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A simple background elimination method for miniaturized fiber-optic Raman probe

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A SIMPLE BACKGROUND ELIMINATION METHOD FOR MINIATURIZED

FIBER-OPTIC RAMAN PROBE

by

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ABSTRACT

Raman scattering is called a photonic - molecular interaction based on the kinetic model of the analytic. Due to the uniqueness of the Raman scattering technique, it can provide a unique fingerprint signal for molecular recognition. However, a serious challenge often encountered in Raman measurement comes from the requirements of fast, real-time remote sensing, background fluorescence suppression, and micro-environmental detection.

A new Miniaturized Fiber-Optic Raman Probe (MFORP) for Raman spectroscopy, used especially for eliminating background fluorescence and enhancing sampling, is presented. Its main purpose is to provide an overview of excellent research on the detection of very small substances and to address the drawbacks of modern optical fiber Raman sensors that cannot be separated from background fluorescence interference. After a brief introduction of the traditional fiber Raman technology, the experimental operation of the design optimization of the new MFORP was discussed. We successfully combined several multi-mode fibers as one fiber taper for Raman spectral analysis by using the fiber tapering technique. The sensing principle and the fabrication of MFORP were discussed. In order to verify that MFORP is a better solution, we used traditional Fiber-Optic Raman sensor and MFORP to experiment on a variety of materials and compare the experimental results. We observed that MFORP not only effectively removes the background fluorescence of the fiber itself, but also improves the energy collection of the Raman spectrum, which provides an argument.

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LIST OF ABBREVIATIONS

Abbreviation	Full name
MFORP	Miniaturized Fiber-Optic Raman Probe
FORP	Fiber-Optic Raman Probe
MRI	Magnetic Resonance Imaging
RS	Rayleigh scattering
SRS	Stoke Raman Scattering
ASRS	Anti- Stoke Raman Scattering

1. INTRODUCTION

The particularity of the Raman spectrum has been a popular spectral analysis method in the wide application of spectroscopy. In theory, Raman spectroscopy is a spectral technique based on the inelastic scattering of monochromatic light (laser source). After the light source laser is excited, the wavenumber of the photons in the monochromatic light interacts with the sample, and the photon of the laser is absorbed by the sample and then re-emitted, which is called inelastic scattering. After interacting with the sample, the wavenumber of the re-emitted photon moves up or down compared with the original photon. This effect is commonly known as the Raman Effect.

1.1. BACKGROUND AND REVIEW

According to this optical phenomenon of the molecular vibration, rotation, and transition information changes, biochemical research has opened up a new field. Each substance has its own unique molecular form. Therefore, the ejection photon that is generated after being hit by the monochromatic light of the source will bring about different Raman shifts. The chemical sensitivity can be greatly improved by using the wavenumber to calibrate the substance. As an extension of this field, Raman technology can also provide the ability to analyze solution samples in vitro and in vivo without changing the chemical properties of the samples [1]. In addition, Raman spectroscopy can also be used in cell research, biology, water quality testing, environmental pollution testing, and clinical pharmacy [2-13].

The development of the application range of Raman spectroscopy faces more and more challenges and demands. In today's medical field, it is very common to use light to

judge the information of relevant clinical tissues, such as optical microscope, fluorescence microscope and spectral analysis [9-10]. However, large scale Raman spectroscopic devices face significant challenges when it comes to the detection of small substances, remote control or ultraviolet-level molarity. The advent of the optical fiber provides a new opportunity to solve current application problems [14-15]. Optical fiber is a very good light guide material. In terms of material, the main component of the optical fiber is silicon dioxide, which is very cheap and robust. Due to the limitations of the fiber's structure, the excited photons are confined to the fiber core, thus reducing the consumption of light energy.

1.2. FIBER-OPTIC SENSOR FOR RAMAN SENSING

Over the past few decades, Raman spectroscopy has proved to be a great technique for molecular analysis by numerous research groups. Compared with the traditional Raman sensing device, the fiber optical Raman device has its unique advantage such as compact size, light weight, low cost, and high accuracy. Due to the particularity of the Raman spectrum, this sensing technique has been found in various sensing and measurement applications.

1.2.1. Review of Current Fiber-Optic Raman Probe in Clinical Application.
Among all the developed fiber optical Raman probe (FORP), the clinical sensing application is the most popular research topic [10-17]. FORP has the unique technique can be used to analyze the inelastic scattering of laser by the molecule in the sample. Since the molecules that make up the material differ, the energy transfer of the scattered light through the vibrations of the molecules varies greatly. Through this technique, Raman spectroscopy

has been widely used in medical research. Based on the micro material properties of optical fiber materials, optical fiber Raman was used to study micro materials in medical research. Raman spectroscopic instruments can visually distinguish between cells or molecules, and they are often used in medical research to separate diseased tissue from healthy tissue. The morphological changes of the disease were expressed by spectral analysis of the scattered light absorbed by Raman spectrometer.

1.2.2. The Need for MFORP in Raman Sensing Technique. Although Raman spectroscopy has good chemical specificity, the low probability of inelastic scattering events hinders the further development of Raman spectroscopy. In the millions of photons excited by the laser interacting with the target molecule, only one or a few photons may be inelastic scattered. This phenomenon greatly increases the difficulty of absorbing Raman signals. In addition, the application of Raman spectroscopy in the field of biomedicine also needs to overcome the obstacle of the wide background generated by biological samples. Since the background fluorescence signal is several orders of magnitude larger than the Raman signal, in order to effectively use the Raman spectrum in sample analysis, the removal of background fluorescence has been a popular research topic. Several methods, including instrumental and computational methods, have been proposed to remove the background fluorescence signal [18-23]. The instrumental method was mainly discussed by using frequency shift to remove the background signal. This filtering method starts from the multi-excitation Raman spectrum and filters the Raman signal through the displacement of the Raman spectrum which has the characteristics of excitation frequency and static response [23]. However, this filtering technique requires complicated experiment design and huge experimental data. The computational method involves frequency-domain

