Polymer Waveguide Sensor Based on Localized Surface Plasmon Resonance for NaCl Solution Detection

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***Abstract*—In this paper, a polymer waveguide sensor based on localized surface plasmon resonance (LSPR) of gold nanoparticles was demonstrated. Gold nanoparticles with diameter of 20 nm were synthesized. Polymer SU-8 3050 material was used as core material to fabricate waveguides by standard photolithography. After silanization process, gold nanoparticles were efficiently and firmly bound to the polymer waveguide surface. Different concentrations of NaCl solution with the refractive index between 1.342 and 1.379 were detected by the polymer waveguide sensor coated with gold nanoparticles. A set of test system for polymer waveguide sensor was established and used to do the absorbance test in NaCl solution. The sensitivity is 4.016△A/RIU which is about 38 times higher than that of polymer film.**

Keywords—polymer waveguide sensor; polymer film; gold nanoparticle; LSPR

I. INTRODUCTION

In recent years, localized surface plasmon resonance (LSPR) of noble metal nanoparticles has attracted much attention due to its potential applications in the sensors[1-6]. When noble metal nanoparticles are excited by visible light of the wavelength matching the resonant frequency of the surface plasmon, the localized surface plasmon resonance can be generated[7]. This results in strong light absorption and scattering. The location and intensity of absorption peak mainly depend on the size, shape of the metal nanoparticles as well as their surrounding environment[8,9].Compared to other noble metals, gold has stable chemical properties, such as anti-oxidation, anti-corrosion. In general, the sensors based on LSPR of gold nanoparticles can be classified into three categories: chip-based[10,11], optical fiber-based[12,13] and solution-phase-based[14,15] sensors. Polymer waveguide sensor is a kind of chip-based sensor. It has many advantages, such as low cost, simple fabrication process, easy integration and relatively high sensitivity.

In this paper, gold nanoparticles were synthesized and immobilized on the polymer SU-8 film. The absorbance test of the polymer SU-8 film coated with gold nanoparticles in NaCl solution was done. Polymer waveguides were fabricated and coated with gold nanoparticles. A set of test system for polymer waveguide sensor was established and used to do the absorbance test in NaCl solution.

978-1-7281-2458-2/19/$31.00 ©2019 IEEE

II. EXPERIMENT

A. Synthesis of Gold Nanoparticles

Gold nanoparticles were synthesized by the method of reduction of gold chloride with sodium citrate in aqueous solution[16,17]. Fig.1 was the TEM image of the gold nanoparticles. The average diameter of the gold nanoparticles is ~20 nm.

B. Immobilization of Gold Nanoparticles on the Polymer Waveguide Surface

According to the papers[18,19] acid solution can create enough –OH groups (which can bind to the silane monomer) on the polymer SU-8 surface. And thus APTMS (3-Aminopropyl trimethoxysilane) molecule can be attached on the polymer SU-8 surface to form a uniform aminosilane layer so that gold nanoparticles can be bound electrostatically to the amine group.

We added 2% APTMS solution to a mixture of ethanol and water. 6% acetic acid was added into aforementioned solution. We formed a layer of polymer SU-8 on the glass substrate. And then the polymer surface interacted with this kind of silane solution. In the Fig.2(a), we can see that the absorbance of the polymer film coated with gold nanoparticles increases as increasing the interact time of the polymer surface with the silane solution, because the enough interact time helps more gold nanoparticles to be immobilized on the polymer film. However, the interact time can not be too long, because the surface of the polymer film may be destroyed. So we chose 20 minutes as the condition.

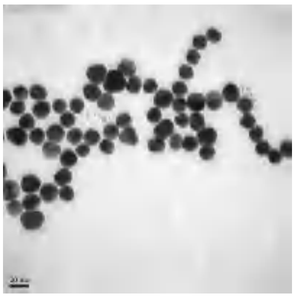

Figure 1. TEM image of gold nanoparticles.

