Research Article

High-Sensitivity Biosensor-Based Enhanced SPR by ZnO/MoS2 Nanowires Array Layer with Graphene Oxide Nanosheet

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A novel SPR biosensor that can achieve a high sensitivity is proposed; therefore, a new prism coupling structure based on metal nanowires array layer is designed in this paper. The thickness of each medium layer for the structure is analyzed to obtain the optimal SPR spectrum, by the finite element method, so that the sensitivity is able to be enhanced greatly. The optimal thicknesses of each medium layer are given, and the sensitivity of the SPR biosensor can reach as high as 210.75°/RIU for the refractive index of the sensing medium, from 1.30 to 1.38.

1. Introduction

Surface plasmon resonance (SPR) is the resonance for free electrons with collective oscillations in the metal surface when excited by the incident light, and the energy of the incident light would be absorbed by free electrons during the resonance, so that the energy of the output light would be decreased to some extent [1–3]. The decreasing degree of the output light is related to the incident light, and the SPR angle is the incident light as the output light is decreased to the minimum. SPR can be excited in a variety of ways, such as prism coupling, grating coupling, and optical fiber coupling, and SPR has been extensively used in sensing of various physical, chemical, and biochemical parameters [4–6].

The surface plasmon resonance biosensor (SPR biosensor) has a remarkable capability of real-time detection and monitoring of biomolecule [7–9]. There are various factors that significantly affect the function of the SPR biosensor, which are needed to be considered for designing a stable and highly sensitive SPR biosensor. The two features, the high detection sensitivity and the good SPR peak for better precision, are critical to the function implementation of the SPR biosensor as well as its application. The SPR biosensor has been studied during the past thirty years [8,9]. There are many studies on the sensitivity of the SPR biosensor before, such as transition metal dichalcogenides (TMDC) materials [10], magneto-optic (MO) material layer [11], magneto-plasmonic (MP) transducers [12], graphene [13,14], graphene-MoS2 hybrid nanostructures [15], and graphene and silicon layers [16]. However, a new prism coupling structure with the TiO2-ZnO layer and MoS2-graphene oxide (GO) was present. Based on this, a novel SPR biosensor capability of achieving a higher sensitivity was proposed in this paper which can provide a further theoretical preparation for making the SPR biosensor detecting instrument in the future.

2. Design Consideration and Theoretical Model

2.1. Design Consideration. In this paper, there are various nanosheets considered to be added into the structure, in order to enhance the sensitivity of the SPR biosensor. MoS2 has high optical absorption and there exists direct bandgap (1.8 eV) for the monolayer MoS2 [17]. Graphene oxide (GO) has several advantages because of its extraordinary optical and structural properties, and it was studied that there was four times greater sensitivity for the SPR biosensor based on GO than that based on the conventional gold film [18–20]. Then, the GO-MoS2 hybrid nanolayer was chosen to strengthen the SPR effect.

Zn oxide (ZnO) is a semiconductor with a wide energy band (3.37 eV), and also has the high exciton binding energy [21–23]. TiO2 has the important characteristics that the
electric field would be enhanced by local SPR, and also the form of electron and hole pairs would be increased for TiO$_2$, as there exists plasmon enhancement because of the light absorption [24, 25]. And therefore, TiO$_2$-ZnO hybrid nanolayer is able to benefit the sensitivity of the SPR biosensor and can be chosen to enhance the sensitivity.

The model of the proposed biosensor is a prism coupling structure with seven-layer, as shown in Figure 1. The structure is composed of a prism, TiO$_2$-ZnO, Au, MoS$_2$, GO, and a sensing medium layer successively. ZnO and MoS$_2$ nanolayer are designed to be nanowires array layers. The refractive index of the prism is 1.54. The refractive index of TiO$_2$, ZnO and Au is 2.5837, 2.9497 + 0.0227i, and 0.0585 + 4.2665i, respectively. The refractive index of MoS$_2$ is 5.9 + 0.8i, the monolayer thickness is 0.65 nm, and the multilayer thickness is $L \times 0.65$ nm. The refractive index of GO is 2 + 0.56i, the monolayer thickness is 1.6 nm, and the multilayer thickness is $L \times 1.6$ nm. $L$ is the number of thicknesses for MoS$_2$ and GO layer. The refractive index of the sensing medium layer of the biosensor is from 1.30 to 1.38. The wavelength of incident light is 632.8 nm.

