Distinguishing Antioxidant Molecules with Near-Infrared Photoluminescence of DNA-Wrapped Single-Walled Carbon Nanotubes

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ABSTRACT: In this study, two biomolecule solutions were distinguished using the capacity difference in the near-infrared photoluminescence (PL) of single-walled carbon nanotubes (SWNTs). Biosensing techniques using sensitive responses of SWNTs have been intensively studied. When a small amount of an oxidant or reductant solution was injected into the SWNT suspensions, the PL intensity of the SWNTs is significantly changed. However, distinguishing between different molecules remains challenging. In this study, we comparably injected saponin and banana solutions, which are known antioxidant chemicals, into an SWNT suspension. The SWNTs were solubilized by wrapping them with DNA molecules. The results show that 69.1 and 155.2% increases of PL intensities of SWNTs were observed after injection of 20 and 59 μg/mL saponin solutions, respectively. Subsequently, the increase in PL was saturated. With the banana solution, 18.1 and 175.4% increases in PL intensities were observed with 20 and 59 μg/mL banana solutions, respectively. Based on these results, the two antioxidant molecules could be distinguished based on the different PL responses of the SWNTs. In addition, the much higher saturated PL intensities observed with the banana solution suggests that the banana solution increased the capacity of the PL increase for the same SWNT suspension. These results provide helpful information for establishing biosensing applications of SWNTs, particularly for distinguishing chemicals.

INTRODUCTION

Single-walled carbon nanotubes (SWNTs) are graphene sheets rolled into cylinders and arranged with hexagonal carbon rings by means of chiral indices n and m. The n and m values, presented in the form (n,m) denoted as chirality, provide information about the diameters of SWNTs and chiral angles of the hexagons of carbon atoms when they are rolled into cylindrical tubes. Chirality also provides information about the types of SWNTs; depending on the n and m indices, SWNTs can be categorized as chiral or achiral and can be further classified as zigzag and armchair. Moreover, chiral indices can differentiate metallic from semiconductor SWNTs.

SWNTs exhibit excellent electrical properties. They have highly stable characteristics, and their highest advantage is that their band gaps can be regulated. Sankar and Kumar reported that in semiconducting SWNTs, the electron band gap is inversely proportional to the diameter. Moreover, they have high strength owing to their superior atomic structures as they are strongly composed of carbon bonds which are stronger than those of diamonds.

Furthermore, the optical properties of SWNTs have been widely studied. SWNTs has been reported to exhibit optical properties such as absorption and fluorescence, and Blancon et al. observed non-resonant absorption in SWNTs, using spatial modulation spectroscopy. Lee et al. reported that the fluorescent efficiency is insignificant in SWNTs, and it was enhanced by wrapping SWNTs with DNA and using reducing agents and also reported that SWNTs have intrinsic characteristics, which make them bright emitters. Wei et al. remarked that to analyze the structures of SWNTs, such as family, diameter, and chiral angle, photoluminescence (PL) quantum yield is necessary and observed that PL intensities depended on the concentration of SWNTs.

The chemical interactions between SWNTs and molecules have attracted significant research attention. Matsuura et al. studied the selectivity of water-soluble proteins by SWNTs by dispersion, and they found that egg white lysozyme and bovine serum albumin could disperse SWNTs, whereas papain and pepsin could not. The SWNTs’ selectivity of nitrogen oxide molecules, sulfur dioxide molecules, porphyrins, peanut allergy-causing protein ara h1, and pyrene molecules, as well as their interactions have been reported. Card et al...
pointed out that SWNTs generally have selective sensitivities to single molecules of analytes.\(^\text{17}\) Saponins are generally derived from plants and aquatic organisms and are known as glycosides composed of triterpenes and steroids.\(^\text{18,19}\) Saponins are useful owing to their enormous beneficial effects on animal health. To date, saponins have shown their ability to digest cholesterol and their anticancer, antioxidant, and antibacterial properties.\(^\text{20}\) In contrast, banana is a tropical fruit that is amply grown in Asia and has various capacities that bring noble health benefits. Moreover, bananas provide antioxidant potencies not only in the pulp but also in the peel, which can have beneficial applications.\(^\text{21}\) Banana is composed of antioxidant-rich components, such as gallic acid,\(^\text{22−24}\) dopamine,\(^\text{25}\) phenolic acids, caffeic acids, and hydroxybenzoic acids.\(^\text{25}\)