filtering, subtraction filtering, and polynomial filtering which is the most common method used nowadays [18-20]. The main idea of these methods is to use simulation method to subtract the background signal. By using the polynomial fitting method, which is the most popular solution, the original spectrum can be found automatically through the system. After polynomial fitting transformation, the signal noise is processed by using peak elimination technique and endpoint constraint. However, using the computational method to subtract the background signal place limitations on energy collecting. The spectrum filtered by these computational filtering methods has a high probability of wiping out the spectrum of the sample itself, thus greatly reducing the accuracy of the experimental data. In this paper, the proposal of MFORP effectively solves the shortcoming of removing Raman background fluorescence. The new technique removes background fluorescence by only changing the structure of the Raman probe without any filtering methods, which improves the collection of scattered light energy. By using the optical fiber pull taper, the multi-mode optical fibers are fused together. The theoretical basis of this method is to eliminate the background signal of the silicon itself by using different optical fibers for excitation and collection.

Moreover, more and more optical devices are used in the medical field, such as fluorescence microscopes, confocal microscopes, and remote optical system. However, large optical sensors are no longer enough to support the exploration and study of small objectives. Several groups of researchers have been working on the Raman taper, but the compact size of the probe is not competitive, and it is also a time-consuming technique [24-28]. Compared with the commercial Raman probe, the MFORP has a similar working principle with small a diameter range. The commercial Raman probes use fibers to deliver

the excitation laser beam to the selected sample. Some modified commercial Raman probes have band pass inline filter which can help to remove the excitation wavelength that is reflected. The commercial Raman probes are increasingly used in health monitoring applications [29]. Due to optical fiber insensitivity to electromagnetic fields, probes can be used in combination with magnetic resonance imaging (MRI) techniques. However, the compact size of the Raman probe is the most important aspect for biochemical research. The introduction of MFORP will make up for the shortcomings of the current Raman probe.
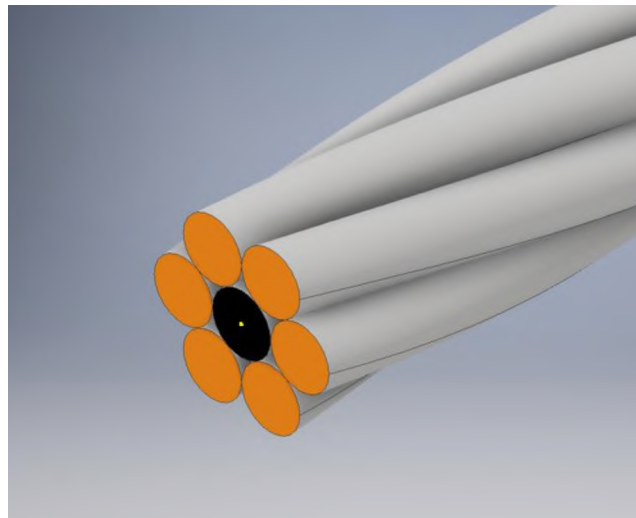
Figure 1.1. Cross section of MFORP.

As shown in the cross-section simulation figure in Figure. 1.1, we deduced that the MFORP is composed of several multi-mode fibers. Six collection fibers (orange) wrapped one excitation fiber (black) in the middle. By using the fiber tapering technique, the diameter of the new MFORP can reach from 20um to 30um. Since the MFORP has been proposed, it has advantages of small compact size, easy operation, and low cost.

1.3. RESEARCH OBJECTIVE

The main objective of this thesis is to design miniaturized optical fiber sensors that can eliminate the silicon background signal for Raman sensing application.

1. Investigate the fundamental physics and theoretical model of Raman sensing.

2. Investigate the traditional Raman optical fiber sensor.

3. Develop the fiber taper machine to combine several fibers as one single fiber by using fiber tapering technique.

4. Develop a remote, miniaturized, background signal eliminated Raman sensor.

5. Demonstrate the new MFORP advantages by comparing them with the Traditional Fiber-Optic Raman probe (TFORP).

6. Using the new Raman probe to devote to the one single cell pH value detection in biochemical research.

1.4. THESIS OVERVIEW

The project aims to develop a Miniaturized Fiber- Optic Raman sensor, which is fabricated by the fiber tapering device that can work in tiny areas and harsh conditions and a eliminate the silicon background signal for Raman sensing application. This thesis will mainly focus on the miniaturized fiber-optic Raman sensor development and the measurement result analysis.

Section 2 focused on the fundamental physics and theoretic model of the proposed miniaturized fiber-optic Raman probe (MFORP). The sensing principle of the traditional fiber-optic Raman probe (TFORP) was also discussed.

Section 3 focused on the fabrication method of the proposed MFORP. A fiber tapering method is developed to fabricate several fibers together as a fiber probe.

Section 4 described the MFORP sensing mechanism and experimental results of MFORP and TFORP in different materials.

Section 5 summarized the conclusions and future work.

