Femtosecond Laser Double-pulse Fabrication of Fiber Tips with Different Roughness and Its Application to SERS Sensor

Yuyin Wei[1,a], Furi Gao[1,b] and Sumei Wang[1,c,*]
[1]Laser Micro Fabrication Laboratory School of Mechanical Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China
a. wyyfrom2@163.email, b. 523842904@qq.com, c. wangsumei@bit.edu.cn
**corresponding author: Sumei Wang*

Keywords: SERS sensor, femtosecond laser, double-pulse fabrication.

Abstract: Fiber Tips with different roughness are fabricated and deposited with silver nanoparticles for SERS detection. Firstly, femtosecond laser double pulses are used to improve the surface roughness of ablated fiber by adjusting the power， scan speed and the pulse-delay. Secondly, silver nanoparticles are reduced by laser-induced method on the fabricated optical fibers with different surface roughness. The size and distribution of silver nanoparticles deposited on rough surfaces are better than that on smooth surfaces, which attributes to that the micro- and nanostructure on the rough tip surface can make the adsorption of silver nanoparticles easier and enhance the intensity of laser field at the output end. The best deposition effect is achieved at 7 mW induced deposition power and 7.5 min deposition time. When the Ra is 0.331, the prepared SERS sensor has the best performance and the lowest detection concentration is 10-6M. The SERS sensor prepared by depositing silver nanoparticles on the rough fiber tip has good performance and broad application prospects.

1. Introduction

When ordinary SERS sensors are used in medical and biochemical sensing, the samples to be tested must be prepared in advance and tested on the sample holder of Raman spectrometer, so remote in-situ detection cannot be realized， while the optical fiber SERS sensors can be directly inserted into the solution[1], living tissues or cells[2,3], to achieve remote detection[4,5], which greatly simplifies the testing process and is widely used in biochemistry, environmental science, medicine, food safety and other fields. Deposition of noble metal nanoparticles on the tip of optical fibers has been proved to be a simple and common method for fabricating optical fiber SERS sensors[6-8]. The micro- and nanostructure of the tip of optical fiber is an important factor affecting the deposition effect of noble metal nanoparticles and the ultimate performance of optical fiber SERS sensors[9]: Rough fiber tip surface can not only improve the adsorption of noble metal nanoparticles, but also generate local surface plasmon resonance "hot spots" to improve the sensitivity of optical fiber SERS sensors.

Published by CSP © 2020 the Authors

Femtosecond laser is an effective tool for processing micro- and nanostructures on optical fibers. However, most of the previous studies were limited to the processing of micro- and nanostructures on fiber surface, and did not pay attention to the quantitative influence of different processing parameters of femtosecond laser on the surface roughness of the processed fibers. The influence of different processing parameters such as laser power and scanning speed on surface roughness is analyzed in this paper. The improvement effect of femtosecond laser double-pulse on surface roughness is also studied. As well as the effects of different roughness on the deposited SERS substrate are also analyzed. The micro- and nanostructure of the tip surface of the optical fiber SERS sensors is one of the key factors affecting the performance of the sensors. Under the same conditions, the SERS signal generated by the rough tip surface is much stronger than that generated by the smooth. Rough surface structure and noble metal nanoparticles can produce local surface plasmon resonance(SPR) with higher enhancement factor, which is the main factor of electromagnetic field enhancement, and electromagnetic enhancement plays a dominant role in SERS enhancement. Therefore, the preparation of rough tip surface micro- and nanostructures has become an important research direction in the field of optical fiber SERS sensors.

