Research article

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Topological insulator overlayer to enhance the sensitivity and detection limit of surface plasmon resonance sensor

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Abstract: Surface plasmon resonance (SPR) sensors have been applied in a wide range of applications for real-time and label-free detection. In this article, by covering the topological insulators nanosheets on the surface of the noble metal (Au), the sensitivity of the SPR sensor is greatly enhanced because of the strong interaction of light with Au–bismuth selenide (Bi_2Se_3) heterostructure. It is shown that the sensitivity of proposed SPR sensors depends on the concentration of Bi_2Se_3 solution or the thickness of the coated Bi_2Se_3 film. The optimised sensitivity (2929.1 nm/RIU) and figure of merit (33.45 RIU⁻¹) have been obtained after three times drop-casting, and the enhancement sensitivity of proposed sensors is up to 51.97% compared to the traditional Au–SPR sensors. Meanwhile, the reflection spectrum is simulated by using the method of effective refractive index, and the reason for the increase of sensitivity is analysed theoretically. For researching the application of modified SPR sensor, heavy metal detection is employed to detect in the last part. Our proposed SPR

sensors have potential applications in heavy metal detections and biosensing.

Keywords: topological insulators; wavelength interrogation; SPR sensor; heavy metal detection.

1 Introduction

Surface plasmon polariton (SPP) is an electron densification wave propagating along the interface of the dielectric medium and the metal, which was first noticed in 1902 by Wood [1]. Surface plasmon polaritons are generally stimulated by the incident light through prism coupler in the Otto geometry or Kretschmann configuration [2, 3], and the phenomenon of surface plasmon resonance (SPR) occurs [4] when the wave vector of SPP matches well with the evanescent wave vector of the incident light. Surface plasmon wave is very sensitive to the changes in the refractive index (RI) of the surrounding environment, so even a tiny change occurring in sensing medium (such as the interaction of biological macromolecules) will arouse the great changes of resonance, such as wavelength, angle, phase, or intensity [5–7]. With these features, a series of sensors have been designed in biological analysis, chemistry, gas detection, and so on [8–11]. The means of optical sensing are becoming more diversified, playing an important role in the application field [12–16]. In some recent literatures, the enhancement sensitivity for SPR sensors based on two-dimensional (2D) materials draws great attention. For example, Wang et al. [17] proposed a wavelength modulation SPR sensor with large sensitivity of 2459.3 nm/RIU based on tungsten disulphide, and Xiong et al. [18] proposed an SPR sensor based on graphene oxide sheets overlayer (2715.1 nm/RIU), and so on. However, it is still not clear how to achieve higher sensitivity in experiments and design the multichannel SPR systems.

With the preparation and development of a series of new materials, such as phosphorene, antimonene, black

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phosphorus (BP), and so on, they are more widely used in improving the performance of traditional optical devices [19–26]. The topological insulator is also a typical kind of new material and bulk insulator with a chiral Dirac cone on its surface, which is a new state of quantum matter with internal insulation but the electric conduction for the interface. Since the theory was predicted by Zhang et al. [27], bismuth selenide (Bi_2Se_3) has attracted much attention. Bi_2Se_3 has excellent performance in thermoelectric and electronic band structure due to morphology and size, which can be modulated by varying reaction conditions [28–31], unlike thin vertical thickness of the classic 2D material such as graphene, BP, and so on [32, 33]. Besides, with the larger surface-to-volume ratios than bulk materials, Bi_2Se_3 nanostructures can improve the surface effect further and offer additional advantages to forward-looking applications and basic researches. Nowadays, because of its unique performance, Bi_2Se_3 has shown great potential applications in biomedicine, photoacoustic imaging, and high-performance electronic and optoelectronic devices [34–38]. Moreover, Bi_2Se_3 topological insulator has the advantages of simple fabrication and low cost, and it is easy to achieve saturable absorption because of the unique significant gap. In this article, we prepared 2D Bi_2Se_3 nanosheets by solution growth route, which is an effective method to prepare high-quality and controllable 2D Bi_2Se_3 nanosheets [39–41].

In this research, we have experimentally demonstrated that Bi_2Se_3 can improve the sensitivity of SPR sensors. First, by sensing different RI mixed solutions of deionised water and ethylene glycol, we illustrate that the proposed sensor can effectively improve bulk RI sensitivities. Besides, we have discussed the performance of the proposed SPR sensor and analysed the reasons for the increased sensitivity. Finally, by detecting the small concentration of Pb^{2+} heavy metal ions, we demonstrate that the sensor can sensitively monitor molecular activities in the sensing surface. In this section, we use the units of ppb to express the concentration of Pb^{2+} solutions, as $1 \text{ ppb} = 10^{-9} \text{ g/ml}$.

