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A novel surface plasmon resonance biosensor based on the PDA-AgNPs-PDA-Au film sensing platform for horse IgG detection

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Abstract

Herein we report a novel polydopamine-silver nanoparticle-polydopamine-gold (PDA-AgNPs-PDA-Au) film based surface plasmon resonance (SPR) biosensor for horse IgG detection. The PDA-AgNPs-PDA-Au film sensing platform was built on Au-film via layer-by-layer self-assembly. Ag ion was reduced in situ to AgNPs in presence of PDA. The top PDA layer can prevent AgNPs from being oxidized and connect with antibody via Schiff alkali reaction directly. The morphology and thickness of the modified gold film were characterized using scanning electron microscope and Talystep. Experimental results show that the PDA-AgNPs-PDA-Au film sensing platform is stable, regenerative and sensitive for horse IgG detection. The detection limit of horse IgG obtained with the present biosensor is 0.625 μg mL^{-1}, which is 2-fold and 4-fold lower than that obtained with biosensor based on PDA modified Au film and conventional biosensor based on MPA, respectively. Furthermore, when challenged to real serum samples, our sensor exhibited excellent specificity to horse IgG, suggesting its potential for industrial application.

Keywords: Surface plasmon resonance; polydopamine; Ag nanoparticles; horse IgG

1 Introduction

Surface plasmon resonance (SPR) sensor can be used for label-free, real-time analysis of molecular interactions and determination of target molecules. The SPR sensor is highly sensitive to change in refractive index [1]. To enhance the sensitivity of SPR sensor, the emphasis has been given on improving sensing layer including efficient immobilization of receptor and introduction of nanomaterials for signal amplifications [2-5]. The SPR sensors have been widely applied to biochemistry [6, 7], disease diagnosis [8, 9], food analysis [10, 11], and environmental monitoring [12, 13].

In 1982, Lee et al. first reported synthesis of Ag nanoparticles (AgNPs) by reducing silver nitrate ($AgNO_3$) with trisodium citrate salt in an aqueous solution [14]. Although AgNPs are easily oxidizable, these inexpensive nanoparticles have been widely used in SPR sensors because of their chemical and optical properties [5, 15-17]. In SPR sensors, the electronic coupling between Ag and surface plasmon wave leads to amplification of SPR response, resulting in enhanced sensitivity of SPR biosensor.

Dopamine (DA), a neurotransmitter found in mussel adhesive proteins, plays an important role in mammalian central nervous system [18-20]. It contains catechol and amine functional groups and self-polymerizes at alkaline medium to form thin adherent

polydopamine (PDA) film, which is able to attach to virtually all types of inorganic and organic surfaces through formation of covalent and noncovalent bonds [21-23]. PDA not only exhibits unique adhesive ability, better chemical properties, biocompatibility and easy bioconjugation, but it also reduces some noble metal ions under basic environment. For example, PDA could induce the reduction of Ag^{+} into AgNPs without introduction of other reductants [24]. In some ways, PDA's ability to function as a reducing agent is related to the oxidation of monomer. The as-formed PDA layer is hydrophilic in nature, and due to its chemical versatility, it can perform as platform for secondary reactions [25]. The PDA has been applied to various interfaces of different fields such as surface modification [26-28], enhancement of electronic properties [29, 30], nanoparticles stabilization [31], biological applications [29, 32, 33], and cell adhesion [34].

Layer-by-layer assembly, a surface modification method, relies on sequential adsorption of polymers onto bulk surfaces from solution, gradually forming complex multilayered films [35]. The films are formed by alternately adsorbing positively and negatively charged polymers or polymers containing complementary hydrogen-bond donors and acceptors onto the substrate [36]. Other building blocks, such as inorganic nanoparticles, have been used layer-by-layer assembly [35]. The advantages of layer-by-layer assembly method lies in its simple operation and retention of bulk properties.

The objective of this work was to construct a PDA-AgNPs-PDA-Au film based SPR biosensor for horse IgG detection. The sensing platform was built on Au film by layer-by-layer self-assembly. PDA film was formed by DA self-polymerization on Au film under low basic environment, and Ag^{+} was reduced to form AgNPs on the film. Another layer of PDA film was grown on the surface of AgNPs through self-polymerization of DA, and finally, antibody was immobilized onto the surface of sensing platform by Schiff alkali reaction. We investigated the performance of this novel sensing platform. The antibody immobilization and antigen recognition capacities of the biosensor were compared with biosensor based on PDA modified Au film and MPA based conventional biosensor, respectively. We studied the stability, regenerability, and applicability of the novel sensor to detect horse IgG in real samples. Furthermore, the binding constant (Ka) between the antibody and antigen was obtained.

