Communications in Physics, Vol. 18, No. 3 (2008), pp. 151-156

ON THE NEW TYPE OF OPTICAL BIO-SENSOR FROM DNA-WRAPPED CARBON NANOTUBES

DO PHI HUNG, DAO LE HIEN, DO THI NGA,
NGO VAN THANH, AND NGUYEN AI VIET
Institute of Physics and Electronics, 10 Daotan, Badinh, Hanoi.

Abstract. *Recently, Daniel A. Heller et al. (Science* **311**, *508 (2006)) demonstrated that carbon nanotubes 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. We study a simple model of this new optical bio-sensor by wrapping a piece of double-stranded DNA around the surface of single-walled carbon nanotubes, in much the same fashion as a ribbon wraps around a cylinder. The DNA starts out wrapping around the nanotube with a certain shape that is defined by the negative charges along its backbone. Based on a theory of exciton in carbon nanotubes and we investigated transition of DNA secondary structure from the native, right-handed "B" form to the alternate, left-handed "Z" form. We've shown that our simple model can explain the working principle of this optical bio-sensor from DNA and carbon nanotubes.*

I. INTRODUCTION

Carbon nanotubes (CN) were first described by Sumio Iijima [2] which can be thought of as a sheet of graphite rolled into a cylinder. Since their discovery, CNs have been the focus of intensive theoretical and experimental studies, due to their potential applications which utilize their unique electronic and mechanical properties [3]. The band structure of CN has been obtained by means of tight-binding method [4]. It has been shown that CN's change between metal and semiconductor depending on their structure such as the diameter and the helical arrangement. The condition for such a characteristic change can be derived based on the band structure of a two-dimensional graphite sheet, this characteristic change can be well reproduced in the $\mathbf{k} \cdot \mathbf{p}$ method [5]. Many works have been carried out to investigate the electronic and optical properties of carbon nanotubes [6, 7, 8], due to the optical characterization is an important technique for understanding the physical properties of nanostructures.

Recently, the prospects of nanotechnology in cardiology it is stated: In vivo sensors which could constantly monitor O_2 blood concentrations and cardiac function to detect problems during sleep. In addition, heart-specific antibodies tagged with nanoparticles may allow doctors to visualize heart movement while a patient experiences sleep apnea to determine both short- and long-term effects of apnea on cardiac function. Carbon nanotubes can be used for optical nanosensors, because they typically fluoresce in the near infrared (n-IR) spectral region, where human tissue and biological fluids are characteristically transparent. An example is the application of Single-Walled Carbon Nanotubes (SWNTs) to monitor blood glucose [9]. As shown in [1], SWNTs wrapped with DNA can be placed inside living cells in order to detect trace amounts of harmful contaminants

at the subcellular level. When the DNA is exposed to ions of certain atoms (e.g., calcium, mercury and sodium) the DNA changes shape, perturbing the electronic structure of SWNT and shifting the nanotube's fluorescence to lower energy.

In this paper, we have discussed the working principle of the new type of optical bio-sensor SWNT-DNA. By using our simple theoretical model and the theory of exciton in carbon nanotubes, we have investigated the phase transition of DNA from the native "B" form (right-handed) to the alternate "Z" form (left-handed). Our results indicate the range of parameters for workable of bio-sensor.

II. EXCITON IN SWNT AND DNA STRUCTURAL TRANSITION

Exciton theory is useful to explain the optical properties of materials especially of nano-materials. It was known that exciton effects in quasi-one-dimensional materials such as carbon nanotubes are expected to be important due to confinement of electrons and holes [10]. The exciton energy for the quasi-particles is defined by

$$E_{\text{exc}} = E_g - E_{\text{bind}}, \tag{1}$$

where E_g is the band gap energy, and E_{bind} is the exciton binding energy. In the case of SWNT, the expression of exciton binding energy was obtained by fitting to the experimental data [11]

$$E_{\text{bind}} = AR^{\alpha-2}\mu^{\alpha-1}\varepsilon^{-\alpha}, \tag{2}$$

in which, R is the radius of SWNT (nm); ε (a.u.) is the dielectric constant. $A = 24.1(\text{eVnm}^{-3/5})$ and $\alpha = 1.4$(a.u.) are fitting constants. μ is reduced effective mass of exciton which could be described by the expression [10]

$$\mu = \frac{0.03871(\text{nm})}{2R} + \begin{cases} \frac{-0.005083(\text{nm})^2\cos(3\theta)}{4R^2} & \text{if Mod}(n-m,3) = 1 \\ \frac{+0.008533(\text{nm})^2\cos(3\theta)}{4R^2} & \text{if Mod}(n-m,3) = 2 \end{cases} \tag{3}$$

where n, m are indexes of chiral vector, θ is a chiral angle of SWNT.

