Оптический журнал

Оптическое приборостроение

УДК 535.1, 535.3, 535.8

Датчик концентрации сахарозы, использующий нанослой графена и улучшенный поверхностный плазмонный резонанс в матрице золотых нанопроволок, контактирующих с нанопленкой MoS_2

© 2020 г. Zhiquan Li, Xiaogang Wu, Kai Tong, Xiaopeng Jia, Wenchao Li, Qiang Li

Представлен метод определения концентрации сахарозы в водном растворе, основанный на использовании поверхностного плазмонного резонанса. Разработанная структура датчика включает в себя призму, на контактирующую с раствором сахарозы грань которой нанесена гибридная нанопленка из оксида графена и MoS_2, выбранная для усиления поверхностного плазмонного резонанса на основе наночастиц Au. Методом конечных элементов проанализировано влияние толщины каждого из слоев на чувствительность датчика и показано, что последняя может быть существенно улучшена при оптимальном выборе толщины. Определена оптимальная толщина этих слоев, обеспечивающая чувствительность в 0,16° на 1% изменения концентрации. Определена зависимость угла поверхностного плазмонного резонанса от концентрации сахарозы во всем диапазоне изменения концентрации от 0 до 70%.

Ключевые слова: *поверхностный плазмонный резонанс, чувствительность датчика, оксид графена, нанопроволоки из золота, концентрация сахарозы, метод конечных элементов.*

Sucrose concentration sensor based on MoS_2 nano-film and Au nanowires array enhanced surface plasmon resonance with graphene oxide nanosheet

© 2020 Zhiquan Li*, Xiaogang Wu*, Kai Tong*, Xiaopeng Jia**, Wenchao Li**, Qiang Li*

*School of Electrical Engineering, Yanshan University, Qinghuangdao, China
**School of Control Engineering, Northeastern University at Qinhuangdao, Qinhuangdao, China

E-mail: wxgdsmy_2004@126.com

Submitted 25.09.2019

DOI:10.17586/1023-5086-2020-87-01-50-56

A method of sucrose concentration detection based on surface plasmon resonance is proposed. Thus, a novel prism coupling structure is designed for sucrose concentration sensor utilizing the unique feature of graphene oxide to sucrose in water, and the MoS_2-graphene oxide hybrid nano-film is chosen to enhance surface plasmon resonance based on Au nanoparticles. The thickness of each layer for the structure designed are analyzed to get the optimal value by finite element method, so that the sensitivity of sucrose concentration sensor is able to be improved greatly. The optimal thickness of each layer is given, for which the sensitivity of surface plasmon resonance sucrose concentration sensor can reach as high as 0.16°/% conc. within the detection range of sucrose concentration, 0–70% conc. The relationship between sucrose concentration and surface plasmon resonance angle are obtained within the detection range of sucrose concentration.

Keywords: *surface plasmon resonance, sensitivity, graphene oxide, Au nanowires, sucrose concentration, finite element method.*

OCIS Codes: *130.6010, 230.0230, 240.6680, 260.0260*

INTRODUCTION

Sensor devices based on surface plasmon resonance (SPR) are paid more and more attention and become a research hotspot in the field of test and detection [1–3]. A rapid and secure detection of sucrose concentration is an important technology in chemistry. There are several conventional and mature detection methods based on titrimetry, measurements of specific-gravity, detection of acoustic waves [4], and the use of optical fibers [5]. However, there is no research on sucrose concentration detection by means of SPR so far, which could be helpful to develop a new optical detection device for sucrose concentration detection. Thus, in this paper a novel structure based on SPR is designed to make a new sucrose concentration sensor, which has the ability of sucrose concentration detection and has features of higher sensitivity, higher accuracy and easy operation, as compared with conventional sensors and detection methods.