In previous studies, most researchers used sandblasting[6], grinding[10,11], spraying nanoparticles[6,12], chemical reagent corrosion[13-16], ion beam etching[17,18] to roughen the tip surface of optical fibers, and fabricated various surface micro- and nanostructures to improve SERS enhancement factor. However, all of the above methods have certain defects. Sandblasting, grinding and spraying of nanoparticles are easily to damage the fiber and it is difficult to control the roughness. Chemical corrosion has certain safety and pollution problems. Although ion beam etching can precisely control the surface micro- and nanostructure, has high repeatability, but requires expensive ion beam equipment, complicated control procedures, high cost and cumbersome operation. Controllable processing of roughness can be achieved by adjusting laser processing parameters (power, scanning speed, double-pulse delay). SERS substrates can be deposited on the tip of the optical fibers by laser-induced method. Under suitable laser power and deposition time, the quality of laser-induced SERS substrate on rough tip surface is much better than that on relatively smooth surface, so better SERS enhancement effect can be achieved.

2. Methods

Silver nanoparticles are deposited on the tip surfaces of different roughness optical fibers to improve SERS. It can be divide into two steps: first, the "smooth"(cut by precise optical fiber cutter, whose precise roughness was not easily measured, so in this paper, we call it the "smooth" tip surface) and different roughness optical fiber tips were prepared, and then silver nanoparticles were deposited on the prepared optical fiber tips.

2.1. Fabrication of Optical Fiber Tip with Different Roughness

The type of optical fiber used in the experiment is OM1, which is purchased from Fiberhome. For the fabrication of "smooth" optical fiber tip, as mentioned earlier, the precise optical fiber cutter(NNO, VF-77) is used to cut the two ends of the stripped coated optical fiber flat and get the complete smooth tip surface without cracks or impurities. For different roughness of the optical fiber tips, the femtosecond laser double-pulse processing method was adopted. A commercial chirped pulse Ti:sapphire laser(Spectra Physics) was used to generate linearly polarized laser pulses of τ=35fs duration at λ=800nm central wavelength at a repetition rate of 1kHz, and a Gaussian intensity profile. In order to avoid the impact of debris on the subsequent processing, the soaking solution processing scheme was adopted. 40X soaking objective was used, NA = 0.8, laser scanning step was set to 1μm, and depth step was 2μm. The influence is 26.5 J/cm2, and the effects of scanning speed and pulse delay on the roughness of the fabricated fiber tip were studied. The 3.1 section show more details about this part.

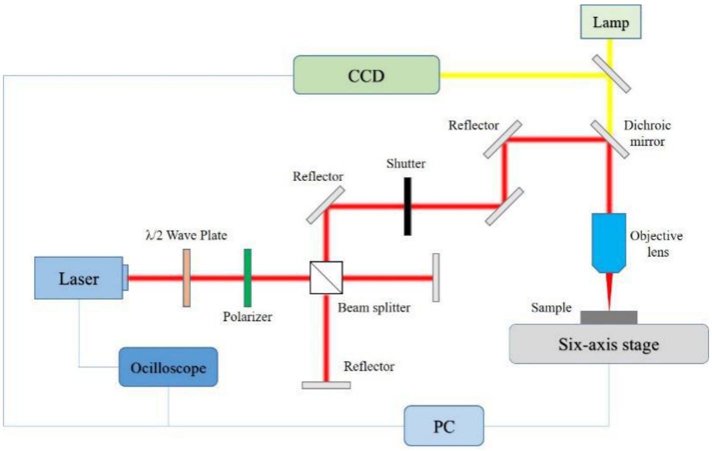

Figure 1: Experimental setup of the fiber tips processing system.

2.2. Deposition of Silver Nanoparticles on Fiber Tips

Silver nanoparticles were deposited on the tip of optical fibers by laser-induced reduction method. A mixed solution of 10-3M silver nitrate (AgNO3, Acros Organics) and 10-3M sodium citrate (Na3CT, Acros Organics) with a volume ratio of 1:1 was prepared. The induced laser was produced by the femtosecond laser pump source, the working medium is Nd:YAG, emitting a continuous wave (CW) laser with a wavelength of 532 nm. The laser was coupled into the 105/125um multimode fiber through a 5X objective lens, and the other end of the fiber was immersed in the prepared mixed solution, and the laser induced the reduction of silver ions and deposited them on the tip of the optical fiber.

