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Enhanced wavelength modulation SPR biosensor based on gold nanorods for immunoglobulin detection

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ABSTRACT

In this study, gold nanorods (GNRs) and graphene oxide (GO) were used to enhance the sensitivity of wavelength modulation surface plasmon resonance (SPR) biosensor to detect bovine IgG. GNRs were prepared by a method of seed-mediated growth and immobilized on the Au film through 1,6-hexanedithiol by covalent attachment. GO was prepared by a modified Hummers and Offeman's method and can be assembled on the sensor surface through electrostatic interaction with GNRs. Meanwhile, GO was used as a support to immobilize antibody directly. The biosensor based on GNRs/GO sensing membrane exhibits a satisfactory response for bovine IgG in the concentration range of 0.075–40.00 μg mL^{-1}. For comparison, the biosensor based on 3-mercaptopropinic acid (MPA) and the biosensor based on GNRs/MPA sensing membrane were also studied for the detection of bovine IgG. The biosensor based on MPA shows a response for bovine IgG in the concentration range of 2.50–40.00 μg mL^{-1}. The biosensor based on GNRs/MPA sensing membrane shows a response for bovine IgG in the concentration range of 0.30–40.00 μg mL^{-1}. As a result, the biosensor based on GNRs/GO sensing membrane was found to be the most sensitive of the three types of biosensors.

1. Introduction

Recently, metallic nanorods have gained significant interest due to their shape-dependent optoeletronic properties such as appearance of a longitudinal plasmon resonance [1], anisotropic chemical reactivity [2], strong surface-enhanced Raman scattering [3] and fluorescence [4], which make them useful for varieties of applications. The morphological anisotropy of nanorods leads to extremely complex physical properties and self-assembly behaviors compared to those of spherical nanoparticles. Metallic nanorods can be synthesized by using rigid templates such as membranes [5], zeolites [6] and nanotubes [7], or by using surfactants as directing agents for electrochemical [8,9] and seed-mediated growth methods [10–12], or by photochemistry [13,14]. Gold nanomaterial is regarded as an excellent material in immunoassay due to its remarkable properties including exceptional optical property, water solubility, good stability, and significant biocompatibility [15], which can be formed in various shapes. Gold nanorods (GNRs) have become a popular research topic and been widely used in biosensing [16–19]. It is known that GNRs exhibit two plasmon absorption bands corresponding to the transverse band assignable to the short axis around 520 nm and the longitudinal band along the long axis which is tunable from visible through near infrared region with nanorod aspect ratio [20]. The longitudinal plasmon absorption band is extremely sensitive to the changes in the dielectric properties of the surroundings and the sensitivity increases as the aspect ratio of GNRs increases [21,22]. This unique optical property of GNRs opens up fascinating applications in biological and chemical sensors.

Graphene is a two-dimensional (2D) carbon material that has attracted great attention because of its outstanding mechanical, thermal, optical, and electrical properties [23–25]. Graphene oxide (GO) is the oxidized graphene with abundant oxygen functional groups (e.g. carboxyl, epoxy, hydroxyl groups), large surface area (theoretical limitation: 2630 $m^2 g^{-1}$) and rich π conjugation structure [26,27], which make it can be served as good supports for biomolecules. And GO has found important application in biosensing. A label-free, regenerative and sensitive surface plasmon resonance and electrochemical aptasensor based on graphene was used for the detection of α-thrombin by Wang et al. [28]. Mao et al. have demonstrated a specific protein detection biosensor using thermally reduced GO sheets decorated with Au nanoparticle-antibody conjugates [29]. Chen and co-workers have designed a GO-based fluorescent biosensor for efficient, selective and real-time biomarker detection on the cancer cell surface [30].