There exists a total internal reflection phenomenon on the interface between two mediums of metal–dielectric with different refractive index so that free electrons in metal surface on the interface will be caused to resonate, which is called surface plasmon resonance, as the incident light penetrates through the interface [6, 7]. The reflection decreased greatly at a certain angle as the surface plasmon resonance occurs, where the angle is called SPR angle [8–10]. However, the SPR angle changes correspondingly, as the refractive index of the sensing medium close to the metal surface varies. This implies that the change of SPR angle could be determined by physicochemical properties of the sensing medium. It is shown in this paper that, because of the change of refractive index changing with sucrose concentration, the SPR angle changes also, and the relationship between the SPR angle and sucrose concentration is given. This can enable a further theoretical preparation for making sucrose concentration SPR detecting instrument.

THEORY AND STRUCTURE DESIGN

There exists a unique adsorption properties of water for graphene oxide (GO), that it can act as a sieve to sucrose solution: the water in sucrose solution is allowed to penetrate the GO membrane, but the sucrose molecules are trapped on the surface when the sucrose adheres to the surface of GO [11–15]. Therefore, the sucrose molecules form a layer covering GO layer, and the thickness of the layer formed will increase with the increase of the sucrose concentration, and finally the refractive index of the sucrose solution layer increases with increase of the sucrose concentration. The relationship between sucrose concentration and refractive index is shown as Fig. 1 [16].

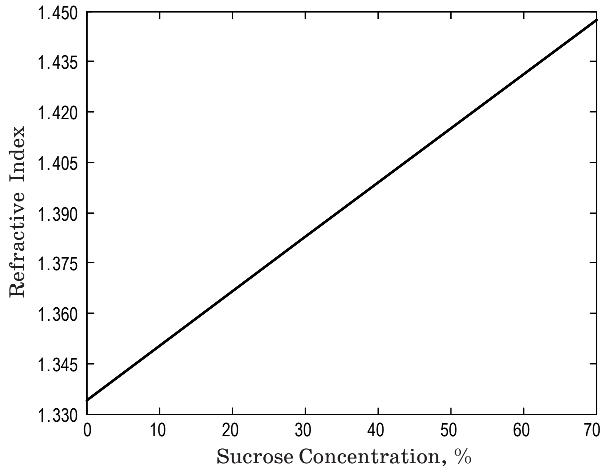

Fig. 1. Relationship between sucrose concentration and refractive index.

Metal nanowire array systems have a strong ability of absorbing incident light at specific frequencies of SPR [17–21]. Compared to conventional SPR sensor based on metal nanofilm, an optimal metal nanowire structure can provide a great sensitivity enhancement (e.g. by 3.44 times [22]). Besides, Au nanowire arrays have good optical extinction properties [23]. Thus, Au nanowire arrays are chosen to improve the sensitivity of SPR sensor designed in this paper.

In this paper, various nanofilms were considered to be added into the structure, in order to improve the sensitivity of sucrose concentration SPR sensor. Two-dimensional nanomaterials have an extremely strong absorption properties, and are very suitable for the adsorption of adsorbate materials because of their large surface-to-volume ratio and highly conductive nature [24]. Monolayer MoS_2 is direct bandgap (1.8 eV) semiconductor [25], and has a variable optical absorption coefficient (near 10%) [26, 27]. So the performance of the SPR sensor can be enhanced by using GO attached to MoS_2, as compared to only GO or only MoS_2.

A novel prism coupling structure was designed for the sucrose concentration sensor, which is composed of a prism (SF10), Au, MoS_2-GO, and the sample medium layer successively, as shown in Fig. 2. The SF10 is a high index material, the refractive index n_0 is 1.723 [28]. The refractive index of Au (n_1) is 0.0585 + 4.2665i respectively [29]. The refractive index of MoS_2 (n_2) is 5.9 + 0.8i [30], the monolayer thickness of which is 0.65 nm, and the multilayer thickness is $L \times 0.65$ nm (L is the layer number). The refractive index of GO (n_3) is 2 + 0.56i [31], the monolayer thickness of which is 1.6 nm, and the multilayer thickness is $L \times 1.6$ nm. The sample medium layer is a sucrose solution, its refractive index depending on the sucrose concentration. The wavelength is chosen of 632.8 nm for the incident light.

