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Studies of Fe_3O_4/Ag/Au composites for immunoassay based on surface plasmon resonance biosensor

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ABSTRACT

A novel method immunosensor based on chemically functionalized Fe_3O_4/Ag/Au nanocomposite was developed. Fe_3O_4/Ag seeds were coated with Au and Fe_3O_4/Ag/Au nanocomposites were obtained. The nanocomposites could be obtained without violent stirring and the operation was easy and convenient. The magnetic nanocomposites can be easily immobilized on Au film of the surface plasmon resonance (SPR) biosensor with a magnetic pillar. The immobilization of Fe_3O_4/Ag/Au nanocomposites on the Au film leads to a large shift in resonance wavelength, which is due to the increase of the sensing membrane thickness, high dielectric constant of Ag and Au particles, and electromagnetic coupling between Fe_3O_4/Ag/Au nanocomposites and the Au film. The effects of Fe_3O_4/Ag/Au nanocomposites on the sensitivity of SPR biosensor were also investigated. As a result, the biosensor based on Au film shows a response for dog IgG in the concentration range of 1.25–20.00 $\mu g\,ml^{-1}$, whereas the SPR biosensor based on Fe_3O_4/Ag/Au nanocomposites shows a response for dog IgG in the concentration range of 0.15–40.00 $\mu g\,ml^{-1}$. The sensitivity of the SPR biosensor based on Fe_3O_4/Ag/Au nanocomposites is higher than that based on Au film.

1. Introduction

Synthesis of magnetic nanoparticles has been of scientific and technological interest due to their potential applications in biosensors [1], drug delivery [2], bioseparation [3] and information storage [4]. However, the application of magnetic nanoparticles has been limited due to its inherent properties. Pure magnetic nanoparticles are likely to form a large aggregate, easily oxidized or dissolved in an acid medium and have fewer activating groups [5]. Therefore, many researchers have focused on preparation of magnetic nanocomposites to obtain novel properties, such as Fe_3O_4/SiO_2 nanocomposites [6], Fe_3O_4–poly(vinyl alcohol) composites [7], CoFe–Fe_3O_4 core–shell nanocomposites [8]. Recently, the incorporation of optically active components onto magnetic nanoparticles has attracted many attentions. Dumbbell-like Au–Fe_3O_4 [9] or core–shell Fe_3O_4–Ag [10] have been synthesized and show interesting optical properties of Au or Ag and magnetic properties of Fe_3O_4. The magnetic nanoparticles coated with Au are an attractive composite system [11,12]. Owing to inner iron oxide core with an outer metallic shell, the nanocomposites may be very stable in corrosive biological conditions and readily functionalized by binding the various biological ligands on the nanocomposites surface. Compared with Au nanoparticles, the absorption coefficient of the surface plasmon band for Ag nanoparticles is approximately four times as large as that for the Au nanoparticles in the same size [13]. Ag nanoparticles have a sharper peak and could be used to enhance the sensitivity of biosensor [14]. The stability and biocompatibility of the Au nanoparticles are far superior to Ag. Therefore, to take full advantages of Fe_3O_4, Au and Ag nanoparticles, core shell Fe_3O_4/Ag/Au nanocomposites were synthesized. The Fe_3O_4/Ag/Au nanoparticles with plasmonic properties make the core shell composite extremely interesting for magnetic, optical and biomedical applications.

Surface plasmon resonance (SPR) is a surface-sensitive analytical technique based on the ability to detect changes in the refractive index. Last two decades, the development of the SPR sensor was noteworthy. Various SPR sensors have been developed and applied in the areas of medical diagnostic, environmental protection, food safety and biotechnology [15]. SPR biosensor has been widely investigated as a bioanalytical tool to analyze biomolecules such as proteins [16], cells [17], hormone [18], oligonucleotides [19], and especially antigens [20]. The SPR biosensor provides a rapid, label-free and highly sensitive assay, and can be especially applicable for immunoassay of biomolecules. Effective immobilization of biomolecules on the sensor surface is crucial in enhancing the sensitivity of SPR biosensor. Magnetic microbeads have unique

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magnetic features which are not present in other materials. So they have increasingly been used in the field of bioscience [21,22]. The magnetic nanocomposites can be immobilized on the surface of the sensing film with a magnetic pillar easily without covalent link between the Au film and the antibody in traditional method of SPR biosensor.