2. Materials and methods

2.1 Chemicals and reagents

Rabbit anti-horse IgG, horse IgG, human IgG and mouse IgG were purchased from Beijing Biosynthesis Biotechnology Company, China. Chicken serum was purchased from Shanghai Jonln Industrial Company, China. Bovine serum albumin (BSA) was purchased

from Ding Guo Biotechnology Company, China. Tris base, 3-hydroxytyramine hydrochloride, silver nitrate, 3-mercaptopropinic acid (MPA), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and N-hydroxysuccinimide (NHS) were purchased from J&K Chemical Ltd., China. All other chemicals were of analytical reagent grade. All the solutions were prepared using ultrapure water, and all the glasswares were cleaned with aqua regia before the experiments.

Rabbit anti-horse IgG, horse IgG, human IgG and mouse IgG were stored at –20 °C, while 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 biosensor was installed in our laboratory. The assembled biosensor consists of an iodine-tungsten lamp, a light guide system, flow cell reactor, a prism-sensing unit, a miniature spectrometer, and a data analysis system. Here is a brief description assembled biosensor. The iodine-tungsten lamp is used as the excitation light source. When the light passes through a polarizer and two lenses, it becomes TM-polarized parallel light. In the sensing platform, Kretschmann configuration is applied to achieve the surface plasmon resonance through attenuated total reflection (ATR) at the interface between a prism and a thin metal layer. A glass slide with Au film is put on base of a prism (K9 glass) using suitable index matching oil. At the interface between the Au

film and the sample solution, the parallel polychromatic light beam passes through the optical prism and excites surface plasmon. Then the output light is guided into the optical fiber and enters the spectrophotometer (HR2000+, Ocean Optics Inc., USA). The detector is a charge-coupled device (CCD). In this work, the volume of the flow cell was about 100 μL. When the sample was injected, the interaction between the analyte in the solution and the biomolecular element immobilized on the SPR biosensor produced a change in refractive index that was observed as a wavelength shift.

2.3 Construction of sensing platform

The sensing platform made of PDA-AgNPs-PDA-Au film was constructed by three steps via layer-by-layer self-assembly. The first step involved the formation of PDA film on Au film. Au film was cleaned with ethanol and dried in a N_2 stream. Dopamine hydrochloride (2 mg mL^{-1}) was dissolved in 5 mL of Tris-HCl buffer (10 mmol L^{-1}, pH 8.5). Au film was then immersed in the dopamine solution for 4 h, and PDA film was formed. The back side of the Au film was cleaned with cotton dipped in alcohol. The second step involved the formation of PDA-AgNPs on Au film surface. The Au film, coated with PDA film, was immersed in 50 mmol L^{-1} of $AgNO_3$ solution for 18 h in dark, and the resulting film was then washed with ultrapure water, followed by drying under N_2 stream. Finally, PDA-AgNPs-PDA-Au film was constructed on Au film surface in the third step, and the method was similar to step-1 except for the concentration of dopamine

hydrochloride — 1 mg mL^{-1} in step-3 instead of 2 mg mL^{-1} in step 1.

2.4 Horse IgG detection with PDA-AgNPs-PDA-Au film sensing platform

All SPR experiments were conducted at room temperature. After constructing the sensing platform of PDA-AgNPs-PDA-Au film, PBS buffer was injected into the flow cell to keep the baseline steady. Different concentrations of rabbit anti-horse IgG were examined to select the optimum concentration of antibody. To block the unbound sites, 1% BSA was used. PBS buffer was injected into the flow cell again to wash unbound antibody and to keep the baseline steady. Next, different concentrations of horse IgG were injected into the flow cell for detection. In order to ensure the reliability of the assay, all experiments were conducted in triplicate. Figure 1a schematically depicts the sensing mechanism using PDA-AgNPs-PDA-Au film biosensor platform. To evaluate the specificity of the sensor, mouse IgG and human IgG were detected. To detect horse IgG, PDA modified Au film was also fabricated, though the detection procedure was same as that of PDA-AgNPs-PDA-Au film biosensor.