Surface plasmon resonance (SPR) biosensor is a powerful tool for biologic analysis which provides a rapid, label-free and high sensitive assay [31]. These advantages make the SPR technique an

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easy, convenient and reliable one for studying the molecular recognition process and binding specificity of individual biomolecules [32]. It is especially suitable for the determination of interaction partners, such as proteins [33], cells [34], nucleic acids [35], hormone [36] and particularly antigens [37]. However, the application of SPR biosensor is hindered since it is difficult to determine analytes in low concentration or of low molecular mass. Thus it is important to improve the existing measurement methods to enhance the sensitivity of SPR biosensor and expand its application fields. Over the years, a number of methods have been employed to enhance the sensitivity of SPR biosensor including the use of liposomes [38], membrane modification such as Ag film [39] and thin films of titanium dioxide [40], and noble nanoparticles such as Au/Ag alloy nanocomposites [41] to modify the sensor surface. The way of immobilizing biomolecules on the surface of biosensor chip is also crucial in the sensitivity enhancement. Usually sulfhydryl compounds are used as a support to immobilize the antibody, by which way the amount of antibody immobilized on the sensor surface is limited. Herein, instead of sulfhydryl compounds, GO was assembled on the sensor surface as a support to immobilize the antibody. Due to the large surface area of GO, the antibody can be immobilized more efficiently.

In this paper, a sensitive SPR biosensor based on GNRs and GO was constructed for the detection of antigen. GNRs can be assembled on the Au film by a disulfide compound since the thiol–gold interaction is strong enough. GNRs were positively charged because of the CTAB on the surface. Then the negatively charged GO can be attached to the sensor surface via electrostatic interaction. The antibody was bound to GO through covalent attachment between the amine group of antibody and the carboxyl group of GO. The bindings of antibody to antigen result in changes in the refractive index on the biosensor surface, which can be detected by the SPR biosensor.

2. Experimental section

2.1. Materials

Bovine IgG, rabbit anti-bovine IgG, human IgG and goat IgM were purchased from Beijing Biosynthesis Biotechnology Company. 3-Mercaptopropinic acid (MPA), 1,6-hexanedithiol (HDT), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and N-hydroxysuccinimide (NHS) were purchased from Jkchemical. Hydrogen tetrachloroauratehydrate ($HAuCl_4 \cdot 3\,H_2O$) was purchased from Acrosl. Graphite powder was purchased from Aladin Ltd. (Shanghai, China). Cetyltrimethylammonium bromide (CTAB), ascorbic acid, $AgNO_3$, H_2SO_4, $NaNO_3$, $KMnO_4$, and all other chemicals were of analytical reagent grade. All the solutions were prepared with ultra pure water, and all the glassware was cleaned with aqua regia before the experiments.

Bovine IgG, rabbit anti-bovine IgG, human IgG and goat IgM were stored at −20 °C. Sodium phosphate buffered saline (PBS, 0.01 mol L^{-1}, pH 7.4) was used as running buffer.

2.2. Equipment

In this paper, the wavelength modulation SPR biosensor installed in our laboratory was used (Fig. S1). The sensing principle was based on fixing the angle of the incident light and modulating the wavelength of the reflected light. Kretschmann configuration was applied to perform the resonant condition by attenuated total reflection (ATR) in a prism. It was involved in measuring the reflected intensity dip versus the change in the refractive index (RI) over a range of incident wavelengths. The interaction between the analyte in the solution and the biomolecule immobilized on the SPR biosensor surface produces a change in RI that is observed as a shift in the SPR resonant wavelength. The incident angle is fixed, at which the strongest coupling occurs and the resonant wavelength is measured. A glass slide with Au film was put on base of a prism (K9 glass) using a suitable index matching oil (cedar oil). A halogen tungsten lamp is used as the excitation light source. The light emitted from the lamp passes through a polarizer and two lenses and becomes TM-polarized parallel light. The parallel polychromatic light beam passes through the optical prism and excites surface plasmon at the interface between the Au film and the analytes. The output light is guided into the optical fiber and then enters the spectrophotometer (Ocean Optics, Inc., USA). A 2048 element linear array charge-coupled device (CCD) was employed as the detector, the resolution of which is 0.22 nm. The wavelength range that can be detected is from 500 nm to 950 nm.

