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Reversible Control of Third-Order Optical Nonlinearity of DNA Decorated Carbon Nanotube Hybrids

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Abstract

Positive and negative third-order optical nonlinearities have been investigated in single-stranded DNA wrapped semiconducting single-walled carbon nanotubes. It is found that the redox reactions of hydrogen peroxide can reverse the sign of the third-order nonlinearity. The observation proves that the lowest unoccupied molecular orbital has a lower density of electronic states than that of the highest occupied molecular orbital. A three-energy-level model is used to explain the effect of the redox reactions. Raman spectroscopy has also been used to investigate the interaction between single-walled carbon nanotubes and single-stranded DNA.

Introduction

Carbon nanotubes are currently the focus of intense research interest worldwide. This attention is not surprising in light of their promise to unique physical properties that could impact broad areas of science and technology, ranging from nanoelectronics to biotechnology.^{1–4} However, one of the most significant hurdles to the practical applications of carbon nanotubes is their separation.^{5–7} Much research has focused on achieving the highest possible degree of dispersion without altering the properties of carbon nanotubes.^{5,6,8} DNA plays a vital role in biology as the carrier of genetic information in all living species. However, because DNA exhibits a remarkable chemical sensing capability to electron transport, it has recently been proven that DNA has great potential in electronics, optics, mechanics, and biosensing.^{9,10} DNA is also one of the polymers possessing ideal structural and molecular-reorganization properties that can be used to disperse carbon nanotubes without the need of poisonous solvent to fabricate nanodevices. Therefore, there is a growing interest in research on the development of multifunctional materials with

unique properties achieved by wrapping DNA on the sidewalls of carbon nanotubes.^{5,6,8,11–15} This hybrid system offers a unique combination of properties of biotechnology and nanotechnology originating from molecular architecture. Research on the electron transport properties of this system is expected to drive the development of molecular-based electronic devices.^{16–18}

In this work, we use single-stranded DNA (ssDNA) to decorate single-walled carbon nanotubes (SWNTs) to fabricate ssDNA–SWNT hybrids. The interactions between ssDNA and SWNTs are studied with Raman spectra. The nonlinear optical absorption properties of these hybrids are investigated under different concentrations of hydrogen peroxide. The influence of the redox process on the nonlinear optical absorption coefficient is observed and explained. The results provide us with useful approaches to control the nonlinear absorption in these hybrids and to develop biosensors based on these materials.

Sample Preparation and Characterization

As-synthesized SWNTs were purchased from Sigma-Aldrich. Their diameters range from 1.2 to 1.5 nm, and they have lengths from 5 nm to 1 μ m. The single-stranded 25-mer DNA oligonucleotide with a sequence of 5'-CTC GAC CGA TGA ATA GTC GTA CGT-3' is used. This ssDNA oligonucleotide with the four nucleotides (A, C, G, T) evenly distributed was purchased from Integrated DNA Technologies, Inc. Dispersion of SWNTs by ssDNA was carried out as described in refs 17, 19, and 20. Briefly, 1 mg of SWNTs was weighted on a microgram-scaled balance and mixed with 1 mL of DNA solution (1 mg of ssDNA/1 mL in 0.1 M Tris EDTA (TE) buffer, pH ~7). The sample was ultrasonicated (Branson 5510R-MTH, 42 kHz, and 135 W) in an ice–water bath for 2 h to disperse the nanotubes and was then centrifuged (Analytical Centrifuge, model 179) for 3 h. The supernatant was extracted. 30 wt % hydrogen peroxide (H₂O₂) solution was purchased from Sigma-Aldrich and was added to the ssDNA–SWNT suspensions in calculated volumes to make ssDNA–SWNT suspensions when we need to investigate the influence of H₂O₂ on the nonlinear optical absorption.

In order to determine the length of DNA, the gel electrophoresis analysis was conducted. ssDNA was analyzed with the 3% (w/v) agarose gel electrophoresis. The ssDNA band was stained with ethidium bromide and visualized under a UV transilluminator. Figure 1 shows that the length of the unsonicated ssDNA is about 25 bases. Considering 1 base $\cong$ 0.34 nm, the length of the ssDNA chain is around 8.5 nm.

