

# Ultrafast Vibrational Energy Transfer from Photoexcited Carbon Nanotubes to Proteins

Tomohito Nakayama<sup>1\*</sup>, Shunsuke Yoshizawa<sup>1</sup>, Atsushi Hirano<sup>2</sup>, Takeshi Tanaka<sup>2</sup>, Kentaro Shiraki<sup>1</sup>, and Muneaki Hase<sup>1</sup>

<sup>1</sup>Division of Applied Physics, Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan

<sup>2</sup>Nanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

**Abstract.** Carbon nanotube (CNT) and protein complexes are one of the most important nanomaterials in physical and biological fields, especially for building biomedical systems based on their unique electronic and optical properties. However, there is little knowledge about ultrafast vibrational phenomena and energy flow in CNT–protein complexes. Here, we study the ultrafast vibrational energy transfer (VET) from photoexcited carbon nanotubes to adsorbed materials, such as protein and surfactant, by observing relaxation dynamics of coherent radial breathing modes (RBMs) of CNT. As a result, we found the vibrational relaxation time of the RBMs depends on phonon density of states (PDOS) of adsorbed materials. Our findings are particularly useful for designing a highly efficient phonon energy flow system from photo-excited CNT to biomaterials, and such vibrational energy transfer can be controlled by the PDOS originated from the structure of coupled biomaterials.

## 1 Introduction

Single-wall carbon nanotubes (SWCNTs) have cylindrical structure, formed by rolling up graphene sheet, which show excellent optical and physical properties. Recently, SWCNTs have been applied for biological applications, such as photo–thermal therapy, by fabricating complexes of the SWCNTs and adsorbed materials [1–3]. In particular, SWCNT–protein complexes are intriguing nanomaterials because SWCNTs can have biological functions through adsorption of proteins, such as antibody that has the ability for treating cancer. To this end, physical properties of the SWCNTs, such as electron–phonon coupling and phonon–phonon coupling, have also been extensively studied [4]. However, there is little knowledge about the vibrational energy transfer from SWCNTs to adsorbed materials in ultrafast time scales.

In this study, we demonstrate that the vibrational energy transfer from photoexcited SWCNTs to proteins is governed by overlap of their phonon density of states (PDOS). The coherent radial breathing mode (RBM) of the SWCNTs was found to decay via two

---

\* Corresponding author: [s1720384@s.tsukuba.ac.jp](mailto:s1720384@s.tsukuba.ac.jp)

relaxation pathways: one is the internal anharmonic population decay and the other is a newly discovered pathway which is governed by the phonon–phonon coupling between SWCNTs and proteins .

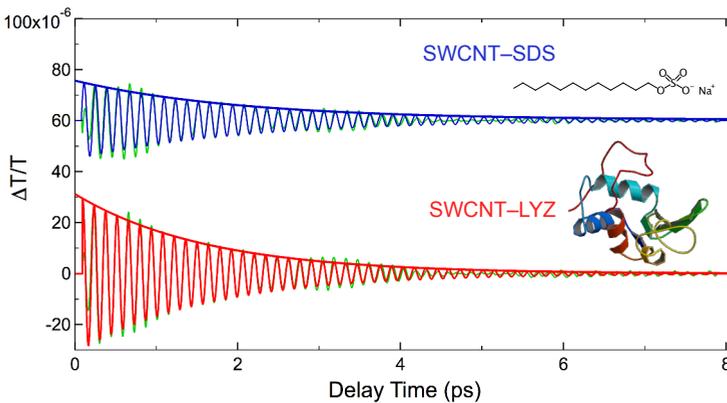
## 2 Experimental Section

The SWCNTs produced via the high-pressure catalytic CO decomposition process (HiPco) were used. We selected two adsorbed materials to compare the difference on the effect of the energy transfer, those are sodium dodecyl sulfate (SDS) and Hen egg-white lysozyme (LYZ). Subsequently, SWCNTs were dispersed by using ultrasonic processor in bulk solution.

The transient transmission ( $\Delta T/T$ ) of SWCNT complexes was measured in a 5-mm-thick quartz cell at room temperature by employing the fast scanning delay method. Optical pump–probe measurements were carried out using a femtosecond Ti:sapphire laser oscillator operated at 80 MHz, which provides near infrared optical pulses with a pulse duration of  $\approx 20$  fs with a central wavelength of 830 nm. The pump and probe pulses were focused on a 70- $\mu\text{m}$ -diameter spot in the sample with a mutual angle of  $\approx 10^\circ$ . The pump power (40 mW) was kept during the measurements.