2.3. Procedures

2.3.1. Preparation of GNRs

GNRs were synthesized by means of a seed-mediated method [12]. At first, the seed solution was prepared by mixing 5 mL of CTAB (0.2 mol L^{-1}) and 5 mL of $HAuCl_4$ (0.5 mmol L^{-1}) aqueous solutions. Subsequently, 0.6 mL of freshly prepared ice-cold $NaBH_4$ solution (0.01 mol L^{-1}) was added under vigorous stirring, which resulted in the color of the solution changing from yellow to brown. The obtained solution was stirred for another 2 min and stored for 2 h at room temprature before further use. To prepare the growth solution, 50 mL of 0.2 mol L^{-1} CTAB solution, 50 mL of 1 mmol L^{-1} $HAuCl_4$ solution and 3 mL of 0.004 mol L^{-1} $AgNO_3$ solution were mixed at room temperature. The solution turned dark yellow and then became colorless upon further addition of 0.7 mL of 0.1 mol L^{-1} ascorbic acid. Finally, 0.24 mL of the seed solution was added into the solution. The resulting solution was kept at 27–30 °C for 24 h to make sure the growth completely. Excess CTAB was removed by repetitive centrifugations at 14,000 rpm for 20 min. The supernatant solution was discarded and the resultant GNRs were redispersed in ultra pure water.

2.3.2. Preparation of GO

GO was produced from natural graphite powder by a modified Hummers and Offeman's method [42]. In a typical synthesis, 1 g of graphite was added into 23 mL of H_2SO_4 with vigorous stirring at room temperature for 24 h. Subsequently, 0.1 g of $NaNO_3$ was added into the mixture and stirred for 30 min. The mixture was kept below 5 °C by ice bath followed by introducing 3 g of $KMnO_4$ slowly. After being heated to 35 °C,the solution was stirred for another 30 min, then diluted by 46 mL of water and mixed for 25 min. Finally, 10 mL of 30% H_2O_2 and 140 mL of water were added into the solution to stop the reaction. The obtained solution was centrifugated for several times to wash the graphite oxide flakes completely. As-synthesized GO was dispersed into individual sheets in distilled water under sonicating.

2.3.3. Modification of Au film

The glass slide with Au film was immersed into fresh ethanol/water solution (v/v, 2:1) containing HDT at the concentration of 10 mmol L^{-1} for 24 h. Then Au film was rinsed several times with ultra pure water, and dried with N_2. As HDT is a disulfide compound, one of the sulfhydryl groups is connected with Au film and the other can be connected with GNRs. The modified Au film was immersed into GNRs solution for 12 h to assemble a monolayer of GNRs, followed by rinsing with ultra pure water and dried with N_2.

2.3.4. Immobilization of antibody

The sensor membrane fabricated as mentioned above were fixed on the SPR instrument equipped with a flow cell. Deionized water was first injected into the flow cell. Then 0.1 mg mL^{-1} GO solution was injected into the flow cell for 1 h. Next PBS solution was injected as the baseline solution. The biosensor surface was activated with NHS under the catalysis of EDC for 20 min, followed by a rinsing with PBS. After the resonant wavelength kept constant, a solution of rabbit anti-bovine IgG was injected into the flow cell to covalently attach to the activated carboxylic acid group. Then 1 mol L^{-1} ethanolamine hydrochloride (pH 8.0) was used to block the non-specific binding sites on the biosensor surface for 10 min. And the non-covalently bound antibody was washed off with PBS buffer, which was also used to stabilize the baseline again.

As a contrast, MPA was also used to covalently immobilize the antibody instead of GO. After Au film modified with GNRs was fixed under the flow cell, 10 mmol L^{-1} MPA was injected into the flow cell. After 2 h, carboxyl group of MPA was activated with NHS under the catalysis of EDC for 20 min. The following processes were the same as that stated above. Meanwhile, the Au film without any modified was also experimented and MPA was injected into the flow cell to immobilize antibody.

