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Sensitivity enhancement of SPR biosensor with silver mirror reaction on the Ag/Au film

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ABSTRACT

Based on well-known silver mirror reaction the Ag film was formed on Au film modified by self-assembled monolayer (SAM) of 1,6-hexanedithiol (HDT). The sensitivity of the biosensor based on this Ag/Au film is enhanced compared to that based on Au film. When the surface plasmon resonance (SPR) biosensor based on this Ag/Au film was used to determine human IgG, the range of concentrations of human IgG that could be determined is 0.30–40.00 $\mu g\,mL^{-1}$. The lowest concentration (0.30 $\mu g\,mL^{-1}$) that could be detected was about 8 times lower than that obtained by the biosensor without modification by Ag film (2.50 $\mu g\,mL^{-1}$), which demonstrated that the biosensor based on Ag/Au film could make the resonant wavelength move to longer wavelength following with the sensitivity enhancement of the SPR biosensor.

1. Introduction

In recent years, sensors based on surface plasmon resonance (SPR) have become more and more important in studying molecular interactions [1]. SPR uses light of defined wavelength [2], angle of incidence [3], and polarity [4] on an Au-coated sensor chip to measure changes in refractive index on the opposite side of the Au film. The most important characteristics of SPR sensor are its versatility and capability in real time monitoring the association or dissociation of biomolecules on the surface of the sensor without the need for fluorescence or labeling of the biomolecules [5]. These characteristics made the SPR technique an easy, convenient and reliable one for determining the concentration and molecular weight, monitoring change in structure, measuring kinetic constant and binding specificity of individual biomolecules. SPR sensors are especially suitable for the determination of interactions between biological molecules [6]. The sensor chip surface is usually coated with a thin hydrogel matrix or sulfhydryl compound bearing covalently immobilized receptor molecules such as antibody for specific analyte capture. Complex formation with ligands such as antigen leads to a change in the refractive index, which can be monitored in real time. Great progress has been made in the field of SPR for the determination of antibody, antigen [7–10], enzymes [11], receptors [12], growth factors [13], glycoproteins [14], nucleic acids [15,16] and drugs [17].

With the development of life science, there is a growing requirement for higher sensitive detection technologies in analysis and the detection of biological samples with low concentration and molecular weight has attached more and more importance. So the studies of sensitivity enhancement of SPR biosensor have also been developed and various measurement formats have been adopted for SPR biosensor [5]. Over the years, colloidal Au and sandwich assay are the techniques most commonly applied for enhancing the sensitivity of wavelength modulation SPR biosensor [18–20]. Other methods also have been used to the sensitivity enhancement of SPR biosensor, such as the use of dispersion from a dye [21], long range surface plasmon resonance (LRSPR) [22], inhibition assay [23], surface functionalization for self-referencing [24], and the use of thin films of titanium dioxide [25]. Based on the theoretical analysis, sensitivity of wavelength modulation SPR biosensor is enhanced with the shift of resonant wavelength towards longer wavelength [5]. In our previous work [26], the sensitivity enhancement of SPR biosensor was also performed by changing baseline solution. In addition, SPR sensor based on wavelength modulation may benefit from the use of Ag [5]. Ag film is ideal for surface plasmon generation, since the behavior of the dielectric constant near the Fröhlich frequency gives rise to an intense absorption in the visible region of the spectrum [28]. In the present paper, we focus on the development of approach to enhance the sensitivity of SPR biosensor by using silver mirror reaction method [27,28] to deposit the Ag film on Au film.

SPR refers to the optical excitation of surface plasmons or charge-density waves at the interface between a conductor and a dielectric. The conductor is a metal that has a high free-electron

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density to support the charge-density waves. Au and Ag are the ideal candidates as metal films in the visible light region. Ag film produces a sharper peak than Au and shows better sensitivity, which could be used to enhance the biosensor sensitivity [29]. The Au film was well stability, strong adhesion with the glass and no reaction with the inorganic ions in the reaction system. As a result, Au film can be used as the substrate due to its stability in the SPR biological systems. In the paper, silver mirror reaction was used to deposit the Ag film on Au substrate film. In order to avoid Ag film falling off from the Au substrate film as weak adhesion, 1,6-hexanedithiol (HDT) was used to modify the Au film, and then thin Ag film was formed on this film by silver mirror reaction. Subsequently, 3-mercaptopropionic acid (MPA) was used to connect Ag film with biological components. In this method, Ag film could be existed stably between HDT and MPA, and this could cause a large shift of the resonant wavelength. The sensitivity of SPR sensor could be enhanced with the shift of resonant wavelength towards longer wavelength. Meanwhile, Ag film gains a more distinct SPR spectrum than Au film and generates a high field enhancement.

