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# The Interaction Between Carbon Nanomaterials and Polypeptide: An *in vitro* and *in silico* Study

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*The interaction of carbon nanotubes (CNTs) and peptide molecule has been investigated by means of experiment and theoretical calculations. For comparison, the graphene-peptide system was investigated with the same manner. It was found that peptide interacts strongly with the CNTs, whereas the interaction of graphene with the peptide is negligibly small. The theoretical calculation supports strongly these findings.*

**Keywords** Carbon nanotube; charge distribution; extended Hückel method; interaction; polypeptide



## 1. Introduction

Recently, carbon nanotubes (CNTs) have been much attention because of their excellent mechanical, electrical and chemical properties and are expected for variable applications such as electric devices, chemical sensor technology, and biomedical technology [1–4]. For biomedical application, the interaction between nanomaterials and biomolecules such as protein, DNA, some ions or water play important key role. Bianco *et al.* investigated that CNTs would be applied for antigen or gene delivery [5]. Kuboki *et al.* suggested that possibility of CNTs for columnchromatography to separate some protein in serum based on the interaction between CNTs and proteins [6]. Tomonari *et al.* reported that aromatic ammonium ions improved the solubility of CNTs in water [7]. Some researchers reported that peptide forms a hybrid with a single-walled carbon nanotube (SWCNT) through pi-stacking. It has also been revealed that the optical and electrical properties of CNTs may be altered by

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the interaction between the CNTs and the peptide [8–10]. However, these studies did not elucidate the interaction quantitatively enough. Though some researchers also reported the interaction of CNTs or graphene based on theoretical calculation, their investigations were focused on small molecules such as metal ions, atoms bound to CNTs [11–13]. In previous study, we also investigated the interaction between nano carbon surface and water cluster based on DFT molecular calculation [14]. Therefore, investigation for the interaction compared with both *in vitro* and *in silico* has not been reported yet.

In this paper, we investigated the interaction between CNTs and peptides based on both experimental and theoretical study. To estimate the interaction, CNTs added into protein solution then the absorption behavior was determined. Also, the structures of protein-carbon nanomaterials complex were optimized and the interaction with proteins was compared between cylindarical CNTs and graphite.



## 2. Materials and Methods

Carbon nanotubes were purchased from CNT Inc. (Korea). They were heated at 500°C and washed with conc. hydrochloric acid for purification. Graphite was purchased from Sigma (U.S.A.) then used without purification. To estimate the protein absorption ability of these carbon nanomaterials, they were soaked into cell-culture medium as a protein solution, which include albumin. During the soaking process, the supernatant was pipetted at several time points. Then the amount of maintained albumin in supernatant was determined with BCA protein assay Kits (Pearce, U.S.A.).

The structures of carbon nanotube (CNT), graphene, peptide-CNT and peptide-graphene interaction systems were fully optimized by means of classical molecular mechanics (MM) method with MM2+ potential function [15]. The electronic states of species are calculated by means of extended Hückel method. The Gaussian 03 program package [16] was used in the calculations.

## 3. Results and Discussion

### A. *Interaction Between Carbon Nano-Materials and Polypeptide*

To estimate the interaction between carbon nano-materials and proteins, two types of nano carbon materials, which structures are based on a graphene sheet, were soaked into solution including albumin then the absorption ability was measured. The protein absorption curves were shown in Figure 1. In the case of graphite, absorption of protein was detected less than 5% even the soaking process reached more than 100 hrs. On the other hand, the amount of absorbed protein to CNTs increased with the soaking time. In early period, the protein was rapidly absorbed to CNTs. Then the amount was saturated. The absorbed amount of protein also increased depending on the soaking amount of CNTs. In this study, the absorption ability is approximately linear in relation to the concentration of CNTs.