The antioxidant potencies of saponin and banana solutions have been analyzed using traditional methods by various research groups.\(^\text{20,21,25−32}\) However, the utilization of the optical responses of DNA-wrapped SWNTs (DNA-SWNTs) in the near-infrared (NIR) region has promised a modern technique for analyzing and distinguishing antioxidant biomolecules. Hamano et al. studied the antioxidant ability of catechin using NIR absorbance (NIR-ABS) values of DNA-SWNTs,\(^\text{33}\) whereas Matsukawa and Umemura analyzed it by means of NIR photoluminescence (NIR-PL) intensities of DNA-SWNTs,\(^\text{34}\) and Yamazaki and Umemura analyzed the antioxidant potencies of epigallocatechin gallate and tannic acid using NIR-PL and NIR-ABS, and the NIR-PL results showed higher antioxidant capacities.\(^\text{35}\) NIR-PL spectroscopy was employed to assess the optical responses of DNA-SWNTs to an oxidant (KMnO\(_4\)) and antioxidant biomolecules (saponin and banana biomolecules). The differences in the PL responses of SWNTs, depending on their chemical interactions with different molecules, such as DNA and biomolecules, were successfully investigated. Moreover, having different PL intensity responses upon injecting two different antioxidant biomolecules, DNA-SWNTs successfully recognized these biomolecules by showing different PL response capacities. Therefore, multiple biomolecules were successfully investigated using a single biosensing tool. NIR-ABS measurements were conducted to confirm the PL capacity of DNA-SWNTs in distinguishing between the two biomolecules. Using atomic force microscopy (AFM), different PL intensities were confirmed depending on the diameter of the DNA-wrapped SWNTs after mixing with the two biomolecules. In summary, this study provides crucial information in the field of biosensing, specifically for distinguishing chemicals.

**RESULTS AND DISCUSSION**

DNA-SWNTs were used to distinguish between biomolecules in the NIR region, using PL measurements. In the NIR-PL measurements, the intensities of the emitted light spectra were determined with the aid of mapping. The various colors in the PL mapping represent only the intensities in the NIR region. The bright spots in the PL maps represent the intensities representing certain chiral indices. Semiconducting SWNTs were prominent in the excitation wavelength range of 500−800 nm and the emission wavelength range of 900−1300 nm, and the red area in top left corner of the PL map represents the Rayleigh scattering with a high intensity (Figures S5 and S6).

In this study, (7,5) and (7,6) chiralities were prominent at an excitation wavelength of 655 nm, whereas (10,2) and (9,4) were prominent at 730 nm. For numerical analysis, the focus was on the (7,5), (7,6), and (9,4) chiralities, whereas the (9,4) chirality was focused on because it showed the highest recovery to the initial state.

**Figure 1** shows the PL maps of the spectra of DNA-SWNTs with and without an oxidant and reductant. From top to bottom: DNA-SWNTs (initial state), injected KMnO\(_4\) (state of oxidation), injected biomolecules after KMnO\(_4\) treatment (state of reduction). In the state of reduction, the biomolecules utilized were (a) saponin and (b) banana solutions.

**Figure 1.** Mapping of the NIR-PL spectra of the DNA-SWNTs with and without an oxidant and reductant. From top to bottom: DNA-SWNTs (initial state), injected KMnO\(_4\) (state of oxidation), injected biomolecules after KMnO\(_4\) treatment (state of reduction). In the state of reduction, the biomolecules utilized were (a) saponin and (b) banana solutions.
When saponin or banana solutions were injected as antioxidant biomolecules into the DNA-SWNTs, the PL intensities recovered. Oxidation can be defined as a chemical process of electron loss, whereas reduction can be defined as an electron-gaining process during a chemical reaction. Antioxidants have properties that are against oxidation, and they have a tendency to donate electrons and generally donate electrons to free radicals, which are atoms or molecules with unpaired valence electrons. They also exhibit the properties of reducing agents or reductants. Because antioxidants have properties that are against oxidation in many ways, the quenched PL intensities were recovered against the state of oxidation, after the injection of antioxidant biomolecules.

In this figure, among all final concentrations, the final concentration of 59 μg/mL was chosen to illustrate the state of reduction because it fully or closely contributed to the saturation of PL intensities of the (9,4) chirality in both cases; additionally, it was attributed to the saturation of the (7,5) chirality in the banana solution case. In the initial state, the (7,5) chirality was the most remarkable; however, in the state of reduction, the (9,4) chirality became the most remarkable at a final concentration of 59 μg/mL. Tanaka et al. investigated the chirality-dependent redox potentials of SWNTs. According to the numerical values of their experiments, the oxidation potential of (7,5) SWNTs was the highest and that of (9,4) SWNTs was the lowest. Hence, (9,4) SWNTs may undergo fewer oxidation reactions with oxidants, whereas (7,5) SWNTs were oxidized with KMnO₄ the most. Therefore, the least PL intensity recoveries from the PL quenching in the oxidation state are expected for (7,5) SWNTs. In contrast, most PL intensity recoveries are expected for (9,4) SWNTs. Additionally, it was observed that the electrochemical band gaps of the (7,5) chirality SWNTs were larger than those of the (9,4) chirality SWNTs. Therefore, it is speculated that the (9,4) chirality SWNTs exhibit the highest PL intensity in the state of reduction.

Figure 2 shows the NIR-PL spectra of DNA-SWNTs with and without the injection of KMnO₄ and solutions of antioxidant biomolecules. In the initial state (navy blue line) of the saponin solution case, the PL intensities of the (7,5), (7,6), and (9,4) chirality SWNTs are 0.505 ± 0.008, 0.384 ± 0.006, and 0.414 ± 0.009, respectively (Table S1). Different chiralities produce different PL intensities. Among all these three chirality SWNTs, (7,5) SWNTs have the smallest diameters. Since light absorption and emission of smaller-diameter SWNTs are superior to those of larger ones, and it can be said that PL intensity has an inverse relationship with diameters of SWNTs, it is clear that (7,5) SWNTs showed the highest intensity in the initial state.