2.3.5. Immunoassay

At room temperature, bovine IgG diluted with PBS buffer was injected into the flow cell. The interaction between bovine IgG in the solution and the rabbit anti-bovine IgG immobilized on the SPR biosensor surface was measured as a shift of resonant wavelength by SPR biosensor in real time. Then PBS buffer was injected into the flow cell and another sample solution was injected. Schematic illustration of the assay procedure is shown in Fig. 1.

To evaluate the selective binding of bovine IgG, human IgG and goat IgM were determined by the same procedure as was used to detect bovine IgG.

3. Results and discussions

3.1. Characterization of GNRs and GO

Fig. 2a shows the UV–vis absorption spectra of GNRs. GNRs have unique and tunable optical properties which are related to two distinct plasmon bands named transverse band and longitudinal band. The long wavelength plasmon band originates from the longitudinal mode of oscillation of the free electrons along the long axis of the rod, while the short wavelength plasmon band

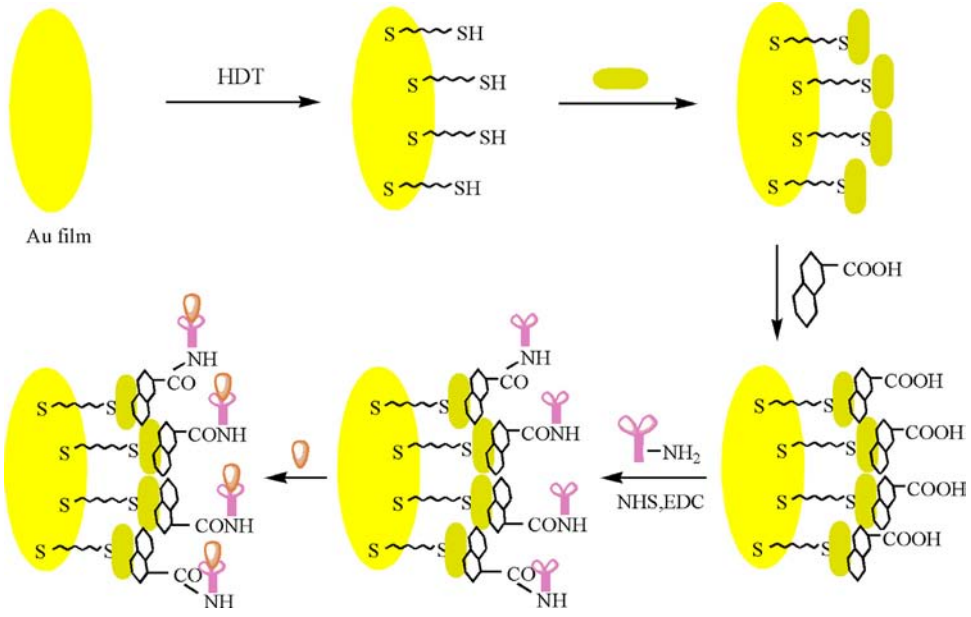

Fig. 1. A schematic diagram of the experimental procedure. ( ) GNRs, ( ) GO, ( ) antibody, ( ) antigen.

