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Differences in the response of the near-infrared absorbance spectra of single-walled carbon nanotubes; Effects of chirality and wrapping polymers

Yuji Matsukawa*, Shusuke Ohura, Kazuo Umemura

Department of Physics, Graduate School of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 1628601, Japan

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ABSTRACT

We detected antioxidant activity of catechin, one of the main components of tea, using SWNTs surface coated with two different biomolecules. Compared to coating with DNA already reported, it can hardly be detected when coated with carboxymethyl cellulose. For nanobiosensing using SWNTs, its sensitivity is not determined only by SWNTs, we found that biomolecules covering the surface are extremely important. In this experiment, we measured the near-infrared absorption spectra of SWNTs coated separately with two different water-soluble polymers; DNA (double-stranded DNA-SWNT complexes) and carboxymethyl cellulose (CMC, CMC-SWNT complexes), and uncovered the differences in their antioxidant properties against the flavonoid catechin. Each dispersion was oxidized with H_2O_2 at 0.03% (final concentration), following which catechin solutions were added to reduce the samples. Our results showed that the magnitude of the change in the absorbance spectra for dsDNA-SWNT complexes in response to oxidation and reduction was superior to that for CMC-SWNT complexes. The CMC-SWNT complexes exhibited almost no change in their spectra even though the same SWNT powder (produced by the high-pressure carbon monoxide (HiPco) method) was used. On the other hand, when (6, 5)-enriched SWNT powder produced by the ComoCat method was used, no significant change in the absorbance was observed, even though (6, 5)-enriched SWNTs are frequently used for nanobiosensing. Our results revealed that both the SWNT chirality and type of polymer for wrapping SWNTs are important factors for establishing nanobiosensing methods utilizing SWNTs.

1. Introduction

Many research groups have reported experiments of nanobiosensing using SWNTs. In many cases, SWNTs are coated with single-stranded or double-stranded DNA, and sensing is performed on the bio-inorganic hybrid surface.

When a double-stranded DNA (dsDNA) solution is mixed with single-walled carbon nanotube (SWNT) powder and sonicated under appropriate conditions, SWNT bundles separate during sonication and the DNA molecules wrap around the SWNT surfaces to form dsDNA-SWNT complexes [1–9]. These complexes are optically sensitive, for example, the near-infrared (NIR) absorbance and photoluminescence (PL) of the hybrids are drastically changed upon slight adjustments of the pH of the suspension [10–16]. Several authors have utilized these optical responses to develop new methods for nanobiosensing [17].

Zhao et al. studied the antioxidant potencies of caffeine-containing beverages with DNA-SWNT hybrids by NIR absorbance spectroscopy [18]. In their experiments, small amounts of caffeine or coffee solutions were injected into a dsDNA-SWNT suspension, following which a significant increase in the NIR absorbance intensities of the SWNTs was observed. The opposite effect of H_2O_2 on the NIR absorbance was also examined using a similar approach. They found that dsDNA-SWNT complexes are useful to quantitatively evaluate the antioxidant potencies of beverages. Ishibashi et al. studied the antioxidant ability of catechin and Japanese tea using dsDNA-SWNT complexes by both NIR absorbance and NIR PL spectroscopy [19]. They found that the PL responses were larger than the absorbance responses. Xu et al. studied the time dependence of H_2O_2 effects on the NIR absorbance spectra of single-stranded DNA (ssDNA) molecules and HiPco SWNTs [20,21]. Tu et al. also reported the effects of H_2O_2 on ssDNA-SWNT hybrids in detail [22–24].

It has been pointed out that not only SWNT itself is not the only factor that determines the sensitivity of nanobiosensing but also the molecules covering the surface are important. Polo et al. employed various polymers including ssDNA to wrap SWNTs to study the effect of polymers on the sensitivity of the PL changes [25,26]. They revealed that the polymers play a central role when redox-active compounds encounter polymer-SWNT complexes. They investigated how reducing

* Corresponding author.
E-mail address: 2214101@alumni.tus.ac.jp (Y. Matsukawa).