In the KMnO₄-oxidized state (purple line), no significant peaks were observed because this is the state in which PL quenching occurs, as shown in the PL maps. When a saponin solution with a final concentration of 59 μg/mL (orange line) was injected, the PL intensities were recovered from the state of oxidation, with numerical values of 0.532 ± 0.013, 0.486 ± 0.009, and 0.643 ± 0.018 for the (7,5), (7,6), and (9,4) chirality SWNTs, respectively.

For the banana solution, the PL intensities of the initial state (navy blue line) were 0.533 ± 0.016, 0.407 ± 0.023, and 0.415 ± 0.046, respectively (Table S2). No peaks were prominent in the oxidation state (purple line) or in the state of reduction (orange line); the PL intensities were 0.581 ± 0.013, 0.540 ± 0.020, and 0.721 ± 0.033, for the (7,5), (7,6), and (9,4) chirality SWNTs, respectively.

Focusing on the initial states, the (7,5) SWNTs exhibited the highest PL intensities in both biomolecule solution cases. When solutions of biomolecules with a final concentration of 59 μg/mL were injected, the (9,4) SWNTs exhibited the highest recoveries in PL intensities, as shown in the PL maps. Mistry et al. wrapped large-diameter SWNTs with two different kinds of polymers: PFO-BPy and PFO-A. According to their observations, the former polymer did not show any selectivity toward these large-diameter SWNTs, whereas the latter showed interactions with certain chiralities. Therefore, it is also speculated in this study that the selectivity of SWNTs may be one of the factors responsible for the sudden PL intensity increases in the case of the (9,4) chirality when solutions of biomolecules were injected. Because DNA and the other two biomolecules are different types of molecules, the selectivity of different SWNT chiralities by these molecules at the initial state may be different from that of the reduced state.

Figure 3 shows the graph of relative intensity vs the final concentration. Herein, the relative intensity is defined as the ratio of the PL intensity of DNA-SWNTs to that of DNA-SWNTs after the injection of KMnO₄ and the antioxidant biomolecule solutions. In other words, it is the ratio of the PL intensity achieved in the initial state to the PL intensity achieved in the state of reduction. The graph reveals two main points: how PL intensities vary with the final concentrations of solutions of biomolecules and how biomolecules are distinguished. This graph focuses on the PL intensities of the (9,4) chirality of DNA-SWNTs when different concentrations of biomolecule solutions were injected. The PL intensities of the (7,5) and (7,6) chiralities for different concentrations of biomolecule solutions are presented in the Supporting Information.
depending on the analytes that they react with. Suspension of SWNTs and final concentrations of solutions of those in the case of the saponin solution, even though the same results show that the recovery percentages of PL intensities SWNTs) when more saponin solution was injected. The dilution of SWNTs (a decrease in the final concentration of both biomolecule cases, and the recovery percentage of the spectra of DNA-SWNTs when the banana solution was injected was lower than that of the saponin solution. If the PL intensity of the initial state is taken to be 100%, the recovery percentages were 69.1 and 18.1% for the saponin and banana solutions, respectively. At 40 μg/mL, the recovery rates went up drastically to 153.2 and 135.4%, respectively; however, the recovery of DNA-SWNTs was still weaker in the case of the banana solution. Starting from 59 μg/mL, the recovery rates of the PL intensities became saturated in both cases; however, the PL intensities increased when the banana solution was injected, even though they were weaker at lower concentrations. The recovery percentages were 155.2% in the saponin solution case and 175.4% in the banana solution case. In the case of the banana solution, the PL intensities continued to saturate up to 96 μg/mL, with 179.2% recovery rates; however, the recovery rates of the PL intensities dropped to 148.2% in the case of saponin solution. This may be due to the dilution of SWNTs (a decrease in the final concentration of SWNTs) when more saponin solution was injected. The results show that the recovery percentages of PL intensities were slightly higher in the case of the banana solution than those in the case of the saponin solution, even though the same suspension of SWNTs and final concentrations of solutions of biomolecules were used. This reveals that the banana solution expanded the optical responses of DNA-SWNTs. Therefore, DNA-SWNTs are useful biosensing tools for distinguishing biomolecules, based on NIR-PL intensities. Card et al. pointed out that SWNTs show heterogeneity in optical characteristics depending on the analytes that they react with. Different analytes produce different variations in optical responses. This may explain why different optical responses of DNA-SWNTs were achieved when saponin and banana solutions were injected.

NIR-ABS measurements were conducted to validate the antioxidant properties of the two molecules distinguished by the NIR-PL measurements (Figures S7 and S8). The observed chiralities were speculated to be (7,5), (8,4)/(9,4)/(7,6), (8,6)/(12,1)/(11,3), and (10,5)/(8,7). After oxidation with KMnO₄, the antioxidant abilities of the two biomolecule solutions were noticeably different. The recovery percentages of the saponin solution were lower than those in the initial state for all chiralities. In contrast, the banana solution exhibited higher recovery percentages compared with the initial state for (10,5)/(8,7) chirality. Hence, it was observed that the saponin solution did not fully recover the NIR-ABS spectra of all SWNTs oxidized by KMnO₄ whereas the banana solution enhanced the absorbance peak of a certain chirality. Therefore, these two biomolecules can be distinguished.