The finite element method is used for theoretical analysis. The incident p-polarized light falls on the metal layers through the prism by the total reflection.

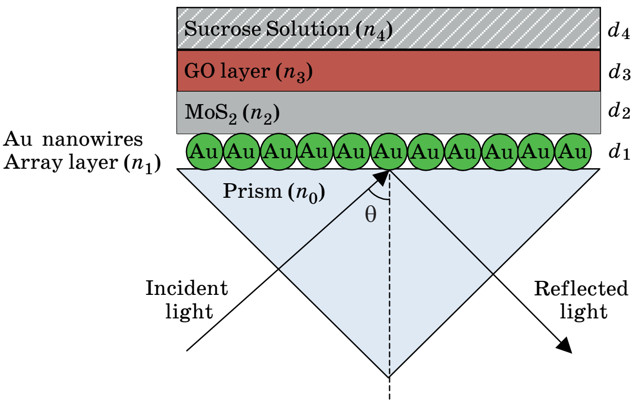

Fig. 2. Structure designed for the sucrose concentration sensor.

There exists an evanescent wave whose amplitude is decayed exponentially normal to the interface by the total reflection. When $k_{x0} = \mathrm{Re}(k_{sp})$, surface plasmons, at the interface of metal and dielectric, are excited by the evanescent wave. The relationship between them are given as follows:

$$\varepsilon_j = n_j^2, \tag{1}$$

$$k_{sp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_j \varepsilon_{j+1}}{\varepsilon_j + \varepsilon_{j+1}}}, \tag{2}$$

$$k_{x0} = \sqrt{\varepsilon_0}\,\frac{\omega}{c}\sin\theta, \tag{3}$$

where k_{x0} is the wave number vector of the incident light across the medium, k_{sp} is the wave number vector of the surface plasmon wave, ε_j ($j = 0, 1, 2, 3, 4$) are the dielectric constants of each medium layer including the prism, Au, MoS_2, GO, and the sensed medium layer respectively. n_j ($j = 0, 1, 2, 3, 4$) are the refractive indices correspondingly, c is the speed of light in vacuum, ω is the frequency, and θ is the angle of incidence.

When the incident light is p-polarized, the reflection coefficient R can be given, according to the Fresnel equation and the reflectivity equation, as follows:

$$R = |r_{04}|^2 = \left|\frac{r_{01} + r_{14}\exp(2ik_{z1}d_1)}{1 + r_{01}r_{14}\exp(2ik_{z1}d_1)}\right|^2, \tag{4}$$

where

$$r_{pq} = \frac{n_p^2 k_{zq} - n_q^2 k_{zp}}{n_p^2 k_{zq} + n_q^2 k_{zp}}$$

is the reflection ratio of the strength for the electric field at the interface between the two adjacent medium, and

$$k_{zj} = \sqrt{\left(\frac{\omega}{c}\right)^2 n_j^2 - k_{x0}^2},$$

$$(p = 0, 1, 2, 3,\ q = 1, 2, 3, 4,\ j = 0, 1, 2, 4).$$

3. RESULTS AND DISCUSSION

The optimal thickness values are 40 nm, 1×0.65 nm and 1×1.6 nm for Au, MoS_2, and GO respectively, which are obtained by means of changing one dielectric thickness while other dielectric thicknesses fixed. The thickness of Au layer is 40 nm. The SPR spectra for different thicknesses of Au layer for d_{Au} = 35, 40, 45, and 50 nm are shown as Fig. 3, where the thicknesses are 1×0.65 nm and 1×1.6 nm for MoS_2 and GO respectively, the spectra A stands for $n = 1.330$ and the spectra B stands for $n = 1.450$ for the refractive index of sensed medium. It can be seen from Fig. 3, the SPR peak spectra are not good for the two limit refractive indices at d_{Au} = 35 nm and d_{Au} = 45 nm, and only when d_{Au} = 40 nm, the SPR peak spectrum is both good for them. It was is also found that, the thickness 40 nm of Au layer is also optimal and suitable for other thicknesses of all other layer media.