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and oxidizing small molecules affect the near-infrared fluorescence of polymer-wrapped SWCNTs. Their results show that the polymer plays an essential role. Reduced molecules such as ascorbic acid significantly increased the near-infrared fluorescence but only if SWCNTs were suspended in negatively charged polymers such as DNA or poly acrylic acid (PAA). In comparison with this, it is reported that SWNTs covered with positively charged poly allyl amine (PAH) did not react at all and quenched. They also evaluated the oxidation and reduction reactions of SWNTs / polymer complexes by spectroscopic electrochemistry, but report that they can not explain all observed patterns with only redox potential, and concluded that it depends on molecules such as DNA covering SWNTs. In particular, it is important to cover SWNTs with negatively charged molecules.

Kruss et al. have found significant increases in the fluorescence efficiency of individual DNA-wrapped SWNTs upon addition of reducing agents, including dithiothreitol, Trolox, and β-mercaptoethanol. They explained this effect by transient reduction of defect sites of the SWCNT sidewall. Although many previous studies have been conducted so far, the mechanism of antioxidant action by polymers around SWNTs has not been elucidated [17]. In other words, how to prepare the bio-inorganic surface composed of the biomolecule used for surface coating and SWNTs are one of the important points for establishing nanobiosensing method using SWNT. Recently, there are reports one after another that the chirality of SWNTs is also important.

Furthermore, direct comparison of the data in the studies mentioned above is impossible because the types of SWNTs and polymers/DNA were different among the different research groups. Zhao et al. and Ishibashi et al. used high-pressure CO conversion (HiPco) SWNTs [27,28], for which major absorbance peaks appeared between 1100 and 1300 nm [29]. They mainly analyzed the (9, 4) chirality. Polo et al. employed (6, 5)-enriched SWNTs and analyzed the absorbance near 1000 nm arising from the (6, 5) chirality. Some groups used dsDNA while others employed ssDNA. On the other hand, it is also known that DNA of a specific sequence adsorbs well to SWNTs of specific chirality [11,14,20]. The importance of biomolecules to be coated on the surface will attract attention in future in order to further examine the effects of chirality.

In this study, we systematically compared the wrapping of HiPco SWNTs with dsDNA and carboxymethyl cellulose (CMC). This is also a useful approach for elucidating the mechanism of antioxidant action by polymers surrounding SWNTs. CMC has been shown to function as an effective dispersant for exfoliating SWNT bundles [30,31], and like DNA, it is negatively charged at neutral pH. However, the properties of SWNTs wrapped with CMC against redox action have not been reported. Therefore, we compared the characteristics of CMC with those of dsDNA using the same SWNTs. Furthermore, we compared HiPco SWNTs and (6, 5)-enriched SWNTs with the same dsDNA wrapping to determine the effects of chirality on dsDNA-SWNT applications in nanobiosensing. In this study, although the difference in absorption spectral intensity between negatively charged dsDNA and CMC coated SWNTs was clarified, the mechanism of antioxidant action by polymers around SWNTs has not been elucidated.

2. Materials and methods

SWNTs produced by the HiPco synthesis method were purchased from Raymor Industries Inc. (Boisbriand, Qyebec, Canada). (6, 5)-enriched SWNT powder and dsDNA (deoxyribonucleic acid sodium salt from salmon testes, D1626) were obtained from Sigma-Aldrich Co. LLC (St. Louis, MO, USA). CMC (No. 1110) was purchased from Daicel Fine Chem. Ltd. (Chuo-ku, Tokyo, Japan). Hydrogen peroxide (abt. 30%, 084-07441) and catechin (553-74471) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka city, Osaka, Japan).

A 1 mg/mL dsDNA solution was prepared with 10 mM tris(hydroxymethyl)aminomethane - HCl (Tris-HCL) buffer (pH 7.9). To untangle the dsDNA molecules, the solution was sonicated in a bath-type ultrasonicator(80 W)for 90 min on ice. Finally, the dsDNA solution was gently shaken for 3 h. For preparation of the dsDNA-SWNT complexes, 0.5 mg of SWNT powder and 1 mL of the dsDNA stock solution were mixed and sonicated for 2 h using a probe-type sonicator (3 W, VCX-130, Sonic & Materials, Inc., Newtown, CT, USA) on ice. The supernatant of the prepared dsDNA-SWNT dispersion was stored after centrifugation at 17360 G for 3 h at 8 °C. [32–34].