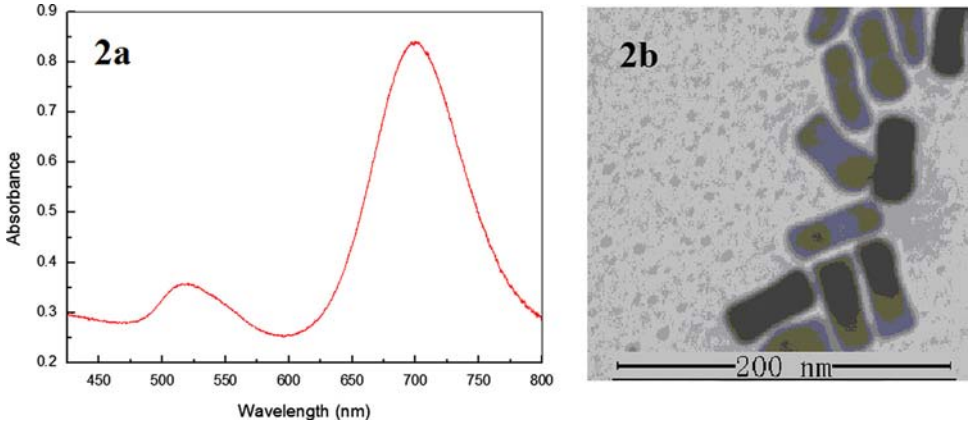

Fig. 2. UV–vis absorption spectra (a) and TEM images (b) of GNRs.

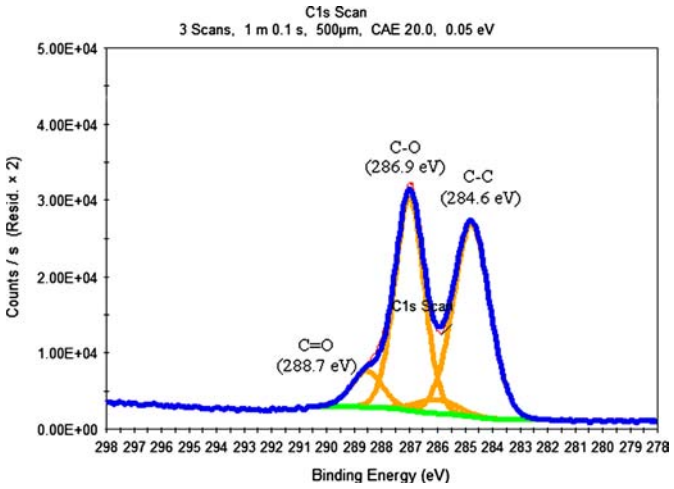

Fig. 3. C 1 s XPS spectra of GO.

originates from the transverse mode perpendicular to the former one. As shown in Fig. 2a, GNRs exhibit two well-defined absorption bands, the transverse band located at 520 nm and the longitudinal band located at 702 nm. Fig. 2b shows the transmission electron microscopy (TEM) image of GNRs synthesized by the seed-mediated growth method in the presence of CTAB. It can be seen that the prepared GNRs are nearly monodisperse and homogeneous. The average size is about 58×24 nm, respectively. GO was characterized by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 3, when the C 1 s XPS spectra was deconvoluted, the peaks at 284.6, 286.9, and 288.7 eV are associated with C–C, C–OH, and C═O, respectively.

3.2. Preparation of SPR biosensor based on GNRs

Traditionally, the SPR biosensor surface is usually modified with a self-assembled monolayer as a sensing membrane. Then the antibody can be covalently immobilized on the monolayer for specific immunoreaction. Complex fabrication of sensing membrane results in a change of refractive index, which can be observed as a shift of resonant wavelength measured by SPR biosensor. Here a GNRs-based SPR biosensor is constructed. GNRs were synthesized by the seed-mediated growth method in the presence of CTAB, which not only plays a role as a stabilizer but also facilitates the transport of Au ions and directs the anisotropic growth. The glass slide was fixed under the flow cell after GNRs were immobilized on the Au film. When the water was injected into the flow cell, a red shift of the resonant wavelength due to the connection with GNRs could be seen. This is due to the increase of the thickness of the SPR sensing membrane and the plasmon coupling between GNRs and Au film. The red shift of resonant wavelength in certain wavelength range is conductive to the sensitivity enhancement of wavelength modulation SPR biosensor [40]. Different concentrations of GNRs were injected into the flow cell to select the optimal condition. Fig. 4 shows that the resonant wavelength shifts increase gradually when the concentrations of GNRs increase from 0.10 g mL^{-1} to 0.60 g mL^{-1}. It is found out that the resonant wavelength reaches a level at the concentration higher than 0.50 g mL^{-1}.

