Sensitivity Improved Surface Plasmon Resonance Sensor Based on Graphene and Gold Nanorods

Shuwen Zeng[1,2,3*], Mathieu Sylvain Bergont[2], Aurelien Olivier[2], Xuan-Quyen Dinh[2], Xia Yu[3], Ken-Tye Yong[1*]

[1]School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, 639798

[2]CINTRA CNRS/NTU/THALES, UMI 3288, Research Techno Plaza, 50 Nanyang Drive, Border X Block, Singapore, 637553

[3]Singapore Institute of Manufacturing Technology, 71 Nanyang Drive, Singapore, 638075

[*]Email: szeng2@ntu.edu.sg; ktyong@ntu.edu.sg

Abstract

In this study, we proposed a new sensing configuration for enhancing the surface plasmon resonance (SPR) based on graphene and gold nanorods (Au NRs). Both analytical modeling based on Fresnel equations and numerical analyses through finite element method (FEM) are performed to optimize the number of graphene layers and the aspect ratio (AR) of Au NRs. The improved sensitivity up to 10^6 degree/ RIU can be achieved by adding a monolayer of graphene onto the Au sensing film with coupling of localized SPR of Au NR (AR=2).

Keywords: Surface plasmon resonance, sensor, graphene, gold nanorods

Introduction

Surface Plasmon resonance (SPR) has been widely studied in the past decade for their potential as a highly sensitive probe to detect biological and chemical interactions in real time [1-4]. This optical phenomenon is associated with electromagnetic waves that consist of collective oscillations of free electron gas propagating along the interface between metal and dielectric. A well-known method to excite SPR is proposed by Kretschmann [5]. The configuration is based on a prism coupler, the light energy will transfer from photons to surface plasmons when the incident angle equals to the resonance angle (θ_{SPR}). This SPR resonance angle is always larger than θ_c, thus total light reflection would occur. The reflective light signal (intensity and phase) can be measured. For example, the reflectivity (R) would decrease to almost zero when SPR excites. However, conventional SPR sensors are limited for sensing of tiny molecules such as cytokine and TNT. There are two main strategies that can further improve the sensitivity: (i) using phase measurement method – sharper signal change than that of intensity and wavelength (ii) exploring new sensing structures such as functionalization the sensing film with nanoparticles and graphene[6-9].

Recently, graphene-based photonics have attracted great attention in various applications such as optical modulators, photovoltaic devices, saturable absorbers and ultrafast lasers, etc[10]. Another important application is to enhance the sensitivity of SPR [11-15]. It has been demonstrated that monolayer graphene only absorbs 2.3% of transmitted light and there will be a charge transfer when graphene makes contact with metals [16-17]. Furthermore, the structure of hexagonal cells existing in graphene is similar to the carbon ring in most of chemical and biological molecules. Thus, the π-stacking interactions will help the sample molecules adsorb more tightly to the sensing film of SPR. But many researchers only focus on the interactions between graphene and the metallic sensing film, few of them studied the sensitivity enhancement by coupling of functionalized metallic nanoparticles on the graphene-modified sensing film, even the metallic nanoparticles such as gold nanorods (Au NRs), have a high electron density on their surface and the localized SPR (LSPR) of Au NRs can strongly couple with the surface plasmon wave (SPW) on the sensing film. Compared to spherical nanoparticles, nanorods are more flexible in tuning the LSPR peak by changing the aspect ratio (AR) and also more suitable for longer wavelength light excitation source (785 – 1064 nm). In this paper, we propose a new sensing configuration for enhancing the sensitivity of SPR based on graphene and gold nanorods. A sensitivity up to 10^6 degree/ RIU is achieved by adding a monolayer of graphene onto the Au sensing film with coupling of LSPR of Au NR (AR=2).

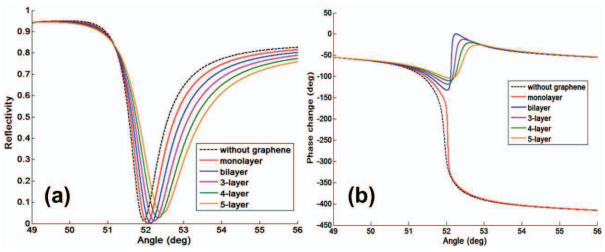

Fig.1. The effects of different number of graphene layers on (a) SPR angle and (b) phase of *p*-polarization.

