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Surface plasmon resonance biosensor based on graphene oxide/silver coated polymer cladding silica fiber

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ABSTRACT

A graphene oxide/silver coated polymer cladding silica fiber optical surface plasmon resonance (SPR) human IgG detection biosensor with a high sensitivity and a low limit of detection is presented. Due to the graphene oxide (GO), the intensity of the confined electric field surrounding the sensing layer can be enhanced, the sensitivity of refractive index (RI) of the graphene oxide/silver SPR sensor reached 3311 nm/RIU in the RI range of 1.3334–1.3731 compared with 2875 nm/RIU in the range of 1.3328–1.3739 of the silver film SPR sensor. Afterwards, SPR optical fiber biosensor was developed based on graphene oxide/silver coated optical fiber when staphylococcal protein A and goat anti-human IgG were immobilized on the surface of the graphene oxide film. The sensor can be used to detect different concentrations of human IgG, a high sensitivity of 0.4985 nm/(μg/mL) and a low limit of detection 0.04 μg/mL were observed. Therefore, the graphene oxide/silver film SPR human IgG detection biosensor with high sensitivity and low limit of detection shows a great promise for the future biochemical and biomedical application.

1. Introduction

In recent years, optical fiber surface plasmon resonance (SPR) biosensors have been studied intensively, as they are widely used for a variety of important industry applications, such as food safety detection, antigen-antibody interaction monitoring and environment monitoring [1–4]. Based on the measurement of refractive index change of the reagents near the surface, the SPR biosensors can achieve a real-time, repeatable and high sensitive detection for target analyze [5–7]. However, there are some challenges for the SPR biosensor. First, preparing a fiber optic SPR sensor requires some special rotation vacuum evaporation or the sputtering system to ensure that the gold film is deposited as evenly as possible on the fiber sensor surface. Second, it still has a demand for more efficient methods of immobilizing functional molecules in order to achieve more binding sites for target molecules and achieve a higher SPR sensitivity analysis [8].

For an optical fiber SPR sensor, a thin metal film is coated on the sensor surface. The gold film is usually preferred because it has good antioxidant and corrosion resistance in different situations. However, to our knowledge, the biomolecules immobilized efficiency is inefficient and the number of absorbed molecules is not enough for just only rely on the thiol groups, which restricts the development of gold film for biosensors [9]. Besides, gold film coated SPR sensor need some special rotation vacuum evaporation or the sputtering system using expensive and complicated equipment. As another option for applying the metal film coating, chemical method has drawn great attention in the fabrication of the SPR sensors [8,10]. Compared with sputtering, chemical method does not need any expensive or complicated equipments, and the thickness and quality of the coating film can be adjusted by controlling the reagent dosage and reaction time. Silver film SPR sensor showed a very sharp resonance peak and high detection accuracy [11]. However, silver is oxidized easily. In recently years, GO was widely used for SPR sensors [9,12–15]. One reason is graphene and GO could stop the oxygen molecules to pass through the surface of silver film, so it prevents the oxygenation of the silver film [14]. Graphene is an allotrope of carbon in the form of a two-dimensional, atomic-scale, hexagonal lattice in which one atom forms each vertex. Graphene has unique optical properties with an unexpectedly high opacity and huge specific surface area for an atomic monolayer, therefore, it is suitable for gas sensing [16], humidity [17] and temperature detection [18] etc. Moreover, compared with graphene, GO shows advantageous properties due to its excellent biocompatibility, solubility and selectivity [19]. The enriched functional groups of GO can interact in an ionic, covalent or non-covalent manner, so that the GO provides the highest extraction efficiency of biomolecules per unit area in principle [15].

The reagents immobilized on the surface of the metal film or sensor

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part are also important in the performance of the SPR biosensor. Amine groups were linked to the carboxyl surface activated by using *N*-hydroxysulfosuccinimide (NHS) and 1–ethy-3-(3-(dimethylamino) propyl)-carbodiimide hydrochloride (EDC) that displayed a better antibody immobilization efficiency [20]. Furthermore, the polydopamine or protein A has been modified on the gold film to immobilize antibody in biosensor [8,21,22]. In this paper, we proposed an SPR biosensor based on graphene oxide/silver coated polymer cladding silica fiber. First, we test the silver film-coated polymer cladding silica SPR sensor, which have a high sensitivity of 2875 nm/RIU with the refractive index change. Second, we modified the graphene on the surface of the silver film, which showed a higher sensitivity of 3311 nm/RIU compared to be better with the silver film SPR sensor. It also confirmed that the graphene oxide provided the highest extraction efficiency of biomolecules per unit area. Therefore, an SPR biosensor was developed based on graphene oxide/silver coated optical fiber, when staphylococcal protein A and goat anti-human IgG were immobilized. The sensor can be used to detect different concentrations of human IgG. The proposed biosensor has a low limit of detection of 0.04 μg/mL and a high sensitivity of 0.4985 nm/(μg/mL). Such a graphene oxide/silver film SPR human IgG detection biosensor shows a great promise for the future biochemical and biomedical application.

2. Materials and methods

2.1. Materials

The fabrication of the graphene oxide/silver coated biosensor mainly used the following materials: Graphene oxide (GO) (Nanjing Xian Feng Nanometer Materials Technology Co. Ltd). Goat anti-human IgG, human IgG, staphylococcal protein A (SPA), phosphate buffered saline (PBS, 0.01 M, pH = 7.4), and bovine serum albumin (BSA) (Beijing Ding Guo Chang Sheng Biotechnology Co. Ltd). *N*-hydroxysulfosuccinimide (NHS) and 1–ethy-3-(3-(dimethylamino)propyl)-carbodiimide hydrochloride (EDC) (Shanghai Aladdin Biochemical Technology Co. Ltd). Mercapto hexylamine (Shandong West Asia Chemical Industry Co. Ltd).