2. Experimental

2.1. Reagents

Human IgG and rabbit anti-human IgG were purchased from Beijing Biosynthesis Biotechnology Company. 3-Mercaptopropionic acid was purchased from Sigma. 1,6-hexanedithiol was purchased from Jkchemical. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS) were purchased from Pierce. Silver nitrate, glucose, ammonia water, sodium hydroxide and all other chemicals were of analytical reagent grade. All solutions were prepared with ultrapure water. Human IgG and rabbit anti-human IgG were stored at −20 °C, and all other biological reagents were stored at 4 °C. PBS buffer (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. It is working with Kretschmann configuration to achieve the resonant condition by attenuated total reflection (ATR) in a prism. A K9 glass slide was used whose diameter and thickness were 12 and 0.7 mm, respectively. A 2 nm adhesive layer of Cr followed by a 50 nm layer of Au was deposited on the glass slide, then the 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 in conjunction with a constant voltage transformer. The light from this source 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 analyte. The output light is guided into the optical fiber and then enters the full wave spectrophotometer (Ocean Optics, Inc., USA). A 2048 element charge-coupled device (CCD) linear array detector was used as the detector. A 100 μL volume flow cell was used. The interaction between the analyte in the solution and the biomolecular element immobilized on the SPR biosensor produces a change in refractive index (RI) profile that is observed as a shift in the SPR resonant wavelength. The surface plasmon resonance manifests itself on a characteristic dip in the wavelength dependence on the intensity of reflected light and the intensity of reflected light is minimum value at the resonant wavelength. A schematic diagram of a typical multilayer SPR device is shown in Fig. 1. Here, two kinds of sensing membranes were used. The sensing membrane based on Au film consists of Au film, MPA layer and antibody layer, and that based on Ag/Au film consists of Au film, HDT layer, Ag film, MPA layer and antibody layer.

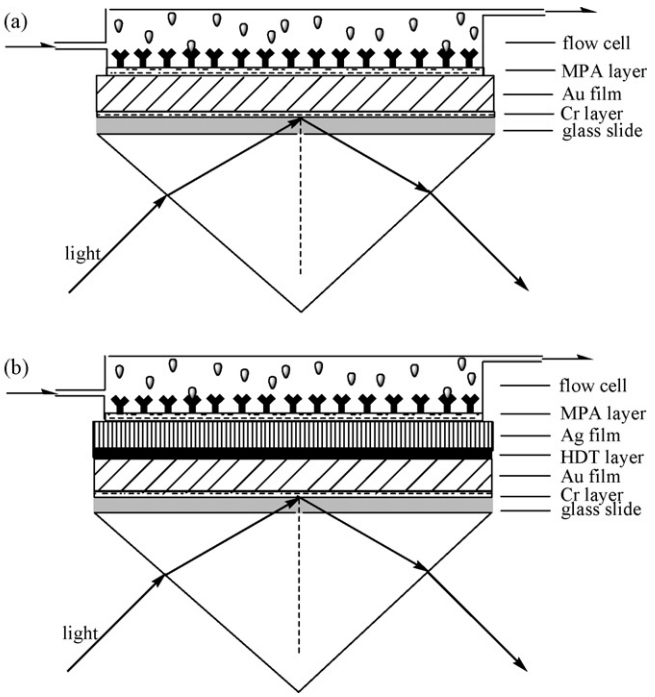

Fig. 1. Schematic diagram of the SPR sensor based on Au film (a) and Ag/Au film (b). (Y) Antibody, (O) antigen.