2. FUNDAMENTAL PHYSICS AND RAMAN SENSING APPLICATION

2.1. FUNDAMENTAL PHYSISCS OF RAMAN SPECTROSCOPY

Raman spectroscopy was named by an Indian physicist. His experiments revealed that a special scattered light could be used to determine the vibrational patterns of molecules, as well as to observe the rotation of the system and other low-frequency patterns. Since then, Raman spectroscopy technology has been widely used in medical inspection, environmental detection, and water pollution treatment. According to the optical theory, when a light source is excited, a beam of light follows a path to the sample [30]. When the photons are scattered by contact with the sample, most of the photons follow elastic scattering (Rayleigh scattering). As shown in Figure. 2.1, the scattered photons have the same energy as the incident photons, but in a different direction. Compared with the Rayleigh scattering (RS), stoke Raman scattering (SRS) and anti-stoke Raman scattering (ASRS) absorb different excitation energy levels.
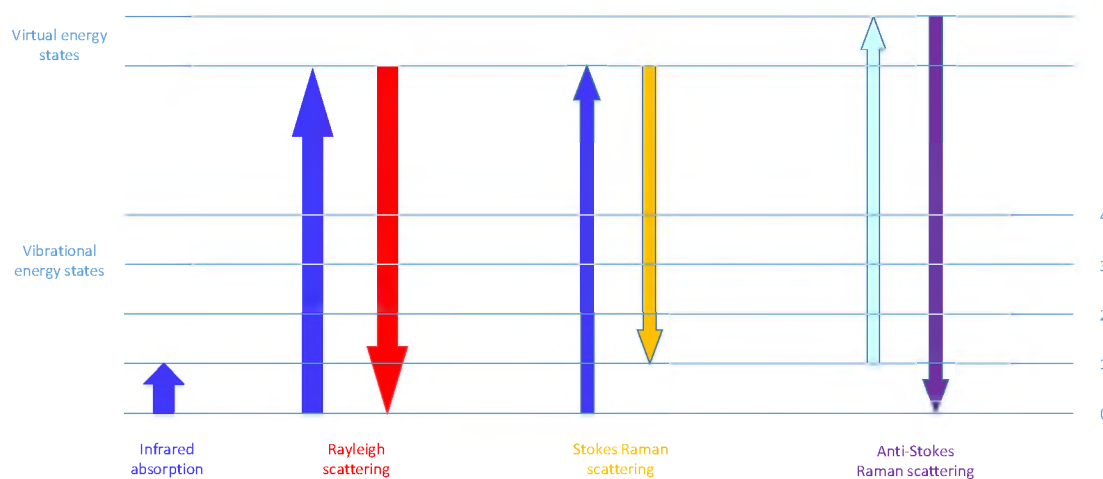

Figure 2.1. Energy-level diagram showing different states in Raman spectroscopy

Of these three cases, the final state initially has the same electronic energy. However, depending on the wavenumbers, researchers use Vo as the wavenumber of the excited laser and, V_m as the wavenumber of the vibrational state. SRS is higher than RS and ASRS in vibrational state which gives a wavenumber of $V_0 - V_m$. $V_0 + V_m$ is given to ASRS because it is lower in vibrational transition [31]. According to thermodynamic equilibrium theory, the transition from a low state to a high state leads to a higher transition rate [32]. Therefore, SRS has higher scattering peak energy than ASRS. Due to the fact that Raman scattering is extremely difficult to collect, the high scattering peak of SRS becomes a powerful basis for its diverse application.

Wavenumber is also named as "Raman shift". In past physical science research, the wavenumber is generally referred to as the spatial frequency of the wave [33]. It is measured in cycles per unit distance or radians per unit distance. The wavenumber can be used to determine distance, time frequency, and unit time. It is not difficult to deduce the theoretical formula that the wavenumber is equal to the true frequency divided by the speed of light, or the inverse of the wavelength (λ). The wavenumber (Δv) can be derived by the following equation,

$$\Delta v = (\frac{1}{\lambda_0} - \frac{1}{\lambda_1}) \qquad (1)$$

where λ_0 is the excitation wavelength and, λ_1 is the Raman spectrum wavelength. the Raman shift is symbolled as Δv that expressed in wavenumber. In general, scientists prefer to use CGS to express wavenumbers [33]. By using the system of units (CGS), the unit of wavenumber is cm^{-1}. The difference in spectral lines can be explained as the difference in

energy levels. The energy level is proportional to the frequency and the wavenumber. The formula of wavenumber calculations is given below,

$$\Delta\varpi(\text{cm}^{-1}) = \left(\frac{1}{\lambda_0(\text{nm})} - \frac{1}{\lambda_1(\text{nm})}\right) \times \frac{(10^7 nm)}{(cm)} \qquad (2)$$

where $\Delta\varpi$ is the Raman shift that is expressed in wavenumber (cm⁻¹).

2.2. FIBER OPTICAL RAMAN SENSING PRINCIPLE

According to the perspective of optical theory, Raman spectroscopy can be considered as a spectral measurement of molecular medium with inelastic scattering of monochromatic radiation. In this process, photons and molecules exchange energy so that the energy of the scattered photon is higher or lower than that of the incident photon, which is called Raman phenomenon. Fiber-Optic Raman sensing is based on absorbing the inelastic photon to provide chemical and structural information.
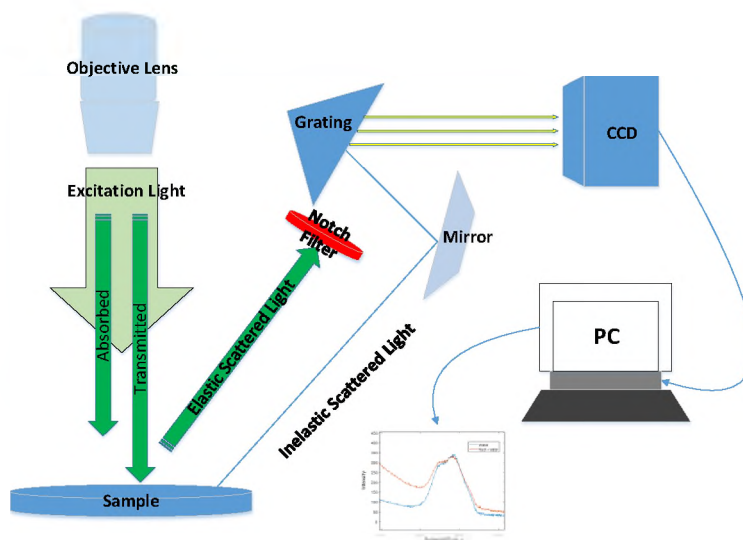
Figure 2.2. Fiber-Optic Raman system diagram.