2 Experimental section

2.1 Materials and reagents

Bismuth (III) acetate [$\text{Bi}(\text{CH}_3\text{CO}_2)_3$, $\geq 99.99\%$ trace metals basis], hydroxylamine solution (NH_2OH , 50% weight in H_2O , 99.999%), sodium selenite (Na_2SeO_3 , $\geq 99\%$), polyvinylpyrrolidone [PVP, molecular weight (MW) $\approx 58,000$] were bought from Sigma-Aldrich (Shanghai, China).

Ethylenediamine ($\geq 99.5\%$), ethylene glycol (EG), and glacial acetic acid ($\geq 99.99\%$) were acquired from Aladdin (Shanghai, China). Chitosan (MW = 50,000 and degree of deacetylation $\geq 95\%$) was purchased from Macklin (Shanghai, China). The standard solution (1000 ppm and 1 mol/L HNO_3) of Pb^{2+} was purchased from Ruiqi (Shanghai, China).

2.2 Preparation of chemical reagents

The classic preparation method of 2D Bi_2Se_3 is solution-based synthesis; we first dissolve 0.3 mmol $\text{Bi}(\text{CH}_3\text{CO}_2)_3$ and 0.4 g PVP in 10 ml EG and then add 0.45 mmol Na_2SeO_3 and 1 ml glacial acetic acid in the above solution and keep stirring until a clear solution disappeared. The clear solution should be further heated to 170°C , and then 1 ml NH_2OH and EG are rapidly injected in it, finally quickly turning black, which indicates that the required Bi_2Se_3 nanosheets are well prepared. In the experiment, different RI-sensing medium was acquired by mixing the EG solution and deionised water and measured using the Abbe refractometer. The chitosan solution was a mixture of 0.4 g chitosan and 1% acetic acid (50 ml), and the different concentration of heavy metal (Pb^{2+}) was obtained by diluting with deionised water.

2.3 Optical characterisation instrument

The Raman spectroscopy measurements were performed by using a Raman system (WITec Alpha300 R, Ulm, Baden-Württemberg, Germany). The Raman scattering signal excited by a continuous wave laser of 532 nm was collected by the $100\times$ objective lens with the spot size of $\sim 1 \mu\text{m}$. The crystal structure of the prepared Bi_2Se_3 material was measured by X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) (XRD, D8 ADVANCE, Bruker, Camarillo, CA, USA). The atomic force microscopy (AFM) (Bruker, Dimension Icon, Santa Barbara, CA, USA). with the ScanAsyst mode under ambient conditions was carried out to determine the surface topography of Bi_2Se_3 . The morphology of as-prepared Bi_2Se_3 was detected by field emission scanning electron microscopy (SEM, Supra 55 Sapphire, Carl ZEISS, Baden-Württemberg, Germany).

2.4 The schematic of the SPR chip

Figure 1A exhibits the detail of the SPR chip, where the chip consists of 50 nm Au film and 3 nm Cr on the BK7 glass. Bi_2Se_3 -Au heterostructure was prepared by using

Figure 1: The schematic diagram of the SPR sensor.

(A) Three-dimensional structure model of designed sensor chip based on Bi₂Se₃. (B) Crystal structure of Bi₂Se₃.

drop-casting technology, which is prepared by the method of magnetron sputtering. The thickness of Bi₂Se₃ film on the Au surface can be controlled by the times of drop-casting. Bi₂Se₃-Au heterostructure is attached to the top of the prism with matching liquid, and the peristaltic pump is used to transfer and recover liquid. A more detailed experimental optical circuit device for sensing detection is shown in Figure S1.