2.5 Horse IgG detection with MPA modified Au film sensor

The conventional SPR biosensor was constructed using MPA modified Au film. Au film was immersed in 10 mmol L^{-1} of MPA and incubated for 3 h. Au film modified with –COOH was then activated with NHS and EDC (30 mg L^{-1}, respectively) for 20 min. Rabbit anti-horse IgG was injected into the reactor for antibody immobilization, and the

non-specific binding sites were blocked with 1% BSA. PBS buffer was used to wash unbound matrix and to stabilize the baseline. Finally, different concentrations of horse IgG were injected into the flow cell for detection. The analysis was conducted in triplicate. Figure 1b shows the sensing procedure for the MPA modified Au film biosensor.

2.6. Regeneration

The prism was taken away from the reactor after a series of immunoassay was completed. The glass slide underwent prolonged ultrasound with ethanol and distilled water separately, and then dried with gaseous nitrogen. The cleaned Au film was reused for performing the new round of immunoassay.

3 Results and discussion

3.1 Characterization of the sensing platform

We characterized the morphology of the modified gold film using scanning electron microscope (SEM). Figure 2 illustrates SEM images of bare Au film, PDA modified Au film, PDA-AgNPs modified Au film, and PDA-AgNPs-PDA modified Au film. SEM images revealed the attachment of PDA onto the gold film and reduction of silver ions to silver nanoparticles of about 55 nm in size. The thickness of bare Au film, the thickness of PDA layer between AgNPs and Au film, and the thickness of the top layer of PDA were 50

nm, 50 nm and 30 nm, respectively; each layer thickness was measured using Talystep.

3.2 Construction of sensor platform

DA (3,4-dihydroxy-L-phenylalanine) is a non-toxic material. DA self-polymerizes to form PDA film under low basic conditions because of the presence of oxidizable phenolic hydroxyl and amino groups on DA. According to the studies examining the mechanism behind DA self-polymerization, the process is somewhat complex [37-40]. The self-polymerization reaction occurs without adding other reaction reagents and condition. As the reaction proceeded, we observed that the color changed from colorless to pale brown and finally turning to deep brown. Next, we immersed the coated Au film into 50 mmol L^{-1} of $AgNO_3$ solution, thus inducing the reduction of Ag^+ into AgNPs [41]. The in situ formed AgNPs were tightly bonded onto the surface of PDA. Finally, the resulting film was immersed into DA solution so that the PDA film, formed over the AgNPs, could prevent the nanoparticles from being oxidized, and the antibodies were immobilized onto the film via Schiff alkali reaction directly.

3.3 Immobilization of rabbit anti-horse IgG

Once the PDA-AgNPs-PDA-Au film sensing platform was ready, we immobilized antibody onto PDA film surface directly. We monitored the resonant wavelength shift in real-time as the antibody was injected. To optimize antibody concentration, a series of antibody solutions with different concentrations were injected the flow cell separately. We

found maximum resonant wavelength shifts of 7.0 nm, 9.4 nm, 11.2 nm for antibody concentrations of 50 μg mL^{-1}, 75 μg mL^{-1}, and 100 μg mL^{-1}, respectively (Fig. 3). Moreover, we found that the immobilized antibody reached saturation in 40 min. Therefore, the optimal concentration is 100 μg mL^{-1}at which the resonant wavelength shifts reached the maximum. Figure 4A depicts the kinetic adsorption curves of immobilized rabbit anti-horse IgG on the PDA-AgNPs-PDA-Au film, PDA-Au film, and MPA modified Au film, respectively, and the maximum resonant wavelength shifts are 4.6 nm, 9.6 nm and 11.2 nm based on the MPA modified Au film, PDA-Au film and the PDA-AgNPs-PDA-Au film respectively at 100 μg mL^{-1} antibody concentration. This confirms that the immobilization capacity of PDA-AgNPs-PDA-Au film sensing platform is higher than that of PDA-Au film and MPA modified Au film.