As shown in Figure. 2. 2, when the photon excited by incident light hits the sample, the incident photon and the sample molecule exchange energy. A part of the photons with elastic scattering are filtered by notch filter, while a small part of the photons with inelastic scattering are captured by the spectrometer and sent back to the computer. Next, a spectrum with Raman shift verse power intensity will be processed.

2.3. RAMAN SPECTROSCOPY APPLICATION AND ADVANTAGES

It is well known that the discovery of Raman spectroscopy has given great impetus to scientific research. Through its unique molecular identification technique, fiber optic Raman has been applied in many fields [34].

2.3.1. Application of Raman Spectroscopy in Polymer Materials. Raman spectroscopy can provide important information about the structure of polymer materials, such as molecular structure and composition, stereoscopic regularity, crystallization and direction, intermolecular interaction, and surface and interface structure [35]. In the application of fiber Raman technology, the tiny fiber probe can provide more accurate information of polymer. Experiments show that the stereo chemical purity of the polymer can have the width of the property Raman peak. The Raman peak of the random position sample is weak and wide, while the Raman peak of highly ordered sample is strong and sharp.

2.3.2. Application of Raman Spectroscopy in Biochemical Research. The primary application of Raman spectroscopy is in biochemical studies. In organic chemistry, Raman spectroscopy is used to determine and identify molecular interactions [37]. For different substances, the size, strength, and Raman wavelength shift

(wavenumber) are an important basis for identifying chemical bonds and functional groups. In addition, Raman spectroscopy can also be used to judge the isomers of molecules by their polarization properties. In chemistry, the catalyst itself and the Raman spectrum can provide structural information about the surface material, as well as real-time analysis of the catalyst preparation process. At the same time, Raman spectroscopy is an important method for working electrode/solution interface structures and properties that can be further studied based on the problems of electrochemical interface structures, and adsorption reactions at the molecular level; it can be applied to the electrical, etching, and electroplating techniques. In the field of biology, Raman spectroscopy is one of the most powerful tools in the study of biomolecules [16-17]. The Raman spectrum of water is very weak in Raman spectroscopy. Therefore, based on the spectrum of water, Raman spectroscopy can change the structure and biological macromolecules in a state close to nature and obtain a lot of valuable information.

2.3.3 Application of Raman Spectroscopy in Materials Science Research. Raman spectroscopy has a great function for studying materials in the grain boundary structure, phase composition interfaces, and other topics related with materials. Raman spectroscopy has been wildly used to study the structure of thin films and to detect and identify CVD films. In addition, Raman spectroscopy can also be used to study the structure of monocrystalline silicon, polycrystalline silicon, micro-silicon and amorphous silicon, as well as the structure of bronzed amorphous silicon, hydrogenated amorphous silicon, diamond and diamond-carbon and other layered films [37]. In civil engineering, Raman spectroscopy can also be used to detect the material composition of bridges or buildings [38]. The composition and proportion of the building material or cement are

inferred using quantitative methods based on Raman spectral information. In the field of semiconductor materials, Raman spectroscopy can measure the distribution of semiconductor damage after ion implantation, the composition of semi-magnetic semiconductor, the mass of the epitaxial layer and the component carrier concentration of epitaxial mixture.

2.3.4 Advantages of Raman Spectroscopy. Raman spectroscopy has several advantages. Since Raman spectrometers use lasers in the visible area, flexible silicon fiber optic cables can be used to excite samples and collect scattered radiation, and these cables can be very long if necessary. Since visible light is used, samples can be stored in glass or quartz. In the study of chemical reactions, this means that the Raman probe can be inserted into the reaction sample, or the Raman spectrum can be collected through internal windows such as external reaction sample circulation or circulation pool. The microfiber Raman technique ensures that the probe will not affect the structure of the reaction sample when inserted. The miniature Raman probe can also be used for precise research and measurement. Secondly, the on-line Raman spectroscopy technique is very useful for the in situ real-time reaction of the catalytic surface. Another advantage of Raman spectroscopy is that hydroxyl bonds do not have Raman activity, which makes it possible to use Raman spectroscopy directly in water. The Raman spectrum is considered nondestructive, although some samples may be affected by laser radiation. One factor to consider when choosing this method is the fluorescence of a particular sample. Raman scattering is a weak phenomenon, and fluorescence may suppress the signal, making it difficult to collect quality data. However, the MFORP proposed in this paper can fully solve the problem of background fluorescence.

In the aspect of reaction analysis, Raman spectroscopy is sensitive to many functional groups, but it performs well in obtaining molecular backbone information by providing its unique molecular fingerprint information. Because Raman spectroscopy uses bond polarization and has the potential to measure lower frequencies, it is sensitive to lattice vibration and can provide users with polycrystalline information that is difficult to obtain by FTIR. This makes Raman spectroscopy very effective for studying crystallization and other complex processes.

3. RAMAN FIBER TAPER FABRICATION AND WORKING PRINCIPLE

3.1. RAMAN FIBER TAPER FABRICATION

A miniaturized fiber Raman probe (MFORP) for eliminating silicon background signals is proposed. The idea is to use different fibers on the collection and excitation state. The background fluorescence generated by the excitation fiber will not be collected by the other collection fibers; the background fluorescence can be eliminated from the beginning which completes the non-filtering Raman device. According to different experimental requirements, 3-in-1, 5-in-1, and 7-in-1 fiber tapers can be made by the fiber tapering device. This paper mainly introduces the 7-in-1 fiber probe. The tapered length of the probe is 1-2cm, and the tip diameter is 20-40μm. Due to the difficulty of Raman spectrum acquisition, we chose the core size of 62.5μm multimode fiber to better collect the scattering signal. To ensure the accuracy of the fiber probe, a self-made fiber tapering device is made, as shown in Figure. 3.1.
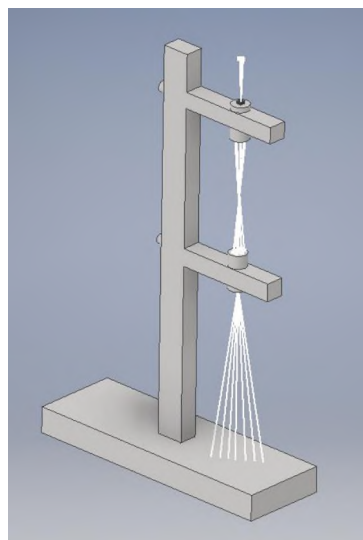