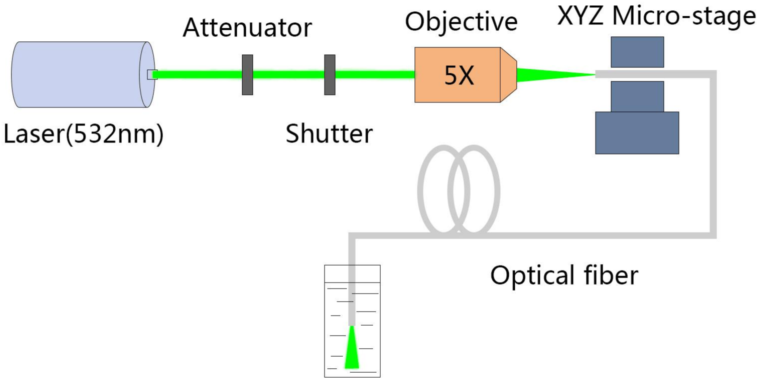

Figure 2: Schematic of the laser induced deposition on the fiber tips.

Different morphologies of silver nanoparticles were obtained by controlling the power and deposition time of the induced laser. The experimental results are shown in 3.2 section, and the additional videos show the deposition process.

3. Results and Discussion

3.1.1. Fabrication of Optical Fiber Tips with Different Roughness

After the fabrication of the optical fiber tip surface, its roughness was characterized by atomic force microscopy (AFM). The tip surface of the fiber cut by the precise fiber cutter was extremely smooth, and the accuracy of the roughness was not easily measured under AFM. The rough fiber tip was processed by femtosecond laser double- pulse. The variation of Ra value with different pulse delays at two scanning speeds of 50um/s and 150um/m was studied. The results are shown in Figure 3(a).

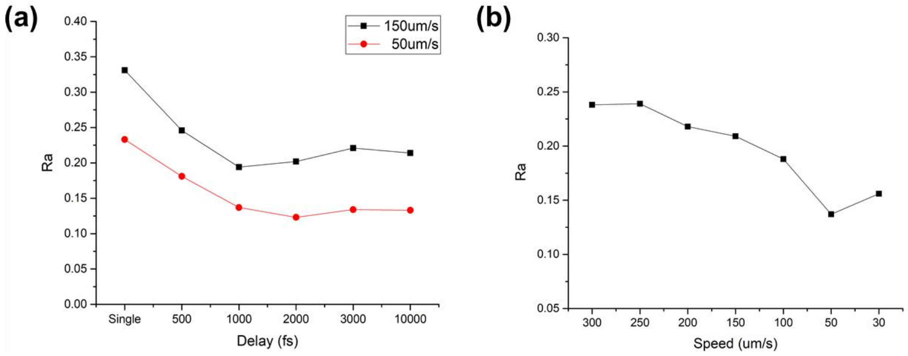

Figure 3: (a) Effect of pulse delay on Ra at two different scanning velocities.(b) Effect of different scanning speeds on Ra under femtosecond laser double-pulse(pulse delay=3000fs).

It can be seen from Figure 3(a) that the variation trend of Ra is similar at two different scanning speeds. With the increase of double pulse delay, the surface roughness of ablated optical fibers decreases at the beginning, however, when the pulse delay increases to a certain value, the surface roughness tended to be stable and did not change with the change of the delay. Even if the delay increased to 120 ps, the measured surface roughness did not change much. There was a minimum value of Ra at both scanning speeds. The minimum Ra was obtained at a delay of 2000 fs when the scanning speed was 50 um/s, and the minimum Ra was obtained at a delay of 1000 fs when the scanning speed was 150 um/s. This is mainly due to the fact that the temporal shaped femtosecond laser double-pulse can reduce the ablation crater depth of the silica.[19]

