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Research on HCPCF SERS Sensing for Melamine Qualitative Detection

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In the face of the current urgent food safety situation, the qualitative detection of trace amounts of illegal food additives is of great significance. The Hollow Core Photonic Crystal Fiber Surface-Enhanced Raman Scattering (HCPCF SERS) based sensing system was proposed to achieve qualitative detection of melamine. The system adopted the reverse-direction light collection scheme, and the silver SERS substrate was produced by ion sputtering, and the PCF taper was selectively filled, and the output signal was collected by the spectrometer. The proposed system was utilized to detect melamine liquid sample qualitatively, the distinct SERS spectrum of melamine was acquired, and the detection limit is 0.25 g/L. The experimental results showed that the sensing system can achieve trace qualitative detection of melamine.

1. Introduction

In recent years, with the development of technology, Cheng Zi-qiang et al (2018) and Bing Pi-bin et al (2014) reported that metal nanoparticles have been fully utilized as new optical, electrical and magnetic materials. Fu Guang-wei et al (2016) reported that the fiber-optic SERS sensor combined with low-loss fiber and SERS has been widely used in many fields. However, the fiber SERS sensor has some main defects, one is the amount of particles in active region is less, another is higher laser intensity or longer time is require to excite to obtain the ideal SERS spectrum. So its application is limited. The proposal and successful development of PCF enabled it to develop rapidly as an ideal platform for SERS sensor. Udaya Rahubadde et al (2018) reported that the unique properties of PCF combined with SERS sensors form a new type of sensor, namely the PCF SERS sensor, which is widely utilized in chemical, biological and environmental detection. At present, the food safety problem that has emerged in an endless stream has caused widespread concern. For some food illegal additives, Shi Shu-dong et al (2012)reported that it has a great impact on people's health. In particular, the "Sanlu milk powder" incident has had a great impact on us. Based on this, this paper utilized PCF SERS sensing technology to carry out qualitative trace detection on food illegal additives.

2. Experimental scheme

In this paper, the SERS PCF sensing system was studied, and the ultra-low concentration sample detection was realized by the perfect combination of PCF and SERS sensors. The experimental content was to detect melamine in the sample solution through the proposed SERS PCF sensing system.

2.1 Experimental principle

The principle of this experimental protocol is the combination of SERS sensing and PCF sensing. According to the actual requirement, the experimental scheme of reverse acquisition of SERS signal was designed. The experimental schematic diagram was shown in Figure1.

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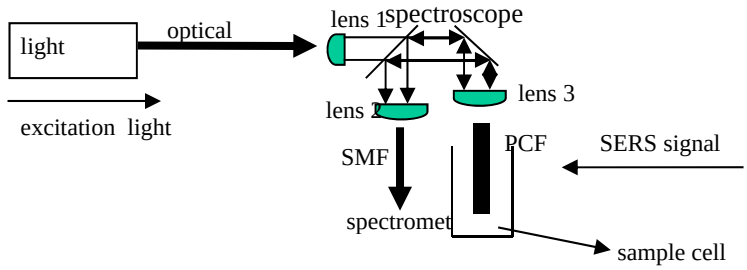


Figure 1:Schematic Diagram of Reverse Light Acquisition Experiment

First, the suitable SERS substrate was manufactured in the prepared PCF air hole, second, the liquid sample were injected into the air hole of PCF, and then the excitation light of 785 nm was coupled into the PCF to excite the SERS signal. Finally, the generated SERS signal was detected by a spectrometer.
In Figure 1, the light source emits excitation light through the lens 1 and is collimated and focused to the spectroscope 2. After being reflected, it is coupled into the PCF through the lens 3 to excite the SERS signal in the PCF. After the SERS signal is reflected, it is collected by the lens 3. The spectroscope 2 reflects and then is reflected by the spectroscope 1 into the lens 2. The lens 2 is collimated and coupled to the spectrometer for spectral measurement. The experimental protocol for this structure is suitable for real-time monitoring of samples.

