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PH-DEPENDENCE OF THE OPTICAL BIO-SENSOR BASED ON DNA - SEMICONDUCTOR GRAPHENE NANORIBBONS

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Abstract. *The pH dependence of the optical biosensor from DNA and semiconductor graphene nanoribbonds (SGR) is investigated. Heller et al (Science 311, 508 (2006)) [1] have demonstrated the first model of this kind of nano biosensors by wrapping a piece of double-stranded DNA around the surface of single-walled carbon nanotubes CN. This new type of optical biosensor in the first time can be placed inside living cells and detect trace amounts of harmful contaminants using near infrared light. In our design model, instead of CN with cylinder shape we take semiconductor graphene nanoribbonds (SGR) with flat geometry. Using the simple exciton theory in nanostructures, the periodic boundary conditions neglecting the edge effect, and the phenomena of B-Z structural phase transition of DNA [2], we investigate working principle and pH dependence of this new class of optical biosensor DNA-SGR responded to the presence of target ions. We have shown the range of parameters for workable conditions of this biosensor. It is indicated that the solution should have pH from 6 to 9, which is applicable for the living environments.*

I. INTRODUCTION

Graphene has rapidly received significant attention since its discovery in 2004 by Novoselov, Geim and co-workers [3]. It has been found that graphene has many unique electrical, mechanical and physical properties, such as massless Dirac quasiparticles [4], high carrier mobilities and capacities [3-4]. It is extremely important in many applications, such as genomics, clinical diagnosis and pharmaceutics because of the ability to precisely detect chemical and biological species .The symmetric band structure of graphene makes it directly amenable to chemical and physical modification. In addition, the high carrier mobility of graphene makes the modification detectable by simply monitoring its conductivity change. Since the discovery of graphene, there is great potential for building graphene-based high-sensitivity, label-free, miniaturized electrostatic or electrochemical sensors. One of the key challenges in current research and development of graphene-based sensors is material handling and device fabrication . In 2006, Daniel A. Heller et al. [1] demonstrated that carbon nanotubes (CNNTs) wrapped with DNA can be placed inside living cells and detect trace amounts of harmful contaminants using near infrared light. This discovery could lead to new types of optical sensors and biomarkers at the sub cellular level. The working principle of this optical biosensor from DNA and CNNTs can be explained by a simple theoretical model which was introduced in [5]. Based on this model,

a new design model of this sensor was introduced in [6], in which the CNNTs is replaced by a semiconductor graphene ribbon (SGR). Using a simple theory of exciton in SGRs [7], the transition of DNA secondary structure from the native, right-handed B form to the alternate, left-handed Z form is investigated. This structural phase transition of DNA is the working principle of this optical biosensor at the sub cellular level from DNA and semiconductor graphene ribbons. It is proved that the AGNR-DNA based biosensors are more sensitive than CNT-DNA based biosensors in [2]. pH is a measure of the acidity or alkalinity of a certain solution and this optical bio-sensor based from DNA and SGR is effected by pH of solution in some way, and investigating its properties vs pH is an indispensable job as for biosensor from DNA and CNNTs. In this paper, we have shown the working principle of this optical biosensor vs pH of solution. In particular, the pH-dependence of DNA and the pH-dependence of solution around SGR are shown by using data analysis method. We have shown the range of parameters for workable conditions of this biosensor was indicated that the solution should have pH from 6 to 9, which is applicable for the living environments.

II. MODEL

II.1. Theoretical model

In this paper, we investigated transition of DNA secondary structure from the native, right-handed B form to the alternate, left-handed Z form by using a simple theory of exciton in SGRs[8-10] . This structural phase transition of DNA is the working principle of this optical biosensor at the sub cellular level from DNA and semiconductor graphene ribbons. The theoretical model of biosensor based on DNA v SGR has been presented in [6].

Here, we used a GNR that has w in width and an atomic layer in thickness. The DNA strand is considered as a ribbon wrapping the GNR. The pitch along the axis of helical DNA is b, and the width of DNA strand is a. Following previous work [6] the system is depicted in Fig.1.