Base on above experimental model, we consider DNA as a ribbon with the width of w (nm). This ribbon regularly wraps around surface of cylinder radius of R (nm) with period along the axis of cylinder b (nm) (see Fig. 1.). Therefore, effective dielectric constant of medium surrounding SWNT can be written as $\varepsilon = f\varepsilon_{\text{DNA}} + (1-f)\varepsilon_w$ [12], where ε_{DNA} and ε_w are dielectric constants of DNA and water, respectively; $f = (w\ell)/(2\pi Rb)$ is the ratio of surface area covered by DNA per total cylindrical surface area, in which $\ell = \sqrt{4\pi^2r^2 + b^2}$ is the length stretching out of DNA in one period.

By using the model of helical spring for DNA [13], we can write the expression of f as a function of structural parameters of DNA. Total energy is, therefore, expressed by: $U_{\text{tot}} = U_B + U_T + U_G$ where U_B, U_T and U_G are bending, twisting and gravitational potentials, respectively. For the case of nano-system, the gravitational potential can be neglected, so U_B and U_T could be written in the forms

$$U_B = \frac{1}{2}EI_1L(\kappa - \kappa_0)^2, \qquad U_T = \frac{1}{2}GI_2L(\tau - \tau_0)^2, \tag{4}$$

here E and G are Young's and shear modulus, I_1, I_2 are second moments of area of the perpendicular section of the wire about diameter and a normal axis through the center, and L is the stretched-out length of the wire; κ_0, τ_0 are initially curvature and torsion,

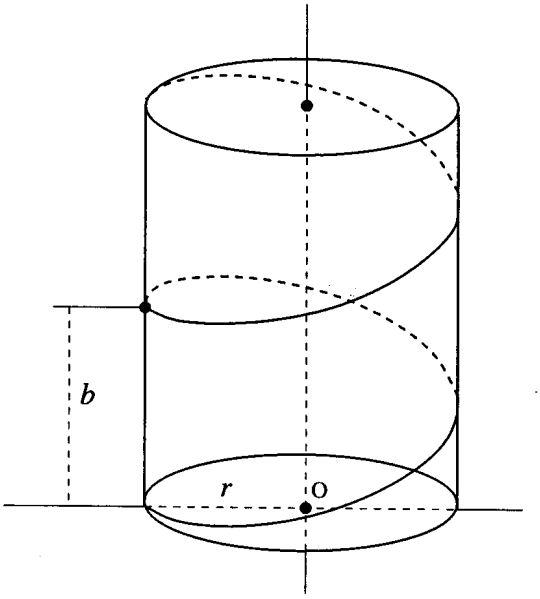


Fig. 1. Theoretical model of optical bio-sensor

respectively, these describe its configuration with no load. It is convenient to be able to express κ and τ in term of measurable quantities, and for this purpose z and φ, the coordinates of the free end of the spring are introduced, are then shown to be:

$$\kappa = \frac{\varphi(L^2 - z^2)^{1/2}}{L^2}, \qquad \tau = \frac{z\varphi}{L^2}. \tag{5}$$

Consider the curvature and torsion in one period, the expression (5) becomes:

$$\kappa = \frac{4\pi^2 r}{4\pi^2 r^2 + b^2}, \qquad \tau = \frac{2\pi b}{4\pi^2 r^2 + b^2}, \tag{6}$$

Substituting (6) into (4), the total potential U_{tot} is following:

$$U_{\text{tot}} = \frac{1}{2} EI_1 L \left(\frac{4\pi^2 r}{4\pi^2 r^2 + b^2} - \frac{4\pi^2 r_0}{4\pi^2 r_0^2 + b_0^2} \right)^2 + \frac{1}{2} GI_2 L \left(\frac{2\pi b}{4\pi^2 r^2 + b^2} - \frac{2\pi b_0}{4\pi^2 r_0^2 + b_0^2} \right)^2. \tag{7}$$

In case of equilibrium system, using minimum energy condition of DNA, we have:

$$b = \sqrt{\frac{r}{r_0}(4\pi^2 r_0^2 + b_0^2) - 4\pi^2 r^2}, \tag{8}$$

Because SWNT is covered by DNA, then we can replace r by R in Eq. (8)

$$b = \sqrt{\frac{R}{r_0}(4\pi^2 r_0^2 + b_0^2) - 4\pi^2 R^2}, \tag{9}$$

Finally, we obtained the expression of the ratio f as a function of structural parameters of DNA and radius of SWNT:

$$f = \frac{w}{2\pi R} \sqrt{\frac{4\pi^2 r_0^2 + b_0^2}{4\pi^2 r_0^2 + b_0^2 - 4\pi^2 R r_0}}, \tag{10}$$

Note that, the electronic structure of SWNT change with changing the structure of DNA, so that the energy of nanotube's natural n-IR fluorescence is changed.