3.3. Immobilization of rabbit anti-bovine IgG

GNRs are positively charged due to the adsorption of the positively charged surfactant CTAB on the surface of GNRs, while GO has many negative charge groups such as carboxylic acids, hydroxyl groups, and epoxides. Then GO can be assembled on the

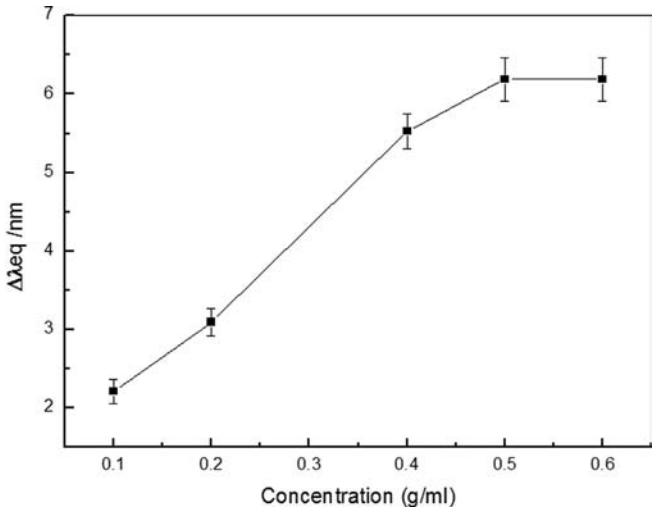

Fig. 4. The relationship between the shifts of resonant wavelength and different concentrations of GNRs.

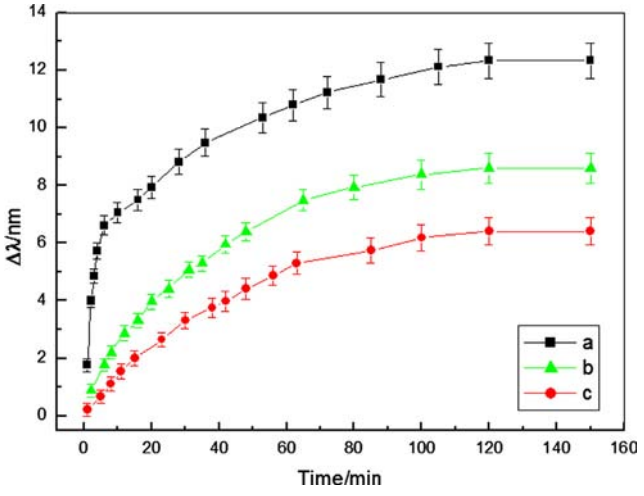

Fig. 5. Kinetic assembling curves of rabbit anti-bovine IgG at the concentration of 100 μg mL^{-1}. (a) The biosensor based on GNRs/GO layer (b) the biosensor based on GNRs/MPA layer (c) the biosensor based on MPA.

sensor surface through electrostatic interaction. After the carboxyl group of GO was activated, rabbit anti-bovine IgG at the concentration of 100 μg mL^{-1} was injected into the flow cell to covalently attach on GO. The kinetic adsorption curves of rabbit anti-bovine IgG on the sensor surface are shown in Fig. 5. After 12 h, PBS buffer was injected into the flow cell and 1 mol L^{-1} ethanolamine hydrochloride (pH 8.0) was used to block the non-specific binding sites on the biosensor surface. Figs. 5a and 5b shows the kinetic adsorption curves of rabbit anti-bovine IgG on the biosensor based on GNRs/GO layer and GNRs/MPA layer, respectively. Fig. 5c shows the kinetic adsorption curves of rabbit anti-bovine IgG on the biosensor based on MPA layer. It can be seen that the resonant wavelength show obvious shift at first and then grows slowly with the time increasing. At last, the resonant wavelength tends to be stable in 120 min, which presents the immobilization of rabbit anti-bovine IgG on the biosensor surface was completed. As shown in Fig. 5, the maximum resonant wavelength shift for immobilization of rabbit anti-bovine IgG on the biosensor surface of MPA, GNRs/MPA and GNRs/GO layer are 6.41 nm, 8.61 nm and 12.34 nm, respectively. It can be seen that the amount of rabbit anti-bovine IgG immobilized on the biosensor surface increases greatly when GNRs and GO were applied. The antibody can be immobilized on

the sensor surface through covalently attachment between the amine group of antibody and the carboxyl group of GO. The surface of GO is relatively rough due to the abundant functional groups, which results in the space of the sensor surface expanded. The large surface area and the space effect are both beneficial for the immobilization of antibody.