Analytical Modeling

In our Kretschmann configuration, the incident light passes through an equilateral SF11 prism onto a graphene-coated Au thin film evaporated on a BK7 glass slide and then reflected out through the other edge of the prism. First, we use Fresnel equation and transfer matrix method (TMM) to optimize the number of graphene layers that are transferred onto the Au thin

film[18]. The refractive indices for each layer at excitation wavelength 785nm are 1.76652 for SF11 prism, 1.51108 for BK7 glass slide, 0.14891 + *i* 4.7830 for 50nm Au thin film and 2.90 + *i* 1.50 for graphene (0.34nm for monolayer)[19-21]. As it is reported that SPR curves are not affected by the thickness of glass slide, we set it as 100nm for simplification [22-23]. Fig.1 shows the effects of different number of graphene layers on the SPR dip angle and on the phase of *p*-polarization. One can see that both monolayer and bilayer graphene exhibit more pronounced SPR signal changes than that of without graphene. For angular measurement, the monolayer graphene-coated Au thin film experience a much lower reflectivity at SPR angle, which means that more light energy has been transferred to surface plasmons. For phase measurement, it also has a sharper phase change at SPR angle which indicates larger signal change when the concentration of sensing medium changes. Here, we suggested a differential phase measurement method for detection of biological and chemical molecules[6]. Since SPR only affect the intensity and phase of *p*-polarization light (ϕ_p), the phase of *s*-polarization light (ϕ_s) can serve as a reference channel to effectively eliminate the environmental noise (See Fig. 2). According to the results shown in Fig. 2, the sensitivity for monolayer graphene-coated Au thin film is estimated to be 2.387×10^4 °/RIU ($S = \Delta\phi_d$ / Δn, $\Delta\phi_d = |\phi_p - \phi_s|$).

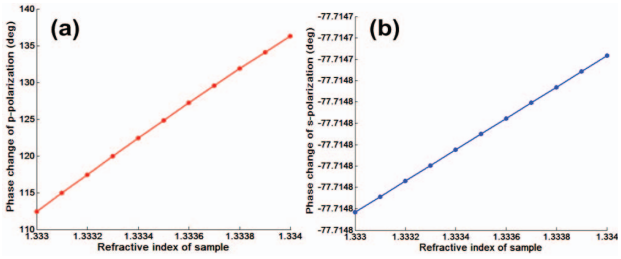

Fig.2. The relations between sample refractive index and phase of (a) *p*-polarization(ϕ_p) and (b) *s*-polarization(ϕ_s).

Numerical Analysis

To further study the perturbation of electric field when SPR excites, we employed finite element method (FEM) to have close observations on the field intensity distribution inside the multi-layer sensing structure. The solution space is set as 1.5 $\mu m \times 1.2\ \mu m$ which is larger than the wavelength of incident light 785nm in order to avoid diffraction effects. In Fig. 3(a), the media in the modeling from left to right are respectively, SF11 prism, BK7 glass slide, Au thin film and water. One can see that when the incident angle is at SPR angle, clear evanescent waves are excited and penetrate to the sensing medium. The red line in Fig. 3(a) shows the cross section range of the total electric field that we are interested in. The center of the line is in the middle of 50nm thick-Au thin film. When a monolayer graphene is coated on the Au thin film, the total electric field is enhanced by almost 4 times compared to that of without graphene as shown in Fig. 4(b). It has been demonstrated that the field intensity is linearly related to the sensitivity of the whole SPR system [24].

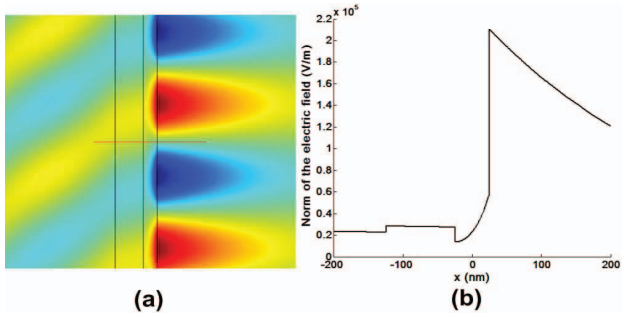

Fig.3. (a) Electric field in y component (b) Cross-section plot of total electric field, in the case of without graphene and Au NR.