The effects of thickness of MoS_2 layer, different layer number $L = 0$, 1, 2, and 3, on SPR angle, for different sucrose concentrations 0 and 70%, are shown as Fig. 4a, where the thicknesses are 40 nm and 1×1.6 nm for Au and GO respectively. It is viewed that, the SPR angle move towards large values both for 0 and 70%, that is, the SPR angle increases both for 0 and 70%, with the layer number of MoS_2 increasing. However, the SPR angle increases more for 70% than that for 0%, as the layer number of MoS_2 increase. Thus, the sensitivity is improved when the layer number of MoS_2 increases, but there is a better SPR peak at monolayer than that at other three layers numbers. The optimal thickness of MoS_2 layer is obtained 1×0.65 nm basing on the improvement of sensitivity.

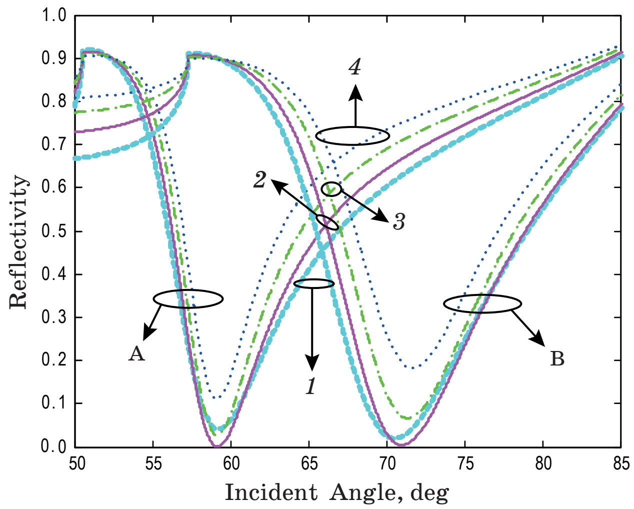

Fig. 3. Surface plasmon resonance spectra for different thickness of Au layers for d_{Au} = 35 (line *1*), 40 (*2*), 45 (*3*), and 50 (*4*) nm. The spectra A and B stand for the refractive index of sensing medium $n = 1.330$ and $n = 1.450$ respectively.