In microscopic viewpoint, graphite and CNTs have almost same chemical structure consisted a graphene sheet. But the absorption abilities for protein were mark different. The absorption ability of graphite is very low, while that of CNTs shows markedly high ability compared with the former. One of the different points between

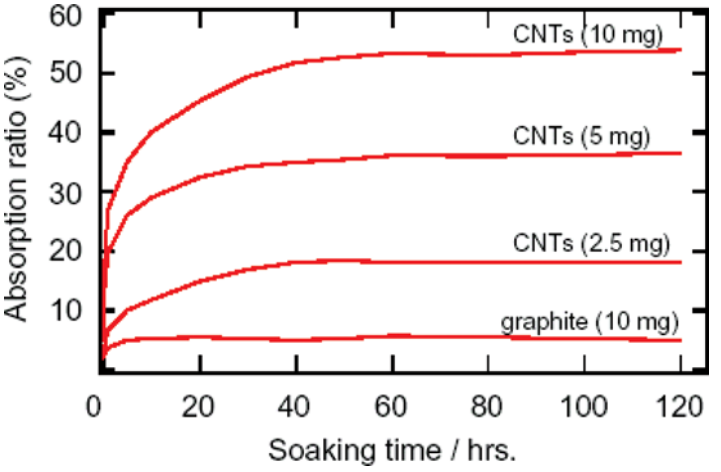


**Figure 1.** Comparison of protein absorption ability of carbon nanomaterials.

those materials is geometrical structure. Though graphite has a planer sheet structure, CNTs has a cylinderical structure with tens of nm for diameter. To elucidate the mechanism, we carried out estimation of the interaction between proteins and nanomaterials base on theoretical calculation.

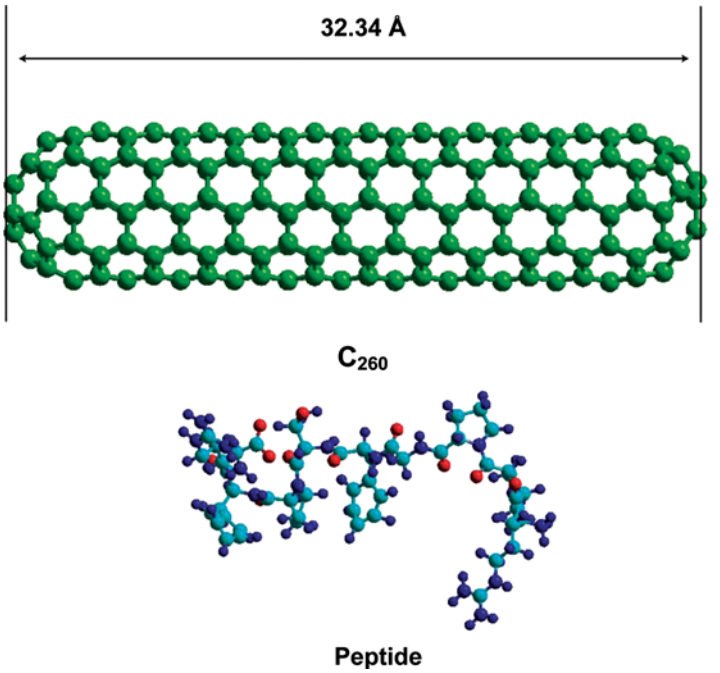


**Figure 2.** Optimized structures of carbon nanotube (CNT) and peptide molecule used in the present study.

### B. *Structures of Carbon Nanotube and Peptide*

The structures of CNT and peptide molecule used in the present study are illustrated in Figure 2. As a peptide molecule model, we used angiotensin that is a kind of small protein-hormones in human body and is part of the renin-angiotensin system. The structures are fully optimized by classical molecular mechanics (MM) method. The energy gradient method was used in the geometry optimization of all systems. The molecular length of CNT is 32.34 Å, while the CNT is composed of 260 carbon atoms ($C_{260}$). The peptide has two benzene rings. In this study, we carried out the calculations using a small CNT structure as a preliminary model.