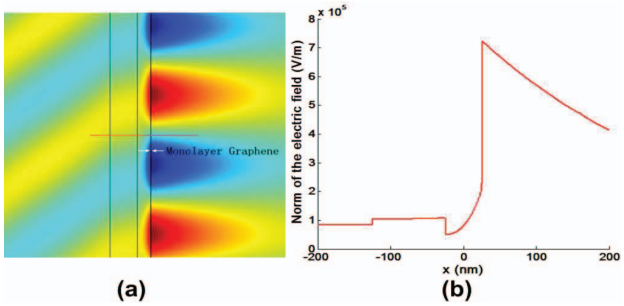

Fig.4. (a) Electric field in y component (b) Cross-section plot of total electric field, in the case of with monolayer graphene but without Au NR.

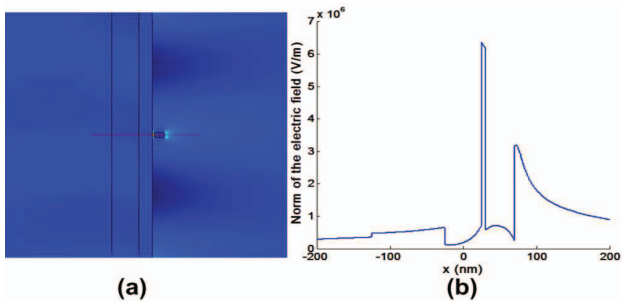

Fig.5. (a) Electric field in x component (b) Cross-section plot of total electric field, in the case of without monolayer graphene but with Au NR (20nm in width, 40nm in length, AR=2).

Then we coupled Au NRs with AR=2 (20nm in width and 40nm in length) with a gap of 5nm to the sensing film and it shows that even without graphene-coated on the Au thin film, the maximum electric field is enhanced by 30 times compared to that of without Au NRs (See Fig. 5). More importantly, when the Au NR is coupled with monolayer graphene-coated Au thin film, the electric field is further improved by 2 more times as shown in Fig. 6. These inspiring results indicate that the total sensitivity of our proposed SPR system can enhanced by 60 times compared to conventional SPR setups, up to 1.43×10^6 °/RIU.

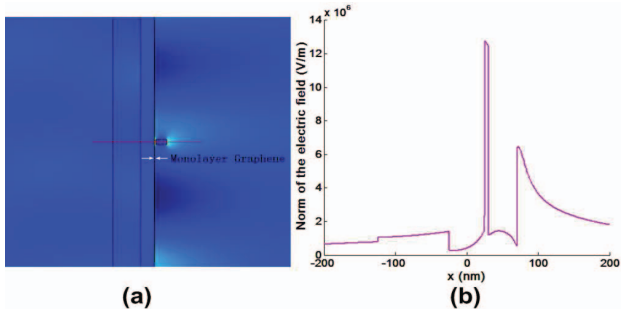

Fig.6. (a) Electric field in x component (b) Cross-section plot of total electric field, in the case of with both monolayer graphene and Au NR (20nm in width, 40nm in length, AR=2).

Conclusions

In summary, a novel SPR sensing structure based on graphene and Au NRs has been proposed and demonstrated to be capable for significantly improving the sensitivity. And it is worth noting that the value can be further enhanced depending on the specific resolution of experimental SPR configurations. The flexible fabrications of uniform and large area graphene-coated metallic thin films promise the realization of this ultrahigh sensitive structure [25-26]. The optimum number of graphene layers is 1 and the aspect ratio for Au NR is 2. Here, the large field enhancement due to strong coupling between LSPR of Au NR and SPW of the graphene-modified Au sensing film plays a key role. Typically, a SPR detection process is that the targeted biological analytes are first flowed onto the functionalized sensing film followed by Au NRs functionalized with capture-analytes. In this way, sandwich structures with targeted analytes between the Au NRs and the sensing film are formed [4, 24]. In our case, the sensing film is monolayer graphene (MG)-coated Au thin film with functional groups such as –SH and $–NH_2$ that are suitable for binding to most of biological analytes.

References

[1] Raether, H., *Surface plasmons on smooth and rough surfaces and on gratings*. 1988, Berlin: Springer-Verlag.

[2] Shuwen Zeng, Ken-Tye Yong, Indrajit Roy, Xuan-Quyen Dinh, Xia Yu, Feng Luan, *A review on functionalized gold nanoparticles for biosensing applications.* Plasmonics, 2011. **6**(3): p. 491-506.

[3] R. Schasfoort and A. Tudos, *Handbook of surface plasmon resonance*. 2008, Cambridge, UK: RSC.

[4] Shuwen Zeng, Xia Yu, Wing-Cheung Law, Yating Zhang, Rui Hu, Xuan-Quyen Dinh, Ho-Pui Ho, Ken-Tye Yong, *Size dependence of Au NP-enhanced surface plasmon resonance based on differential phase measurement.* Sensors and Actuators B: Chemical, 2012.