In order to study the influence of scanning speed on the roughness of the processed fiber tip face furtherly, the relationship between Ra value and scanning speed was studied under the influence of 26.5 J/cm^2, scanning step of 1μm and double pulse delay of 3000fs (From Figure 3 (a), we can know that the effect of pulse delay on Ra is almost unchanged under this delay time). The result is shown in Figure 3(b). It can be found that as the scanning speed decreased, the surface roughness of the ablated fiber decreased too. When the scanning speed was 50 μm/s, the minimum value of Ra was obtained, and after the scanning speed was lowered, the surface roughness was no longer reduced. The reduction of the scanning speed enables the pulsed laser to perform more intensive processing on the same area, which can greatly reduce problems such as poor surface quality caused by factors such as debris, thereby improving the surface roughness. However, when the scanning speed was less than 50 μm/s, multiple processing of the same position will destroy the original better surface quality, resulting in an increase in roughness.

The experimental results show that the desired roughness can be obtained by controlling scanning speed and pulse delay at a certain processing fluence. By this method, five kinds of fiber tip surfaces with Ra roughness of 0.123, 0.194, 0.246, 0.331 and 0.421 were fabricated for subsequent laser-induced reduction deposition experiments.

3.1.2. Laser Induced Reduction Deposition of Silver Nanoparticles

Silver nanoparticles were deposited on the tips of optical fibers by the laser-induced reduction method. The induced laser power affects the overall optical field intensity, which in turn affects the reduction degree, aggregation size and distribution of nanoparticles. Deposition time also affects the deposition effect of silver nanoparticles on the tip surface of optical fibers. Therefore, the deposition effect of silver nanoparticles under different laser power and deposition time was studied. The deposition effect was judged by monolayer, uniformity and particle size, which have a positive impact on SERS according to literature[20].

The influence of laser power and deposition time on deposition effect was studied on the "smooth optical fiber tip" firstly. The different deposition effects of laser power of 5 mW~10 mW and deposition time of 5 min~20 min were studied. When the laser power was small (≤5 mW) or the deposition time was short although the laser power is large(~7 mW,≤7.5 min), the effective deposition can not be realized; when the laser power was too high (≥10 mW) or when the laser power was moderate but the deposition time was longer (~7 mW,≥15 min), the aggregation of multi-layer silver nanoparticles was formed, which would have a certain negative impact on the enhancement of SERS; when the laser power and deposition time were moderate (~7mW, ~10min), the silver nanoparticles deposited were uniform and well covered, the optical and SEM images of the deposited silver nanoparticles are shown in Figure 4.(a) and (b). By comparing the SEM diagrams under different deposition conditions, it can be found that the silver nanoparticles deposited at 7mW for 10min as shown in Figure 4.(a) and (b) have the best effect, with single layer, large particle size and uniform distribution. In conclusion, the optimal condition for deposition of silver nanoparticles on the "smooth" optical fiber tip surface is 7 mW for 10 minutes.

In order to ensure the best performance of the fabricated optical fiber SERS sensors, the laser energy and deposition time required for the best deposition effect are also explored on the rough fiber tip surface. The experimental process is no longer demonstrated. It was found that the laser deposition power of 7 mW and the deposition time of 7.5 min can achieve the best deposition effect on different roughness fiber tips. The morphology of silver nanoparticles deposited on the fiber tip with Ra=0.241 is shown in Figure 4. (c) and (d). Compared with the best morphology of silver nanoparticles deposited on the "smooth" optical fiber end surface, silver nanoparticles have larger particle size and more dense distribution, which means they have better deposition effect.