III. EXCITON ENERGY OF SWNT WRAPPED DNA

When the bio-sensor is in the certain medium where the ionic concentration exceed a critical value, the structure of DNA will be changed over from B to Z form, so the emission energy of SWNT was shifted. The deviation of exciton binding energy can be expressed as

$$\Delta E_{\mathrm{B}\to\mathrm{Z}} = E_{\mathrm{bind-B}} - E_{\mathrm{bind-Z}} = AR^{\alpha-2}\mu^{\alpha-1}\left(\frac{1}{\varepsilon_{\mathrm{B}}^{\alpha}} - \frac{1}{\varepsilon_{\mathrm{Z}}^{\alpha}}\right). \tag{11}$$

Now, we investigate the deviation of energy as a function of structural parameters of SWNT in particularly of radius of SWNT. By using numerical method, we show in Fig. 2 the ratio of surface area covered by DNA per total area for two kinds of DNA form vs radius of SWNT. We see that the ratio covered by DNA in B-form is larger than one in Z-form.

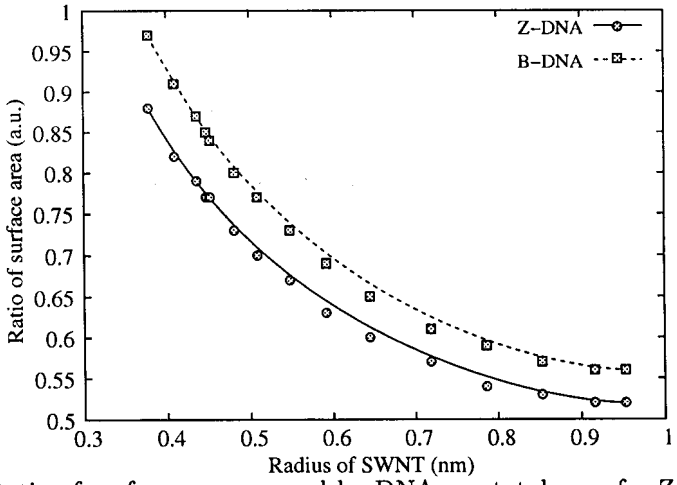
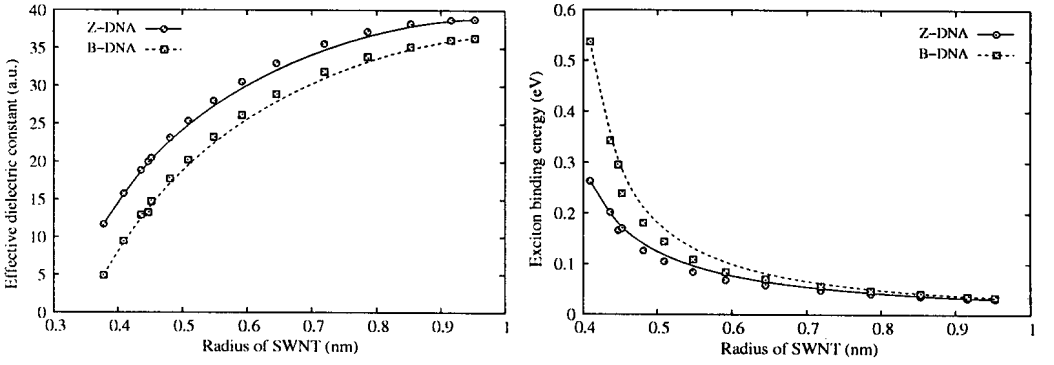


Fig. 2. Ratio of surface area covered by DNA per total area for Z- (circles) and B- (squares) forms

It well known that the dielectric constant of DNA is much smaller than dielectric constant of water, i.e., the effective dielectric constant in B-form must be smaller than that in Z-form, so the exciton binding energy of SWNT in B-form is larger than Z-form (see in Figs. 3(a), 3(b).

In Fig. 4 we shown the dependence of $\Delta E_{\mathrm{B}\to\mathrm{Z}}$ on radius of SWNT. The bio-sensors is only workable in range of small radius.

In the case of low concentration, there is no phase transition of DNA and DNA exists in the B-form only, so the effective dielectric constant could depend on concentration of solution. We shown in Fig. 5(a) the dependence of solution on its concentrations [14], in particularly for sodium chloride solution. Using this result, we investigate exciton energy as a function of ionic concentration (Fig. 5(b)).