3 Theory and experiment

As the primitive cell of Bi₂Se₃ is shown in Figure 1B, hexagonal monatomic crystal planes alternate with each other and stack in ABC order along the *z* axis. Every repeating unit is an ordered sequence of Se-Bi-Se-Bi-Se and forms quintuple layers (QLs), and atomic planes are

covalently bonded within a QL; nevertheless, the adjacent QLs are linked together by weak van der Waals interaction [42–44]. This is why some literature prepared Bi₂Se₃ by solution growth route. As the typical Raman spectrum of the as-prepared nanosheet is described in Figure 2A, the four prominent Raman peaks were located at ~37, ~71, ~130, and ~175 cm⁻¹, corresponding to *E*_{1g}, *A*_{1g}¹, *E*_g², and *A*_{1g}² modes, respectively, which is in accord with some theoretical demonstration that the crystal is in α phase [45, 46]. The relative motion of the various atoms for these observations is plotted in the inset in Figure 2A. It is worth noting that *A*_{1g} and *E*_g modes are out-of-plane and in-plane vibration modes, belonging to the Raman active phonon. Here we can quite clearly see that the intensity of the low frequency is relatively weak, possibly ascribed to the high Rayleigh background [47, 48]. The crystal structure of Bi₂Se₃ is verified by the XRD as displayed in Figure 2B,

Figure 2: Characterisation of the Bi_2Se_3 overlayer.

(A) Raman spectrum of the deposited Bi_2Se_3 overlayer. Inset: schematic diagram of Raman active modes. (B) X-ray diffraction (XRD) pattern of Bi_2Se_3 nanosheets. (C–E) Three-dimensional atomic force microscopy images correspond to zero, three, and four times drop-casting. (F) Line scanning height profile of Bi_2Se_3 overlayer for three and four times drop-casting. (G) The root-mean-square roughness of Bi_2Se_3 overlayer corresponds to three and four times drop-casting.

and the diffraction peaks of rhombohedral Bi_2Se_3 structure (space group: $R\bar{3}m$) can be indexed, which highly maintains consistency of the literature dates (JCPDS no. 33-0214) [49–51].

For a more intuitive description of the Au– Bi_2Se_3 heterostructure, we draw the 3D AFM images as an understanding. Figure 2C is the Au film without Bi_2Se_3 overlayer. The Bi_2Se_3 nanosheets are casually distributed in the surface of the Au film and have a higher concentration

and dense distribution with increasing drop-casting, as shown in Figure 2D and E. The height profile in Figure 2F indicates that the thickness of Bi_2Se_3 overlayers satisfies the normal distribution. The average thicknesses are 256 and 345.738 nm. Meanwhile, the root-mean-square roughnesses (R_q) are 15.6 and 19.4 nm, which manifests that Bi_2Se_3 nanosheets have good dispersiveness. In order to obtain the representative topographical profiles corresponding to the AFM images of Bi_2Se_3 nanosheets, we

provided the SEM images. As shown in Figure S2, the thicknesses of Bi_2Se_3 nanosheets on the Au surface are increased by repeated drop-casting, (240.8 and 281.6 nm corresponding to three and four times drop-casting). The average thickness may be larger than SEM characterisations because of the wide range of measurement for AFM and the aggregation of nanosheets when abundant materials distribute on the surface [17, 18].

Figure 3A–E are the reflectance spectra varying with the resonance wavelength for different RI of sensing

medium, the reflectance broadened, and the SPR dips risen with the growing of drop-casting times, due to the large loss of Bi_2Se_3 . When the RI of sensing medium changes within a certain range, the resonance wavelength changes linearly with the RI of the medium. Therefore, the resonance wavelength is determined by measuring the curve of the reflectivity changing with the wavelength, and the refractive of the medium can be obtained by using the linear relation between the resonance wavelength and the refractivity. And we can clearly see that

Figure 3: The experimental measurements of the reflectance spectrum.

(A–E) The reflectance spectrum of resonance wavelength experimentally changes with the variation of RI 1.3334 to 1.3605 and different drop-casting times of Bi_2Se_3 nanosheets corresponding to zero to four times. (F) Variation of the FWHM and FOM with the increase of drop-casting times for the proposed sensor based on Bi_2Se_3 at the environment of $n_s = 1.333$.

the linearly dependent coefficients (R^2) were 0.98129, 0.98464, 0.9983, 0.9979, and 0.98544 under the condition of zero to four drop-casting times of Bi_2Se_3 nanosheet, respectively. These experimental data exhibited a good linear relationship between the changes of RI of sensing medium and wavelength shifts of SPR resonance, which indicates that the RI of sensing medium changes can be obtained from resonance wavelength shift. On the other hand, the slope of the line can represent the sensitivity of

the sensor. Therefore, the sensitivities for different coating times of Bi_2Se_3 nanosheet suspension are 1927.4, 2140.9, 2303.4, 2929.1, and 2333 nm/RIU for zero to four times drop-casting, respectively.