2.2 Main equipment

The instruments used in the test are light source, lens, wave-limiting plate and spectrometer, which are described as below.
(1) Light source
In the Raman spectroscopy experiments, the commonly used excitation wavelengths are 514 nm, 633 nm, 785 nm, and 1064 nm. The light source used in this experiment was a FC-D-785A type semiconductor laser purchased from Changchun New Industry Optoelectronics Company, with an optical fiber output, an output power of 300 mW, and a stability of 3% or less.
(2) Laser Notch Filter
When the SERS signal was collected in the experiment, the excitation light at 785 nm would have a great influence, so the 785 nm light was filtered out by a laser notch filter. Using a laser notch filter produced by Semrock, USA, the notch bandwidth is 39 nm.
(3) Spectrometer
The spectrometer uses WGD-4B combined multi-function grating spectrometer with a wavelength range of 4000~650 cm-1 and a focal length of 300 mm. The wavelength accuracy is about 4 cm-1, the wavelength repeatability is 1 cm-1, and the resolution is 6 absorption peaks of polystyrene.
The Agilent 86142B spectrometer has a wavelength accuracy of 10 pm, a test range of 600 to 1700 nm, a sensitivity of 90 dBm, and a bandwidth range of 0.2 nm to full scale. This spectrometer is suitable for system testing where power and wavelength accuracy are critical.

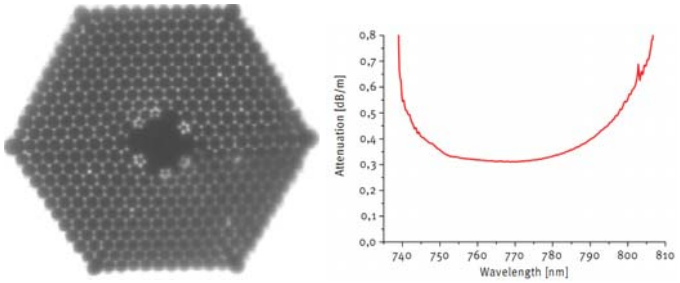
2.3 Experimental preparation

(1)PCF preparation
The Air-6-800 from Crystal Fiber of Denmark is capable of experimenting at an excitation wavelength of 785 nm. The structural parameters of this fiber are shown in Table 1.

Table 1: Air-6-800 technical parameters

Material	Outer layer diameter	Coating diameter	Core hole diameter	Cladding hole diameter	Hole spacing	Transmission bandwidth
Pure silicon	$122\pm5\mu m$	$243\pm10\mu m$	$6\pm1\mu m$	$6\pm1\mu m$	$1.65\ \mu m$	60 nm

Its structure diagram and transmission line are shown in Figure 2.
The Air-6-800 is numerically simulated by COMSOL software. The specific steps are the steps of modeling, parameter setting, region division and calculation, and the input wavelength is 785 nm, and the perfect matching layer was adopted. After simulation, the effective refractive index is 0.995814-1.256822e-9, and its field distribution was shown in Figure 3.



a b

Figure 2: Air-6-800 HCPCF a structure diagram b attenuation VS wavelength

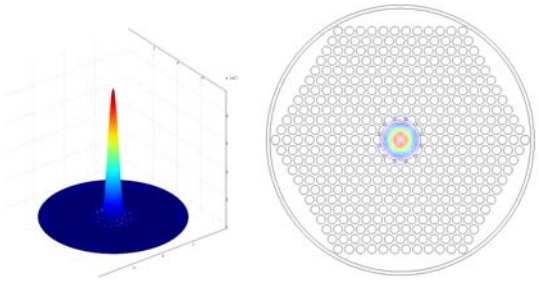


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Figure3:Air-6-800 a three-dimensional field distribution b equipotential field distribution

Selective filling, that is, the liquid sample to be tested is only filled into the core hole of the PCF by some methods, so that the cladding air hole does not enter the liquid. Previously, Cristiano M B Cordeiro et al (2007) and Stephan Smolka et al (2008) reported that the conducted separate experiments to achieve selective filling. In this paper, a new selective filling scheme is proposed, which the taper function of the fiber fusion splicer was utilized to collapse the cladding air hole of the PCF and keep the core hole unchanged, thus achieving selective filling. The specific implementation process is as follows. Firstly, the PCF was cut into segments of about 5 cm. Then the coating in the middle of PCF was removed, and then the taper was performed by a fiber fusion splicer (Ericsson FSU-925). When drawing the cone, the PCF should be placed on the same level. When the cone was pulled, only the cladding hole was collapsed and the core is completely determined by the discharge current, the tensile force and the material heat transfer effect. During the process,Wu Yu-deng et al (2013) reported that the distance d between the PCF and the electrode, the discharge current and the discharge time were necessary to set. The current between the electrodes is expressed as