3.4 Determination of horse IgG

When the immobilized antibody reached saturation, we injected PBS buffer injected into the reactor to keep the baseline steady by flushing out the unbound antibody. To block the non-bonding sites, 1% BSA was injected into the flow cell. Next, a series of different concentrations of horse IgG were injected into the reactor at room temperature. Antigen-antibody interaction leads to the resonant wavelength shift. Thus, kinetic adsorption curve of binding can be determined based on the resonant wavelength change. The SPR biosensor installed in our laboratory is able to determine the minimum resonant

wavelength shift of 0.20 nm, corresponding the lowest detectable antigen concentration. As evident from Fig. 4B, for PDA-AgNPs-PDA-Au film sensing platform, the minimum resonant wavelength shift is 0.20 nm at the lowest detection concentration of horse IgG is 0.625 μg mL^{-1}, and the resonant wavelength shift further moves to 4.2 nm at 40 μg mL^{-1} horse IgG. The SPR biosensor exhibited a good response in the concentration range of 0.625 μg mL^{-1}–40 μg mL^{-1} for horse IgG. For PDA-Au film sensing platform, the minimum resonant wavelength shift is 0.20 nm at 1.25 μg mL^{-1}, and the maximum of resonant wavelength shift is 2.10 nm at 40.00 μg mL^{-1}. For MPA based biosensor, the minimum resonant wavelength shift is 0.20 nm at 2.5 μg mL^{-1}, and the maximum of resonant wavelength shift is 1.90 nm at 40.00 μg mL^{-1}. Therefore, the PDA-AgNPs-PDA-Au film sensing platform indeed performed better than other two sensor platforms (PDA-Au film sensing platform and MPA modified Au film). We can ascribe the better performance by PDA-AgNPs-PDA-Au film sensing platform to the effective antibody immobilization by PDA, while Ag nanoparticles further enhance the sensitivity of the biosensor due to electronic coupling between AgNPs leading to the amplification of the SPR response. Furthermore, we calculated the binding constant (Ka) between the antibody and antigen for PDA-AgNPs-PDA-Au film sensing platform. For 1:1 reaction of antigen (Ag) and antibody (Ab): Ag+Ab=AgAb, the binding constant K_A=[AgAb]/[Ag][Ab] (Eq. (1)). The association phase of the interaction kinetics measured

as SPR signal can be expressed as $d\Delta\lambda/dt = k_a[Ag](\Delta\lambda_{max}-\Delta\lambda)-k_d\Delta\lambda$ (Eq. (2)), where $d\Delta\lambda/dt$ is the rate of the change of SPR response, [Ag] is the concentration of antigen in the solution, k_a and k_d are association and dissociation rate constants, respectively. $\Delta\lambda_{max}$ is a constant for a special sensing membrane, which is corresponding to the maximum capacity of binding antigen on the sensor surface. $\Delta\lambda$ is the bound antigen measured as the biosensor response at time t. At equilibrium, the signal reached a plateau and $\Delta\lambda$ should be expressed as $\Delta\lambda_{eq}$, then $d\Delta\lambda_{eq}/dt=0$. According to $K_A=k_a/k_d$, Eq. (2) becomes $\Delta\lambda_{eq}/[Ag]= K_A\Delta\lambda_{max}-K_A\Delta\lambda_{eq}$. A plot of $\Delta\lambda_{eq}/[Ag]$ against $\Delta\lambda_{eq}$ can be used to obtain K_A from the slope of the plot. Here the binding constant of horse IgG with antibody is 2.93×10^7 L mol^{-1} based on proposed biosensor.

To evaluate the specificity, we challenged the SPR biosensor with mouse IgG and human IgG. Rabbit anti-horse IgG was first immobilized on the surface of the biosensor until it reached saturation, and then mouse IgG and human IgG (10.00 μg mL^{-1}) were separately injected into the flow cell for 40 min. Figure 5 shows no observable shifts of the resonant wavelength for mouse IgG and human IgG, indicating selective binding of horse IgG.

3.5 Analysis of real samples

To evaluate applicability, we challenged PDA-AgNPs-PDA-Au film biosensor with

chicken serum samples spiked with 5 μg mL^{-1}, 10 μg mL^{-1}, and 20 μg mL^{-1} of horse IgG. The PBS solutions containing the same spiked levels of horse IgG were also analyzed using the PDA-AgNPs-PDA-Au film biosensor in the same way. The obtained sensorgrams for real samples are exhibited in Figure 7A. Table 1 shows acceptable recoveries, suggesting the potential of our PDA-AgNPs-PDA-Au film in determining horse IgG in real serum samples.

3.6 Study of stability and regeneration

To investigate the stability, anti-horse IgG was immobilized onto the surface of the PDA-AgNPs-PDA-Au film sensing platform and stored for two weeks. Figure 6A reveals that the SPR biosensor detects 20 μg mL^{-1} horse IgG even after storing for one to two weeks, and the relative decrease in the resonance wavelength shifts is in the range of ±20% only.