The antioxidant abilities of the two biomolecules were investigated without adding KMnO₄ by employing NIR-PL spectroscopy (Figures S9–S11). Without oxidation, the PL enhancements were higher than those of the previous redox reactions. When the two biomolecule solutions were compared, the banana solution enhanced the PL spectra of all (7,5), (7,6), and (9,4) SWNTs more than the saponin solution, even without the oxidation with KMnO₄. Even without the oxidation process, the (9,4) SWNTs showed the highest PL intensities after reduction with antioxidant biomolecules, whereas the (7,5) SWNTs showed the highest PL intensities in the initial state (Figures S9–S11, Tables S3 and S4). Even though largely strong oxidant KMnO₄ was not used, we speculate that it is possible that the DNA-SWNT suspension would be oxidized by the oxygen in the air through the passage of time since the experiments were carried out in open conditions. Since (9,4) SWNTs have the lowest oxidation potential, it is clear that they showed the highest recovery from the oxidation at the state of reduction. However, it is speculated that the oxidation was much weaker than that with KMnO₄ and the recovery rates were higher in this case. According to NIR-ABS, measurements showed that the banana solution enhanced the NIR-ABS spectra of all chiral SWNTs without the oxidation process with KMnO₄ showing its highest recovery percentage of 109.0% for the (10,5)/(8,7) chirality (Figure S8 and Table S5). In contrast, saponin solution did not enhance the NIR-ABS spectra of all chiralities, except (10,5)/(8,7) chirality, and the highest recovery percentages were obtained as only 102.2% for (10,5)/(8,7) chirality (Figure S8 and Table S5). Hence, these two biomolecules were successfully distinguished in various aspects.

For the absorbance measurements, the spectra in the visible region (600–800 nm), which was used for the excitation wavelength range in NIR-PL measurements, was determined. If the 800–1350 nm range represents E₁₁ optical transitions, the 600–800 nm wavelength range is assumed as the representation of E₂₂ optical transitions. Peak 1 and Peak 2 were seen at 654 and 733 nm. 654 nm is speculated as the excitation wavelength for (7,5) and (7,6) chiralities, and 733 nm is for (9,4) chirality. Hence, these results were consistent with those of NIR-PL measurements. For Peak 1 and Peak 2, absorbance enhancements were superior in the case of banana solution than saponin solution (Figures S7 and S8, Table S6), even though the difference was slightly less prominent. We distinguished the two molecules from another aspect.

AFM measurements were performed in air to perform structural analysis of the DNA-SWNTs. DNA-wrapped SWNTs are clearly visible in Figure 4a. A total of 100 heights were randomly selected using 20 SWNTs. The average diameter was 1.03 ± 0.41 nm. Generally, the diameters of individual HiPCO SWNTs range from 0.7 to 1.4 nm, and in this study, the distribution of diameters between 0.7 and 1.4 nm was 63%. In Figure 4b, c, DNA-SWNTs were clearly observed, even after mixing with saponin or banana solutions. The average diameters of DNA-SWNTs mixed with saponin or banana solutions were 1.32 ± 0.48 and 1.74 ± 1.71 nm, respectively. The distributions of the individual diameters ranging from 0.7 to 1.4 nm were 43 and 49%, respectively. The
Figure 4. AFM images of (a) DNA-SWNTs and (b) DNA-SWNTs mixed with saponin solution and (c) DNA-SWNTs mixed with banana solution. Each solution was diluted 25 times with Tris-HCl buffer and analyzed in AFM-air conditions after dropping onto AP-treated mica substrates.

Figure 5. Height distribution histograms for DNA-SWNTs and those mixed with saponin or banana solutions after correcting the diameters with those of the gold colloids. The bin size was chosen as 0.7 nm. The diameters of DNA-SWNTs were distributed in the smallest values in the histograms, whereas the diameters of DNA-SWNTs mixed with saponin or banana solutions were calculated as 1.85 ± 0.67 and 2.44 ± 2.40 nm, and the distributions of the individual diameters ranging from 0.7 to 1.4 nm were 20 and 36%, respectively.

The distribution of diameters between 0.7 and 1.4 nm was calculated as 55%. Therefore, it can be speculated that the SWNTs were abundantly dispersed individually, and some of them were dispersed as small bundles. The average diameters of DNA-SWNTs mixed with saponin or banana solutions were calculated as 1.85 ± 0.67 and 2.44 ± 2.40 nm, and the distributions of the individual diameters ranging from 0.7 to 1.4 nm were 20 and 36%, respectively.

Figure 5 shows the height distributions of DNA-SWNTs and those mixed with saponin or banana solutions after correcting the diameters with those of the gold colloids. The bin size was chosen as 0.7 nm. The diameters of DNA-SWNTs were distributed in the smallest values in the histograms, whereas the diameters of DNA-SWNTs mixed with saponin or banana solutions were calculated as 1.85 ± 0.67 and 2.44 ± 2.40 nm, and the distributions of the individual diameters ranging from 0.7 to 1.4 nm were 20 and 36%, respectively.