To describe the performance of the designed SPR sensor based on Bi_2Se_3 , we define the performance of the sensor by calculating several common parameters, such as sensitivity and FWHM (full width at half maximum), which is referred to the full width of the spectral band

Figure 4: Theoretical simulation of the SPR curve.

(A) Theoretical three-dimensional plot and map of reflection spectra for the traditional SPR sensor based on Au. (B–F) The theoretically calculated reflectance curve for different occupation ratios in the volume of Bi_2Se_3 overlayer of 0, 0.1, 0.2, 0.5, and 1, the incident angle set 74° .

when the maximum height of the absorption spectral band height is half and is used to represent energy resolution, DA (detection accuracy), and FOM (the figure of merit), where $S = \Delta\lambda/\Delta n$, $DA = 1/\text{FWHM}$ and $FOM = S \cdot DA$, respectively [52]. It illustrates that the overall trend FWHM (Figure 3F) shows growth with the increasing number of drop-casting; due to the large loss of increasing Bi_2Se_3 layer, the varying tendency of FOM (Figure 3D) is increasing first and then decreasing, and a large FOM of 33.45 RIU^{-1} can be obtained with three times drop-casting. But beyond that, the stability and repeatability investigations were measured in Figure S3, which showed good stability and durability.

In the simulation process of physical modelling, the approach of Fresnel equations and the transfer matrix method are employed to acquire the reflectance spectrum, which is the formula for incident wavelength (λ_{in}). According to Figure 2C–E, the AFM image is detailed enough to see that the Bi_2Se_3 covering layer is a porous structure on the surface of the Au film; the different RI-sensing medium will be filled with hollowness. Therefore,

the Bi_2Se_3 overlayer and sensing medium are considered as a hybrid structure, and the hybrid dielectric n_{eff} is described as $n_{\text{eff}} = n_{\text{Bi}_2\text{Se}_3} \times f_{\text{Bi}_2\text{Se}_3} + n_s \times f_s$, whereas the $n_{\text{Bi}_2\text{Se}_3}$ and n_s are the RIs, respectively. $f_{\text{Bi}_2\text{Se}_3}$ and f_s are the relevant occupation ratios in volume and added together make 1 [17, 18, 53–55]. In the simulation process, the thickness of the hybrid structure is fixed ($d_2 = 5 \text{ nm}$), whereas $f_{\text{Bi}_2\text{Se}_3}$ is changing; the RIs of Au and Bi_2Se_3 can refer to the relevant literature [56, 57]. Figure 4A is the excitation of SPPs based on Au, and the lowest reflectance intensity can be observed at 74° . Then, we choose a different value of $f_{\text{Bi}_2\text{Se}_3}$ (0, 0.1, 0.2, 0.5, 1) as shown in Figure 4E–F. The resonance wavelengths are constantly generated red shifts with the increasing RI-sensing medium. Meanwhile, the sensitivity first increases and then decreases for different occupation ratios in the volume of Bi_2Se_3 overlayer, which matches the experimental data.

To further explain the reason of red shift and enhancement sensitivity, Figure 5A is the typical electric field for the excitation of the SPP mode based on Au, which is the strongest at the Au-sensing medium interface

Figure 5: Simulation of the electric field.

(A–C) The amplitude distribution of the electric field ($|E_x|^2/|E_0|^2$) for different occupation ratios in the volume of Bi_2Se_3 overlayer of 0, 0.1, and 0.5. (D) The changing resonance wavelength with the varying thickness of the hybrid structure and $n_s = 1.3334$.

and decreases exponentially away from the interface. The field intensity changed obviously when the RI-sensing mediums are gradually increasing. It is because a slight change of the RI-sensing medium near the interface can alter the characteristics of the related surface wave, which means it is sensitive to the variation of the RI-sensing medium. The electric field is defined as $|E_x|^2/|E_0|^2$, while E_x and E_0 are the electric field amplitude and the incident light, respectively. As Figure 3B and C show, the resonance wavelengths become broader with the growth of drop-casting times, which is due to the introduced Bi_2Se_3 overlayer and additional loss, so the field intensity decreases with the increase of $f_{\text{Bi}_2\text{Se}_3}$. However, the field strength continues to increase in the region of the Bi_2Se_3 layer, and $f_{\text{Bi}_2\text{Se}_3} = 0.5$ (as shown in Figure 5C) grows faster than $f_{\text{Bi}_2\text{Se}_3} = 0.1$ (as shown in Figure 5B), corresponding to the sensitivity of the experimental data. The effect of the thickness of hybrid structure d_2 is discussed in Figure 5D, and the resonance wavelengths become broader with the increasing d_2 .