All of the chemicals used were of analytical reagent grade and used without any further purification. The polymer cladding silica (PCS) optical was purchased from Beijing Scitlion Technology Corp., Ltd, with 600 μm core diameter and 0.37 numerical aperture.

2.2. Preparation of the silver film for the optical fiber SPR sensor

The graphene oxide/silver film SPR biosensor is shown in Fig. 1. The left part is the sensing region that was immersed in the measuring liquids, the right part is used to connect the optical fiber coupler. The diameter of the coin is 25 mm.

In this paper, we coated the PCS fiber with silver film by chemical method. The sensing portion (10 mm) of the PCS fiber was soaked in acetone to soften the cladding and removed it manually before coated silver film, as shown in Fig. 2(a).

Fig. 2(b) is the coating silver film operation which is divided into the following steps. (1) The sensing portion was soaked in 0.2% stannous chloride solution for about 20 min, then washed with distilled water. During this time, we can complete the following two steps. (2) Add 2 mL silver nitrate solution (molecular concentration: 0.1 mol/L) to a 10 mL vessel and stir, then add the ammonia solution, then the solution will change from the clear to brown. At this moment, add the ammonia continuously until the solution become clear. (3) Drop 1.4 mL potassium hydroxide (molecular concentration: 0.8 mol/L) to the above mixture, the color of the solution turns black, and then we continue add the ammonia solution until the mixture turns clear. We can get a silver-ammonia solution this time. (4) Remove the optical fiber from the stannous chloride solution and rinse it off with distilled water. Place the sensing portion of the fiber into the silver-ammonia solution prepared above and adjust the position. Pour 5 mL glucose solution (molecular concentration: 0.05 mol/L) into the silver-ammonia solution, it is best to mix the glucose and silver-ammonia solution quickly. At this time, the silver mirror reaction is happening, wait about 10 min, remove the fiber and rinse the fiber with distilled water. At last, dry the probe in a nitrogen stream.

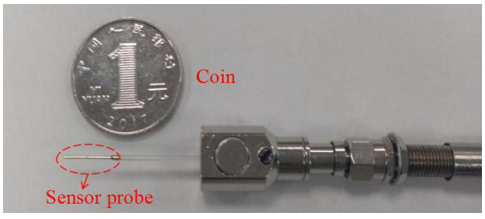

Fig. 1. The optical fiber SPR sensing probe.

2.3. Fabrication of GO/silver SPR sensor

The silver mirror reaction was the same as the above fabrication of silver SPR sensor. Followed by, the silver coated PCS optical fiber was immersed into the mercapto ethylamine (molecular concentration: 0.1 mol/L) for 1 h to form amino on the surface of the silver film, as shown in Fig. 2(c). It is used for covalent bond with the epoxy group of the graphene oxide. The fiber was immersed into the graphene oxide (0.5 mg/mL) for the formation of graphene oxide film on the surface of the fiber, and then rinsed the unbounded graphene oxide with distilled water, as shown in Fig. 2(d). Therefore, we complete the GO/silver film SPR sensor probe.

2.4. SPA and goat anti-human IgG modified biosensor for immunoassay

Functionalization of the sensor surface is an important step in the biosensor development. The covalent immobilization of goat anti-human IgG on GO/silver film surface might lead to improper orientation by masking antibody-binding sites. This shortcoming can be circumvented by using heterobifunctional cross-linkers of EDC/NHS combination [23].

The functionalization process is shown in Fig. 2, the silver mirror reaction and GO deposited were the same as the above fabrication of GO/silver SPR sensor. Afterwards, the GO/silver film SPR optical fiber was immersed into a mixture of EDC and NHS (0.4 mol/L EDC: 0.1 mol/L NHS = 1:1 v/v) at room temperature for 20 min, after which the sensor was rinsed with phosphate buffer solution (PBS). Then, the fiber was immersed into Protein A (200 μg/mL) for 2 h, following washed thoroughly with PBS solution, as shown in Fig. 2(e). Protein A is to achieve the proper orientation as mentioned above and increase the amount of goat anti-human IgG combined. Goat anti-human IgG (100 μg/mL) soaked the fiber for 2 h, to modify on the optical fiber surface, the unbound goat anti-human IgG was washed by PBS solution, as shown in Fig. 2(f). The fiber was immersed in BSA solution (1% w/v) for 1 h to block unbound carboxyl groups, as shown in Fig. 2(g). Thus we complete the functionalization of the sensor surface and are ready to use biosensor to detect the target human IgG, as shown in Fig. 2(h).

2.5. Experimental setup

The schematic diagram of the measurement systems using the optical fiber SPR sensor is shown in Fig. 3. A tungsten-halogen lamp (LS-3000, Biaoqi Scientific Corporation, China) with wide spectrum range of 400 nm–1000 nm is used as the light source. The optical fiber spectrometer (USB2000+, Ocean Optics Inc.) was used to detect the reflection signal. The Y-type 2 × 1 optic fiber coupler (BIF600-VIS-NIR, Ocean Optic Corporation) was used to measure both the sensing signal and the reference signal. The signal obtained could be monitored in real