CONCLUSIONS

In this study, two antioxidant biomolecules, saponin and banana, were successfully distinguished using the PL enhancement of DNA-SWNTs. Compared to the saponin solution, a saturated amount of banana solution can exhibit higher PL enhancement of DNA-SWNTs, with or without oxidation with KMnO$_4$. NIR-ABS measurements supported the results of the NIR-PL measurements, even though the NIR-ABS recovery rates were lower. In the NIR-ABS measurements with the KMnO$_4$ oxidation, the banana solution revealed absorbance increases in (10,5)/(8,7), whereas the saponin solution did not reveal in all SWNTs. In the absence of KMnO$_4$, the banana solution showed absorbance enhancement of all SWNTs, whereas the saponin solution did not enhance the NIR-ABS spectra of all SWNTs, except (10,5)/(8,7), and showed weaker absorbance enhancements in all chiral SWNTs compared to the banana solution. Hence, the absorbance measurements successfully distinguished the two biomolecules, same as the NIR-PL measurements. Even though our research was mainly focused on the study of optical properties, it gives some insights into electrochemical properties of SWNTs. The diameter increases of the DNA-SWNTs were relatively higher when they were mixed with the banana solution than when they were mixed with the saponin solution. Hence, this could provide a useful correlation between the PL enhancement and the diameter increase of DNA-SWNTs measured by AFM. In summary, the two biomolecules were successfully distinguished in various aspects.

METHODS

In this study, the SWNTs produced by the HiPCO method were purchased from NoPo Nanotechnologies India Private Limited (India), and double stranded DNA (deoxyribonucleic acid sodium salt from salmon testes, no. D1626-250 MG), saponin (84510-100G), and banana powder (B4032-500G) were purchased from Sigma-Aldrich Co. LLC (St. Louis, MO, USA).

First, DNA was dissolved in 10 mM tris(hydroxymethyl)aminomethane (Tris-HCl buffer solution, pH 8.0) to prepare a 1.0 mg/mL DNA solution. Dispersion was performed in a bath-type ultrasonicator (80 W) for 180 min on ice to ensure uniformity. The solution was shaken gently in an ice bath for 180 min.

To prepare DNA-SWNTs, 0.69 mg of SWNTs was dissolved in 1.38 mL of the prepared DNA solution, so that the final concentration of the solution was 0.5 mg/mL. The solution was sonicated using a probe-type sonicator (VCX130; Sonics & Materials, Inc. Newtonville, CT, USA) in an ice-water bath for 90 min at 2 W. Subsequently, the solution was centrifuged.
for 3 h at 15,000 rpm (21,500g) at 8 °C. Finally, 70% of the supernatant was stored for further use after removing insoluble residual SWNTs.

Saponin was stored at room temperature (23 °C), and banana powder was stored at 3.5 °C initially. 2.55 mg of saponin was mixed with 1.275 mL of pure water, and the solution was denoted as saponin solution (concentration of 2 mg/mL) and then stored in a refrigerator for further use. Moreover, 2.33 mg of banana powder was dissolved in 1.165 mL of pure water, and the solution was named banana solution (concentration of 2 mg/mL) and then stored in the refrigerator. Saponin and banana solutions were stored at 3.5 °C.

To distinguish between the antioxidant biomolecules, PL measurements were performed using DNA-SWNTs. The PL spectra of the samples were measured using a PL spectrometer (NIR System; Shimadzu Co., Ltd., Kyoto, Japan). To determine the concentration of DNA-SWNTs, absorbance was measured using UV−vis spectrophotometry (V-630, Jasco Corp., Hachioji City, Tokyo, Japan), and the concentration at which the absorbance value was 0.1 at 808 nm was used in the PL measurements. First, the PL excitation wavelength range was chosen from 400 to 1000 nm, and the emission wavelength range was chosen from 850 to 1600 nm. For further experiments, the excitation and emission wavelength ranges were 600–800 and 900–1400 nm, respectively. PL spectroscopy is an optical spectroscopy technique in which emission wavelengths are measured in the near-infrared (NIR) region. The colors indicated in the PL maps, such as blue, green, yellow, and red, are only a visual representation of their PL intensities.

To measure the NIR-PL values, 464 μL of Tris-HCl buffer and 26 μL of the prepared DNA-SWNT solution were mixed in a cuvette, and the spectra were recorded initially. The solution was oxidized by adding 5 μL KMnO₄ (final concentration of 0.5 μM), and after 10 min of incubation, the spectra were recorded. The prepared solution was then treated with 5 μL of saponin solution (final concentration of 20 μg/mL) or banana solution (final concentration of 20 μg/mL), and the spectra were recorded after 10 min of incubation at room temperature (23 °C). The final concentrations were varied by adding 5 μL each time, the resulting concentrations were 40, 59, 78, and 96 μg/mL, and the incubation period each time was 10 min. The experiment was conducted three times, and the results were presented as mean ± standard deviation. The experiment was repeated without the KMnO₄ oxidation process by adding 59 μg/mL solutions of biomolecules to 490 μL of the DNA-SWNTs and Tris-HCl buffer mixture. The experiment was conducted three times, and the results were presented as mean ± standard deviation.

NIR-ABS measurements were performed using the Solid-Spec-3700DUV (Shimadzu Co., Kyoto, Japan) and 980 μL of the mixture solution containing DNA-SWNT solution with Tris-HCl buffer. The concentration for which the absorbance of SWNTs is 808 nm is 0.1. The wavelength range was chosen from 800 to 1350 nm. The solution was oxidized with 10 μL KMnO₄ (final concentration of 0.5 μM) and reduced with 30 μL of the solutions of the biomolecules (final concentration of 59 μg/mL), and the spectra were recorded at each state. The experiment was repeated without the oxidation process, by choosing the final concentration of the biomolecule solution as 59 μg/mL.