3.4. Determination of bovine IgG

In this study, three kinds of sensing membranes including GNRs/GO/antibody (the proposed biosensor), GNRs/MPA/antibody, and MPA/antibody (traditional biosensor) were applied. At room temperature, after the rabbit anti-bovine IgG was immobilized on the surface of the biosensor, sample solutions containing different concentrations of bovine IgG were separately injected into the flow cell and shifts of resonant wavelength due to antibody-antigen immunoreaction were measured in real time. Fig. 6 draws the relationship between the shifts of resonant wavelength and the concentration of bovine IgG. It can be seen from Fig. 6a that the SPR biosensor based on GNR/GO sensing membrane shows a good response to bovine IgG in the concentration range of 0.075–40.00 μg mL^{-1}. The minimum shift of resonant wavelength is 0.22 nm at 0.075 μg mL^{-1} and the maximum of resonant wavelength is 4.62 nm at 40.00 μg mL^{-1}. Fig. 6b shows that the SPR biosensor based on GNR/MPA sensing membrane exhibits a good response to bovine IgG in the concentration range of 0.30–40.00 μg mL^{-1}. The minimum shift of resonant wavelength is 0.22 nm at 0.30 μg mL^{-1} and the maximum of resonant wavelength is 3.97 nm at 40.00 μg mL^{-1}. For the traditional assay, Fig. 6c shows that the SPR biosensor based on MPA sensing membrane exhibits a good response to bovine IgG in the concentration range of 2.50–40.00 μg mL^{-1}. The minimum shift of resonant wavelength is 0.22 nm at 2.50 μg mL^{-1} and the maximum of resonant wavelength is 2.43 nm at 40.00 μg mL^{-1}. As mentioned above, the experimental results indicated that the application of GNRs and GO highly enhanced the sensitivity of the wavelength-modulation SPR biosensor. The limit of quantification (LOQ) is defined as the lowest concentration of an analyte that can be quantitatively determined by the proposed method. Under identical conditions, the LOQ obtained from the biosensor modified with GNRs and GO is 32 times lower than that obtained from MPA membrane biosensor and 4 times lower than that obtained from the biosensor modified with GNRs and MPA. Since the SPR

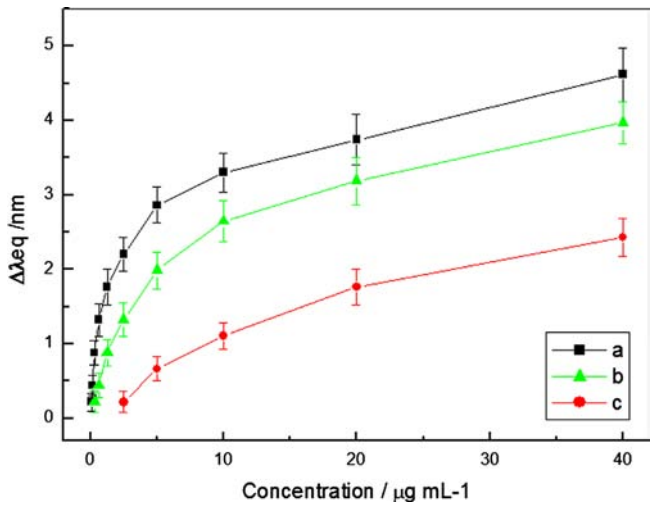

Fig. 6. The relationship between the concentrations of bovine IgG and the shifts of resonant wavelength. (a) The biosensor based on GNRs/GO layer (b) the biosensor based on GNRs/MPA layer (c) the biosensor based on MPA.