In this paper, Fe_3O_4/Ag/Au nanocomposites were synthesized and used in the SPR biosensor. The Fe_3O_4/Ag/Au nanocomposites have the advantages of Fe_3O_4, Au and Ag nanoparticles. The nanocomposites could be immobilized on the sensing film without any chemical covalent binding. Due to the good stability and biocompatibility of Au shell and high sensitivity of Ag, the nanocomposites can be very stable and have high sensitivity and good biocompatibility. Thus the Fe_3O_4/Ag/Au nanocomposites could be one of the excellent candidates for protein immobilization on the SPR biosensor surface and could play an important role in the sensitivity enhancement of the biosensor.

2. Material and methods

2.1. Reagents

Dog IgG and rabbit anti-dog IgG were purchased from Beijing Biosynthesis Biotechnology Company. 3-Mercaptopropionic acid (MPA) was purchased from Jkchemical. Hydrogen tetrachloroauratehydrate ($HAuCl_4{\cdot}4H_2O$) was obtained from Acrosl. *N*-hydroxysuccinimide (NHS) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) were purchased from Pierce. Silver nitrate, sodium borohydride, 2-propanol, Triton X-100, n-hexanol, cyclohexane, cetyltrimethylammonium bromide (CTAB), ascorbic acid and all other chemicals were of analytical reagent grade. All solutions were prepared with ultra pure water. Dog IgG and rabbit anti-dog IgG were stored at −20 °C and all other biological reagents were stored at 4 °C. Sodium phosphate buffered saline (PBS, 0.01 mol l^{-1}, pH 7.4) was used as running buffer.

2.2. Equipment

The wavelength modulation SPR analyzer installed in our laboratory was used [23]. It is working with Kretschmann configuration to achieve the resonant condition by attenuated total reflection (ATR) in a prism. A 2 nm adhesive layer of Cr followed by a 50 nm layer of Au was deposited on a K9 glass slide, then the glass slide with Au film was put on base of a prism (K9 glass). The light emitted from a lamp passes through the optical prism and excites surface plasmon at the interface between the biosensor chip surface and analytes. The output light is guided into the optical fiber and then enters the spectrophotometer. A charge-coupled device (CCD) was used as the detector. Magnetic pillar was immobilized under the optical prism. The diameter and height of the magnetic pillar are 25 and 12 mm, respectively.

2.3. Procedures

2.3.1. Preparation of Fe_3O_4/Ag/Au nanocomposites

Fe_3O_4 nanoparticles were prepared by chemical coprecipitation method [23]. 2.6 g of $FeCl_3{\cdot}6H_2O$, 1.0 g of $FeCl_2{\cdot}4H_2O$ and 0.425 ml of HCl (12 mol l^{-1}) were added in 12.5 ml deionized water to prepare a stock solution. 125 ml of NaOH (1.5 mol l^{-1}) solution was heated to 80 °C in a flask. Then the stock solution was added dropwise into the flask under nitrogen gas protection and vigorous stirring. After 3 h, the obtained Fe_3O_4 nanoparticles were separated from the solution using a permanent magnet and washed with deionized water three times. The precipitate was dispersed in 100 ml deionized water.

Fe_3O_4/Ag nanocomposites were synthesized by the reverse micelle technology [24]. 0.4 ml of Fe_3O_4 nanoparticles solution, 7.0 ml of Triton X-100, 7.0 ml of n-hexanol and 37.5 ml of cyclohexane were mixed uniformly with vigorous stirring. Then, 1 ml of 0.1 mol l^{-1} $AgNO_3$ was added. After 30 min, 1 ml of 0.2 mol l^{-1} $NaBH_4$ was added into the solution which was stirred at room temperature. After 4 h, the black Fe_3O_4/Ag nanocomposites were precipitated by adding excess acetone, and then separated from the mixture using a permanent magnet. The precipitate was washed with ethanol and deionized water several times and then dispersed in 20 ml deionized water.