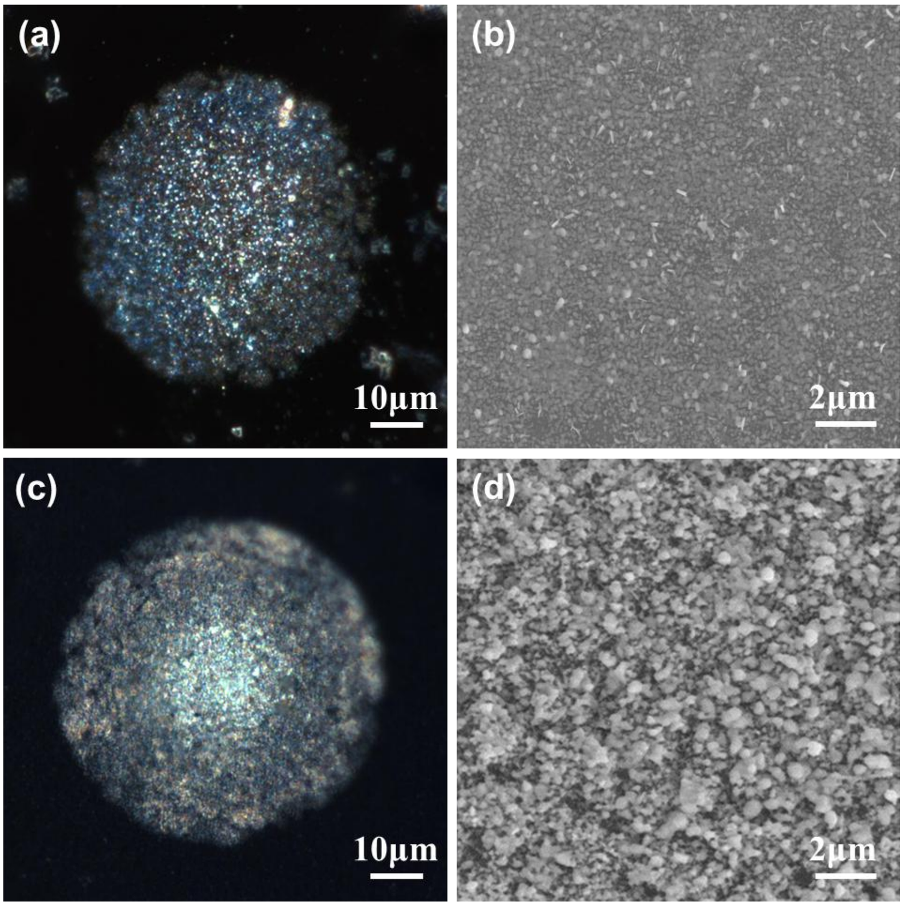

Figure 4: Morphology of silver nanoparticles deposited on the "smooth" tip of the fiber at a laser power of 7 mW and a deposition time of 10 min: (a)optical microscope image; (b)SEM image. Morphology of silver nanoparticles deposited on the tip of the fiber with Ra=0.241 at a laser power of 7 mW and a deposition time of 7.5min: (c)optical microscope image; (d)SEM image.

In the process of femtosecond laser ablation of the tip surface of the optical fiber, some debris will remain on the tips. Even if it is ultrasonically cleaned, it cannot be completely cleaned. So it is necessary to conduct elemental energy spectrum analysis on the tip of the fiber to prove that silver nanoparticles are deposited on the surface rather than debris. Take any fiber core region and characterize it by using the elemental component analysis function in the SEM. The results are shown in Figure 5. The Ag element proves the existence of silver nanoparticles on the fiber tip.

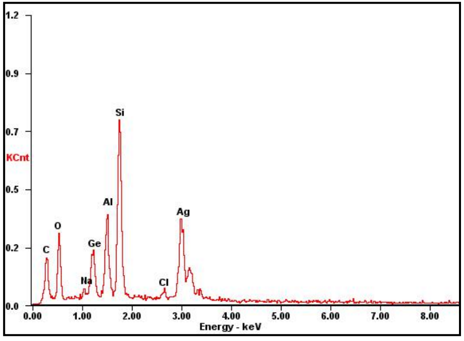

Figure 5: Component analysis of optical fiber tip surface.