[5] Kretschmann, E. and H. Raether, *Radiative decay of nonradiative surface plasmons excited by light.* Z. Naturforsch. A, 1968. **23**: p. 2135.

[6] Wu, S.Y., et al., *Highly sensitive differential phase-sensitive surface plasmon resonance biosensor based on the Mach-Zehnder configuration.* Optics Letters, 2004. **29**(20): p. 2378-2380.

[7] Wang, T.J. and C.W. Hsieh, *Surface plasmon resonance biosensor based on electro-optically modulated phase detection.* Optics Letters, 2007. **32**(19): p. 2834-2836.

[8] Law, W.C., et al., *Nanoparticle enhanced surface plasmon resonance biosensing: Application of gold nanorods.* Optics Express, 2009. **17**(21): p. 19041-19046.

[9] Moirangthem, R.S., Y.C. Chang, and P.K. Wei, *Investigation of surface plasmon biosensing using gold nanoparticles enhanced ellipsometry.* Optics Letters, 2011. **36**(5): p. 775-777.

[10] Kandammathe Valiyaveedu Sreekanth, Shuwen Zeng, Jingzhi Shang, Ken-Tye Yong, Ting Yu, *Excitation of surface electromagnetic waves in a graphene-based Bragg grating.* Scientific Reports, 2012.

[11] Wu, L., et al., *Highly sensitive graphene biosensors based on surface plasmon resonance.* Optics Express, 2010. **18**(14): p. 14395-14400.

[12] Choi, S.H., Y.L. Kim, and K.M. Byun, *Graphene-on-silver substrates for sensitive surface plasmon resonance imaging biosensors.* Optics Express, 2011. **19**(2): p. 458-466.

[13] Verma, R., B.D. Gupta, and R. Jha, *Sensitivity enhancement of a surface plasmon resonance based biomolecules sensor using graphene and silicon layers.* Sensors and Actuators B-Chemical, 2011. **160**(1): p. 623-631.

[14] Maharana, P.K. and R. Jha, *Chalcogenide prism and graphene multilayer based surface plasmon resonance affinity biosensor for high performance.* Sensors and Actuators B-Chemical, 2012. **169**: p. 161-166.

[15] Salihoglu, O., S. Balci, and C. Kocabas, *Plasmon-polaritons on graphene-metal surface and their use in biosensors.* Applied Physics Letters, 2012. **100**(21).

[16] Nair, R.R., et al., *Fine structure constant defines visual transparency of graphene.* Science, 2008. **320**(5881): p. 1308-1308.

[17] Giovannetti, G., et al., *Doping graphene with metal contacts.* Physical Review Letters, 2008. **101**(2).

[18] Hansen, W.N., *Electric Fields Produced by the Propagation of Plane Coherent Electromagnetic Radiation in a Stratified Medium.* J. Opt. Soc. Am., 1968. **58**(3): p. 380-388.

[19] Weast, R.C., *CRC Handbook of chemistry and physics*. 68th ed. 1987, Boca Raton, Fla: CRC Press.

[20] Johnson, P.B. and R.W. Christy, *Optical constants of the noble metals.* Physical Review B, 1972. **6**(12): p. 4370-4379.

[21] Weber, J.W., V.E. Calado, and M.C.M. van de Sanden, *Optical constants of graphene measured by spectroscopic ellipsometry.* Applied Physics Letters, 2010. **97**(9).

[22] Xiao, C.D. and S.F. Sui, *Numerical simulations of surface plasmon resonance system for monitoring DNA hybridization and detecting protein lipid film interactions.* European Biophysics Journal with Biophysics Letters, 1999. **28**(2): p. 151-157.

[23] Xiao, C.D. and S.F. Sui, *Characterization of surface plasmon resonance biosensor.* Sensors and Actuators B-Chemical, 2000. **66**(1-3): p. 174-177.

[24] Law, W.C., et al., *Sensitivity improved surface plasmon resonance biosensor for cancer biomarker detection based on plasmonic enhancement.* Acs Nano, 2011. **5**(6): p. 4858-4864.

[25] Eda, G., G. Fanchini, and M. Chhowalla, *Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material.* Nature Nanotechnology, 2008. **3**(5): p. 270-274.

[26] Song, B., et al., *Graphene on Au(111): A highly conductive material with excellent adsorption properties for high-resolution bio/nanodetection and identification.* Chemphyschem, 2010. **11**(3): p. 585-589.