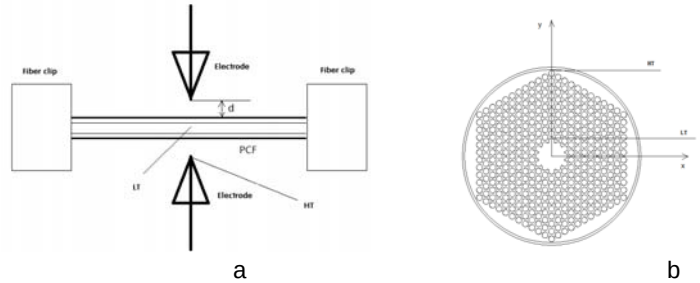
$$i(r,z)=\frac{I_0}{2\pi\sigma^2(z)}\exp(-\frac{r^2}{2\sigma^2(z)}) \tag{1}$$

$$\sigma(z)=\sigma_0(1+z^2)^{-1/3} \tag{2}$$

Where I_0 is the total current, $\sigma(z)$ and σ_0 is the Gaussian width at z and at z = 0 respectively. The space temperature is determined by the current density,

$$T(r,z)\propto i^2(r,z) \tag{3}$$

The temperature distribution diagram was shown in Figure 4.



a b

Figure 4: a. fiber fusion splicer electrode b. space temperature distribution of PCF

It was found from the figure that the temperature is highest at the tip of the electrode, and the temperature is the highest at the surface of the PCF and that is the lowest at the core. So the thermal conductivity of PCF is gradually reduced from cladding to core because of the presence of air. And if the heating rate is

$$V_{collapse} = \frac{\gamma}{2\eta(T)} \tag{4}$$

the collapse will happen in cladding hole . Where, γ is the surface tension, η is the viscosity of silicon.

With the increase of the temperature, the viscosity drops rapidly, so the air holes in high temperature region will collapse faster, so that the cladding air holes will be collapsed quicker than the core holes. So the PCF cladding air hole collapses only by setting appropriate taper parameters.

For Ericsson FSU-925, after adjusting the parameters, the taper has the best effect when the spacing $d = 0\mu m$, the discharge current is 11 mA and discharge time is 400 ms. The effect diagram is shown in Figure 5.

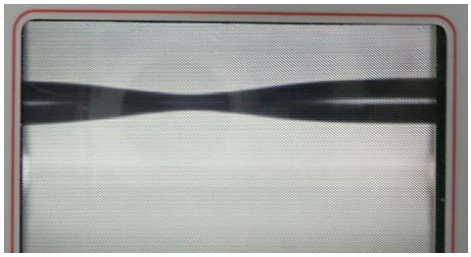


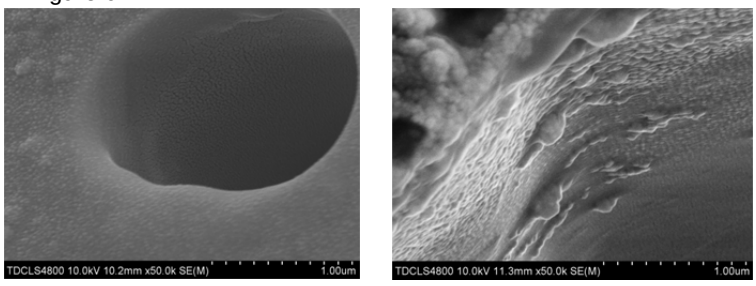
Figure 5: Effect diagram after PCF taper

Through the above processed PCF, selective filling can be achieved. That is, only the liquid sample is immersed in the core air hole, and the cladding hole is still air.

(2)Preparation of SERS substrate

Shi Ye-xin and Li J.S (2018) reported that there are many methods for preparing SERS substrates, taking into account the advantages and disadvantages of various methods. In order to facilitate the control of nanoparticles, ion sputtering was utilized to prepare SERS substrates. The coating method has high purity and compactness, and the film thickness can be controlled. In order to realize the coating of the inner wall of the PCF air hole, this paper used the HTCY-JS type ion sputtering instrument produced by Beijing Hetong Venture Technology Co., Ltd. to coat the PCF. This device is convenient for controlling the sputtering time and current.

For comparison, the sputtering current was set to 10 mA for the first coating, the pressure was $6\times10^{-1} mbar / par$, and the sputtering time was 2 minutes. The second sputtering time was 5 minutes, and the PCF after two coatings was observed with a Hatchi S-4800 scanning electron microscope, as shown in Figure.6.



a 2min b 5min

Figure 6: Effect diagram of ion sputtering coating

It can be seen that the nanoparticles of b were obviously larger than that of a. Therefore, for the ion sputtering method to vaporize the nano film, the evaporation time will have an important influence on the thickness, that is, the size of the nanoparticles.

