the rough metallic surface. A microscope objective focuses laser light on the surface, and collects the scattered Raman light. The Raman signal is proportional to the solid angle subtended by the objective, or to the square of its Numerical Aperture (NA).

For *in-vivo* applications a long narrow probe is desirable to minimize invasiveness. A single mode optical fiber, terminated in a rough metallic surface, would be ideal. We will show that such a fiber produces a SERS signal comparable to that of a microscope objective of the same NA. Unfortunately, in a long fiber the signal from the specimen is masked by Raman scattering from the fiber itself.

Systems are available which avoid this problem by using one fiber to transmit the exciting light and a second fiber to collect the Raman scattered light (Fig. 1). The rough metallic surface is replaced by metallic nano-particles disbursed in the specimen. To propagate a Raman signal a nano-particle must be within the NA cones of both fibers. The Raman light must also be directed toward the second fiber's core. We will show that for common values of fiber and core diameters the Raman signal is thousands of times smaller than for a single fiber. In addition there are transmission losses through the tissue and comparisons between sites depend on the reproducibility of the dispersion of the nanoparticles.

We have retained the advantages of a single fiber by coupling a short length to the spectrometer via a 1 meter long air path in an articulated mirrored arm disclosed at a previous EIPBN conference.[1] The probe (Fig. 2) contains a commercial graded index (GRIN) lens/fiber combination (Thor Labs). The fiber is epoxied within a 0.5 mm outside diameter stainless steel needle. About 20 nm of gold are sputtered on a sacrificial sheet of aluminum foil. Gold has poor adherence to aluminum, as it has to many materials, and forms a collection of nanoparticles on the foil. The foil is epoxy bonded under pressure to the end of the fiber, and removed in a KOH etch, leaving the rough gold bonded to the fiber by a submicron layer of transparent epoxy.

Spectra were obtained with the articulated arm and the single fiber probe inserted into blocks of gelatin prepared with dissolved Rhodamine 6G dye (Fig. 3). In a biological application, spectra were obtained with the probe inserted into a chilled pellet of cancerous mouse tumor cells (Fig. 4).

[1]H.-C.Hou et al, 59th EIPBN, San Diego, CA, May 29, 2015
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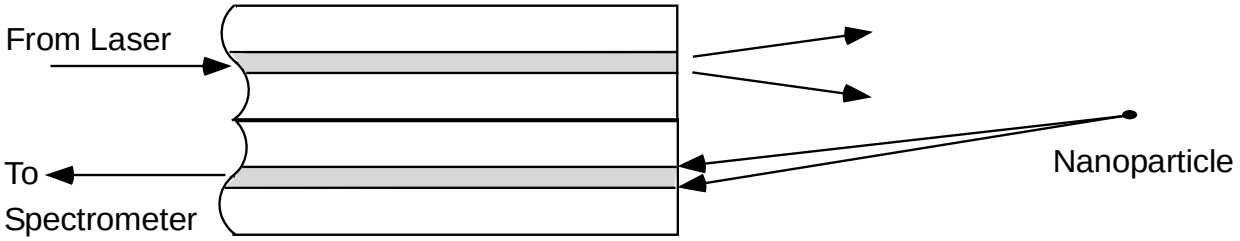

Fig. 1. Laser light exits the top fiber and illuminates nanoparticles in the specimen. Some of the Raman light emitted by the nanoparticles enters the core of the bottom fiber, but only light which originates within its NA propagates to the spectrometer. For clarity only one nanoparticle is shown.

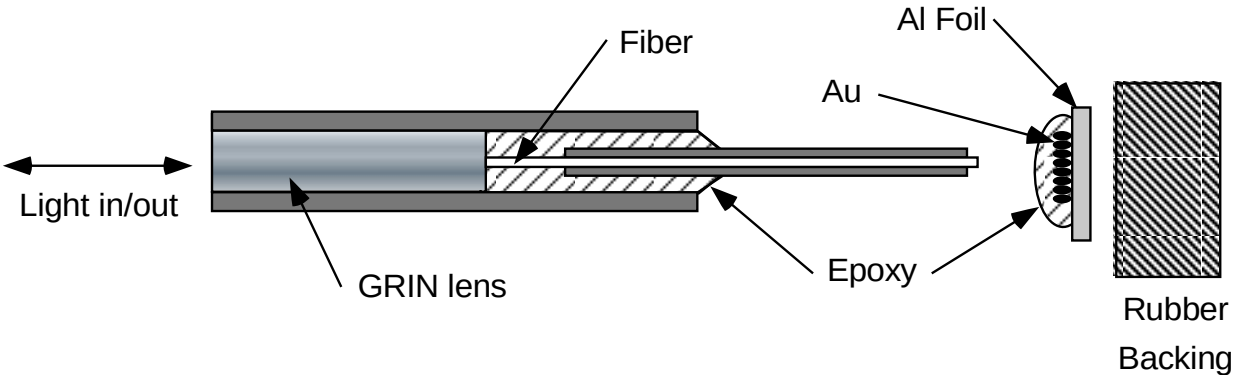

Fig. 2. Exploded sketch of the single fiber probe (not to scale). The fiber is sealed in a 0.5 mm OD stainless steel needle. The tip of the fiber is pressed against gold deposited on aluminum foil, and is bonded to it with a submicron thickness of epoxy. A subsequent etch removes the foil.

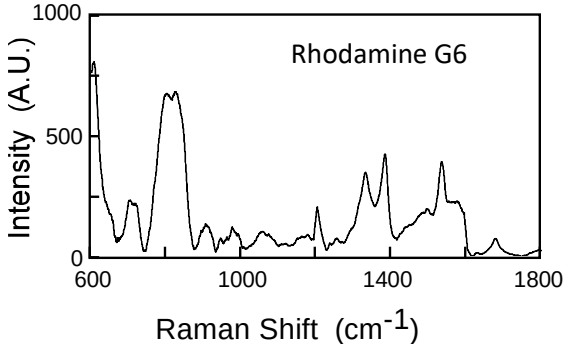

Fig. 3. Raman spectrum of 1 mM of Rhodamine 6G dissolved in gelatin, obtained through a 1 meter long articulated arm with a single fiber probe.

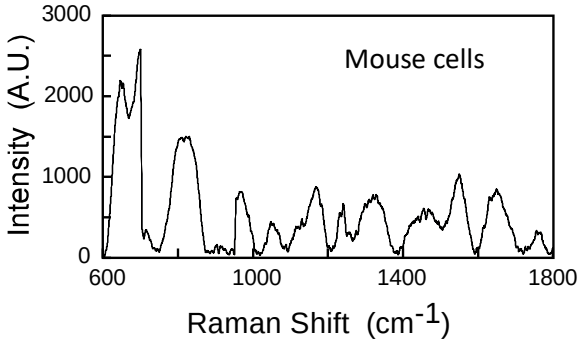

Fig. 4. Raman spectrum of chilled mouse cells from a cancerous tumor. The spectrum was obtained with a single fiber probe.