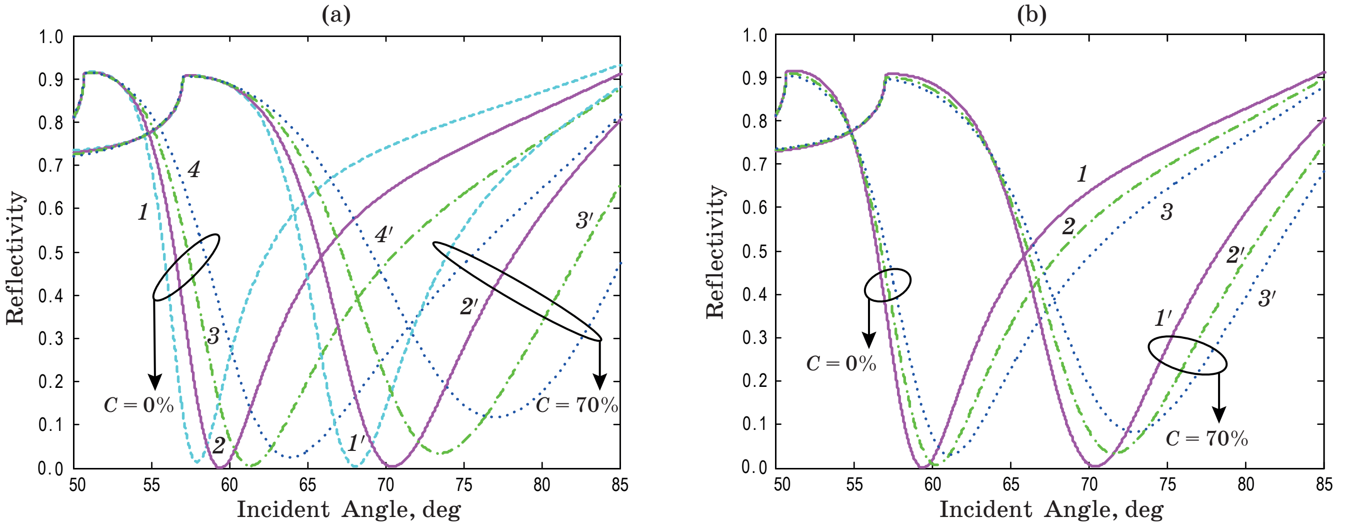

Fig. 4. Surface plasmon resonance spectra (a) for different number of MoS_2 layers for $L = 0$ (lines *1*, *1′*), $L = 1$ (*2*, *2′*), $L = 2$ (*3*, *3′*), and $L = 3$ (*4*, *4′*), (b) for different number of GO layers for $L = 1$ (lines *1*, *1′*), $L = 2$ (*2*, *2′*), and $L = 3$ (*3*, *3′*). The curves *1*–*4* stand for $C = 0\%$, the curves *1′*–*4′* stand for $C = 70\%$.

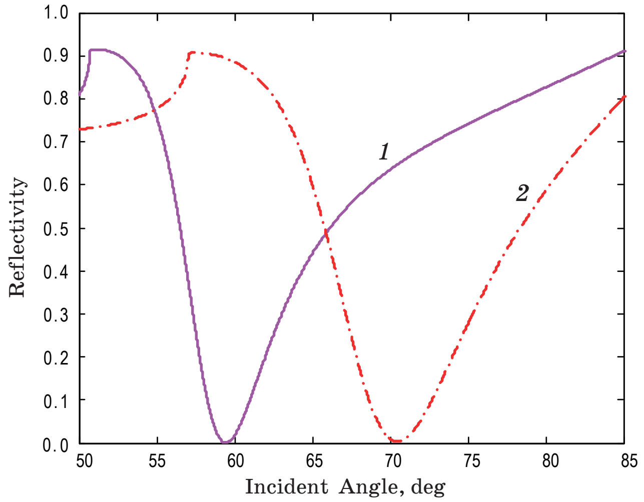

Fig. 5. Surface plasmon resonance spectra with different sucrose concentrations, $C = 0\%$ (line *1*) and $C = 70\%$ (*2*).

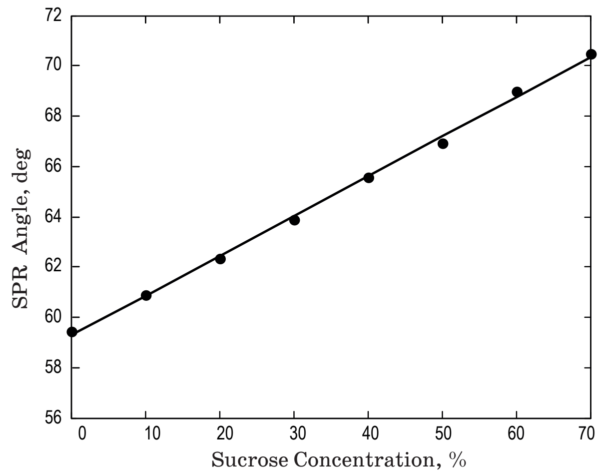

Fig. 6. Relationship between SPR angle and sucrose concentration (experimental value — points, theoretical value – line).