(3). Experimental process

Liquid sample injection

Since the core hole of the PCF is relatively thin, it is difficult to inject the liquid. Claire Gu et al (2007) used siphoning to inject, but the inhalation was slower. In this paper, a syringe was utilized to inject the liquid sample, as shown in Figure 7.

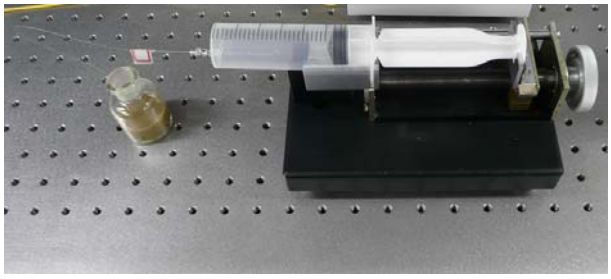


Figure 7: PCF liquid sample injection device diagram

2.4 Experiment and result analysis

After the above preparation, the sample can be tested. The experimental scheme used in this paper is to collect SERS signals in the same direction. The experimental physical map is shown in Figure.8.

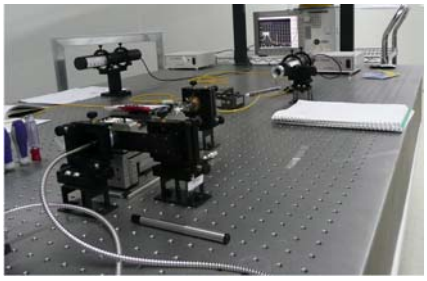


Figure 8: PCF SERS sensing system physical map

During the experiment, low concentrations of melamine in aqueous solution were tested. The experiment was done in superclean room.

(1) Solution preparation

First, 0.5 g of melamine was dissolved in 1 liter of distilled water to prepare a standard intermediate test solution having a concentration of 0.5 g/L. Next, 50 mL of the intermediate test solution was taken, and then placed in 25mL, 50 mL, 100 mL, and 200 mL of distilled water to obtain concentrations of 0.33 g/L, 0.25 g/L, 0.125 g/L, and 0.0625 g/L.

(2) Experimental test

The prepared PCF is immersed in the liquid to be tested, and is extracted by a syringe to accelerate the speed at which the liquid enters the PCF core. After a period of time, it is taken out and tested by a designed experimental system. As a result, only the liquid having a concentration of 0.33g/L and 0.25 g/L was able to detect a characteristic SERS spectrum of melamine, as shown in Figure 9.

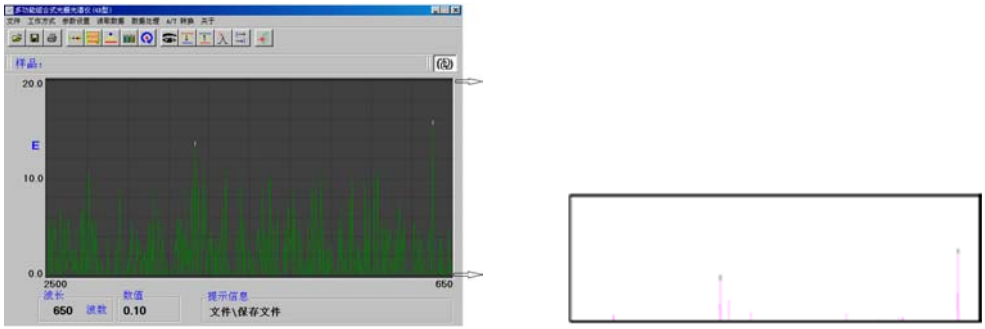


Figure 9: Melamine SERS spectrum

It can be seen from figure 9 that the SERS spectrum of melamine has obvious characteristic peaks around 750 cm^{-1} and 1500 cm^{-1}, and the detection results were basically consistent with the literature by Kalachyova Y et al (2018), thus the presence of melamine could be qualitatively detected.

3. Conclusions

The PCF SERS sensor used to detect Melamine was proposed in this paper. First, the HCPCF suitable for SERS sensor was designed by COMSOL software, then the proposed HCPCF was selective filled by drawing the cone to obtain the liquid core PCF. Second, the high – gain SERS substrate was manufactured by filling Ag nanoparticles in air core of HCPCF, and then liquid core HCPCF SERS sensor was acquired. Finally this sensor was utilized in trace detection of Melamine solution, and the detection limitation can reach 0.25 g/L.

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