Figure 3.1. Simulation model of fiber tapering device

The device is manufactured on the upper and lower stations; 7 multi-mode optical fibers are inserted horizontally into the self-made 7-hole mold; the terminal is fixed with a splint to ensure all fibers are strongly stabilized.
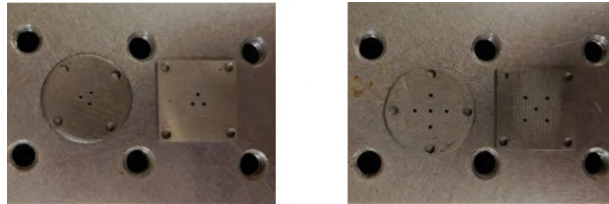
Figure 3.2. Fiber mold chip for taper fabrication.

The self-made fiber mold shown in Figure. 3.2, has two sets of the upper and lower stage respectively, which allow the fiber to pass freely. The molds were constructed in strict accordance with the standard hexagonal pattern to ensure that the optical fiber remains horizontal during the drawing process. The upper stage mold is round so that it can rotate the fibers together. The mold on the lower stage is designed as a square to better fix the fiber and ensure the vertical and horizontal position stabilized of the fiber during the tapering process, as shown in Figure. 3.3.

Figure 3.3. Fiber taper device installation process illustration.

To make the 7-in-1 optical fiber taper, a pencil flame torch is placed perpendicular to the torsion area of the fiber. The torch is powered by butane and has a sustained temperature of about 1400 degrees Celsius. Horizontal tapering has been found to be a major factor leading to brittle and unsafe tapered tips. In order 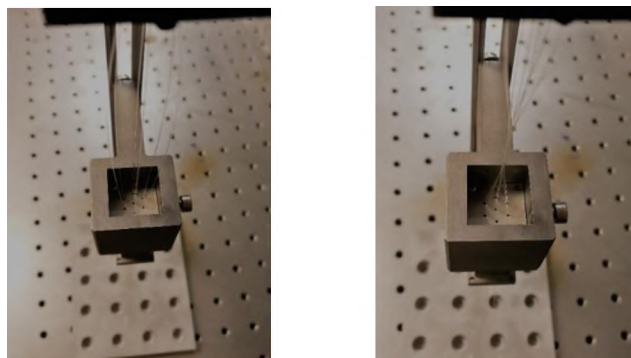to make the probe more ductile, we used the gravity vertical fiber thinning method. Under the lower stage, seven optical fibers are weighted with homemade buttons to achieve simultaneous application of gravity and temperature. Through the interaction of gravity and temperature, each fiber in the light tip cone is controlled to be uniformly stressed and heated.

Table 3.1. Fiber taper key parameter information for MFORP.

Parameter information	Parameter value
Fiber type	Multimode fiber with core diameter of 62.5μm
Taper length	1-2 cm
Taper diameter	20-40 μm
Working stage distance	6-10 cm
Twisting angle	1440-2180 degrees (4-6 turns)
Taper structure	One central excitation fiber with several absorption fibers surrounded
Pencil torch	1400 degrees Celsius

After the heating and tapering process, the tip was cut by the diamond knife to ensure that the fibers are horizontal. According to different experimental requirements, the

number of turns of the fiber and the distance between the upper and lower worktables are also different. If the sample to be measured is small, the number of fiber optic torsional turns should be 4 or more and the distance between the upper and lower worktables should be no less than 6cm. The parameters of the fiber probe processed in this paper are illustrated in Table. 3.1. After repeated experiments, the probe machined, constructed under the equipment parameters has excellent detection performance and is not easily damaged.

3.2. RAMAN FIBER TAPER WORKING PRINCIPLE

The 7-in-1 MFORP works in a different way from ordinary fiber Raman. As shown in Figure. 3.4, the tip of 7-in-1 MFORP is pointed to the sample, and the other section is divided into two parts by optical fiber connection.
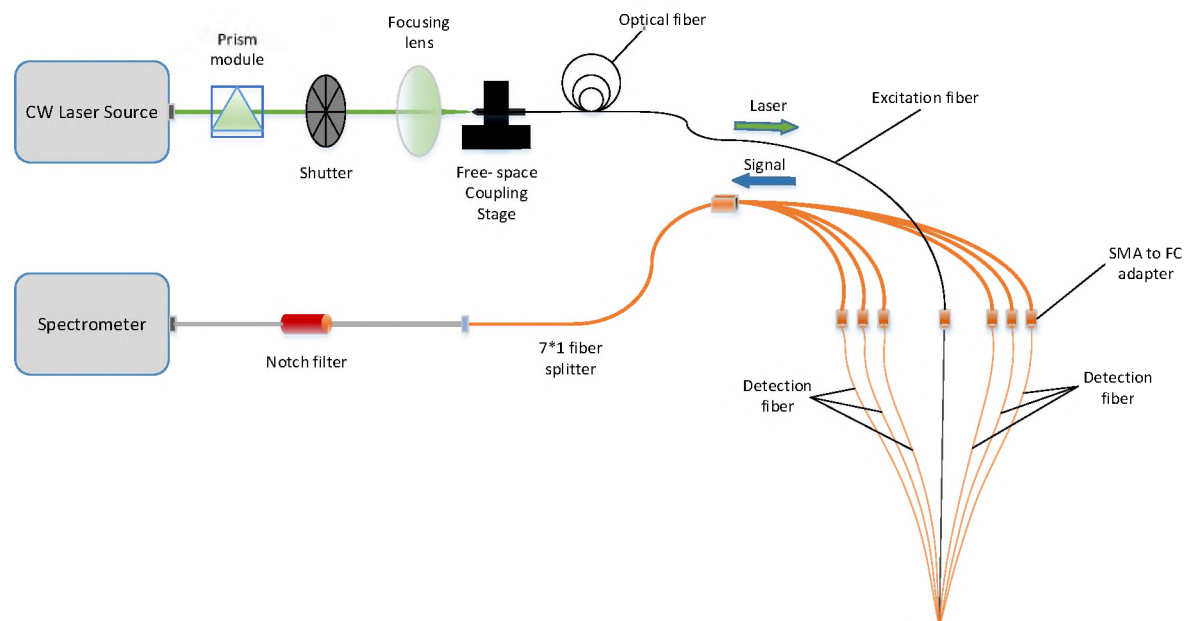
Figure 3.4. The schematic diagram of MFORP system.