Furthermore, we examined the regeneration for recycling of gold films after performing a series of antibody-antigen binding assays and found that the relative resonant wavelength shifts were lower than ±10% for five-cycles of regeneration (Fig. 6B). In addition, a sensorgram that shows the regeneration of the reused Au film for five times is provided in Figure 7B. Although the resonant peak becomes wider, the resonant wavelength turns back to be the original position, revealing the success of regeneration.

Therefore, the PDA-AgNPs-PDA-Au film sensing platform immobilized with antibody is stable and regenerative.

4 Conclusions

This study proposes a stable PDA-AgNPs-PDA-Au film based SPR biosensor, constructed via layer-by-layer assembly for horse IgG detection. We used non-toxic polydopamine, instead of conventional chemical reagents, for more effective immobilization of antibody onto the sensing platform. AgNPs were used as signal-enhancing label, and antibody was immobilized via Schiff alkali reaction directly. The new PDA-AgNPs-PDA-Au film based SPR biosensor exhibited 4-fold and 2-fold lower detection limit compared with that of the PDA modified Au film based biosensor and MPA based conventional SPR biosensor, respectively. Furthermore, when challenged with chicken serum samples spiked with horse IgG, the sensor exhibited acceptable recoveries. The new sensor is remarkably stable and regenerative. The findings of this study show potential of this new SPR biosensor to be used for practical purposes. However, further investigation is required to build sensor chip based on this new sensor for industrial application.

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Figure Captions

Fig. 1 Schematic diagram of experimental procedure. PDA-AgNPs-PDA-Au sensor platform (a) MPA modified Au film(b).

Fig. 2 Scanning electron microscope (SEM) images of Au film (a), PDA modified Au film (b), PDA-AgNPs modified Au film (c), and PDA-AgNPs-PDA modified Au film (d).

Fig. 3 The SPR spectra for anti-horse IgG immobilization onto PDA-AgNPs-PDA-Au film at 0 min (—),40 min (—) and 120 min (—) for concentrations of 50 μg mL^{-1} (a),75 μg mL^{-1} (b), and 100 μg mL^{-1} (c).

Fig. 4 The kinetic adsorption curves of immobilizing rabbit anti-horse IgG with the concentration of 100 μg mL^{-1} (A) and the relationships between the shifts of the resonant wavelength and concentrations of horse IgG (B) based on MPA-Au film (a), PDA-Au film (b) and PDA-AgNPs-PDA-Au film (c).

Fig. 5 The shifts of resonant wavelength measured with different antigens in different assays.

Fig. 6 The stability of the anti-horse IgG immobilized on PDA-AgNPs-PDA-Au film sensor platform (A) and the repeatability test of PDA-AgNPs-PDA-Au film sensor platform and relative detection response (B).

Fig. 7 The sensorgrams of detecting real samples (A) and regeneration of the reused Au

film for five times.

Table

Table 1. Analytical results of horse IgG in chicken serum.

Content of horse IgG ($\mu g\ mL^{-1}$)	Spiked ($\mu g\ mL^{-1}$)	Shifts in PBS (nm)	Shifts in serum (nm)	Recovery (%)
None	5	1.4	1.5	107.1
None	10	1.8	2.0	111.1
None	20	2.4	2.6	108.3