The effects of thickness of GO layer, different layer number of $L = 1$, 2, and 3, on SPR angle, for different sucrose concentrations 0 and 70%, are shown in Fig. 4b, where the thicknesses are 40 nm and 1×0.65 nm for Au and MoS_2 respectively. It can be seen that the SPR angle moves towards the large values both for 0 and 70%, that is, the SPR angle increases both for 0 and 70%, with the layer number of GO increasing. However, the SPR angle increases more for 70% than for 0%, as the layer number of GO increases. Thus, the sensitivity is improved when the layer number of GO increase, but there is a better SPR peak at monolayer than that at other two layers number. The highest improvement of sensitivity is obtained at the thickness of GO layer equal to 1×1.6 nm.

Thus, the thicknesses of 40, 0.65, and 1.6 nm are chosen for Au, MoS_2, and GO respectively, for the structure designed. The figure of merit is SPR spectrum *vs* the sucrose concentration. The SPR spectra for the sucrose concentrations 0 and 70% are given Fig. 5. Generally speaking, the SPR spectrum moves towards the higher sucrose concentration, the SPR angle shifts to the higher sucrose concentration and increases significantly.

The sensitivity of the SPR sensor or SPR sucrose concentration sensor can be defined as

$$S_n = \frac{\Delta\theta_{SPR}}{\Delta n}, \quad S_e = \frac{\Delta\theta_{SPR}}{\Delta C}, \qquad (5)$$

where $\Delta\theta_{SPR}$ is the change in resonance angle, Δn is the the change in refractive index, ΔC is the change in sucrose concentration, S_n and S_e are the sensitivity of SPR sensor and SPR sucrose concentration sensor respectively.

The relationship between SPR angle and sucrose concentration are given, as shown in Fig. 6. There is linear relationship between SPR angle and sucrose concentration, and the SPR angle got the maximum when the sucrose concentration is 70%. The SPR angle shifts significantly, ranging from 59.45 to 70.47°. Thus, the detection range of sucrose concentration sensor is 0–70%, the shift of SPR angle is 11.02° at the detection range, and also the sensitivity reached as high as 98.96°/RIU in terms of refractive index change, which is the highest value as compared with other sensor, such as the sensors with sensitivity of 59.5°/RIU [32], 75.0°/RIU [33], 83°/RIU [34]. In terms of sucrose concentration detection, the sensitivity of SPR sucrose concentration sensor reaches 0.157°/% conc.

CONCLUSION

In this paper, a novel prism coupling structure based on SPR is designed for the sucrose concentration sensor, and the thickness of each layer was optimized to get the good SPR spectrum and the high sensitivity. The sensitivity can reach 98.96°/RIU in terms of refractive index change, which gives, for the sensitivity of SPR sucrose concentration sensor, the sensitivity value 0.16°/% conc. within the detection range of sucrose concentration, from 0 to 70% conc. The relationship between SPR angle and sucrose concentration is given, based on this, the making of a new optical detection device, SPR detecting instrument with a higher sensitivity, has a sufficient theoretical preparation.