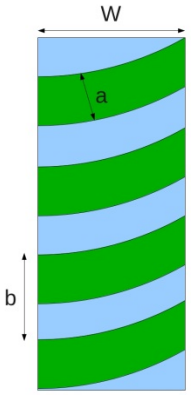

Fig. 1. The scheme of GNR-DNA based biosensor model

In this model, the effective dielectric constant of DNA and surrounding medium is given:

$$\varepsilon = f.\varepsilon_{DNA} + (1-f).\varepsilon_W \tag{1}$$

Here ε_{DNA} and ε_W are the dielectric constants of DNA and solution, respectively, and f is the ratio of DNA-covered surface area per total surface area of the GNR:

$$f = \frac{al}{2bW} \tag{2}$$

Where l is the straight length in a period of DNA. l is approximately calculated by the following expression:

$$l = 2\sqrt{\frac{b^2}{4} + W^2} \tag{3}$$

And minimizing the potential energy in order to find the equilibrium system:

$$f = \frac{a}{2W}\sqrt{\frac{4\pi^2.r_0^2 + b_0^2}{4\pi^2 r_0^2 + b_0^2 - 4\pi.r_0 W}} \tag{4}$$

Where r_0 is the equilibrium radius, and b_0 is the equilibrium pitch. In the case of equilibrium system, here r_0, b_0, and a is 1nm, 3.32nm, and 0.51 nm, respectively, for B-DNA; and $r_0 = 9$ nm, $b_0 = 4.56$ nm, and $a = 1.18$ nm for Z-DNA.

By using the separation of variables and solution of the Wannier model have been applied to the 2D semiconductor systems and AGNR systems, the exciton energy levels are given by:

$$E_{exc} = E_g - \frac{\mu.e^4}{2\hbar^2\varepsilon^2}\frac{1}{(n+1/2)^2} + \frac{\hbar^2 K^2}{2(m_e+m_h)} \tag{5}$$

where E_{exc} is the exciton energy, E_g is the band gap, e is the relative dielectric constant, n is an integer, and K is the wave vector. The second term is the binding exciton energy, denoted by E_B.

The binding exciton energy shifts at $n = 0$ when DNA change the form from Z-DNA to B-DNA

$$\Delta(E_{BZ}) = \frac{2\mu.e^4}{\hbar^2}(\frac{1}{e_Z^2} + \frac{1}{e_B^2}) \tag{6}$$

Here e_B and e_Z are the effective dielectric constant when DNA is in the form of B and Z, respectively.

II.2. Experimental parameters

When the pH of solution varies, the dielectric constants of DNA and solution around the SGR change, it brings about the variation of effective dielectric constant. Therefore, the optical signals of our sensor change. So, it is important to investigate the pH-dependence of dielectric constants of component parts, DNA and CNNTs. The pH-dependence of the dielectric parameters of DNA was investigated in [11] by experiences.

In this paper, we assumed that the dependence on the pH of the biosensor SGR-DNA and biosensor CNNTs-DNA is the same. According to fitting results in [11], we have:

$$\Delta\varepsilon_{DNA}(pH) = \varepsilon_s - \varepsilon_\infty = 0,44.pH^3 - 0,89.pH^2 + 5,93.pH - 6,24 \tag{7}$$

The dielectric increment $\Delta\varepsilon$ which is a measure of the magnitude of the dielectric dispersion is given by: $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ where ε_s and ε_∞ are the low-frequency and high-frequency relative permittivities describing the relaxation process, respectively. In our problem, we just paid attention in the dielectric constant at low-frequency. Because ε_∞ is quite invariable and its value is around waters one. In our computation, we seted it equal to 80. According to [2], we have:

$$\frac{A(pH) - A_p}{A_d - A_p} = \frac{K_p}{[H^+]^n + K_p} = \frac{K_p}{10^{-npH} + K_p} \tag{8}$$

Or

$$A(pH) = (A_d - A_p)\frac{K_p}{[H^+]^n + K_p} + K_p \tag{9}$$

Here, K_p is the reaction equilibrium constant, A_p and A_d as the absorption intensities of the protonated and deprotoanted states. Approximately, the values of lnK_p range from -36.39 to -33.97 [8] and the average number of protons reacting per protonated entity was determined to be $n = 3$.