Due to the compatibility of the fiber probe materials, MFORP can easily insert the probe into a liquid sample if the test is required. The central excitation fiber was connected to the excitation wavelength λ= 532 nm CW laser. The other six fibers were connected back to the QE Pro spectrometer through the connection of 7*1 fiber combiner by using SMA to FC adapter. When the laser light source is turned on, the excited photons are shot into the sample from the excitation fiber (Black) in the image. The excited photon scatters on the sample and the scattered photon is absorbed by the other six absorption fibers (Orange). The Raman background fluorescence generated by the optical fiber itself is eliminated, because the background fluorescence collected by the excitation fiber is not absorbed into the spectrometer.

4. EXPERIMENTS AND MEASUREMENT RESULT

4.1. FIBER TAPER FIBRICATION RESULT

Raman spectroscopy has always been known for its high precision and accuracy. The molecular detection in biology, chemistry and materials has become a hot topic at present. As in the result shown in Figure. 4.1, we proposed the MFORP, a very tiny Raman probe with high stability.
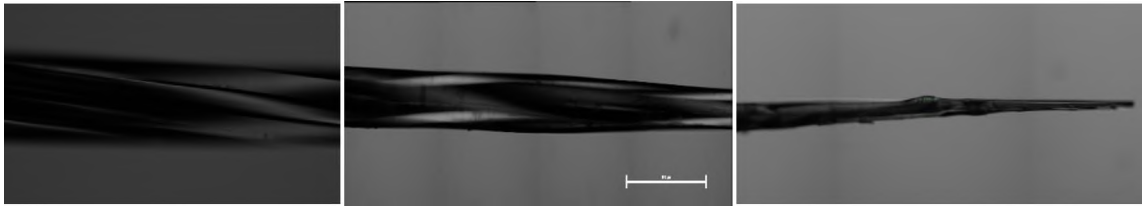
Figure 4.1. Confocal microscope image of MFORP.

The spiral traces can be clearly seen when the probe is under the confocal microscope. The seven multimode fibers work closely together through a high-temperature tapering technique. These three small graphs represent the three positions of the probe. The total length of the probe tip is approximately 1.5cm. The cross-section diameter of the probe is approximately 30 microns. In order to see the size of the probe more clearly, we also captured the image of the probe under a normal microscope. As shown in Figure. 4.2, the max diameter of the cross section of the tip measures 38μm.

Figure 4.2. Microscope image of probe tip.

As expected, the seven strongly twist fibers were gradually extended parallel to the tips. As a result, from the original 125μm*7, the total diameter length of all 7 fibers decreased to tip diameters as 38 microns. This tapering technique optimized the probe structure to reduce the scattered excited light and maximize the emitted signal. In other words, compar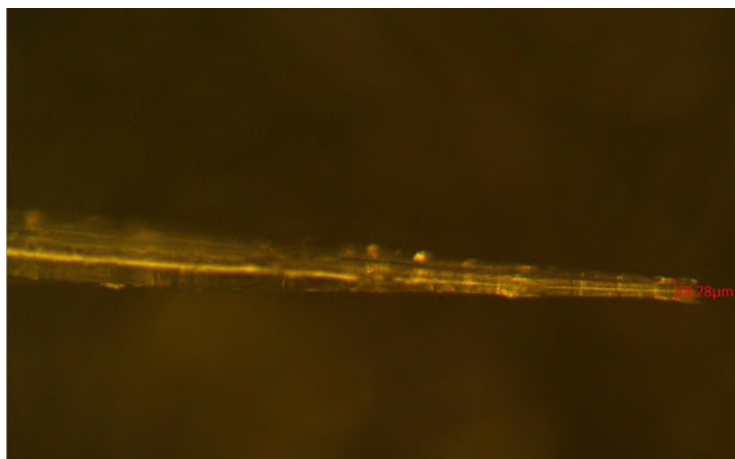ed with the traditional FORP, two-in-one optical fiber couplers are used to excite and emit light through the same induction axis. This causes the excited photon to encounter the sample and the scattered photon to return to the spectrometer along the original path. The collected Raman spectrum is interfered by a large background fluorescence and the data cannot be read normally. In contrast, the new MFORP structure is designed to overcome the challenge of completely separating the excitation and emission of light. In the field of Raman spectroscopy research, such separation is necessary to improve sensitivity and miniaturize probes for single-cell analysis, molecules detection, and so on. However, the key is to eliminate the fluorescence signal coupled by the fiber itself.