Fe_3O_4/Ag/Au nanocomposites were synthesized by a new seed growth method [25,26]. The nanocomposites could be prepared without violent stirring and the operation was more convenient compared with others. 49.6 μl of 1 g ml^{-1} $HAuCl_4{\cdot}4H_2O$ and 2 ml of 0.1 mol l^{-1} CTAB were separately added into 80 ml of water. Then, 600 μl of 0.1 mol l^{-1} ascorbic acid was added into the solution. This resulting solution was referred to as the growth solution. 20 ml of Fe_3O_4/Ag nanocomposites was added into the growth solution. After 12 h, the precipitate was separated from the solution using a permanent magnet, and washed with deionized water five times. Finally, the Fe_3O_4/Ag/Au nanocomposites obtained were dispersed in 20 ml deionized water.

2.3.2. Characterization of the nanocomposites

The morphologies of Fe_3O_4, Fe_3O_4/Ag and Fe_3O_4/Ag/Au nanocomposites were tested using transmission electron microscopy (TEM). The samples for TEM were obtained by placing drops of each sample on a copper grid. The UV-visible absorption spectra of the Fe_3O_4/Ag and Fe_3O_4/Ag/Au nanocomposites were measured with a UV–vis spectrophotometer. The samples were diluted with deionized water and treated using ultrasound to make them disperse homogeneously. The composition of Fe_3O_4/Ag/Au nanocomposites was determined using X-ray photoelectron spectroscopy (XPS). The samples for XPS were obtained by placing drops of sample on a thin glass slide.

2.3.3. Preparation of Fe_3O_4/Ag/AuNPs-MPA-antibody

Deionized water was injected into the flow cell as the baseline solution. Then the Fe_3O_4/Ag/Au nanocomposites were introduced into the flow cell equipped with a magnetic pillar under the prism. The modified magnetic nanocomposites can be immobilized on the Au film by the magnetic pillar. The immobilization of magnetic nanocomposites on the Au film surface could produce change of refractive index that could be observed as a red shift in the SPR resonant wavelength. The magnetic nanocomposites at the same concentration were injected into the flow cell. When the shifts of resonant wavelength reach about 10 nm, the amounts of nanocomposite immobilized with magnetic pillar are almost the stable.

After 4 h, deionized water was injected into the flow cell, and then 10 mmol l^{-1} MPA was injected for 5 h. PBS was injected into the flow cell. Then a solution containing NHS (30 mg ml^{-1}) and EDC (30 mg ml^{-1}) was introduced to activate the carboxyl group of MPA for 20 min, followed by a rinsing with PBS. After the resonant wavelength kept constant, a solution of rabbit anti-dog IgG was injected into the flow cell to covalently attach to the activated carboxyl group. Then 1 mol l^{-1} ethanolamine hydrochloride (pH 8.0) was used to block the nonspecific binding sites on the biosensor surface. After 10 min, PBS was injected into the flow cell and the Fe_3O_4/Ag/AuNPs-MPA-antibody sensing membrane was formed. A schematic diagram of the immobilization of antibody on the surface of the Au film is shown in Fig. 1.

The magnetic pillar was immobilized under the prism on the whole experiment process.