2.3. Procedures

2.3.1. SPR biosensor based on Au film

The glass slide with Au film was first rinsed with ethanol and deionized water respectively. Then glass slide was fixed under the flow cell (Fig. 1a). Deionized water was injected into the flow cell. After the resonant wavelength kept constant, 10 mmol L^{-1} MPA was injected into the flow cell for 6 h. Then PBS was injected into the flow cell as the baseline solution. After –COOH group was activated with NHS under the catalysis of EDC for 20 min, rabbit anti-human IgG (50 μg mL^{-1}) was injected into the flow cell for 12 h to organize the processing antibody on the sensing membrane and thus the biosensor membrane was stable. Then, 1 mol L^{-1} ethanolamine hydrochloride (pH 8.5) was used to block the non-specific binding sites on the biosensor surface for 10 min. Finally, at room temperature, different concentrations of human IgG diluted with PBS buffer were separately injected into the flow cell over the immobilized antibody surface prepared and shifts of the resonant wavelength ($\Delta\lambda$) were measured as time prolonged. After 40 min, PBS buffer was injected over the surface to monitor the dissociation of antigen from antibody for 30 min. When the antigen was completely dissociated from the antibody surface, another sample containing human IgG at different concentration was injected into the flow cell.

2.3.2. SPR biosensor based on Ag/Au film

The glass slide with Au film was first cleaned with ethanol and deionized water respectively. Then, the glass slide was immerged into ethanol solution containing the HDT at the concentration of 12.5 mmol L^{-1} for 24 h. Au film was rinsed several times with ethanol and deionized water, and dried with gaseous nitrogen.

After the immobilization of HDT, a thin Ag film was formed on the modified Au film by means of the silver mirror reaction. The concentration of $AgNO_3$ is an important factor affecting

the thickness of Ag film. The different concentrations of $AgNO_3$ (0.2%; 0.4%; 0.6%; 0.8%; w/w) were used to prepare Ag film on Au film. 55 μL 5% NaOH solution was added into 3 mL $AgNO_3$ aqueous solution until a fine brown precipitate of Ag_2O was formed. Then 6% ammonia solution was added into this mixture drop by drop until the precipitate was completely dissolved to form $[Ag(NH_3)_2]^+$. Then 6% $AgNO_3$ solution was added until the solution became pale brown/yellow. After 1 drop of 6% ammonia water was added, the solution became transparent again. This $[Ag(NH_3)_2]^+$ solution was mixed with 1 mL 35% glucose solution and 0.5 mL methanol. Then the solution went black. The glass slide with the modified Au film was immersed in this solution and left for approximately 1 h under 35 °C. After that, the glass slide was ultrasonically cleaned with distilled water for 60 s and immerged in PBS buffer for 10 min, then ultrasonically cleaned again for 30 s. Finally, the glass slide was rinsed with distilled water and dried with gaseous nitrogen.

After the glass slide with modified Au film was fixed under the flow cell (Fig. 1b), deionized water was first injected into the flow cell. Then, 10 mmol L^{-1} MPA was injected into the flow cell for 6 h. The next procedures were the same as that mentioned above.

2.3.3. Regeneration

When the immunoassay was finished, the prism was taken away from the flow cell. The glass slide was ultrasonically cleaned with ethanol and distilled water respectively, then dried with gaseous nitrogen. The Au film could be used repeatedly. All measurements using this system were carried out at room temperature under atmospheric pressure.

3. Results and discussion

3.1. Preparation of Ag/Au film

Au and Ag are the most widely used metals for the SPR experiments [5]. At the wavelength of 632.8 nm, the dielectric constant ($\varepsilon = \varepsilon_r + \varepsilon_i$, where ε_r and ε_i are the real and the imaginary part of dielectric constant respectively) of Au is $-10.92 + 1.49i$ and Ag is $-18.22 + 0.48i$. The response curve of SPR is very sensitive to ε_r and ε_i, because they account for reflection and absorption of light in the metal, respectively [29]. The sharpest peak is produced by the metal whose dielectric constant has the highest $|\varepsilon_r/\varepsilon_i|$ ratio ($|\varepsilon_r/\varepsilon_i|$ for Ag is 38.0 and $|\varepsilon_r/\varepsilon_i|$ for Au is 7.33) [30–32]. Compared with Au, Ag has higher $|\varepsilon_r/\varepsilon_i|$ ratio and shows better sensitivity. Ag film could be used to enhance the sensitivity of the biosensor, while Au film can be used as the substrate due to its stability in the SPR biological systems.