4.2. EXPERIMENT TEST RESULT

4.2.1 Comparison Test of Raman Measurement Between Proposed MFORP and TFORP. After introducing the principle and fabrication method of the Fiber-Optic probe, the prediction of the function of the new probe needs to be verified by many experiments. In order to test the Raman spectral properties of the new probe and whether it has the function of removing fluorescent background light, we combined the probe with a 532nm wavelength, 100MW laser. The excitation fiber in the center is connected to the laser through a SMA to FC adapter. Excitation light is provided by fiber coupling, with volume holographic grating (VHG) stable 532 nm laser diode and single-mode output capability. A notch filter is positioned on the return path, which was connected with the remaining six collection fibers, preventing the subsequent noise based on the reflection signals. To facilitate the following experimental measurements, we used about 2 meters of optical fiber as the excitation and collection optical fiber. Using a longer fiber prevents the probe from breaking due to a shorter fiber and can also be used in some special experiments. We first experimented with the Raman signal of this method water because in Raman spectroscopy, the Raman spectrum of water is very weak. We demonstrated the advantages of the new Raman probe in spectral collection by detecting low-energy Raman spectral samples. The experiment processing procedure for Raman sensing in detail is as follows:

Step 1: Take a small measuring cup of water as an experimental sample and fix the beaker on an optical bench to prevent vibration.

Step 2: Dip the fiber taper into water and attach the probe to a rack perpendicular on the top of the beaker to reduce the error caused by vibration during the experiment.

MFORP and TFORP were used to conduct experiments on the Raman spectrum of water respectively. The experimental results are shown in Figure. 4.3.
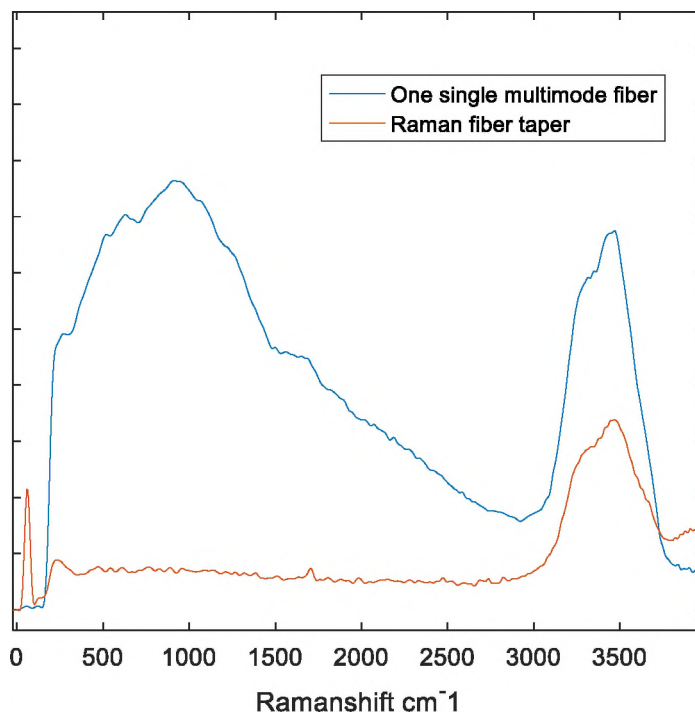
Figure 4.3. Water Raman signal measurement result.

In the experimental data, MFORP is represented by blue lines. The traditional Raman probe of single multimode fiber is represented by an orange line. In the experiment, we used 3s as the acquisition time and get the average result from 10 times repeat to ensure the data is stabilized. One spectrum takes about 30s to process. The traditional Raman probe has a strong background fluorescence between Raman shift $100cm^{-1}$ and $1500cm^{-1}$, while the new MFORP performs well in the experiment. It can effectively eliminate the background fluorescence signal that was excited by the material of the fiber itself, and the

spectral intensity of the six collected fibers is much better than that of conventional Raman fiber probe.

In addition, in the experiment of measuring liquid Raman, we also selected ethanol for the second group of measurement experiment. Considering the strong volatility of ethanol, the high concentration of ethanol would lead to inaccurate experimental data. We extracted the 98% ethanol to water; 50% ethanol compounded in the determined cylinder. The optical fiber probe was also perpendicular to the cylinder containing the ethanol sample and is fixed with a table. After the fiber probe was submerged into the sample, 2 second acquisition time and the average result of 10 times repeat was selected for Raman spectrum acquisition. The experimental results are shown in Figure. 4.4.
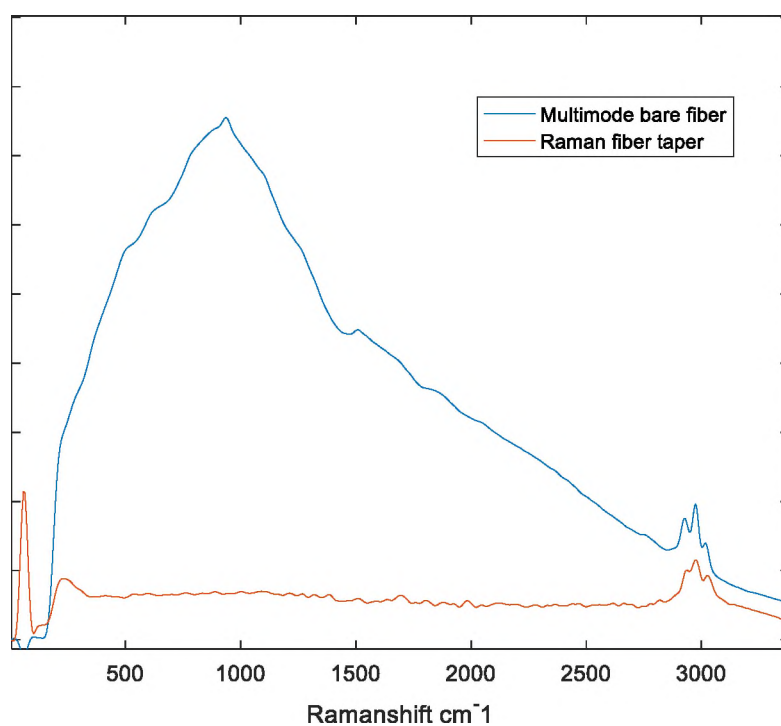

Figure 4.4. Ethanol Raman signal measurement result.