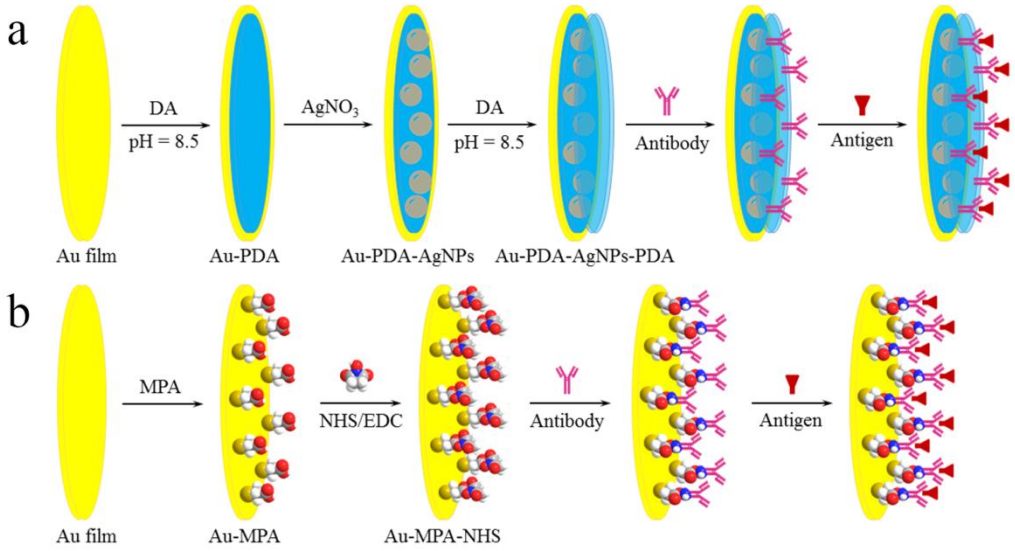
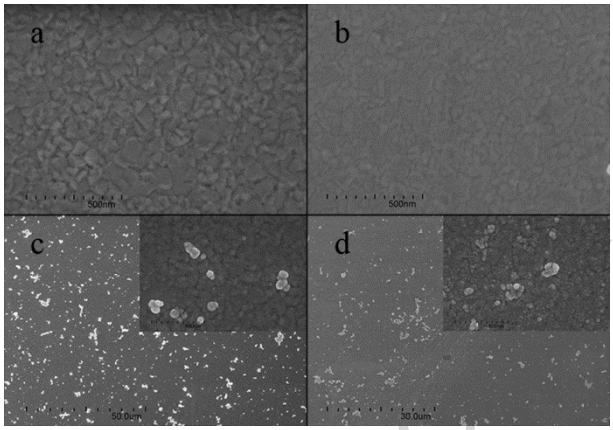


Fig. 1



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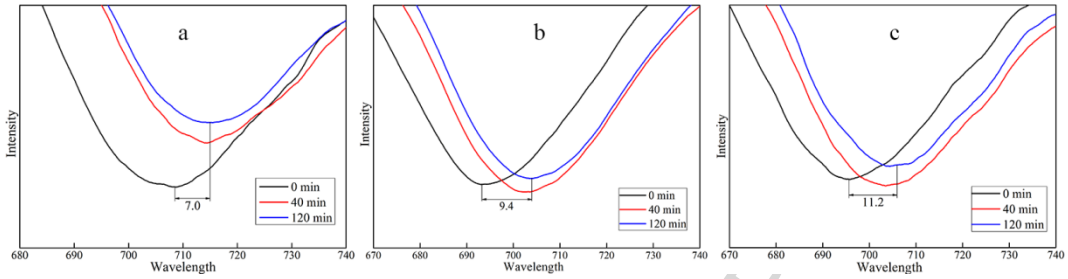

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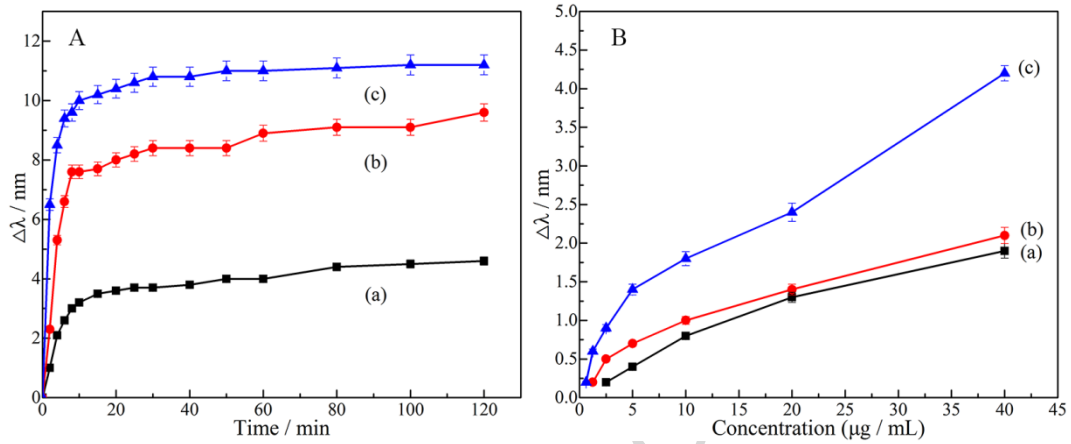