In order to actually characterize the SERS enhancement effect of the deposited silver nanoparticles, the Raman spectroscopy of the fiber SRES sensor prepared under the best deposition conditions on the "smooth" and the above five kinds of roughness fiber tips was carried out. The microconfocal laser Raman spectrometer (inVia-Reflex) manufactured by Renishaw Company was used. Rhodamine-6G solution (R6G) with was chosen as the solution to be measured, which the concentration was 10^{-6}M. The excitation laser power was 0.05% of the total power, the integration time of 10s, and the integral number of 1. The experimental results are shown in Figure 6.

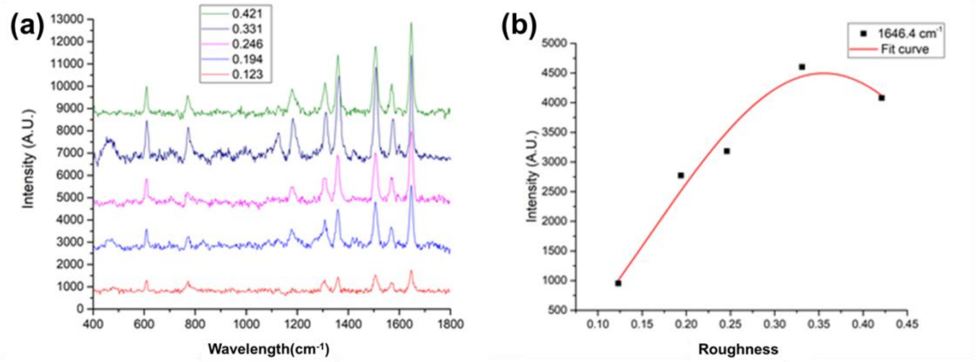

Figure 6: (a) R6G Raman spectroscopy of optical fiber SERS sensor with different roughness end faces. (b) variation of characteristic peak intensity at 1646.4 cm^{-1}.

In the Figure 6. (a), the roughness of the tip face represented by each curve increases from bottom to top, and the Raman signal intensity first increases and then decreases. The Raman signal reaches the strongest when Ra is 0.331, that is because that when the surface roughness is low, the enhancement effect of surface micro- and nanostructures on the light field is weak, and the enhancement of the adsorption of silver nanoparticles is relatively insignificant, so the Raman signal is weak. With the increase of surface roughness, the Raman signal also increases. However, if the surface roughness is too high, the surface quality will be poor during the preparation process, which has a negative impact on the experimental results and makes the Raman signal weaker. The optical fiber SERS sensor prepared by depositing silver nanoparticles on the "smooth" fiber tip can only obtain weak signals and has no reference significance. It can be seen that the performance of the SERS sensor prepared by the rough tip surface compared to the "smooth" has been greatly improved.

When the roughness is low, the surface micro- and nanostructure has a weak enhancement effect on the light field, and the adsorption of silver nanoparticles is relatively insignificant, so the Raman signal is weak. The Raman signal increases with the increase of surface roughness, but when the surface roughness is too high, the surface quality is poor during the preparation process, so the experimental results have a certain influence, which causes the Raman signal to decrease.

4. Conclusions

The optical fiber SERS sensor, which is widely used in biological, medical, chemical and other fields, was studied, and the effect of different parameters of femtosecond laser processing on the surface roughness of quartz fibers was explored. The morphology and distribution of silver nanoparticles under different parameters in the preparation of optical fiber SERS substrate by laser-induced method were also studied. Based on the experimental results, the fiber tip surfaces with different roughness were prepared and silver nanoparticles were deposited on it as SERS sensors, which had good SERS enhancement effect.

We hope you find the information in this template useful in the preparation of your submission.

Acknowledgments

This work was supported by the National Natural Science Foundation of China(NSFC) (Grant No. 51575053).