The Ag film formed on Au substrate film without the modification by HDT is easy to be destroyed, so HDT layer was constructed on the Au film. The glass slide with Au film was immerged in HDT ethanol solution for 24 h and a monolayer of HDT was formed on the Au surface. As HDT is a disulfide compound, one of sulfhydryl groups is connected with Au and the other can be connected with Ag. After the immobilization of HDT on the Au film, the Ag film could be formed on the modified Au film by means of the silver mirror reaction. The thickness of Ag film produced by the silver mirror reaction is related to the concentration of $AgNO_3$ in solution. As the increase of concentration of $AgNO_3$ from 0.2% to 0.8%, the thickness of Ag films was changed from 10 to 15 nm, which were measured by Dektak 150 Surface Profiler. This indicates that the thickness of Ag/Au film is 60–65 nm. From a series of experiments, it was found that the thickness of Ag/Au film in 60–65 nm has the almost same effect on the sensitivity of SPR biosensor. In this paper, 0.4% $AgNO_3$ was chosen for preparing the Ag film by the silver mirror reaction.

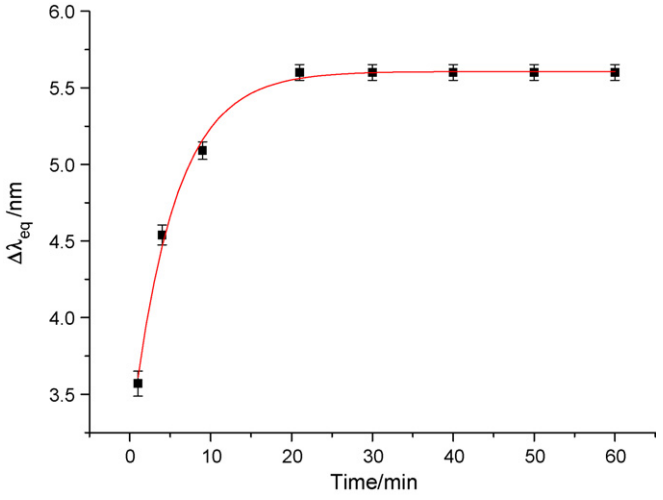

Fig. 2. Kinetic adsorption curve of MPA on the sensor surface based on Au film.

After the silver mirror reaction on the Au film, the glass slide with modified Au film was fixed under the flow cell. When the water was injected into the flow cell, a red-shift of the resonant wavelength for the sensor based on Ag/Au film could be seen. The shift of resonant wavelength was 21.89 nm compared to the sensor based on Au film. This is due to the change of the thickness of the SPR biosensor film and the interparticle interactions in the Ag/Au film. In wavelength modulation SPR biosensor, the shift of resonant wavelength towards long wavelength could increase the sensitivity of the sensor [5].

3.2. Preparation of the MPA self-assembled monolayer

The formation of monolayer is driven by a strong, specific interaction between the thiol and the metal surface. Due to the strong affinity, the traditional method of antibody immobilization was performed by sulfhydryl compounds [33]. In the biosensor based on Au film, the adsorption curve of MPA by self-assemble on the Au film is shown in Fig. 2. It can be seen clearly that the shift of the resonant wavelength reached about 80% of its total shift within 20 min and after 6 h the maximum shift of the resonant wavelength for the formation of this monolayer is 7.13 nm. These results indicate that the MPA monolayer was formed well.

For the biosensor based on Ag/Au film, HDT can effectively connect Au and Ag film and the stable molecular self-assembled layer can be formed. After the modified Au film was fixed under the cell flow, MPA was injected into the flow cell for 6 h. Then the biosensor surface was rinsed with water to remove unbound MPA. The adsorption curve of MPA at the Ag film is shown in Fig. 3. It can be seen clearly that the shift of the resonant wavelength reached about 75% of its total shift within 1 h. After 6 h, the maximum shift of resonant wavelength for the formation of this monolayer is 49.78 nm. This experimental result indicated that a good monolayer membrane of MPA was formed.

For the biosensor based on Ag/Au film, the immobilization of MPA on the Au film was fast while the shift of the resonant wavelength was not significant. Compared with Au film, the rate of immobilization of MPA on Ag film was slower and the shift of the resonant wavelength was more significant. These results are in agreement with the theory that the sensitivity of SPR biosensor based on Ag film is much higher than that based on Au film and the sensitivity of the sensor increases with the shift of resonant wavelength towards longer wavelength in wavelength modulation SPR biosensor [34].