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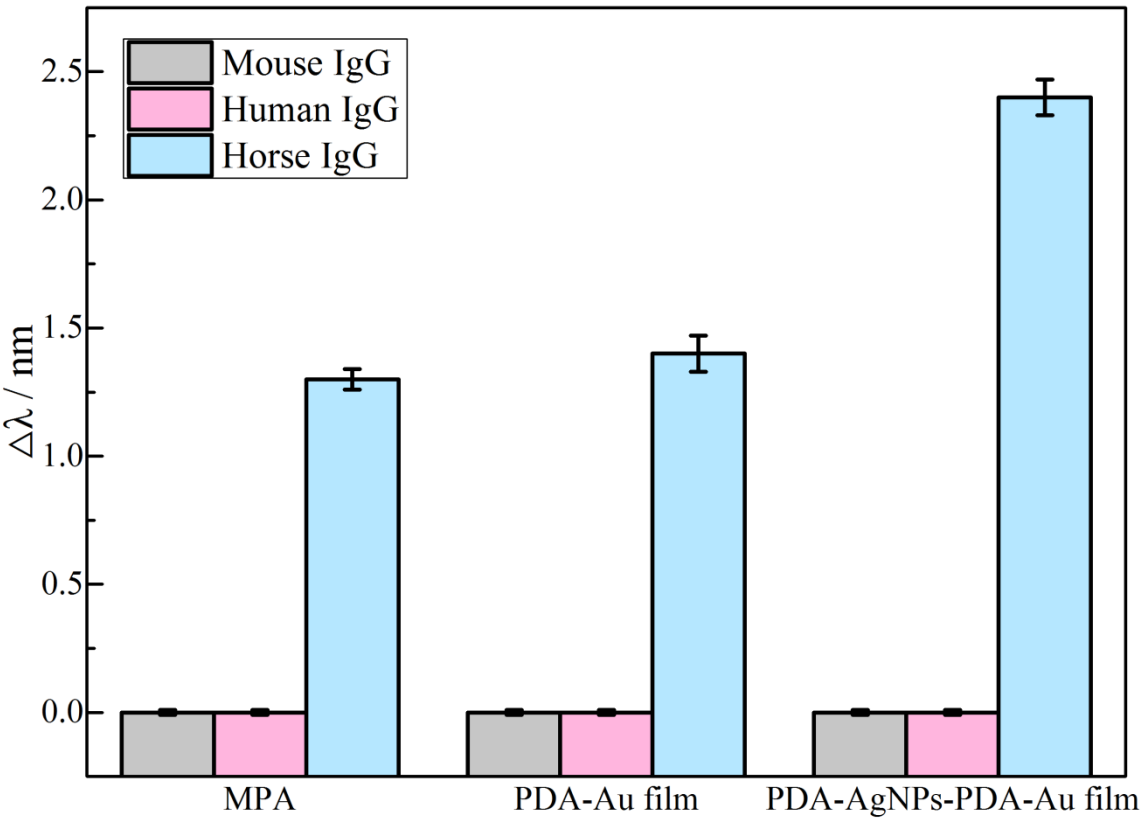
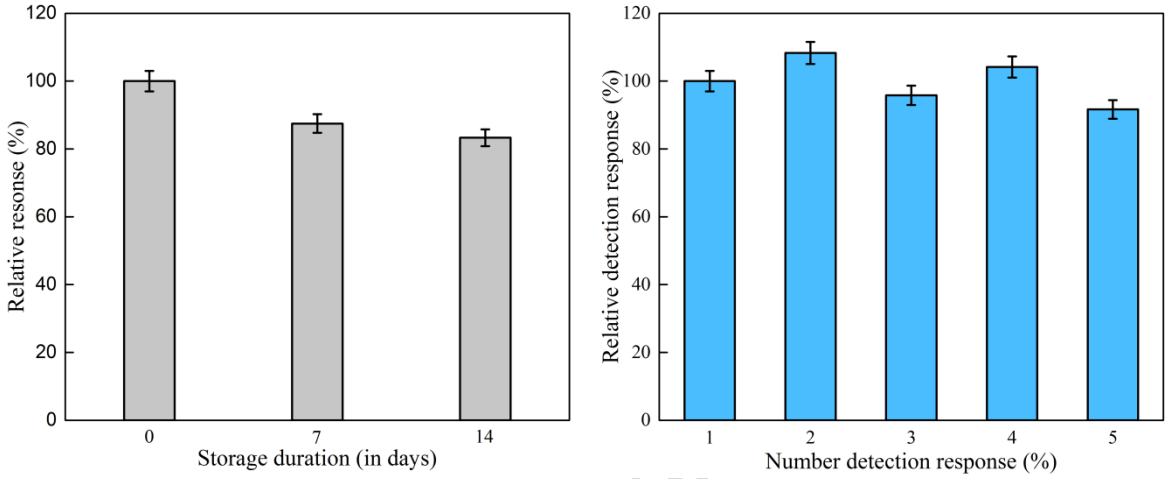