In Figure 4.4, the orange signal represents the experimental data results of MFORP. Compared with the experimental data of the ordinary Raman sensor, the new MFORP maintains good performance in the measurement of ethanol as well. Most of the background fluorescent signals were effectively eliminated. And there was an effective increase in the spectrum of collection.

4.2.2. Liquid Sample Raman Measurement Test of Proposed MFORP. Raman spectroscopy has a very strong molecular detection technique, which can analyze the molecular spectrum through the different vibration energy levels of different molecules. In the following experiment, we added salt to pure water and mixed it into normal saline. Since the Raman characteristic peak of saline and water is very similar, the obvious difference lies in the change of Raman peak energy. There were two significant Raman characteristic peaks in water and NaCl water at Raman shift 3200 cm^{-1} and 3450 cm^{-1}. The higher the concentration of normal saline, the higher the composition of sodium ion and chloride ion in solution.
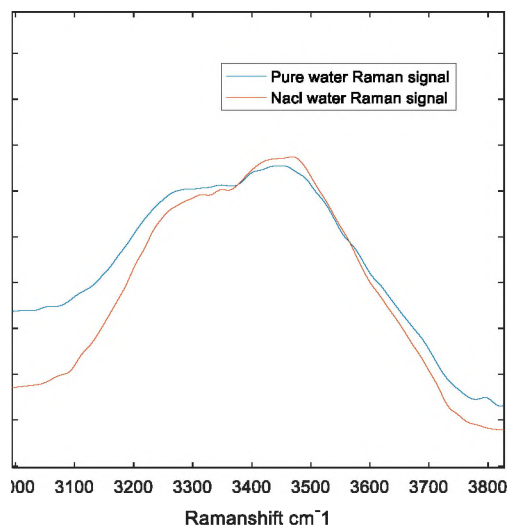

Figure 4.5. Nacl water Raman spectrum measured by MFORP.

As a result, shown in Figure. 4.6, when the concentration of saline increases, the spectrum intensity of the first Raman peak decreases and the second Raman peak increases. In this experiment, we first adopted Raman spectroscopy as the reference signal for the pure water. Then, we added a certain amount of salt into the cup without changing the fiber position. We used a centrifugal blender to accelerate the decomposition of salt in water. After decomposition and stirring for 1 h, we adopted the Raman spectrum of normal NaCl water. The orange line represents the Raman spectrum of pure water. After adding salt, the Raman characteristic peak of salt water (blue) can be clearly seen to change, thus verifying the accuracy of the experimental data.

After determining that the new MFORP can obtain different Raman spectra by changing the solution composition, we also tested the stability and sensitivity of the new MFORP. The Raman spectrum of ethanol has three characteristic peaks, and the energy of the Raman spectrum will change with the change of different concentration of ethanol. To determine the sensitivity of the new MFORP probe, an ethanol concentration experiment was performed.
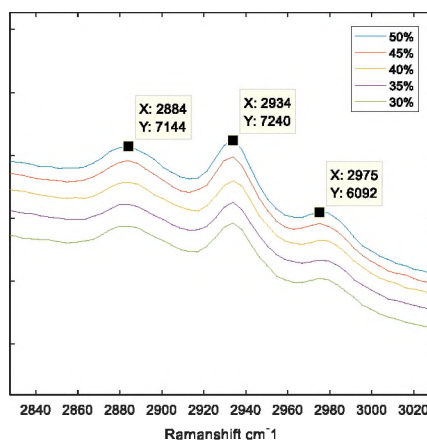
Figure 4.6. Ethanol concentration test result measured by MFROP

Without changing other parameters, the concentration of ethanol was degraded by adding pure water to the sample to detect whether the change of ethanol concentration would affect the peak energy of Raman. Considering the accuracy of the experimental data, we chose 50% ethanol as the initial measurement value because of its high volatility. As shown in Figure. 4.7, we selected 30%-50% ethanol concentration as the detection index of this experiment. It can be concluded from the figure that the energy of the characteristic peak of ethanol Raman decreases with the decrease of the concentration of ethanol.

5. CONCLUSION AND FUTURE WORK

In this paper, we have successfully developed a new type of fiber-optic Raman probe (MFORP). The diameter of the new Raman probe can reach 20-40 microns by using the processing method of high temperature with gravity tapering method. The effect of fluorescence of optical fiber on Raman spectrum acquisition was successfully solved by processing seven-in-one optical fiber taper. At the same time, the spectral energy collected by the six absorbed optical fibers was also improved, compared with traditional optical fiber Raman equipment. Experiments show that MFORP has high sensitivity. By using a 532nm laser to analyze the sample with 2s acquisition time, the concentration change and composition change of the sample can be clearly perceived through the change of the Raman spectrum.

In previous studies, the Raman fiber probe has been widely used in biochemistry, materials science, and related medical research. In the field of medicine, preventing cancer has always been an important research topic. The first signs of cancer are changes in the cell's acidity or alkalinity. Cells that become cancerous at the first stage tend to be acidic and expand in the body. In future work, we would like to measure the cell pH by using the novel MFORP. Based on the advantages of small MFORP, strong stability, and high sensitivity, coating pH sensitive polymer on the end face of MFORP to conduct pH measurement experiments will be our primary task to achieve. By working into the field of biochemical study, enhancing the ability of Raman signal detection will also be the important task for us to work on in the future. The Focus Ion Beam will be applied to cut the end face of probe to maintain the fibers are in the same orientation. Moreover, during

the project experimenting process, the end face of the new MFORP would be damaged in the long period experiment measurement. The main reason is that the optical fiber probe is exposed without protection and in direct contact with the sample. Finally, we will develop a protective mold that can embed MFORP without changing other parameters to meet the experimental requirements of long-term detection.

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