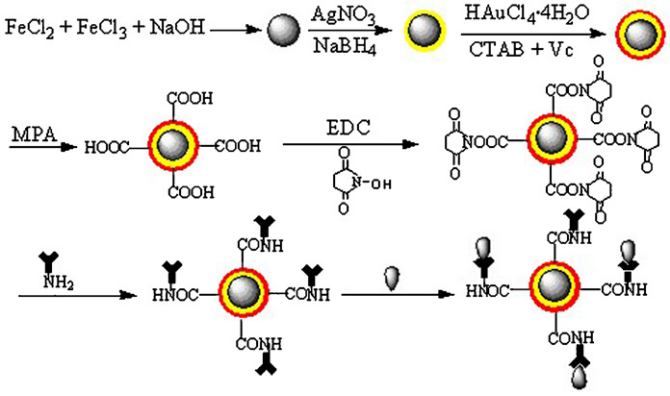

Fig. 1. A schematic diagram of the immobilization of antibody on the surface of the Au film. ( ) Fe_3O_4/Ag/Au nanocomposites, ( ) Fe_3O_4 nanoparticles ( ) antibody, ( ) antigen.

2.3.4. Preparation of MPA-antibody

For comparison, the MPA-antibody sensing membrane without nanocomposites modified was also constructed. PBS was used as the baseline solution and 10 mmol l^{-1} MPA was injected into the flow cell for covalent binding to the Au film. After 5 h, carboxyl group of MPA was activated with NHS under the catalysis of EDC for 20 min. Then 100 μg ml^{-1} rabbit anti-dog IgG solution was injected. Then PBS was used to wash off noncovalently bound antibody. And then 1 mol l^{-1} ethanolamine hydrochloride (pH 8.0) was used to block the nonspecific binding sites on the biosensor surface. PBS was injected into the flow cell and MPA-antibody sensing membrane was formed.

2.3.5. Immunoassay

All SPR experiments were conducted at room temperature. Different concentrations of dog IgG diluted with PBS were separately injected into the flow cell of the SPR biosensor system. Thus free antigens could bind to antibodies immobilized on the biosensor surface and the shifts of resonant wavelength due to antibody–antigen immunoreaction were measured. After 40 min, PBS was injected into the flow cell for 20 min. Then another sample solution was injected into the flow cell.

To evaluate the selective binding of dog IgG, human IgG and bovine serum albumin were determined by the proposed procedure.

3. Results and discussion

3.1. Characterization of Fe_3O_4/Ag/Au nanocomposites

The morphologies of the magnetite nanocomposites were characterized by TEM. Fig. 2 provides the TEM photographs of the prepared Fe_3O_4, Fe_3O_4/Ag and Fe_3O_4/Ag/Au nanocomposites. The average particle sizes are about 10 nm, 22 nm and 35 nm, respectively. The TEM photographs show a relatively homogeneous distribution of particles. Fig. 3 shows the UV–vis absorption spectra for the Fe_3O_4, Fe_3O_4/Ag and Fe_3O_4/Ag/Au nanocomposites and the absorption spectrum in inset is a close-up view of the absorption spectrum (c). The absorbance of Fe_3O_4 decreases with the increase of the wavelength in the range 300–800 nm and no obvious absorption peak is observed. The Fe_3O_4/Ag nanocomposites have a characteristic peak at 400 nm which result from the typical surface plasmon resonance of silver nanoparticles [13]. This result demonstrates that silver was deposited on the surface of Fe_3O_4 successfully.

The resonance wavelength obtained with the biosensor based on metal nanoshell is much longer than that based on the solid