Otherwise, the absorbance of photons is given by the golden rule:

$$A(pH) = Const\frac{e^2}{\varepsilon_s(pH)}|\langle\widehat{e}.p_{cv}\rangle|^2\delta(E_v + \hbar\omega - E_e) \tag{10}$$

In case, the SGR is in the normal solution at a neutral pH, the dielectric constant is ε_0 (equal to the dielectric constant of water of 80), the neutral absorbance of photons A_0 would be:

$$A_0 = \frac{e^2}{\varepsilon_0}|\langle\widehat{e}.p_{cv}\rangle|^2\delta(E_v + \hbar\omega - E_e) \tag{11}$$

Dividing (10) to (11), and substituting (9) into the obtained equation then gives:

$$\frac{\varepsilon^s}{\varepsilon_0} = \frac{A_0}{(A_d - A_p).\dfrac{K_p}{[H^+]^n + K_p} + A_p} \tag{12}$$

III. RESULTS

Dielectric constants of DNA and solution around SGR are varied when thesolution pH changes. So, the pH dependence of effective dielectric constant will be expressed as:

$$\varepsilon(pH) = f.\varepsilon_{DNA}(pH) + (1 - f).\varepsilon_s(pH) \tag{13}$$

The effective dielectric constant of solution around sensor versus pH curves is illustrated in Fig. 2

The exciton binding energy of SWNT in the solution would be written as follow:

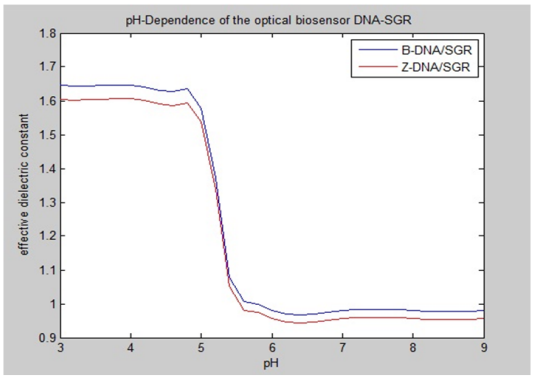

Fig. 2. pH-Dependence of the dielectric constant

$$E_{bind}(pH) = A.R^{\alpha-2}\mu^{\alpha-1}\varepsilon^{-\alpha}(pH) \tag{14}$$

And the neutral exciton binding energy is:

$$E_{bind}(pH) = A.R^{\alpha-2}\mu^{\alpha-1}\varepsilon_0^{-\alpha} \tag{15}$$

Dividing (14) to (15), the exciton binding energy of SGR in the solution is written as:

$$\frac{E_{ext}(pH)}{E_\beta^{(0)}} = \frac{E_g}{E_\beta^{(0)}} = \left(\frac{\varepsilon_0}{f.\varepsilon_{DNA}(pH) + (1-f).\varepsilon_s(pH)}\right)^\alpha \tag{16}$$

The pH-dependence of the exciton binding energy is insulated in Fig.4

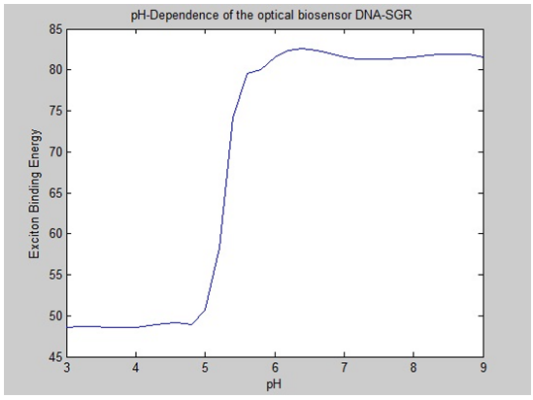

Fig. 3. The pH-dependence of the exciton binding energy

IV. CONCLUSIONS

This new combining structure of DNA and SGR is really interesting. The biosensor based on DNA and GNR open new prospects of CNNT applications on nanotechnology in the future, due to their potential applications. By using a simple model for DNA, we have investigated the environment-dependent properties of biosensor. We showed the expression of effective dielectric constant of medium. The pH dependence of the optical biosensor from DNA and semiconductor graphene nanoribbonds (SGR) is investigated and we can see that, the workable solution for sensor should has pH from 6 to 9. Therefore, we can choose the best parameters for the model. The sensors properties depend on temperature, pKa, pressure, etc are still such interesting ways for studying more.

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