For the absorption spectra in the visible region (600–800 nm) with or without the oxidation process with KMnO₄, experiments were carried out using UV−vis spectrophotometry (V-630, Jasco Corp., Hachioji City, Tokyo, Japan). The concentrations for DNA-SWNT, KMnO₄, saponin, and banana solutions were the same as those used in NIR-ABS measurements.

An atomic force microscope (MFP-3D microscope, Asylum Research, Santa Barbara, CA, USA) was employed for the structural analysis of the DNA-SWNTs. Experiments were conducted in the AC-AFM mode in air with the application of a silicon cantilever PPP-NCSTR-W (NANOSENSORS, Nanoworld AG, Neuchatel, Switzerland). Mica substrates were treated with 0.01% 3-aminopropyl triethoxysilane (Shin-Etsu Chemical Co., Ltd. Tokyo, Japan) for use in the AFM measurements. The DNA-SWNT solution was diluted 25 times with Tris-HCl buffer. Then, 10 μL of the prepared sample was dropped onto the center of the mica substrates. After incubating for 10 min at room temperature, the sample was washed twice with 1 mL of pure water and dried at room temperature for one day. Finally, structural analysis of the prepared sample was performed using AFM. Twenty DNA-SWNTs were chosen randomly, and 100 heights were selected.

For the structural analysis of DNA-SWNTs mixed with saponin or banana solutions, 464 μL of Tris-HCl buffer, 26 μL of DNA-SWNT solution, 15 μL of saponin solution (saturated concentration in the PL measurement), or 25 μL of banana solution (saturated concentration in the PL measurement) were mixed together in a container in each experiment. The solution (100 μL) was mixed with 29 μL of Tris-HCl buffer again in the case of saponin solution or 26 μL of Tris-HCl buffer in the case of banana solution, so that the dilution of DNA-SWNTs was 25 times in each experiment. The subsequent processes were the same as those used for the measurement of DNA-SWNTs without the saponin solution.

In the structural analysis of saponin or banana solutions only, 519 μL of water and 15 μL of saponin solution or 515 μL of water and 25 μL of banana solution were mixed in each case. The solution (10 μL) was dropped onto the center of the mica substrates, and the same processes were followed.

Focusing on the tip convolution effects, AFM measurements were carried out by diluting 5 nm gold colloids (EM. GC5, BBI Chemical Co., Ltd. Tokyo, Japan) for use in the AFM measurements. The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02038. The Supporting Information contains additional experimental details and figures related to the study.
increases in absorbance of (7,5), (7,6), and (9,4) SWNTs in the state of reduction; AFM images of saponin, banana, and colloids; histograms of DNA-SWNTs with saponin or banana solutions; PL intensities and emission wavelengths of DNA-SWNTs with or without KMnO₄; Absorbances and wavelengths of DNA-SWNTs with or without KMnO₄ at the 800–1350 and 600–800 nm wavelength range (PDF)

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**Author Contributions**

The manuscript was written through contributions of all authors.

**Notes**

The authors declare no competing financial interest.

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**ABBREVIATIONS**

AFM, atomic force microscopy; AP-mica, mica treated with 3-amino propyltriethoxysilane; DNA, deoxyribonucleic acid; DNA-SWNTs, DNA-wrapped single-walled carbon nanotubes; HiPCO, high-pressure carbon monoxide; PL₆, photoluminescence; NIR, near-infrared; NIR-ABS, NIR absorbance; NIR-PL₆, NIR photoluminescence; KMnO₄, potassium permanganate; PL₆, photoluminescence; SWNT, single-walled carbon nanotube; UV–vis, ultraviolet–visible

**REFERENCES**

(1) Hofferber, E. M.; Stapleton, J. A.; Iverson, N. M. Review-Single Walled Carbon Nanotubes as Optical Sensors for Biological Applications. J. Electrochem. Soc. 2020, 167, 037530.

(2) Liu, B.; Wu, F.; Gu, H.; Zheng, M.; Zhou, C. Chirality-controlled synthesis and applications of single-wall carbon nanotubes. ACS Nano 2017, 11, 31–53.

(3) Rodríguez, K. R.; Malone, M. A.; Nanney, W. A.; A Maddux, C. J. A.; Coe, J. V.; Martínez, H. L. Generalizing thermodynamic properties of bulk single-walled carbon nanotubes. AIP Adv. 2014, 4, 127149.

(4) Odom, T. W.; Huang, J. L.; Lieber, C. M. Single-walled carbon nanotubes - From fundamental studies to new device concepts. Molecular Electronics II; Aviram, A., Ratner, M., Mujica, V., Eds.; New York Academy of Sciences, 2002; Vol. 960, pp 203–215.

(5) Chen, J.-Y.; Kim, M.; Yoo, C.-S. High structural stability of single wall carbon nanotube under quasi-hydrostatic high pressures. Chem. Phys. Lett. 2009, 479, 91–94.

(6) Blackburn, J. L. Semiconducting single-walled carbon nanotubes in solar energy harvesting. ACS Energy Lett. 2017, 2, 1598–1613.