Sterilized water was placed in a beaker and CMC (1 g) powder was added to prepare an aqueous CMC solution with a weight ratio of 1%. To prepare the CMC-SWNT complexes, 2.5 mg of SWNTs and 10 mL of CMC solution (ratio 1:4) were mixed and sonicated for 2 h using the probe-type sonicator (3 W) on ice. CMC-SWNT dispersions in a ratio of 1: 2 and 1: 8 were also prepared. The supernatants of the prepared CMC-SWNT dispersions were stored after centrifugation at 17360 *g* for 3 h at 8 °C.

Thereafter, 0.5 mg of (6, 5)-enriched SWNT was suspended in 1 mL of dsDNA solution. Samples were sonicated using the probe-type sonicator (3 W) for 2 h, followed by centrifugation at 17360 *g* for 3 h at 8 °C. The supernatant was collected as a dsDNA– (6, 5)-enriched SWNT suspension.

An NIR spectrometer (SolidSpec-3700DUV, Shimadzu Corporation, Kyoto city, Kyoto, Japan) was employed for absorbance measurements (1000–1350 nm). For NIR measurements of dsDNA-SWNT complexes, 100 μL of a dsDNA-SWNT suspension and 880 μL of Tris-HCL buffer solution were mixed in a cuvette, and the initial spectra recorded. Subsequently, 10 μL of H_2O_2 diluted with sterilized water (final concentration 0.03%) was added to the samples followed by incubation for 30 min at 21 °C. The spectra of the samples were measured. Finally, 10 μL of catechin solution (final concentration 15, 1.5, 0.15, 0.075, and 0.03 μg/mL) was added to the samples, and the spectra were measured after 10 min incubation at 21 °C.

For NIR measurements of CMC-SWNT complexes, 100 μL of CMC-SWNT suspension and 880 μL of sterilized water were mixed in a cuvette, and the initial spectra recorded. Subsequently, 10 μL of H_2O_2 diluted with sterilized water (final concentration 0.03%) was added to the samples, followed by incubation for 30 min at 21 °C. The spectra of the samples were measured. Finally, 10 μL of catechin solution (final concentration 15, 1.5, 0.75, and 0.3 μg/mL) was added to the samples, and the spectra were measured after 10 min incubation at 21 °C.

For dsDNA– (6, 5)-enriched SWNT suspensions, a UV–vis spectrophotometer (V-630, JASCO CORPORATION, Hachioji city, Tokyo, Japan) was employed for NIR spectra measurements. For this, 50 μL of dsDNA– (6, 5)-enriched SWNT complex and 440 μL of buffer solution (pH 7.9) were mixed in a cuvette, and the initial spectra recorded. Subsequently, 5 μL of H_2O_2 diluted with sterile water was then added to the samples (final concentration 0.03%), and incubated for 30 min at 21 °C. The spectra of the samples were measured. Finally, 5 μL of catechin solution (final concentration 15 μg/mL) was added to the samples, and the spectra were measured again after 10 min incubation at 21 °C.

Triplicate NIR measurements for each experiment were recorded to verify the reproducibility.

3. Results and discussion

Fig. 1 shows a conceptual diagram of the experiment. DsDNA-SWNT, CMC-SWNT, and dsDNA– (6, 5)-enriched SWNT suspensions were oxidized with H_2O_2 and catechin was added to detect changes in the absorption spectra.

DsDNA-SWNT suspension, CMC-SWNT suspension and dsDNA–(6,5)-Enriched SWNT were oxidized with H_2O_2 and catechin was added to detect changes in NIR-ABS spectra. Final H_2O_2 concentration was 0.03%. For comparison of these samples, the catechin concentration was 15 μg/ml.

We directly compared dsDNA and CMC using the same SWNTs to investigate the influence of the molecules covering the SWNTs on the