2.2. Calculation Method. The structure of the proposed SPR biosensor in this paper is shown in Figure 1. The incident light and p-polarized light falls on the metal layers through the prism by the total reflection. There exists an evanescent wave whose amplitude is decayed exponentially normal to the surface plasmon, at the interface of the metal and dielectric, and excited by the evanescent wave. The relationship between them is given as follows:

$$\varepsilon_j = n_j^2,$$
$$k_{jp} = \frac{\omega}{c} \sqrt{\varepsilon_j},$$
$$k_{x0} = \sqrt{\varepsilon_0} \frac{\omega}{c} \sin \theta,$$

where $k_{x0}$ is the wave number vector of the incident light across the medium, $k_{jp}$ is the wave number vector of the surface plasmon wave, and $\varepsilon_j$ ($j = 0, 1, 2, \ldots, 6$) is the dielectric constants of each medium layer including the prism, TiO$_2$, ZnO, Au, MoS$_2$, GO, and the sensing medium layer, respectively. $n_j$ ($j = 0, 1, 2, \ldots, 6$) is the refractive index corresponding, $c$ is the speed of light in vacuum, $\omega$ is the frequency, and $\theta$ is the angle of incidence.

When the incident light is p-polarized light, the reflection coefficient $R$ for the whole structure designed can be given, according to the Fresnel equation and the reflectivity equation, as follows [26]:

$$R = |r_{00}|^2 = \frac{r_{01} + r_{16} \exp(2i k_{zL} d_{L})}{1 + r_{01} r_{16} \exp(2i k_{zL} d_{L})},$$

where $r_{pq} = \frac{\left( (n_p^2 k_{x0} - n_q^2 k_{zL}) (n_p^2 k_{zL} + n_q^2 k_{x0}) \right)}{\left( (n_p^2 k_{x0} + n_q^2 k_{zL}) (n_p^2 k_{zL} + n_q^2 k_{x0}) \right)}$ is the reflection ratio of the strength for the electric field at the interface between the two adjacent medium, and

3. Results and Discussion

3.1. Thickness of Au, MoS$_2$ and Graphene Oxide. The effect of the number of MoS$_2$ nanowires array layers on the SPR spectrum, when the refractive index of the sensing medium layer is 1.30, 1.32, 1.34, 1.36, and 1.38 is shown in Figure 2. The thickness of TiO$_2$, ZnO, Au, and GO layer is 20 nm, 10 nm, 40 nm, and 1 $\times$ 1.6 nm, respectively. As shown in Figures 2(a)–2(d), it is obviously found that there exist a good SPR spectrum and shift of the SPR angle for all the refractive indices of 1.30, 1.32, 1.34, 1.36, and 1.38, when MoS$_2$ nanowires array is monolayer. And also, the conclusion is still effective for other thicknesses of TiO$_2$, ZnO, Au, and GO layer, as the same case of the refractive index for the sensing medium layer.

The effect of the number of GO layers on the SPR spectrum, when the refractive indices of the sensing medium layer are 1.30, 1.32, 1.34, 1.36, and 1.38, is shown in Figure 3. The thickness of TiO$_2$, ZnO, Au, and MoS$_2$ layer is 15 nm, 10 nm, 46 nm, and 1 $\times$ 0.65 nm, respectively. As shown in Figures 3(a)–3(d), it is obviously found that the shift of the SPR angle increased gradually, with the increase in the number of GO layers from $L = 0$ to $L = 4$. However, only when the number of GO layers is three ($L = 3$), there would exist a good SPR spectrum for all the refractive indices of the sensing medium layer from 1.30 to 1.38. It is shown from the beginning that the number of GO layers is four ($L = 4$), the SPR curves begin to become not obvious. As a result, it is shown by the research that the number of GO layers is three ($L = 3$) which is a benefit of the generation of SPR tip and the shift of SPR angle, which shows reasonable agreement with the other cases of different thicknesses of TiO$_2$, ZnO, Au, and MoS$_2$ layer.

The effect of thickness of Au layer on the SPR spectrum, when the refractive index of the sensing medium layer is 1.30 and 1.38, is shown in Figure 4. The thickness of TiO$_2$, ZnO, MoS$_2$, and GO layer is 15 nm, 10 nm, 1 $\times$ 0.65 nm, and 3 $\times$ 1.6 nm, respectively. As shown in Figure 4, it is found that there is an obvious SPR peak when the thickness of Au layer is between 45 nm and 60 nm for $n = 1.30$, and also, there is an obvious SPR peak when the thickness is between 40 nm and 50 nm for $n = 1.38$. Moreover, it is shown by the research that
46 nm, the thickness of Au layer, is the optimal thickness because of the good SPR peak as well as the large shift of the SPR angle, for the refractive index from 1.30 to 1.38.

3.2./Thickness of TiO2 and ZnO Layers. The sensitivity of the SPR biosensor can be defined as

\[ S_n = \frac{\Delta \theta_{SPR}}{\Delta n} \]  

where, \( \Delta \theta_{SPR} \) is the change in resonance angle, \( \Delta n \) is the change in refractive index, and \( S_n \) is the sensitivity of the SPR biosensor.