The electronic states of CNT are calculated by means of the extended Huckel method. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are given in Figure 3. HOMO is delocalized over the CNT, especially, the orbital is delocalized on tip of CNT. The LUMO is also

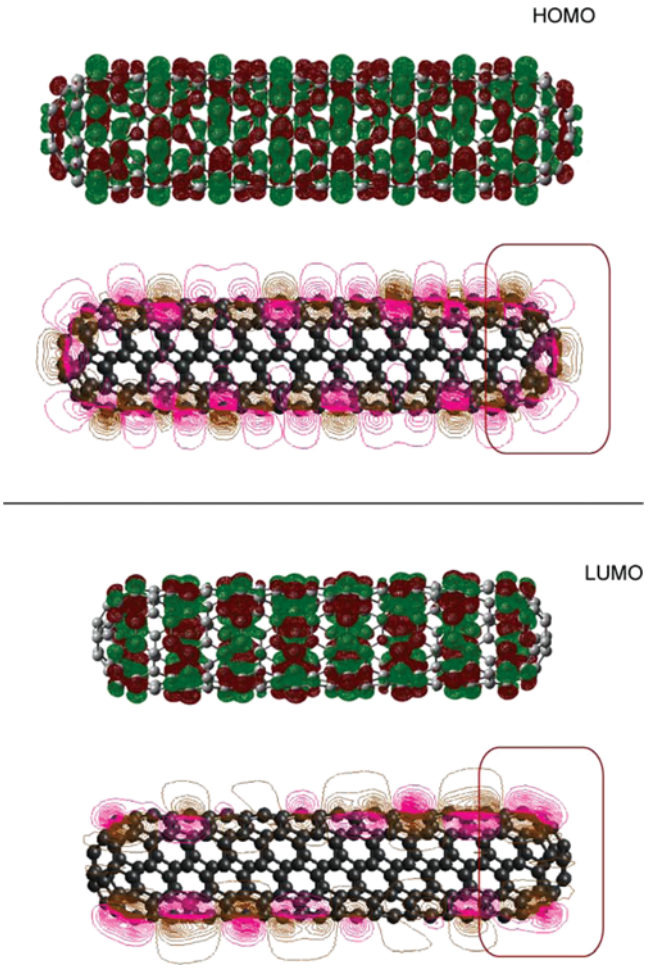


**Figure 3.** HOMO and LUMO of CNT calculated by means of Extended Hückel method.

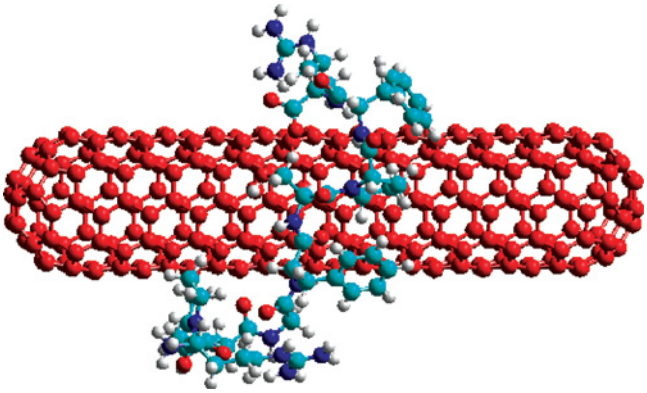

**Figure 4.** Optimized structure of CNT-peptide system.

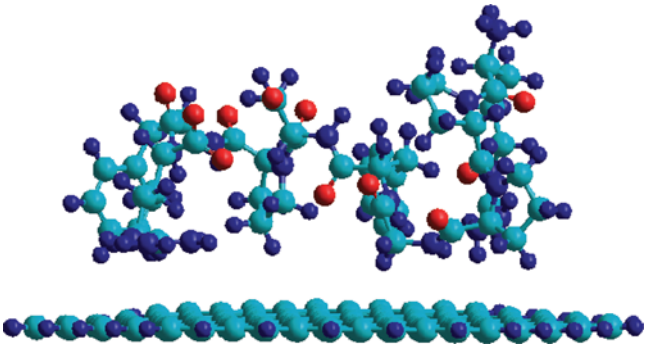

**Figure 5.** Optimized structure of graphene-peptide system.



delocalized on the CNT, but the orbital is not distributed over the tip. This is main difference between HOMO and LUMO. The HOMO-LUMO band gap is calculated to be 0.24 eV. The orbital feature implies that the electron donor molecule interacts with a body of CNT, whereas the electron acceptor molecule interacts mainly with both body and tip.