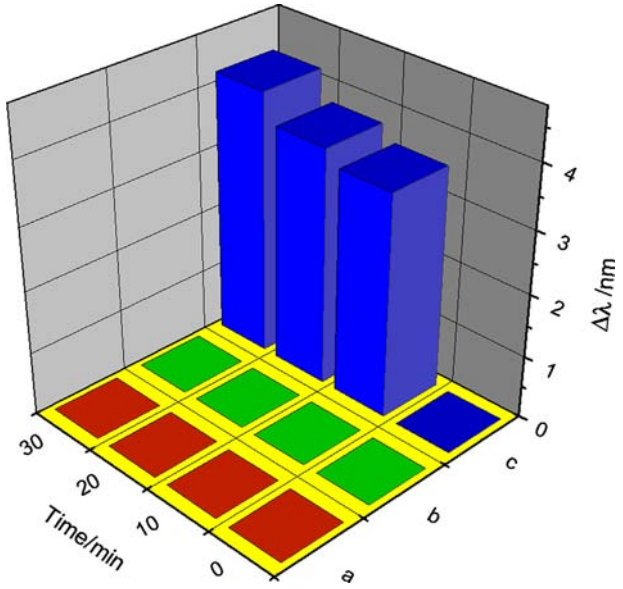

Fig. 7. Kinetic response of human IgG (a), goat IgM (b) and bovine IgG (c) detected by SPR biosensor based on GNRs/GO layer.

biosensor used in this study is installed in our laboratory, it is compared to the previous work we did. The LOQ obtained from the biosensor based on Ag film is 0.3 μg mL^{-1} [39]. For another, the LOQ obtained from the biosensor modified with Au/Ag alloy nanocomposites is 0.15 μg mL^{-1} [41]. As a result, in this study, the LOQ obtained from the biosensor modified with GNRs and GO is lower than that obtained from other biosensors.

When GNRs and GO were applied in the SPR biosensor, the thickness of sensing membrane increases and the resonant wavelength moves to longer wavelength. GNR has its own localized surface plasmon resonance due to the collective oscillations of its conduction electrons. The longitudinal band of GNRs have been found to be more sensitive to the changes in the local environment. The coupling of the localized surface plasmon resonance of GNRs with the propagating plasmon in the Au film might lead to large changes in SPR reflectivity, which further increases the shift of resonant wavelength. Moreover, GO has a large surface area and contains carboxyl groups, which contribute to the immobilization of antibody. The amount of the antibody immobilized on the sensor surface plays a role in the sensitivity enhancement. GO will also modify the propagation of surface plasmon polariton, resulting in the increase of the refractive index. All the above factors lead to the sensitivity enhancement of the wavelength modulation SPR biosensor.

The evaluation of the specificity was performed by detecting human IgG and goat IgM. After the rabbit anti-bovine IgG was immobilized on the surface of the biosensor, human IgG and goat IgM at the concentration of 10 μg mL^{-1} were separately injected into the flow cell for 40 min. As shown in Fig. 7, there were no observable shifts of the resonant wavelength, which indicated the selective binding with bovine IgG.

4. Conclusions

The sensitivity enhancement of wavelength modulation SPR biosensor based on GNRs/GO sensing membrane for the detection of bovine IgG was studied. GNRs have specific optical characters and are more sensitive to the changes in the dielectric properties of the surroundings. GO was proved to be an ideal support to antibody due to its unique structure and good biocompatible. The

experimental results indicate that the biosensor based on GNRs/GO sensing membrane exhibits a satisfactory response to bovine IgG in the concentration range of 0.075–40.00 μg mL^{-1}. The lowest concentration of bovine IgG that could be detected with the proposed biosensor is lower than that with the biosensor based on MPA and the biosensor based on GNRs/MPA sensing membrane. Therefore, GNRs and GO can be used to enhance the sensitivity of the SPR biosensor significantly for the determination of bovine IgG.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.06.059.

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