After the above process, the polymer surface was exposed to gold nanoparticles solution. In the Fig.2(b), we can see that the absorbance of the polymer film coated with gold nanoparticles increases as increasing the interact time of the polymer surface with the nanoparticles solution because more interact time helps more gold nanoparticles to be immobilized on the polymer surface. But too long interact time may cause the polymer waveguide to fall off. So we chose 4 hours as the condition. Finally, the polymer film was cleaned by deionized water to remove unbound gold nanoparticles and then the polymer film was kept for 24 hours at room temperature for forming stable gold nanoparticles layer.

C. Localized Surface Plasmon Resonance of Gold Nanoparticles on the Polymer SU-8 Surface

Afterward, the glass substrate was exposed to different concentrations of NaCl solution with the refractive index between 1.333 and 1.370. The normalized absorbance spectrum was recorded by the UV-visible spectrophotometer (UV-1780), as shown in Fig.3(a). The wavelength range was from 400 nm to 800 nm. In the Fig.3(a), the absorption peak of the polymer SU-8 film coated with gold nanoparticles appears and its intensity increases as the concentration of the NaCl solution increases. In the Fig.3(b), we can see that the sensitivity, defined as the ratio of the change in absorbance to the change in refractive index, is 0.11△A/RIU for the polymer SU-8 film coated with gold nanoparticles.

D. Fabrication of Polymer Waveguide

In order to improve the sensitivity, the polymer SU-8 waveguides were fabricated using standard photolithography. Firstly, the polymer SU-8 3050 was spin-coated onto a Si substrate with 2 μm thickness silicon dioxide film to form the core layer. Secondly, a group of 50 μm height and 100 μm width waveguides were fabricated by standard photolithography. This size of waveguide matched with the size of input/output optical fiber and reduced the loss at the joint, so we chose it. Finally, the gold nanoparticles were immobilized on the surface of polymer waveguide according to aforementioned process.

Fig.4 is the TEM image of the polymer waveguide with gold nanoparticles. By the aforementioned process, we knew that the uniform aminosilane layer in the waveguide could bind the nanoparticles tightly and the uniform aminosilane layer only existed in the surface of polymer waveguide. So in Fig.4, we can see that the gold nanoparticles on the surface of polymer waveguide are very dense, while the gold nanoparticles on the silicon dioxide are very sparse. This proves the importance of choosing the optimal time in gold nanoparticles immobilizing process.

E. Measurements Setup

An experimental setup for the polymer waveguide sensor was established, as shown in Fig.5. For efficient coupling the LED light source into the waveguide input, a fiber-coupled LED light source (Thorlabs, MBB1-F1-Broadband) was used. Compared with microscope objectives, which were usually utilized to couple signal beams in previous reports[23,24], it did not need complicate optical adjustment operations and coupling efficiency was greatly improved for the 100 μm × 50μm cross section of waveguide. The output signal from the waveguide was coupled to a fiber optical spectrometer (Ocean Optics, USB 2000+).

F. Localized Surface Plasmon Resona of Gold Nanoparticles on the Polymer Waveguide

To prove that LSPR affected the absorbance intensity, we compared the absorbance of the polymer SU-8 waveguides with and without gold nanoparticles. In the Fig.6(a), the polymer waveguide without gold nanoparticles doesn't show any absorption peak when the refractive index of NaCl solution changes from 1.342 to 1.379. While for the polymer waveguide coated with gold nanoparticles, the absorption peak appears and the intensity increases as the concentration of the NaCl solution increases, as shown in the Fig.6(b). This proves that it is LSPR effect of the nanoparticles which are immobilized in the waveguides' surface affecting the absorbance intensity.