### C. *Peptide-CNT and Peptide-Graphene Interaction Systems*

The optimized structure of peptide-CNT is illustrated in Figure 4. The chain of peptide is twisted around the CNT at the most stable structure. Namely, the peptide can interact strongly with the CNT. The optimized structure of peptide-graphene is given in Figure 5. The graphene has a planer structure. The peptide molecule interacts weakly with the planer graphene. In this study, we carried out the calculations using a graphene sheet structure as a preliminary model of graphite. The surface of graphene is composed of pure 2 pz orbital. On the other hand, the surface of CNT has sp(n) (n = 2.5–2.8) hybrid orbital. Therefore, the interaction of CNT with the pectide is stronger than that of graphene.

## Conclusion

The interaction of carbon nanotubes (CNTs) and peptide molecule has been investigated by means of experiment and theoretical calculations. For comparison, the graphene-peptide system was investigated with the same manner. It was found that peptide interacts strongly with the CNTs, whereas the interaction of graphite with the peptide is negligibly small. The theoretical calculation supports strongly these findings.

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## References

[1] Majumder, M., Zhan, X., Andrews, R., & Hinds, B. J. (2007). *Langmuir*, *23*, 8624.
[2] Shim, B. S., Tang, Z. Y., Morabio, M. P., Agarwal, A., Hong, H. P., & Kotov, N. A. (2007). *Chem. Mater.*, *19*, 5467.
[3] Li, X., Fan, Y. B., & Watari, F. (2010). *Biomed. Mater.*, *5*, 22001.
[4] De Jong, W. H., & Born, P. J. (2008). *Int. J. Nanomedicine*, *3*, 133.
[5] Prato, M., Kostarelos, K., & Bianco, A. (2008). *Accounts. Chem. Res.*, *41*, 60.
[6] Kuboki, Y., Koshikawa, T., Takita, H., Fujisawa, R., Li, M. H., Abe, S., Akasaka, T., Uo, M., Watari, F., & Sammons, R. L. (2010). *Dent. Mater. J.*, *29*, 369.
[7] Tomonari, Y., Murakami, H., & Nakashima, N. (2006). *Chem. Eur. J.*, *12*, 4027.
[8] Heller, D. A., Jeng, E. S., Yeung, T.-K., Martinez, B. M., Moll, A. E., Gastala, J. B., & Strano, M. S. (2006). *Science*, *311*, 508.
[9] Kawamoto, H., Uchida, T., Kojima, K., & Tachibana, M. (2006). *J. Appl. Phys.*, *99*, 094309.
[10] Cha, M., Jung, S., Cha, M.-H., Kim, G., Ihm, J., & Lee, J. (2009). *Nano Lett.*, *9*, 1345.
[11] Suzuki, T., Hasegawa, T., Mukai, S., & Taomi, H. (2003). *Carbon*, *41*, 1933.
[12] Tachikawa, H., & Shimizu, A. (2006). *J. Phys. Chem. B*, *110*, 20445.
[13] Kelly, K. F., Chiang, I. W., Mickelson, E. T., Hauge, R. H., Margrave, J. L., Wang, X., Scuseria, G. E., Radloff, C., & Halas, N. J. (1999). *Chem. Phys. Lett.*, *313*, 445.
[14] Abe, S., Nagoya, Y., Watari, F., & Tachikawa, H. (2010). *Jpn. J. Appl. Phys.*, *49*, 01AH071.
[15] Rappé, A. K., Casewit, C. J., Colwell, K. S., Goddard, III W. A., & Skiff, W. M. (1992). *J. Am. Chem. Soc.*, *114*, 10024.
[16] Gaussian 03, Revision A.1, Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, J. A., Jr., Vreven, T., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G. A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J. E., Hratchian, H. P., Cross, J. B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Ayala, P. Y., Morokuma, K., Voth, G. A., Salvador, P.,

Dannenberg, J. J., Zakrzewski, V. G., Dapprich, S., Daniels, A. D., Strain, M. C., Farkas, O., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Ortiz, J. V., Cui, Q., Baboul, A. G., Clifford, S., Cioslowski, J., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Gonzalez, C., & Pople, J. A. (2003). *Gaussian, Inc.*, Pittsburgh: PA.