To further describe the performance of the designed SPR sensor based on Bi_2Se_3 nanosheets, we apply it to the sensing experiment of heavy metal detection (Pb^{2+} , changing from 0 to 1 ppb with a step of 0.25 ppb). Traditional sensor based on gold film did not have the ability to detect the heavy metal, and the common method of detecting the heavy metal was realised by adding chitosan on the surface of the gold film. We experimentally measured the changes of resonance wavelength for conventional SPR sensor based on Au + chitosan and proposed sensor based on Au + chitosan + Bi_2Se_3 with different concentrations of Pb^{2+} solution, and the wavelength shifts in conventional SPR sensor (Figure 6A) are significantly less than the proposed sensor based on Au + chitosan + Bi_2Se_3 (Figure 6B). For a more intuitive expression, we compared the performance of the three types of SPR sensors in Figure 6C: the pink line is the SPR sensors without chitosan, the yellow line is the SPR sensors with chitosan, and the purple line is the SPR sensors with chitosan + Bi_2Se_3 . Figure 6D shows the wavelength shifts for different SPR sensors in

Figure 6: Comparison of different structures applied to the detection of lead ions.

(A, B) Reflection spectra of SPR sensor without Bi_2Se_3 coating and proposed SPR sensor based on Bi_2Se_3 overlayer for different concentrations of Pb^{2+} . (C) The corresponding line graph of resonance wavelength. (D) The wavelength shifts for different SPR sensors in detecting heavy metal.

Table 1: Comparison of the latest literature of the enhancing methods for SPR-sensing performance.

Plasmonic interface	Detection range (RI)	Sensitivity (nm/RIU)	Enhanced fold	FOM	Theoretical/experimental	Referents
$Au + WS_2$	1.333–1.360	2459.3	1.266	15.23	Experimental	[17]
$Au + MoS_2$	1.333–1.360	2793.5	1.357	24.58	Experimental	[53]
$Au + (GO)$	1.333–1.360	2715.1	1.202	19.53	Experimental	[18]
$Au + MoSe_2$	1.333–1.360	2524.8	1.363	16.2	Experimental	[55]
$Au + Bi_2Se_3$	1.333–1.360	2929.1	1.52	33.45	Experimental	This work

detecting 0 to 1 ppb Pb^{2+} solution. The wavelength shifts of the proposed sensor based on $Au + \text{chitosan} + Bi_2Se_3$ have been enhanced by 51.07% compared with the SPR sensors with chitosan, which indicates that the proposed Bi_2Se_3 nanosheets could improve the sensitivity and detect a lower concentration of heavy metal.

In the final section, we have listed some literature about SPR sensors based on different 2D materials. According to the sensing target, materials, and data acquisition method, we sorted out Table 1 to compare the performance. The SPR sensor based on the Bi_2Se_3 overlayer has larger sensitivity and FOM, which will make a great contribution to the practical application of the sensor.

4 Conclusion

In summary, we have designed an SPR sensor based on Bi_2Se_3 nanosheets in this article, and a higher sensitivity (up to 2929.1 nm/RIU) and FOM (33.45 RIU⁻¹) can be acquired through experimentally measuring RI sensing. The enhancements of sensitivity and FOM are 51.97% and 67.35% compared to the traditional SPR based on gold film without Bi_2Se_3 nanosheets. We have employed the method of effective RI to explain why the sensitivity increases first and then decreases with increasing times of drop-casting. The proposed SPR sensor based on Bi_2Se_3 has a linearly dependent coefficient of 99.79% in detecting the RI of sensing medium ranging from 1.3334 to 1.3605, more than the Bi_2Se_3 overlayer can protect the metal from oxidation. In the final section, we apply the proposed SPR sensor to lead ions detection, and the lower concentration of lead ions can be detected. Compared with the traditional heavy metal detection sensors based on $Au - \text{chitosan}$, the enhancement of wavelength shift (51.07%) was obtained. We convinced that the optimisation of SPR sensors with the Bi_2Se_3 nanosheet overlayer will have widespread applications in heavy metal detection and biosensing.

5 Supplementary material

The supplementary information can be found with the online version of the article: Experimental device for the SPR technique; Characterisation of SEM; The stability and repeatability of the SPR sensor based on the Bi_2Se_3 overlayer.

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