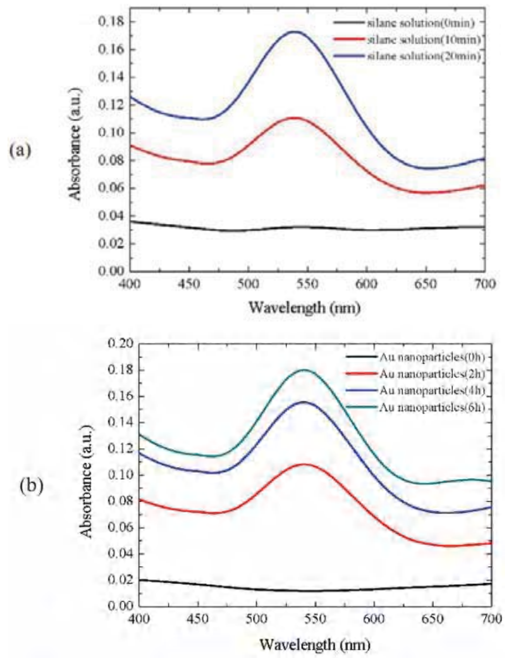

Figure 2. (a) The relationship between the interact time of the SU-8 polymer film with the silane solution and the absorbance of the polymer film coated with gold nanoparticles; (b) The relationship between the interact time of the SU-8 polymer film with the nanoparticles solution and the absorbance of the SU-8 polymer film coated with gold nanoparticles.

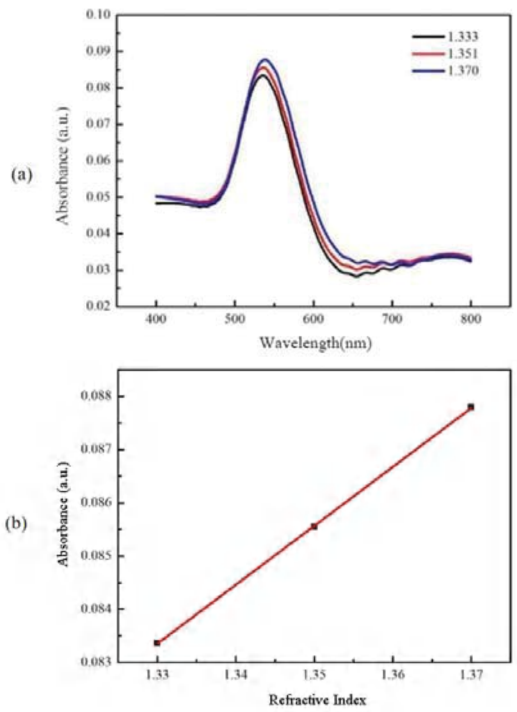

Figure 3. (a) The normalized absorbance spectrum of the polymer film exposed to different concentrations of NaCl solution with the refractive index between 1.333 and 1.370; (b) The linear relationship between the refractive index of NaCl solution and the absorbance of the polymer film coated with gold nanoparticles.

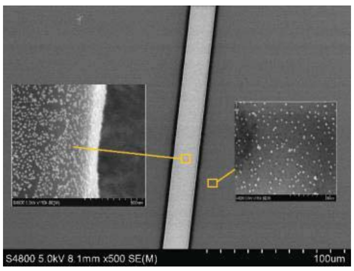

Figure 4. The SEM images of polymer waveguide coated with gold nanoparticles.

In the Fig.6(b), the shift of obtained resonance wavelength is very hard to see. This may be the reason that the resolving power of our spectrometer is too low to detect the shift of resonance wavelength when the refractive index of different concentrations of the NaCl solution changes by 0.02 and the light source is broadband light source which is hard to see the change of shift. Therefore, We used the peak point of the absorption peak to characterize the sensor response like many other papers[20-22]. In the Fig.6(c), We can see that the absorbance of the peak increases linearly as increasing the refractive index of NaCl solution. The sensitivity, defined as the ratio of the change in absorbance to the change in refractive index, is 4.016△ A/RIU.

We compared the sensitivity of the polymer film and polymer waveguide. The results were shown in TABLE.1. The sensitivity of polymer waveguide is about 38 times higher than that of polymer film. This is because the LSPR effect of gold nanoparticles covered on a 2 cm-length waveguide can be fully stimulated, while for thin polymer film, only gold nanoparticles within the range of the signal spot (μm2) on the film's surface can be stimulated.