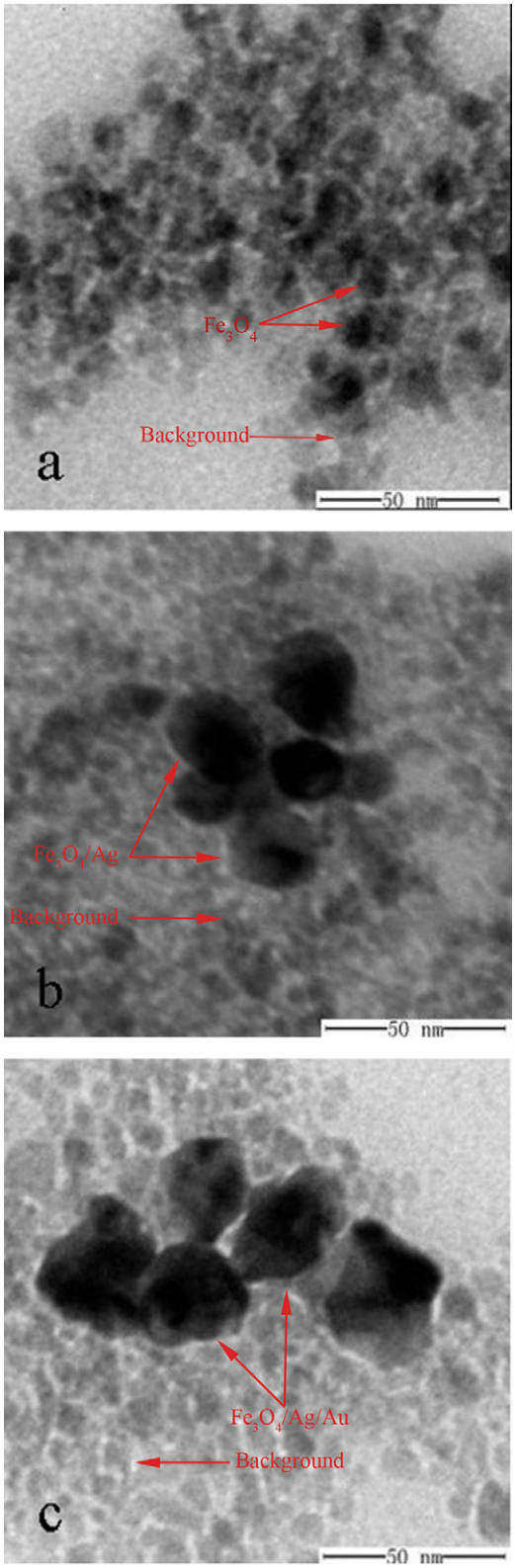

Fig. 2. Transmission electron microscope (TEM) images of Fe_3O_4 nanoparticles (a), Fe_3O_4/Ag nanocomposites (b), and Fe_3O_4/Ag/Au nanocomposites (c).

metal nanoparticles [27]. After Fe_3O_4/Ag nanocomposites were coated with Au nanoparticles, the resonance wavelength is 550 nm, which has redshift compared with that of Ag nanoparticles. The resonance peaks of Ag and Au plasmon for these nanocomposites were not observed and the results indicated that these nanocomposites

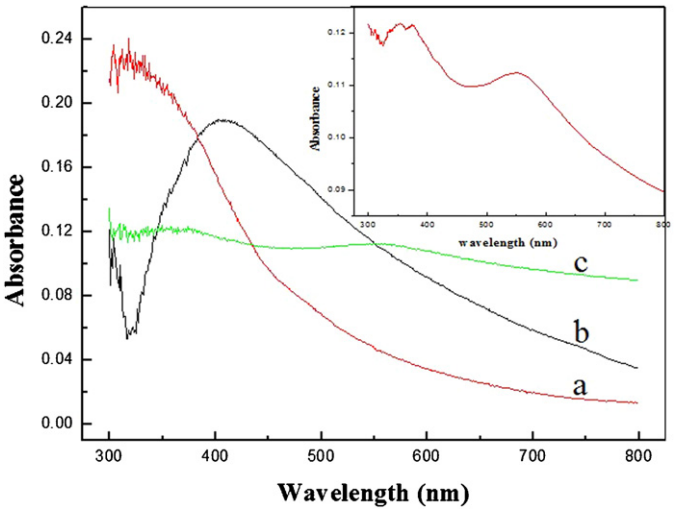

Fig. 3. UV–vis absorption spectra of Fe_3O_4 (a), Fe_3O_4/Ag (b) and Fe_3O_4/Ag/Au nanocomposites (c). Inset: the close-up view of the absorption spectrum of (c).