## 3 Results and Discussion

Figure 1 shows the coherent phonon oscillation of the SWCNT–SDS and SWCNT–LYZ samples together with those obtained by curve fitting analysis and with the structures of adsorbed materials. It should be noted that the coherent phonon oscillation were obtained by subtracting the signal of electronic response with exponentially decaying functions from the raw data.



**Fig. 1.** Coherent phonon oscillations of SWCNT complexes observed using 830-nm excitation. The green line represents the experimental data, whereas the blue and red lines show the fits with Eq. (1). The upper and lower data correspond to SWCNT–LYZ and SWCNT–SDS, respectively. Insets show the structures of SDS and LYZ.

The data of the time-domain oscillation were fitted by a linear combination of damped harmonic oscillators,

$$\Delta T/T = A_1 e^{-t/\tau_1} \cos(2\pi\nu_1 t + \phi_1) + A_2 e^{-t/\tau_2} \cos(2\pi\nu_2 t + \phi_2) + A_3 e^{-t/\tau_3} \cos(2\pi\nu_3 t + \phi_3), \quad (1)$$

where  $A$  ( $A_1, A_2, A_3$ ),  $\tau$  ( $\tau_1, \tau_2, \tau_3$ ),  $\nu$  ( $\nu_1, \nu_2, \nu_3$ ), and  $\phi$  ( $\phi_1, \phi_2, \phi_3$ ) are the amplitude, the relaxation time, the frequency, and the initial phase of the three coherent RBMs of the first ( $\nu_1 = 6.5$  THz), the second ( $\nu_2 = 6.9$  THz), and the third ( $\nu_3 = 7.2$  THz) modes, respectively. We notice that the exponential decay curve for the dominant mode (7.2 THz) depends on the adsorbed materials; specifically, the relaxation time for the SWCNT–LYZ (1.41 ps) is significantly shorter than that for the SWCNT–SDS (2.04 ps). Although the decay of the coherent RBM for the SWCNT–SDS is generally accounted for by anharmonic phonon–phonon energy relaxation into underlying acoustic phonons, the change in the relaxation time observed in Fig. 1 cannot be explained by the anharmonic phonon–phonon energy relaxation; note that this relaxation depends only on the temperature, whereas the present experiment was performed at room temperature. Therefore, there should be another relaxation pathway. Here, we proposed that the total relaxation rate  $1/\tau$  is expressed by the sum of two relaxation pathways: the pathway for anharmonic phonon–phonon energy relaxation and the newly discovered pathway,

$$1/\tau = 1/\tau_{\text{anharmonic}} + 1/\tau_{\text{new}}, \quad (2)$$

where the latter pathway ( $\tau_{\text{new}}$ ) corresponds to the vibrational energy transfer from photoexcited SWCNTs to LYZ protein. The vibrational energy transfer was caused by overlap of the PDOS of the SWCNTs and that of the adsorbed materials [5].

### 3 Summary

We found the vibrational energy transfer between SWCNTs and adsorbed materials, i.e. SDS and LYZ, by means of the ultrafast transient transmission measurements. The vibrational relaxation time of the RBMs changed depending on the PDOS of the adsorbed materials.

### References

1. L. Nair, Y. Ngaoka, T. Maekawa, D. Sakthikumar, and R. Jayasree, *Small*, **10**, 2771–2775 (2014)
2. M. Zhang, T. Murakami, K. Ajima, K. Tsuchida, A. Sandanayaka, O. Ito, S. Iijima and M. Yudasaka, *Proc. Natl. Acad. Sci.* **150**, 14773–14778 (2008)
3. Z. Chen, S. M. Tabakman, A. P. Goodwin, M. G. Kattah, D. Dranciang, X. Wang, G. Zhang, X. Li, Z. Liu, P. J. Utz, K. Jiang, S. Fan and H. Dai, *Nat. Biotechnol.* **26**, 1285, (2008)
4. K. Makino, A. Hirano, K. Shiraki, Y. Maeda and M. Hase, *Phys. Rev. B*, **80**, 245428 (2009)
5. T. Nakayama, S. Yoshizawa, A. Hirano, T. Tanaka, K. Shiraki and M. Hase, *Appl. Phys. Express*, **10**, 125101 (2017)