Gold nanoparticles modified double-tapered fiber for SERS detection

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Abstract. Double-tapered fiber probes modified with gold nanoparticles were fabricated for the surface-enhanced Raman scattering (SERS) sensing. Its performance was compared with the fiber SERS probes of flat end and of single-tapered structure. The remote detection performances of three fiber probe structures were compared by detecting rhodamine 6G (R6G) aqueous solutions with the different concentrations. The results of remote detection of R6G aqueous solution indicate that double-tapered fiber probe with the detection limit of 10⁻⁹ M is the most sensitive.

1. Introduction

As a SERS sensor, its ability to detect solutions with low concentration is an issue parameter to judge its performance. The use of flat-end fiber (FEF) probe realized the fiber SERS sensors from double fiber detection (one fiber propagates excited laser and the other collects Raman scattering light) to single fiber detection [1]. However, the performance of FEF probe in remote detection cannot reach the optimum effect. Single-tapered fiber (STF) probe with an optimal cone angle can achieve superior performance for optical fiber SERS detection, due to it increasing the SERS active surface [2], transmitting the evanescent field to the surroundings with an increased magnitude [3], and good collection efficiency [4]. Also, the STF probe with the needle structure would be used to biomedical techniques for living cells, and obtain the lives period information of cells. STF tips with silver nanoplates have been fabricated to detect the 10⁻⁷ M 4-ATP [5], and STF tips with gold nanoparticles could detect the 10⁻⁸ M solution of R6G [6]. Single molecule detection was demonstrated by the SERS technique in different environments [7], even in single living cell [8]. It is worth noting that the silver nanoparticles is deleteriousness for cells or biological tissue. Therefore, the gold nanoparticles were used as our SERS enhancement substrates, though the gold nanoparticles perform worse than silver nanoparticles in enhancement substrates. In order to increase the SERS active surface and detect lower concentration solution, the double-tapered fiber (DTF) was proposed. It was confirmed that with the optimized geometry, fiber-optic sensor could detect the SERS spectra from a 10⁻⁹ M solution of crystal violet in distilled water both with measurements performed in solution and with a “dip and dry” technique [2]. That the large area of column increase the interaction opportunity between the detection molecules and evanescent wave, would be the reason.

In this paper, we prepared three types of fiber SERS probes with FEF, STF and DTF. Their performance for SERS sensing were compared. All fiber probes were modified with gold
nanoparticles by the electrostatic self-assembly technology. Raman spectra of R6G aqueous solutions with different concentrations were detected by these fiber probes in remote mode.

2. Materials and methods

2.1. Experimental reagents
HF acid (40%), chlorauric acid, trisodium citrate, rhodamine 6G (R6G) and anhydrous ethanol were purchased from Sinopharm Chemical Reagent. Potassium hydroxide (95%) and iso-octane were purchased from Aladdin Reagent online. Milli-Q deionized water (resistivity = 18.2 MΩ cm−1) was used throughout the experiment.

2.2. Probe preparation and SERS detection
A multimode fiber with a cladding of 125 μm and a core of 50 μm were used in our experiment. There were two steps to fabricate our three types of SERS fiber probe. The first step was to fabricate the fiber probes. Three multimode fibers were removed the coating layers and were cleaned with anhydrous ethanol. The FEF probe was obtained by directly cutting the fiber end with a flat surface. For the DTF probe, we put the FEF into a beaker with 40% hydrofluoric acid aqueous solution covered with iso-octane over-layer for etching 55 min, lift up 1 mm for etching 8 min, and finally obtain the double-tapered structure. After etching, the DTF was rinsed with deionized water. The method of prepared STF was similar with that of reference [6]. The second step was to modify these fiber probes with gold nanoparticles. The gold nanoparticles with around 55 nm in diameter were prepared by citratereduction of chloroauric acid. And the gold nanoparticles were solidified on the tapered fiber probe by electrostatic self-assembly technology [9].