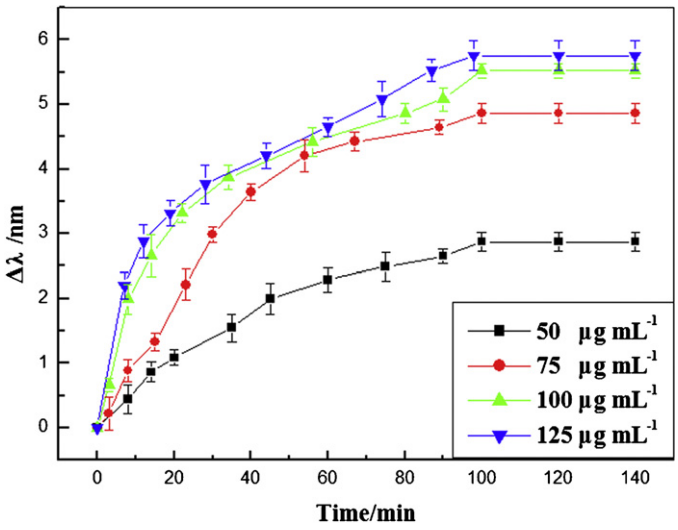

Fig. 4. The kinetic adsorption curves of immobilization of rabbit anti-dog IgG at different concentrations.

were aggregates of the different metal particles instead of a simple mixture of the metal particles.

3.2. XPS analysis

The composition of prepared Fe_3O_4/Ag/Au nanocomposites was determined using XPS. It can be seen from Fig. S1 there are two obvious peaks of Ag 3d, which are consistant with the results of bimetallic nanocomposites [28]. The signal of Au is weak and the reason may be that there is a small amount of Au in the shell [25]. The Fe 2p spectrum is also resolved into two spin–orbit components. Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peaks occur at a BE of 711.1 and 724.7 eV, respectively, which are consistent with metallic Fe spectrum [29]. The results indicated that Fe_3O_4/Ag/Au nanocomposites were synthesized successfully.

3.3. Immobilization of Fe_3O_4/Ag/Au nanocomposites on SPR biosensor

Traditionally, molecular self-assembly was used to form a sensing layer on the Au film substrate. However, in the work the nanocomposites can be easily immobilized on the bare Au film with magnetic pillar. In addition, Au and Ag nanoparticles are widely employed in SPR experiments [30]. Compared with Au, the Ag shows a higher enhancement in the visible light region [31]. However, it should be noted that Ag is unstable and not biocompatible. Therefore, Au was used as the protective agent for the Ag nanoparticles and Fe_3O_4/Ag/Au nanocomposites are of considerable interest. On one hand, due to the magnetic property of Fe_3O_4, the immobilization of the Fe_3O_4/Ag/Au nanocomposites can be simplified. On the other hand, the underneath Ag may provide extra enhancement of sensitivity of the biosensor. Thus, a new SPR biosensor was fabricated based on Fe_3O_4/Ag/Au nanocomposites.

The redshift of the resonant wavelength due to the magnetic nanocomposites immobilized on the Au film reached about 10 nm because the thickness of the SPR sensing membrane changes and the interparticle interactions in the Fe_3O_4/Ag/Au nanocomposites leads to change in the refractive index at the bare Au film surface. The result demonstrated that the Fe_3O_4/Ag/Au nanocomposites were immobilized on the sensor film.