(a) (b)

Fig. 3. a) Effective dielectric constant for Z- (circles) and B- (squares) forms. b) Exciton binding energy of SWNT for Z- (circles) and B- (squares) forms.

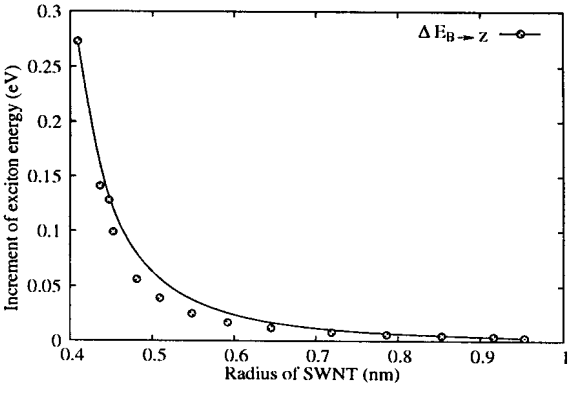
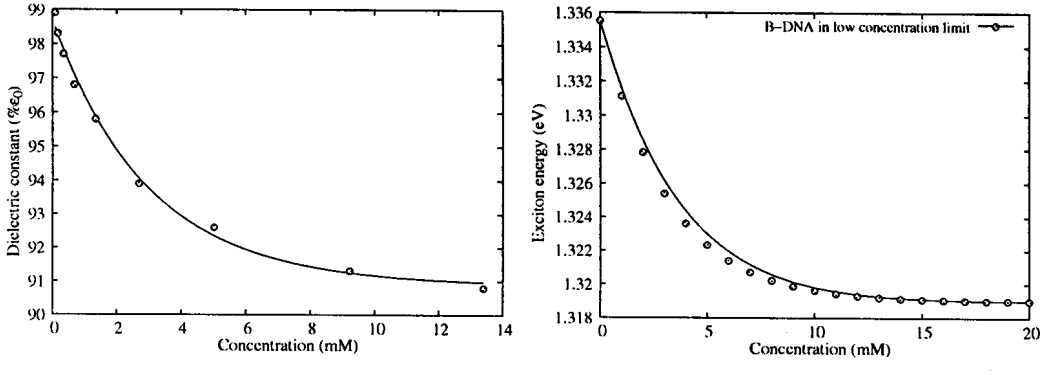


Fig. 4. Increment exciton energy in structural transition of DNA from B to Z form.



(a) (b)

Fig. 5. a) Dielectric constant of sodium chloride solution, here ε_0 is the dielectric constant of pure water; b) Exciton energy of SWNT in low salt concentration limit.

IV. CONCLUSIONS

By using our new simple model, we can explain the working principle of bionano-sensor SWNT-DNA as well as estimation and detected the presence of small amount of ions in medium. This model can be also used to calculate for various of SWNT and ionic solutions, these results are useful for the experimental study. The working mechanism of this bio-sensor can be controlled by the relevant parameters, this project will be investigated in future.

REFERENCES

[1] Daniel A. Heller, Esther S. Jeng, Tsun - Kwan Yeung, Brittany M. Martinez, Anthonie E. Moll, Joseph B. Gastala, Michael S. Strano, *Science* **311** (2006) 508.
[2] S. Ijima, *Nature*, **354** (1991) 56 .
[3] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon nanotubes*, Imperial College Press, London, (1998).
[4] R. Saito, M. Fujita, M.S. Dresselhaus, and G. Dresselhaus, *Phys. Rev.* **B 46**, 1804 (1992).
[5] H. Ajiki and T.Ando, *J. Phys. Soc. Japan* , **62** (1993) 1255; *ibid.* **63** (1994) 4267.
[6] M. F. Lin, *Phys. Rev.* **B 62** (2000) 13153.
[7] O. J. Korovyanko, C. X. Sheng, Z. V. Vardeny, A. B. Dalton, and R. H. Baughman, *Phys. Rev. Lett.* **92** (2004) 017403.
[8] T. Ando, *J. Phys. Soc. Japan*, **66** (1997) 1066.
[9] Paul W. Barone, Seunghyun Baik, Daniel A. Heller and Michael S. Strano, *Nature Material*, **4**, (2005) 86.
[10] Thomas G. Pedersen, *Carbon*, **42** (2004) 1007.
[11] Vasili Perebeinos, J. Tersoff, and Phaedon Avouris, *Phys. Rev. Lett.* **92** (2004) 257402.
[12] J-P. Demaret, and M. Gueron, *Biophysical Journal*, **65** (1993) 1700.
[13] Ronald Geralle, *Amer. J. Phys*, **26** (1958) 287.
[14] V. I. Little, *Journal of Science Instruments*, **36** (1959) 129.

Received 31 December 2007.