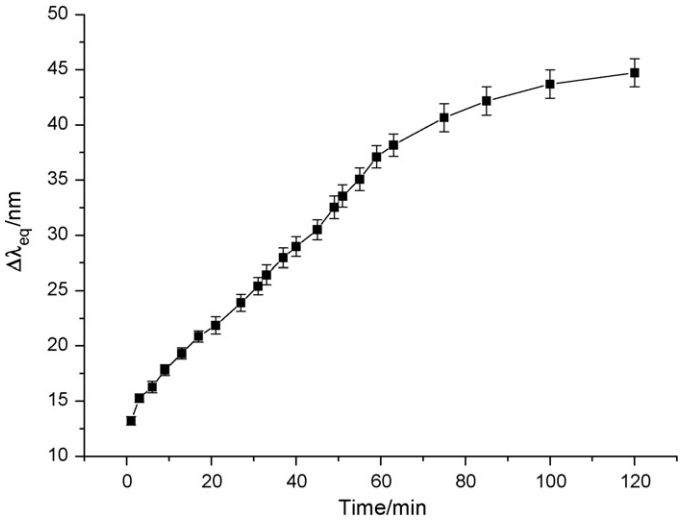

Fig. 3. Kinetic adsorption curve of MPA on the sensor surface based on Ag/Au film.

3.3. Immobilization of rabbit anti-human IgG

After –COOH group reacted with NHS under the catalysis of EDC for 20 min, the rabbit anti-human IgG diluted with PBS buffer at the concentration of 50 μg mL^{-1} was injected into the flow cell to perform its binding on the activated surface. The assembling curve of antibody on surface of sensor based on Au film is shown in Fig. 4. It can be seen that rabbit anti-human IgG sensing membrane formed well within 1 h. The maximum resonant wavelength shift for the immobilization of rabbit anti-human IgG is 11.19 nm. The assembling curve of antibody on surface of sensor based on Ag/Au film is also shown in Fig. 4. It can be seen that the shift of the resonant wavelength is fast at first and then slow and the sensor response seems to increase steadily within 1 h. Rabbit anti-human IgG sensing membrane also formed well on the sensing film within 1 h and the maximum resonant wavelength shift for immobilization of rabbit anti-human IgG is 14.19 nm.

For the immobilization of antibody, the shifts of resonant wavelength are 12.21 and 20.27 nm for the sensor based on Au film and Ag/Au film after 12 h, respectively. When PBS buffer was injected into the flow cell, almost no change was observed. These results indicated that the surface prepared with MPA is a strong response to antibody and antibody was bound steadily on the biosensor surface. Then, 1 mol L^{-1} ethanolamine hydrochloride (pH 8.5) was used to block the non-specific binding sites on the biosensor surface. The shifts of resonant wavelength for constructing sensing membrane are shown in Table 1. It can be seen from Table 1 that compared with the sensor based on Au film, the total shift of the resonant wavelength based on Ag/Au film was 72.60 nm after rabbit anti-human IgG was bound on the biosensor surface.

Table 1
The shifts of resonant wavelength for constructing sensing membrane.

Sensing layer	Sensor based on Au film $\Delta\lambda_1$ (nm)	Sensor based on Ag/Au film $\Delta\lambda_2$ (nm)
Ag film	0	21.89 ± 1.02
MPA	7.13 ± 0.25	49.78 ± 1.28
Rabbit anti-human IgG	12.21 ± 0.51	20.27 ± 0.51

3.4. Determination of human IgG

At room temperature, after the rabbit anti-human IgG was immobilized on the surface of the biosensor, human IgG at different concentrations was separately injected into the flow cell. The shifts of resonant wavelength due to antibody–antigen immunoreaction were measured. The monitoring of SPR response of the adsorption and the dissociation of human IgG can be carried out in real time. The SPR biosensor based on Au film shows a good response to human IgG in the concentration range 2.50–40.00 μg mL^{-1}. The minimum shift of resonant wavelength is 0.51 nm at 2.50 μg mL^{-1} and the maximum shift of resonant wavelength is 3.80 nm at 40.00 μg mL^{-1}. The SPR biosensor based on Ag/Au film shows a good response to human IgG in the concentration range 0.30–40.00 μg mL^{-1}. The minimum shift of resonant wavelength is 0.51 nm at 0.30 μg mL^{-1} and the maximum shift of resonant wavelength is 6.09 nm at 40.00 μg mL^{-1}. The lowest concentration determined by the sensor based on Ag/Au film is about 8-fold lower than that obtained by the sensor based on Au film. Fig. 5 shows the relationship between the shift in the resonant wavelength and the concentrations of human IgG. When the Ag/Au film was used, the thickness of the sensing membrane increased. This caused the resonant wavelength to move to longer wavelength, which enhances the sensitivity of the biosensor. On the other hand, when a thin film of Ag was deposited on Au substrate film, the Ag film can change the SPR features of the substrate and has its own localized surface plasmon due to the collective oscillations of its conduction electrons. So, the coupling of the localized surface plas-