(7) Sankar, P. G.; Kumar, K. U. Mechanical and electrical properties of single walled carbon nanotubes: a computational study. Eur. J. Sci. Res. 2011, 60, 342–358.

(8) Blanchon, J.-C.; Paillet, M.; Tran, H. N.; Than, X. T.; Guebrou, S. A.; Ayari, A.; San Miguel, A. S.; Phan, N.-M.; Zahab, A.-A.; Sauvajol, J.-L.; Fatti, N.; Vallée, F. Direct measurement of the absolute absorption spectrum of individual semiconducting single-wall carbon nanotubes. Nat. Commun. 2013, 4, 2542.

(9) Lee, A. J.; Wang, X.; Carlson, L. J.; Snyder, J. A.; Loebsch, B.; Tu, X.; Zheng, M.; Krauss, T. D. Bright fluorescence from individual single-walled carbon nanotubes. Nano Lett. 2011, 11, 1636–1640.

(10) Wei, X.; Tanaka, T.; Li, S.; Tsuzuki, M.; Wang, G.; Yao, Z.; Li, L.; Yomogida, Y.; Hirano, A.; Liu, H.; Kataura, H. Photoluminescence quantum yield of single-wall carbon nanotubes corrected for the photon reabsorption effect. Nano Lett. 2019, 20, 410–417.

(11) Matsuura, K.; Saito, T.; Okazaki, T.; Ohshima, S.; Yumura, M.; Iijima, S. Selectivity of water-soluble proteins in single-walled carbon nanotube dispersions. Chem. Phys. Lett. 2006, 429, 497–502.

(12) Sedelnikova, O. V.; Sysoev, V. I.; Gurova, O. A.; Ivanov, Y. P.; Koroteev, V. O.; Arenal, R.; Makarova, A. A.; Bulusheva, L. G.; Okotrub, A. V. Role of interface interactions in the sensitivity of sulfur-modified single-walled carbon nanotubes for nitrogen dioxide gas sensing. Carbon 2022, 186, 539–549.

(13) Li, W.; Ma, J.-J.; Liu, P.; Pan, Z.-L.; He, Q.-Y. First-principles study of the adsorption sensitivity of Ni-doped single-walled zigzag (n, 0) CNTs (n= 4, 5, 6) toward SO2 molecules. Appl. Surf. Sci. 2015, 335, 17–22.

(14) Li, H.; Zhou, B.; Lin, Y.; Gu, L.; Wang, W.; Fernando, K. S.; Kumar, S.; Allard, L. F.; Sun, Y.-P. Selective interactions of porphyrins with semiconducting single-walled carbon nanotubes. J. Am. Chem. Soc. 2004, 126, 1014–1015.

(15) Sobhan, A.; Oh, J.-H.; Park, M.-K.; Kim, S. W.; Park, C.; Lee, J. Single walled carbon nanotube based biosensor for detection of peanut allergy-inducing protein ara h1. Korean J. Chem. Eng. 2018, 35, 172–178.

(16) Baek, Y.-K.; Jung, D.-H.; Yoo, S. M.; Shin, S.; Kim, J.-H.; Jeon, H.-J.; Choi, Y.-K.; Lee, S. Y.; Jung, H.-T. Label-free detection of DNA hybridization using pyrene-functionalized single-walled carbon nanotubes: effect of chemical structures of pyrene molecules on DNA sensing performance. J. Nanosci. Nanotechnol. 2011, 11, 4210–4216.

(17) Card, M.; Gravely, M.; Madani, M.; Roxbury, D. A Spin-Coated Hydrogel Platform Enables Accurate Investigation of Immobilized Individual Single-Walled Carbon Nanotubes. ACS Appl. Mater. Interfaces 2021, 13, 31986–31995.

(18) Podolak, I.; Galanty, A.; Sobolewska, D. Saponins as cytotoxic agents: a review. Phytochem. Rev. 2010, 9, 425–474.

(19) Mugford, S. T.; Osbourn, A. Saponin synthesis and function. Isoprenoid Synthesis in Plants and Microorganisms; Springer, 2012; pp 405–424.

(20) Desai, D. S.; Desai, D. G.; Kaur, H. Saponins and their biological activities. Pharrarnatics 2009, 41, 13–16.

(21) Reihani, S.; Saifullah, R.; Abbas, F.; Azhar, M. Total phenolics, flavonoids and antioxidant activity of banana pulp and peel flours: influence of variety and stage of ripeness. Int. J. Food Res. Technol. 2012, 19, 1041.

(22) Siji, S.; Nandini, P. Antioxidants and antioxidant activity common eight banana varieties in Kerala. Int. J. Adv. Res. Comput. Sci. Software Eng. 2017, 7, 237219.

(23) Someya, S.; Yoshiki, Y.; Okubo, K. Antioxidant compounds from bananas (Musa Cavendish). Food Chem. 2002, 79, 351–354.

(24) Chueh, C. C.; Lin, L. J.; Lin, W. C.; Huang, S. H.; Jan, M. S.; Chang, S. C.; Chung, W. S.; Lee, T. T. Antioxidant capacity of banana
peel and its modulation of Nrf2-ARE associated gene expression in broiler chickens. *Ital. J. Anim. Sci.* 2019, 18, 1394–1403.