3.4. Covalent immobilization of rabbit anti-dog IgG

After Fe_3O_4/Ag/Au nanocomposites were immobilized on the Au film and the biosensor surface was activated, rabbit anti-dog IgG at different concentrations was separately injected into the flow cell. The rabbit anti-dog IgG can be effectively structured on the surface of the biosensor Fig. 4 through covalent attachment. Fig. 4 shows the kinetic adsorption curves for the immobilization of rabbit anti-dog IgG. It can be seen that the resonant wavelength shows an evident shift at first. With the increase of the time, the resonant wavelength increases slowly and seemed to be unchanged in 100 min, which indicates that the immobilization of antibody on the biosensor surface was completed effectively. With the increase of concentration of rabbit anti-dog IgG, more antibodies were immobilized on the biosensor surface and the resonant wavelength shifts to the longer wavelength. When the concentrations of rabbit anti-dog IgG are 50.0, 75.0, 100.0 and 125.0 $\mu g\,ml^{-1}$, the shifts of resonant wavelength in 100 min are 2.872, 4.862, 5.525, and 5.757 nm, respectively. With the increasing concentration of rabbit anti-dog IgG, the amount of antibody immobilized increases at first and tends to be saturated gradually. After 12 h, PBS was injected into the flow cell to wash off the noncovalently binding antibody. It can be seen the maximum shifts of the resonant wavelength are almost the same when the concentrations of rabbit anti-dog IgG are 100.0 and 125.0 $\mu g\,ml^{-1}$. It means that the amount of rabbit anti-dog IgG on the sensor reaches saturation. The minimum shift of the resonance wavelength that can be measured is about 0.22–0.23 nm in SPR spectra. When the concentration of rabbit anti-dog IgG increased from 100 $\mu g\,ml^{-1}$ to 125 $\mu g\,ml^{-1}$, the resonant wavelength shifted only about 0.232 nm, which may result from the non-special adsorption. When concentration of rabbit anti-dog IgG increased from 75 $\mu g\,ml^{-1}$ to 100 $\mu g\,ml^{-1}$, the resonant wavelength shifted from 4.862 nm to 5.525 nm, which should result from special adsorption. As a result, 100.0 $\mu g\,ml^{-1}$ was chosen as the optimum concentration for the detection of dog IgG.

3.5. Determination of dog IgG

Before going into the details of the immunoassay experiment, it is necessary to emphasize the two kinds sensing membranes including Fe_3O_4/Ag/Au/anti-dog IgG and MPA/anti-dog IgG.

When the Fe_3O_4/Ag/Au nanocomposites were used, the shifts of resonant wavelength due to antibody–antigen immunoreaction

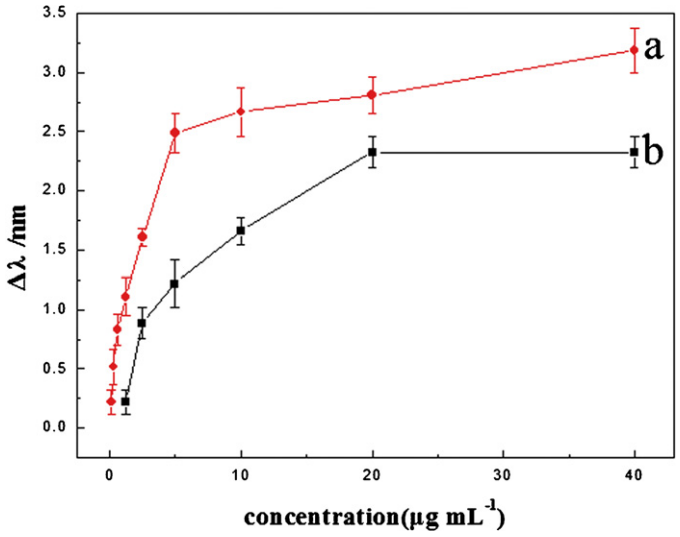

Fig. 5. The relationship between the shifts of the resonant wavelength and the concentrations of dog IgG. The biosensor based on Fe_3O_4/Ag/Au nanocomposites (a), the biosensor based on Au film (b).

were measured. Fig. 5 shows the relationship between the shifts in the resonant wavelength and the concentrations of dog IgG. It can be seen that the SPR biosensor based on Fe_3O_4/Ag/Au nanocomposites shows a good response to dog IgG in the concentration range of 0.15–40.00 μg ml^{-1}. The minimum shift of resonant wavelength is 0.230 nm at 0.15 μg ml^{-1} and the maximum shift of resonant wavelength is 3.186 nm at 40.00 μg ml^{-1}. The SPR biosensor based on MPA/anti-dog IgG shows a good response to dog IgG in the concentration range of 1.25–20.00 μg ml^{-1}. The minimum shift of resonant wavelength is 0.230 nm at 1.25 μg ml^{-1} and the maximum shift of resonant wavelength is 2.324 nm at 20.00 μg ml^{-1}. The experimental results indicate the advantage of the Fe_3O_4/Ag/Au nanocomposites used as the SPR substrate for the immunoassay analysis. Under identical conditions, the limit of quantification (LOQ) obtained with the biosensor based on Fe_3O_4/Ag/Au nanocomposites is about 8 times lower than that obtained with the biosensor based on Au film.