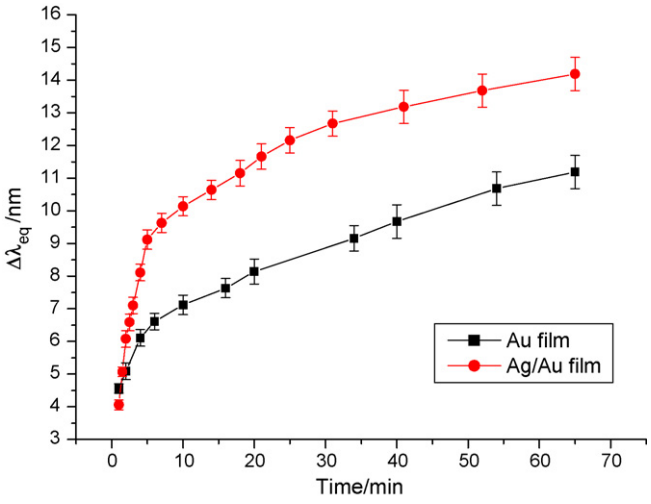

Fig. 4. Kinetic assembling curves of rabbit anti-human IgG on the MPA monolayer.

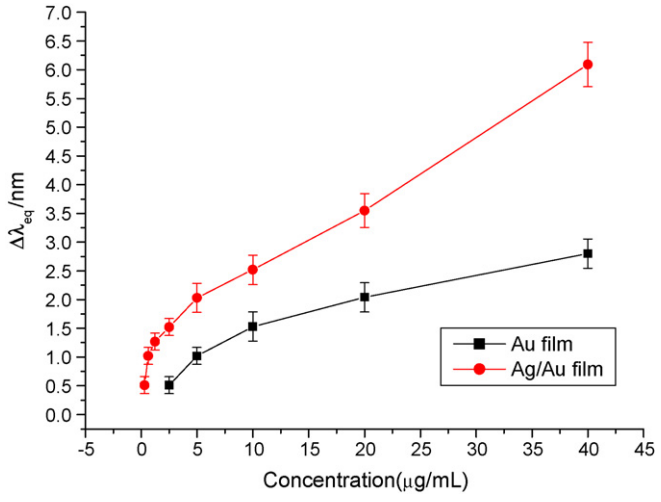

Fig. 5. The relationship between the concentration of human IgG and the shift in the resonant wavelength $\Delta\lambda_{eq}$.

mon of the Ag film with the propagating plasmon in the Au film could enhance the sensitivity of the SPR biosensor [35]. Due to the two factors, the limit of determination for human IgG obtained by the biosensor based on Ag/Au film was about eight times lower than that obtained by the biosensor based on Au film alone.

4. Conclusion

The sensitivity enhancement of SPR biosensor by Ag/Au film is presented. Self-assembled monolayer (SAM) of HDT was formed on the Au film and a well-known experiment as the silver mirror reaction was used to form thin Ag film. By using Ag/Au film, SPR biosensor gains a more distinct SPR spectrum than that obtained with bare Au film, which makes the resonant wavelength of the SPR spectrum move to the longer wavelength. The biosensor based on Ag/Au film, was therefore found to be more sensitive. The limit of determination with sensor based on Ag/Au film is about eight times lower than that obtained with the sensor based on Au film alone.