The thickness of TiO\(_2\)-ZnO layers is a positive factor that enhances the sensitivity of the proposed SPR biosensor. The variation of the SPR spectrum with the thickness of TiO\(_2\) is shown in Figure 5(a). There exists an obvious change for the SPR spectrum as the different thickness of TiO\(_2\) for 10 nm, 15 nm, and 20 nm. The change relation between the change of SPR angle and the thickness of TiO\(_2\) layer is shown in Figure 5(b); it is found that the change of SPR angle reaches the largest when the thickness of TiO\(_2\) layer is 15 nm, which the largest change of SPR angle is 16.86°. The change relation between the sensitivity of the SPR biosensor and the thickness of TiO\(_2\) layer is shown in Figure 5(b), and it is found that the sensitivity of SPR biosensor reaches the highest when the thickness of ZnO nanowires array layer is 40 nm as a result of the largest change of SPR angle, for which the sensitivity can reach 210.75°/RIU.

The variation of the SPR spectrum with the thickness of ZnO nanowires array layer is shown in Figure 6(a). There exists an obvious change for the SPR spectrum as the different thicknesses of ZnO nanowires array layer are 10 nm, 15 nm, and 20 nm. The change relation between the change of SPR angle and the thickness of TiO\(_2\) layer is shown in Figure 5(b); it is found that the change of SPR angle reaches the largest when the thickness of TiO\(_2\) layer is 15 nm, which the largest change of SPR angle is 16.86°. The change relation between the sensitivity of the SPR biosensor and the thickness of TiO\(_2\) layer is shown in Figure 5(b), and it is found that the sensitivity of SPR biosensor reaches the highest when the thickness of ZnO nanowires array layer is 40 nm as a result of the largest change of SPR angle, for which the sensitivity can reach 210.75°/RIU.
Figure 3: SPR spectrum (a) for number of GO layer $L = 0$, (b) for number of GO layer $L = 2$, (c) for number of GO layer $L = 3$, (d) for number of GO layer $L = 4$, for different refractive indices of the sensing medium layer. The curves $A_1$, $A_2$, $A_3$, $A_4$, and $A_5$ stand for the refractive index of sensing layer $n = 1.30$, $n = 1.32$, $n = 1.34$, $n = 1.36$, and $n = 1.38$, respectively. And the thickness is 15 nm, 10 nm, 46 nm, and $1 \times 0.65$ nm for TiO$_2$, ZnO, Au, and MoS$_2$ respectively.

Figure 4: SPR spectrum for different thicknesses of Au layer for $d = 40$ nm (curves $A_1$ and $A_2$), 45 nm (curves $B_1$ and $B_2$), 50 nm (curves $C_1$ and $C_2$), and 60 nm (curves $D_1$ and $D_2$), as the case of $n = 1.30$ and $n = 1.38$ for sensing medium. The curves $A_1$, $B_1$, $C_1$, and $D_1$ stand for the refractive index of sensing layer $n = 1.30$, the curves $A_2$, $B_2$, $C_2$, and $D_2$ stands for the refractive index of sensing layer $n = 1.38$. The thickness is 15 nm, 10 nm, $1 \times 0.65$ nm, and $3 \times 1.6$ nm for TiO$_2$, ZnO, MoS$_2$, and GO layer, respectively.
16.86°. The change relation between the sensitivity of the SPR biosensor and the thickness of ZnO nanowires array layer is shown in Figure 6(b), and it is found that the sensitivity of the SPR biosensor reaches the highest when the thickness of ZnO nanowires array layer is 40 nm as a result of the largest change of SPR angle, for which the sensitivity is 210.75°/RIU.

Therefore, keeping all the results above into consideration, the optimized thickness is found to be 46 nm for Au, 15 nm for TiO$_2$, and 40 nm for ZnO, and the optimized layer number is found to be 1 for MoS$_2$ and 3 for GO, where the thickness is 1 $\times$ 0.65 nm for MoS$_2$ and 3 $\times$ 1.6 nm for TiO$_2$. The proposed SPR biosensor has a big shift of 16.86° and high sensitivity of 210.75°/RIU for the refractive index of the sensing medium from 1.30 to 1.38. The relationship between the SPR angle and the refractive index of the sensing medium is shown in Figure 7.
4. Conclusion

A novel SPR biosensor that can achieve a high sensitivity is proposed in this paper. The SPR biosensor with two nanowires array layers of ZnO and MoS2 has TiO2 nanolayer based on graphene oxide nanosheet; therefore, there is a great enhancement of sensitivity. The thickness of each medium for the structure designed is given. The sensitivity of the SPR biosensor is obtained, which can reach as high as 210.75°/RIU. Also, the sensitivity is greatly improved compared with the traditional SPR biosensor.

Data Availability

The data used to support the findings of this study in the manuscript are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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