(25) Bashmil, Y. M.; Ali, A.; Blk, A.; Dunshea, F. R.; Suleria, H. A. Screening and Characterization of Phenolic Compounds from Australian Grown Bananas and Their Antioxidant Capacity. *Antioxidants* 2021, 10, 1521.

(26) Brahim, M. A. S.; Fadli, M.; Markouk, M.; Hassan, I.; larhshini, M. Synergistic antimicrobial and antioxidant activity of saponins-rich extracts from Paronychia argentea and Spergularia margarita. *Eur. J. Med. Plants* 2015, 7, 193–204.

(27) Akinpelu, B.; Igbenedu, O.; Awotunde, A.; Iwalewa, E.; Oyedapo, O. Antioxidant and antibacterial activities of saponin fractions of *Erythrophleum suaveolens* (Guill. and Perri.) stem bark extract. *Sci. Res. Essays* 2014, 9, 826–833.

(28) Hu, J. L.;Nie, S. P.; Huang, D. F.; Li, C.; Xie, M. Y. Extraction of saponin from Camellia oleifera cake and evaluation of its antioxidant activity. *Int. J. Food Sci. Technol.* 2012, 47, 1676–1687.

(29) Fu, X.-J.; Liu, H.-B.; Wang, P.; Guan, H.-S. A study on the antioxidant activity and tissues selective inhibition of lipid peroxidation by saponins from the roots of Platycodon grandiflorum. *Am. J. Chin. Med.* 2009, 37, 967–975.

(30) Krishnan, S. A.; Sinija, V. Proximate composition and antioxidant activity of banana blossom of two cultivars in India. *Int. J. Agric. Food Sci. Technol.* 2016, 7, 13.

(31) Powthong, P.; Jantrapanukorn, B.; Suntornthiticharoen, P.; Na-Ayudhya, P.; Laohaphatanalert, K. Study of prebiotic properties of selected banana species in Thailand. *J. Food Sci. Technol.* 2020, 57, 2490–2500.

(32) Nakraen, P.; Charoenthaikij, P.; Kerdsum, P. Physicochemical properties and nutritional compositions of foamed banana powders (Pisang Awak, Musa sapientum L.) dehydrated by various drying methods. *Walaik J. Sci. Technol.* 2016, 13, 177–191.

(33) Hamano, R.; Miyashiro, D.; Umemura, K. Selective binding of single-stranded DNA-binding molecules on SWCNTs. *ACS Omega* 2021, 7, 28903–28903.

(34) Matsukawa, Y.; Umemura, K. Chirality luminescent properties of single-walled carbon nanotubes during redox reactions. *Opt. Mater.* 2021, 112, 110748.

(35) Yamazaki, Y.; Umemura, K. Sensing of epigallocatechin gallate and tannin acid based on near infrared optical spectroscopy of DNA-wrapped single-walled carbon nanotube hybrids. *J. Near Infrared Spectrosc.* 2021, 29, 73–83.

(36) Dukovic, G.; White, B. B.; Zhou, Z.; Wang, F.; Jockusch, S.; Steigerwald, M. L.; Heinz, T. F.; Friesner, R. A.; Turro, N. J.; Brus, L. E. Reversible surface oxidation and efficient luminescence quenching in semiconductor single-wall carbon nanotubes. *J. Am. Chem. Soc.* 2004, 126, 15269–15276.

(37) Biswas, S. U.; Karmakar, K.; Saha, B. Oxidation-reduction reactions in geochemistry. *Vietnam J. Chem.* 2021, 59, 133–145.

(38) Lee, C. Y.; Nanah, C. N.; Held, R. A.; Clark, A. R.; Huyneh, U. G.; Maraskine, M. C.; Uzarski, R. L.; McCracken, J.; Sharma, A. Effect of electron donating groups on polyphenol-based antioxidant dendrimers. *Biochimie* 2015, 111, 125–134.

(39) Lobo, V.; Patil, A.; Phatak, A.; Chandra, N. Free radicals, antioxidants and functional foods: Impact on human health. *Phcog. Rev.* 2010, 4, 118.

(40) Padayatty, S. J.; Katz, A.; Wang, Y.; Eck, P.; Kwon, O.; Lee, J.-H.; Chen, S.; Corpe, C.; Dutta, A.; Dutta, S. K.; Levine, M. Vitamin C as an antioxidant: evaluation of its role in disease prevention. *J. Am. Coll. Nutr.* 2003, 22, 18–35.

(41) Phaniendra, A.; Jestadi, D. B.; Periyasamy, L. Free radicals: properties, sources, targets, and their implication in various diseases. *Indian J. Clin. Biochem.* 2015, 30, 11–26.

(42) Sotler, R.; Poljiak, B.; Dahmane, R.; Jukić, T.; Pavan Jukić, D.; Rotim, C.; Trebshe, P.; Starc, A. Prooxidant activities of antioxidants and their impact on health. *Acta Clin. Croat.* 2019, 58, 726–736.

(43) Thorat, I. D.; Jagtap, D. D.; Mohapatra, D.; Joshi, D.; Sutar, R.; Kapdi, S. Antioxidants, their properties, uses in food products and their legal implications. *Int. J. Food Sci. Technol.* 2013, 2, 81.