Fig. 5



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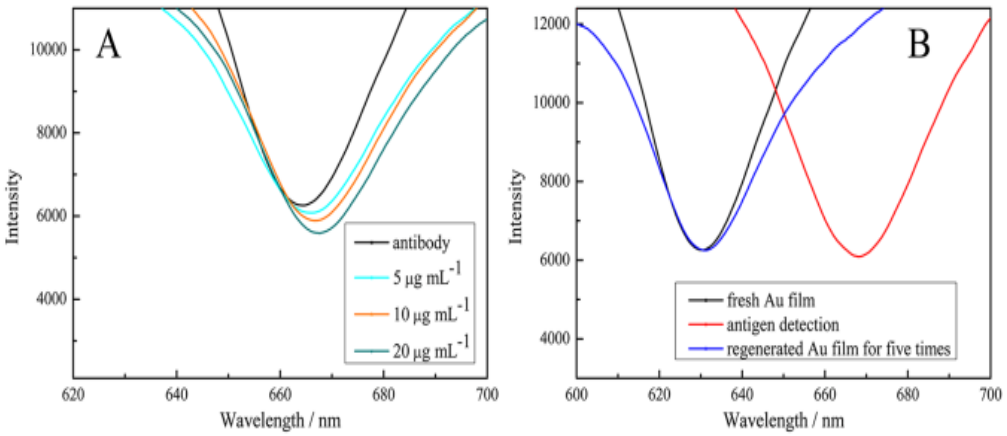
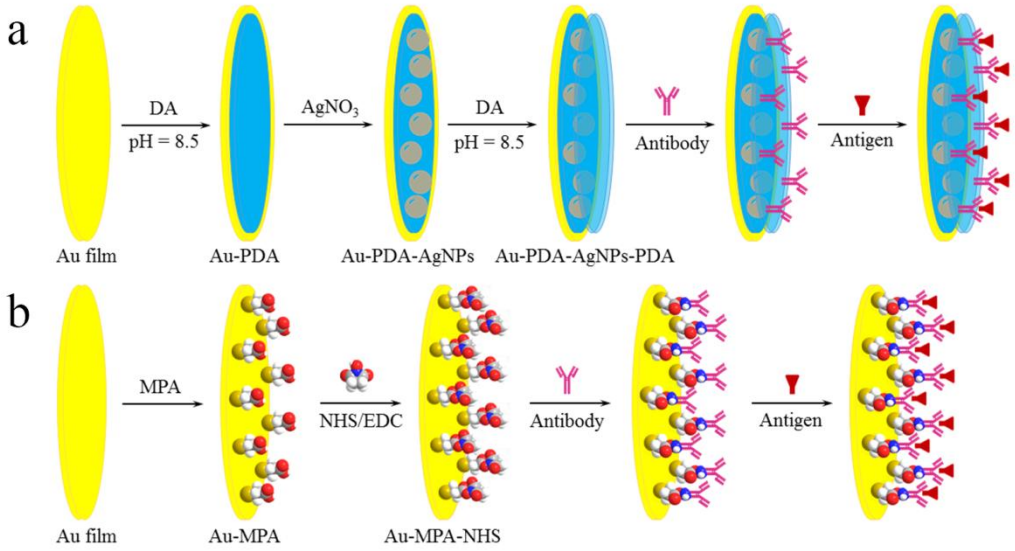


Fig. 7



Graphical abstract

Highlights:

1. A novel sensor platform was constructed via the layer-by-layer self-assembly.
2. The antibody was immobilized on the sensing platform more effectively by using non-toxic polydopamine instead of conventional chemical reagents.
3. Polydopamine was connected with the antibody via Schiff alkali reaction directly, which simplified the process of antibody immobilization.
4. The detection limit decreased by constructing the PDA-AgNPs-PDA-Au film sensing platform.