Take the DTF probe as an example to introduce the solidified progress. Firstly, the DTF tip should be totally cleaned by dipping the DTF tip into a piranha solution (3:1 mixture of 96 % concentrated sulfuric acid and 30 % hydrogen peroxide) for 30 min, and then rinsing twice in deionized water and ethanol respectively. Secondly, the cleaned DTF tip was immersed in the mixture solution with 5 % v/v deionized water, 5 % v/v (3-Aminopropyl) trimethoxysilane (APTMS 97 %) and 90 % ethanol for 30 min. Again, it was rinsed twice in deionized water and ethanol respectively to remove the residual APTMS. Thirdly, it was kept in the incubator at 90 °C for 30 min. Finally, the DTF was cleaned in the ethanol and then immersed into the gold colloids for 48 h. Finally, the gold nanoparticles modified double-tapered fiber probes were obtained.

The final microscope photograph of double-tapered structure with SEM images inset is shown in figure 1.

![figure 1](image_url)

Figure 1. Optical and SEM images of the DTF SERS probe.

The schematic of remotely detecting R6G was shown in figure 2. A confocal micro-Raman spectrometer (Renishaw inVia plus) was used to detect the Raman spectra by the DTF SERS probe with a segment around 28 cm long. Through the 10× microscope objective, 633 nm He-Ne laser as excitation was injected into the fiber from the other flat end. The backward SERS signals of the R6G molecules on the probe surface were collected by the same probe. The exposure time of Raman spectrometer was set to 10 s for each measurement. Raman signals were collected in the spectral range...
from 1000 to 1800 cm\(^{-1}\). The detection of the other two types of fiber SERS probes was the same as above method.

![Raman spectrometer diagram](image)

**Figure 2. Schematic diagram of remotely detecting R6G solution.**

### 3. Results and discussions

The probes of DTF, STF and FEF were used to detect R6G aqueous solution with several concentrations in remote mode, their results shown in figure 3.

For the detection of DTF probe from figure 3 (a), the main Raman characteristic peaks of R6G were clearly recognized, and the intensity of each peak lowers with the concentrations decreasing. The detection limit reached 10\(^{-9}\) M. From figure 3 (c) and figure 3 (d), it can be concluded that for the detection of STF probe and FTF probe, these detection limits reached 10\(^{-8}\) M and 10\(^{-6}\) M, respectively. Comparing the detection limit of three fiber probes from figure 3 (b), we could find that the detection intensity of FEF probe (detection limit corresponding to 10\(^{-6}\) M) is the highest, and the DTF probe is the lowest. The detection limit of FEF probe is, after all, the highest, although its detection sensitivity is the worst. Therefore, the detection intensity of FTF probe is the strongest.

It is obviously that the tapered fibers have larger effect surface area than that of flat end fibers, and the tapered structure increases the contact opportunity between detection molecules and evanescent wave. Furthermore, the tapered structure can be collected more Raman signals from the detection molecules. Therefore, tapered structure is superior to flat end structure. Apparently, the effect surface area of double-tapered structure is the largest, so as for the most sensitivity in the remotely Raman detection.

![Raman intensity graphs](image)
4. Conclusion

The probes of DTF, STF and FEF, modified with gold nanoparticles by electrostatic self-assembly technology, were successfully fabricated. When they were used to detect the standard sample of R6G aqueous solution, the detection limits of DTF, STF and FEF SERS sensor were $10^{-9}$ M, $10^{-8}$ M and $10^{-6}$ M, respectively. The DTF probe has the largest sensitivity, due to the double-tapered structure increasing the contact opportunity between the detection molecules and the evanescent wave. Furthermore, the tapered structure can also increase the collecting efficiency. In the same conditions, the flat end fiber probe is two-order lower than tapered probe because of its little interaction area and lower collecting efficiency. The high sensitive remote SERS detection of DTF will provide a new tool for detecting Raman spectra of kinds of biomolecules.

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