In the novel SPR biosensor based on Fe_3O_4/Ag/Au nanocomposites, the interaction between the localized SPR of the Ag and Au with the propagating plasmon in the Au film might lead to large changes in SPR reflectivity through the collective oscillations of their conduction electrons. So the coupling of the localized surface plasmon of the Fe_3O_4/Ag/Au nanocomposites with the propagating plasmon in the Au film is mostly responsible for the enhancement of SPR signal [32]. Meanwhile, Fe_3O_4/Ag/Au nanocomposites used in the SPR biosensor made the thickness of the sensing membrane increase and the resonant wavelength move to longer wavelength, which also results in the sensitivity enhancement of the wavelength-modulation SPR biosensor [33,34]. In conclusion, due to magnetic property and plasmonic property, Fe_3O_4/Ag/Au nanocomposites can simplify the immunoassay and improve the sensitivity of SPR biosensor. The present biosensor extended the application of magnetic nanocomposites in SPR immunoassay.

As can be seen in Fig. 5, the shift of the resonant wavelength does not linearly increase with the increase of the concentration of dog IgG in certain concentration range. The reaction between antigen (Ag) and antibody (Ab) can be expressed as follows:

Ag +Ab = AgAb

The binding constant is K_A [35].

$$K_A = \frac{[AgAb]}{[Ag][Ab]} \quad (1)$$

where [AgAb] is the concentration of AgAb on the sensor surface, which is corresponding to the SPR biosensor signal $\Delta\lambda_{eq}$, [Ag] is the concentration of antigen in the solution, [Ab] is corresponding to $(\Delta\lambda_{max} - \Delta\lambda_{eq})$. $\Delta\lambda_{max}$ is the SPR response corresponding to the maximum capacity of binding antigen on the sensor surface. So Eq. (1) can be expressed as:

$$\frac{\Delta\lambda_{eq}}{[Ag]} = K_A\Delta\lambda_{max} - K_A\Delta\lambda_{eq} \quad (2)$$

$\Delta\lambda_{eq}$ increases with the increase of concentration of antigen ([Ag]) in the solution. It is also seen from the Eq. (2) that the $\Delta\lambda_{eq}$/[Ag] decreases with the increase of $\Delta\lambda_{eq}$. So the slope of the relationship curve between the shift of the resonant wavelength and the concentration of dog IgG decreases with the increase of the concentration of antigen, which is in accordance with the experimental results.

The specificity was also tested by two control experiments using human IgG and bull serum albumin (BSA) under the same conditions. After the rabbit anti-dog IgG was immobilized on the biosensor surface, human IgG and BSA at the concentration of 10 μg ml^{-1} were separately injected into the flow cell for 30 min. There are no observable shifts of the resonant wavelength (Fig. S2), which indicate the selective binding of dog IgG.

4. Conclusion

Here the Fe_3O_4/Ag/Au nanocomposites were successfully used in wavelength modulation SPR biosensor to detect dog IgG. The structures of the Fe_3O_4/Ag/Au nanocomposites were separately studied by TEM, UV–vis absorption spectroscopy and XPS. The biosensor based on Fe_3O_4/Ag/Au nanocomposites exhibits a good response to dog IgG in the concentration range of 0.15–40.00 μg ml^{-1} and LOQ is about 8 times lower than that obtained with bare Au film. Therefore, this primary study demonstrates that the Fe_3O_4/Ag/Au nanocomposites were beneficial to improve the performance of the SPR sensor.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.colsurfb.2012.08.040.

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