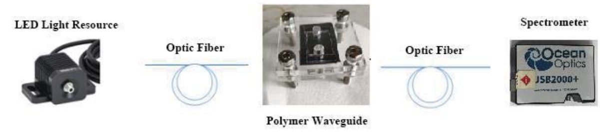

Figure 5. Schematic of measurements setup.

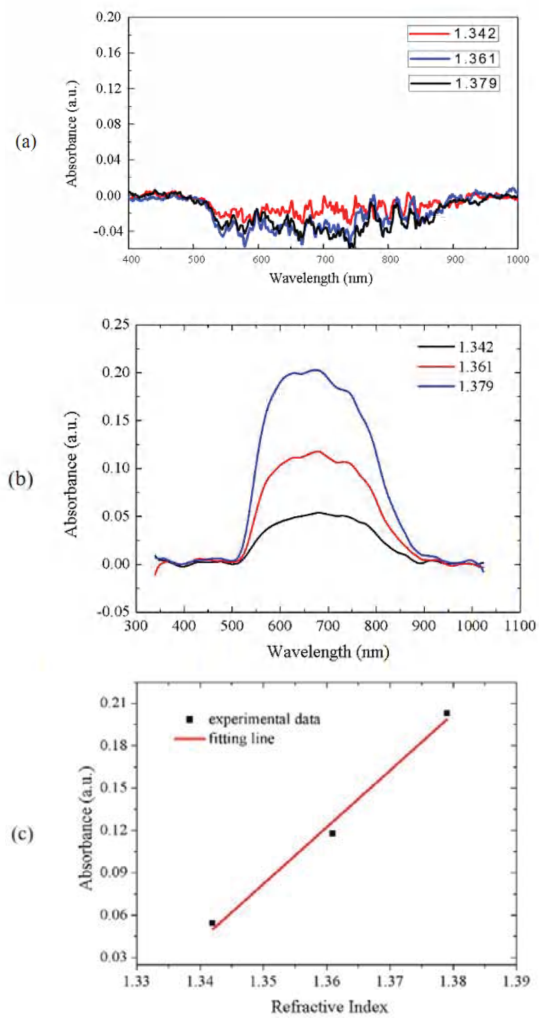

Figure 6. The normalized absorbance spectrum of the polymer waveguide without gold nanoparticles for detecting different concentrations of NaCl solution; (b) The normalized absorbance spectrum of the polymer waveguide coated with gold nanoparticles for detecting different concentrations of NaCl solution; (c) The linear relationship between the refractive index of NaCl solution and the absorbance of the polymer waveguide coated with gold nanoparticles.

TABLE I. THE SENSITIVITY OF DIFFERENT TYPES OF SENSOR

Type	Sensitivity(△A/RIU)
polymer film	0.11
polymer waveguide	4.016

III. CONCLUSION

In conclusion, a polymer waveguide sensor based on LSPR was designed and fabricated. Different concentrations of NaCl solution with the refractive index between 1.342 and 1.379 were detected by using this polymer waveguide sensor. The peak absorption increased linearly as increasing the refractive index of NaCl solution. The sensitivity of this sensor was 4.016△A/RIU which increased by about 38 times comparing to the polymer sensing film (0.11△A/RIU). The reason is that the light in the polymer waveguide can touch more gold nanoparticles than the light in the polymer film.

ACKNOWLEDGMENT

First, I should appreciate the National Natural Science Foundation of China (No.61875170) and the Principal's Fund of Xiamen University (No.20720150086) that support to us. Second, I would like to show my deepest gratitude to my supervisor, Doc. Zhang, who has walked me through all the stages of the writing of this paper. Without her illuminating instruction and patience, this paper could not have reached its present form. Last but not least, I am greatly indebted to all my teachers and classmates who have helped me in my study and life.

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