REFERENCE

1. *Devanarayanan V.P., Manjuladevi V., Gupta R.K.* Surface plasmon resonance sensor based on a new opto-mechanical scanning mechanism // Sensors and Actuators B: Chemical. 2016. V. 227. P. 643–648.
2. *Vachali P.P., Li B., Bartschi A., Bernstein P.S.* Surface plasmon resonance (SPR)-based biosensor technology for the quantitative characterization of protein–carotenoid interactions // Archives of Biochemistry and Biophysics. 2015. V. 572. P. 66–72.
3. *Sankiewicz A., Laudanski P., Romanowicz L., Hermanowicz A., Roszkowska-Jakimiec W., Debek W., Gorodkiewicz E.* Development of surface plasmon resonance imaging biosensors for detection of ubiquitin carboxyl-terminal hydrolase L1 // Analytical Biochem. 2015. V. 469. P. 4–11.
4. *Turton A., Bhattacharyya D., Wood D.* Measurement science and technology liquid density analysis of sucrose and alcoholic beverages using polyimide guided love-mode acoustic wave sensors // Meas. Sci. and Technol. 2006. V. 17. P. 257–263.
5. *Fujiwara E., Ono E., and Suzuki C.K.* Application of an optical fiber sensor on the determination of sucrose and ethanol concentrations in process streams and ef uents of sugarcane bioethanol industry // IEEE Sensors J. 2012. V. 9. P. 2839–2843.
6. *Barnes W.L., Dereux Al., Ebbesen T.W.* Surface plasmon subwavelength optics // Nature. 2003. V. 424. P. 824–830.
7. *Maharana P.K., Bharadwaj S., Jha R.* Electric field enhancement in surface plasmon resonance bimetallic configuration based on chalcogenide prism // J. Appl. Phys. 2013. V. 114. P. 014304.
8. *Wijaya E., Lenaerts C., Maricot S., Hastanin J., Habraken S., Vilcot J.P., Boukherroub R., Szunerits S.* Surface plasmon resonance-based biosensors: From the development of different SPR structures to novel surface functionalization strategies // Current Opinion in Solid State and Materials Sci. 2011. V. 15. P. 208–224.
9. *Abbas A., Linman M.J., Cheng Q.* Sensitivity comparison of surface plasmon resonance and plasmon-waveguide resonance biosensors // Sensors and Actuators B. 2011. V. 156(1). P. 169–175.
10. *Homola J., Yee S.S., Gauglitz G.* Surface plasmon resonance sensors: Review // Sens. Actuator B. 1999. V. 54(1–2). P. 3–15.
11. *Nair R.R., Wu H., Jayaram P.N., Grigorieva I.V., Geim K.* Unimpeded permeation of water through helium-leak-tight graphene-based membranes // Science. 2012. V. 335(6067). P. 442–444.
12. *Joshi R.K., Carbone P., Wang F.C., Kravets V.G., Su Y., Grigorieva I.V., Wu H., Geim K., Nair R.R.* Precise and ultrafast molecular sieving through graphene oxide membranes // Science. 2014. V. 343. P. 752–754.
13. *Cittadini M., Bersani M., Perrozzi F., Ottaviano L., Wlodarski W., Martucci A.* Graphene oxide coupled with gold nanoparticles for localized surface plasmon resonance based gas sensor // CARBON. 2014. V. 69. P. 452–459.
14. *Mikheev G.M., Zonov R.G., Obraztsov A.N., & Svirk Y.P.* Sensitivity of fast-response nanographite photodetector at high temperature // Optical Sensors. 2009. V. 7356. P. 73560X.
15. *Zhang H., Sun Y., Gao S., Zhang J., Zhang H., Song D.* Novel graphene oxide based surface plasmon resonance biosensor for immunoassay // Small. 2013. V. 9. P. 2537–2540.
16. *Bin Mat Yunus W.M., Bin Abdul Rahman A.* Refractive index of solutions at high concentrations // Appl. Opt. 1988. V. 27(16). P. 3341–3343.
17. *Sosnova M.V., Dmitruk N.L., Korovin A.V., Mamykin S.V., Mynko V.I., Lytvyn O.S.* Local plasmon excitations in one-dimensional array of metal nanowires for sensor applications // Appl. Phys. B. 2010. V. 99(3). P. 493–497.

18. *Simsek E.* On the surface plasmon resonance modes of metal nanoparticle chains and arrays // Plasmonics. 2009. V. 4(3). P. 223–230.

19. *Schmidt M.A., Sempere L.P., Tyagi H.K., Poulton C.G., Russell P.S.J.* Waveguiding and plasmon resonances in two-dimensional photonic lattices of gold and silver nanowires // Phys. Rev. B. 2008. V. 77(3). P. 033417.