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References

[1] X. Liu, D.Q. Song, Q.L. Zhang, Y. Tian, L. Ding, H.Q. Zhang, Trends Anal. Chem. 24 (2005) 10.
[2] B. Liedberg, I. Lundström, E. Stenberg, Sens. Actuators B 11 (1993) 63.
[3] R.C. Jorgenson, S.S. Yee, Sens. Actuators B 12 (1993) 213.
[4] A.A. Kruchinin, Y.G. Vlasov, Sens. Actuators B 30 (1996) 77.
[5] J. Homola, S.S. Yee, G. Gauglitz, Sens. Actuators B 54 (1999) 3.
[6] B. Liedberg, C. Nylander, I. Lundstrom, Biosens. Bioelectron. 10 (1995) 1.
[7] W. Lee, B.K. Oh, W.H. Lee, J.W. Choi, Colloids Surf. B 40 (2005) 143.
[8] X. Liu, Y. Sun, D.Q. Song, Q.L. Zhang, Y. Tian, H.Q. Zhang, Talanta 68 (2006) 1026.
[9] S. Toyama, A. Shoji, Y. Yoshida, S. Yamauchi, Y. Ikariyama, Sens. Actuators B 52 (1998) 65.
[10] X. Liu, D.Q. Song, Q.L. Zhang, Y. Tian, H.Q. Zhang, Talanta 62 (2004) 773.
[11] E. Fujii, T. Koike, K. Nakamura, S. Sasaki, K. Kurihara, D. Citterio, Y. Iwasaki, O. Niwa, K. Suzuki, Anal. Chem. 74 (2002) 6106.
[12] B. Hock, M. Seifert, K. Kramer, Biosens. Bioelectron. 17 (2002) 239.
[13] M. Wong, C. Fong, M. Yang, Biochim. Biophys. Acta 1432 (1999) 293.
[14] C. Bertucci, S. Cimitan, L. Menotti, J. Pharm. Biomed. Anal. 32 (2003) 697.
[15] M. Minunni, S. Tombelli, M. Mascini, A. Bilia, Talanta 65 (2005) 578.
[16] J.L. Wang, F. Wang, Z.A. Xu, Y.Z. Wang, S.J. Dong, Talanta 74 (2007) 104.
[17] R.L. Rich, Y.S.N. Day, T.A. Morton, D.G. Myszka, Anal. Biochem. 296 (2001) 197.
[18] X. Liu, Y. Sun, D.Q. Song, Q.L. Zhang, Y. Tian, S.Y. Bi, H.Q. Zhang, Anal. Biochem. 333 (2004) 99.
[19] F. Wang, J.L. Wang, X.Q. Liu, S.J. Dong, Talanta 77 (2008) 628.
[20] Y. Li, J. Ren, H. Nakajima, B.K. Kim, N. Soh, K. Nakano, T. Imato, Talanta 77 (2008) 473.
[21] A. Hanning, J. Roeraade, J.J. Delrow, R.C. Jorgenson, Sens. Actuators B 54 (1999) 25.
[22] G.G. Nenninger, P. Tobiška, J. Homola, S.S. Yee, Sens. Actuators B 74 (2001) 145.
[23] K.V. Gobi, M. Sasaki, Y. Shoyama, N. Miura, Sens. Actuators B 89 (2003) 137.
[24] M.G. Manera, G. Leo, M.L. Curri, P.D. Cozzoli, R. Rella, P. Siciliano, A. Agostiano, L. Vasanelli, Sens. Actuators B 100 (2004) 75.
[25] C. Boozer, Q.M. Yu, S.F. Chen, C.Y. Lee, J. Homola, S.S. Yee, S.Y. Jiang, Sens. Actuators B 90 (2003) 22.
[26] Y. Sun, X. Liu, D.Q. Song, Y. Tian, S.Y. Bi, H.Q. Zhang, Anal. Chim. Acta 569 (2006) 21.
[27] Y. Saito, J.J. Wang, D.A. Smith, D.N. Batchelder, Langmuir 18 (2002) 2959.
[28] Y. Saito, J.J. Wang, D.N. Batchelder, D.A. Smith, Langmuir 19 (2003) 6857.
[29] M. Mitsushio, K. Miyashita, M. Higo, Sens. Actuators A 125 (2006) 296.
[30] W.H. Weber, S.L. McCarthy, Phys. Rev. B 12 (1975) 5643.
[31] R.D. Olney, R.J. Romagnoli, Appl. Opt. 26 (1987) 2279.
[32] J.W. Sadowski, J. Lekkala, I. Vikholm, Biosens. Bioelectron. 6 (1991) 439.
[33] T.Y.B. Leung, M.C. Gerstenberg, D.J. Lavrich, G. Scoles, F. Schreiber, G.E. Poirier, Langmuir 16 (2000) 549.
[34] J. Homola, Sens. Actuators B 41 (1997) 207.
[35] L.A. Lyon, M.D. Musick, M.J. Natan, Anal. Chem. 70 (1998) 5177.