References

[1] Chu H, Liu Y, Huang Y, et al. A high sensitive fiber SERS probe based on silver nanorod arrays[J], 2007, 15(19): 12230-12239.

[2] Haka A S, Volynskaya Z, Gardecki J A, et al. In vivo margin assessment during partial mastectomy breast surgery using Raman spectroscopy[J], 2006, 66(6): 3317-3322.

[3] Liu C, Wang S, Fu C, et al. Preparation of surface-enhanced Raman scattering (SERS)-active optical fiber sensor by laser-induced Ag deposition and its application in bioidentification of biotin/avidin[J], 2015, 31(1): 25-30.

[4] Bello J, Vo-Dinh T J a S. Surface-enhanced Raman scattering fiber-optic sensor[J], 1990, 44(1): 63-69.

[5] Komachi Y, Katagiri T, Sato H, et al. Improvement and analysis of a micro Raman probe[J], 2009, 48(9): 1683-1696.

[6] Viets C, Hill W J S, Chemical A B. Comparison of fibre-optic SERS sensors with differently prepared tips[J], 1998, 51(1-3): 92-99.

[7] Zheng X, Guo D, Shao Y, et al. Photochemical modification of an optical fiber tip with a silver nanoparticle film: a SERS chemical sensor[J], 2008, 24(8): 4394-4398.

[8] Ming-Shan L, Chang-Xi Y J C P L. Laser-Induced silver nanoparticles deposited on optical fiber core for surface-enhanced Raman scattering[J], 2010, 27(4): 044202.

[9] Youfu G, Zhen Y, Xiaoling T, et al. Femtosecond laser ablated polymer SERS fiber probe with photoreduced deposition of silver nanoparticles[J], 2016, 8(5): 1-6.

[10] Mullen K I, Carron K T J a C. Surface-enhanced Raman spectroscopy with abrasively modified fiber optic probes[J], 1991, 63(19): 2196-2199.

[11] Viets C, Hill W J J O R S. Single‐fibre surface‐enhanced Raman sensors with angled tips[J], 2000, 31(7): 625-631.

[12] Stokes D L, Vo-Dinh T J S, Chemical A B. Development of an integrated single-fiber SERS sensor[J], 2000, 69(1-2): 28-36.

[13] Viets C, Hill W J J O M S. Fibre-optic SERS sensors with conically etched tips[J], 2001, 563: 163-166.

[14] Lucotti A, Pesapane A, Zerbi G J a S. Use of a geometry optimized fiber-optic surface-enhanced Raman scattering sensor in trace detection[J], 2007, 61(3): 260-268.

[15] Lucotti A, Zerbi G J S, Chemical A B. Fiber-optic SERS sensor with optimized geometry[J], 2007, 121(2): 356-364.

[16] White D, Mazzolini A, Stoddart P J J O R S a I J F O W I a a O R S, Including Higher Order Processes,, et al. Fabrication of a range of SERS substrates on nanostructured multicore optical fibres[J], 2007, 38(4): 377-382.

[17] Dhawan A, Muth J, Leonard D, et al. Focused ion beam fabrication of metallic nanostructures on end faces of optical fibers for chemical sensing applications[J], 2008, 26(6): 2168-2173.

[18] Dhawan A, Zhang Y, Yan F, et al. Nano-engineered surface-enhanced Raman scattering (SERS) substrates with patterned structures on the distal end of optical fibers[C]. Plasmonics in Biology and Medicine V, 2008: 68690G.

[19] Jiang L, Wang A-D, Li B, et al. Electrons dynamics control by shaping femtosecond laser pulses in micro/nanofabrication: modeling, method, measurement and application[J], 2018, 7(2): 17134.

[20] Xu Y, Geng Y, Wang L, et al. Femtosecond laser ablated pyramidal fiber taper-SERS probe with laser-induced silver nanostructures[J], 2018, 51(28): 285104.