20. *Yang M.R., Chu S.Y., Chang R.C.* Synthesis and study of the SnO_2 nanowires growth // Sensors and Actuators B: Chemical. 2007. V. 122(1). P. 269–273.

21. *Oh W.K., Yoon H., Jang J.* Characterization of surface modified carbon nanoparticles by low temperature plasma treatment // Diamond and Related Materials. 2009. V. 18(10). P. 1316–1320.

22. *Byun K.M., Shuler M.L., Kim S.J., Yoon S.J., Kim D.* Sensitivity enhancement of surface plasmon resonance imaging using periodic metallic nanowires // J. Lightwave Technol. 2008. V. 26(11). P. 1472–1478.

23. *Yao H., Duan J., Mo D., Günel Yu.H., Chen Y., Liu J., Sch pers T.* Optical and electrical properties of gold nanowires synthesized by electrochemical deposition // J. Appl. Phys. 2011. V. 110(9). P. 094301.

24. *Kim J.A., Hwang T., Dugasani S.R., Amin R., Kulkarni A., Park S.H., Kim T.* Graphene based fiber optic surface plasmon resonance for bio-chemical sensor applications // Sens. Actuators B: Chem. 2013. V. 187. P. 426–433.

25. *Mak K.F., Lee C., Hone J., Shan J., Heinz T.F.* Atomically thin MoS_2: A new direct-gap semiconductor // Phys. Rev. Lett. 2010. V. 105. P. 136805.

26. *Ouyang Q., Zeng S., Dinh X.Q., Coquet P., Yong K.T.* Sensitivity enhancement of MoS_2 nanosheet based surface plasmon resonance biosensor // Proc. Engineering. 2016. V. 140. P. 134–139.

27. *Roy K., Padmanabhan M., Goswami S., Sai T.P., Ramalingam G., Raghavan S., Ghosh A.* Graphene-MoS_2 hybrid structures for multifunctional photoresponsive memory devices // Nat. Nanotechnol. 2013. V. 8. P. 826–830.

28. *Lee K.S., Son J.M., Jeong D.Y., Lee T.S., Kim W.M.* Resolution enhancement in surface plasmon resonance sensor based on waveguide coupled mode by combining a bimetallic approach // Sensors. 2010. V. 10(12). P. 11390–11399.

29. *Gupta B.D., Sharma A.K.* Sensitivity evaluation of a multi-layered surface plasmon resonance-based fiber optic sensor: A theoretical study // Sens. Actuators B: Chem. 2005. V. 107(1). P. 40–46.

30. *Castellanos-Gomez A., Agraït N., Rubio-Bollinger G.* Optical identification of atomically thin dichalcogenide crystals // Appl. Phys. Lett. 2010. V. 96(21). P. 213116.

31. *Meshginqalam B., Ahmadi M.T., Ismail R., Sabatyan A.* Graphene/graphene oxide-based ultrasensitive surface plasmon resonance biosensor // Plasmonics. 2017. V. 12(6). P. 1991–1997.

32. *Verma A., Prakash A., Tripathi R.* Sensitivity enhancement of surface plasmon resonance biosensor using graphene and air gap // Opt. Commun. 2015. V. 357. P. 106–112.

33. *Choi M., Kim N.H., Eom S., Kim T.W., Byun K.M., Park H.H.* Fabrication and characterization of gold nanocrown arrays on a gold film for a high-sensitivity surface plasmon resonance biosensor // Thin Solid Films. 2015. V. 587. P. 43–46.

34. *Maurya J.B., Prajapati Y.K., Singh V., Saini J.P.* Sensitivity enhancement of surface plasmon resonance sensor based on graphene-MoS_2 hybrid structure with TiO_2-SiO_2 composite layer // Appl. Phys. A. 2015. V. 121. P. 525–533.