To investigate the binding interactions of ssDNA on SWNTs, Raman scattering studies were performed at room temperature using a Horiba Jobin Yvon HR-800 spectrometer equipped with a charge-coupled detector, a spectrometer with a grating of 600 lines/mm, and a He–Ne laser (633 nm, 1.96 eV) as the excitation source. The laser beam intensity measured at the sample was kept at 5 mW. The microscope focused the incident beam to a spot size of <0.01 mm², and the backscattered light was collected. Raman shifts were calibrated with a silicon wafer at a peak of 521 cm⁻¹. The two curves shown in the lower part of Figure 2 include Raman spectra from ssDNA and SWNTs. The upper spectrum is from a sonicated ssDNA and SWNT hybrid suspension. On the spectrum of SWNTs, one can clearly see the radial breathing modes (RBM) of two peaks at 160.2 and 189.2 cm⁻¹, the disorder-induced band (D) at 1322 cm⁻¹, and the tangential vibration mode band (G) at 1588.38 cm⁻¹.²¹ The two RBM peaks can be used to estimate the diameters d of SWNTs through the relation $\omega_{\text{RBM}} = A/d + B$,²² where A and B are experimental parameters in wavenumber and d is the diameter in nm. For SWNTs within 1 nm $< d < 2$ nm, $A = 223.5$ cm⁻¹ and $B = 12.5$ cm⁻¹. The two peaks correspond to two diameter values of 1.51 and 1.26 nm. These data are essentially consistent with the company's specification (1.2–1.5 nm). After sonicating with ssDNA, the

RBM band has only one peak at 161.2 cm^{-1} , the D band becomes lower, and the G band peak becomes wider (two peaks at 1574.89 and 1588.38 cm^{-1}), as shown in the upper part of Figure 2. This indicates the wrapping of ssDNA affects the RBM and G mode vibrations.⁸

Figure 3 shows a typical absorption curve of DNA–SWNT suspensions. Absorbance was measured in a 2 mm path length quartz cell using a UV–vis absorption spectrometer (Agilent Technologies 83453B). One can see that there is a pronounced absorption band E_{11} between 950 nm (1.30 eV) and 1080 nm (1.15 eV). The absorption measurement beyond 1100 nm is limited by the spectrophotometer. This absorption band arises from the first interband transition, which is the band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of hybridization between the semiconducting SWNTs and ssDNA.^{12,23} The smaller peak between 700 and 800 nm may originate from the second interband transition E_{22} , which is the band gap between the second conduction band and the second valence band. Note the first metallic interband transition absorption band (M_{11} : 400–600 nm)^{8,10,21} is not very clear in these suspensions.

Nonlinear Optical Absorption Effect

There are two types of nonlinear absorption: saturable absorption (SA) and reverse saturable absorption (RSA). Materials that have the SA property can be used in passive Q-switch technology to compress laser pulses.^{22–25} Materials exhibiting RSA can be used to fabricate optical power limiters to manipulate the amplitude of lasers.^{24–27} SA arises from the saturation of electronic transition. In other words, the material is bleached to be more transparent under intense illumination. RSA means the material has larger absorption at high intensities.

When a laser beam propagates in a medium, considering the nonlinear absorption term,^{28,29} the beam intensity change along the propagation direction (for example, z axis) can be written as

$$\frac{\partial I}{\partial z} = -(\alpha I + \beta I^2) \quad (1)$$

where α is the linear absorption coefficient and β is the nonlinear absorption coefficient, which is related to the imaginary part of the third-order susceptibility $\chi^{(3)}$. If $\beta = 0$, that means that only linear absorption exists in the medium. If nonlinear absorption coexists in the medium ($\beta \neq 0$), with increasing input power, the transmission should either increase (SA) or decrease (RSA) faster than linearly. This is the so-called nonlinear absorption effect. Considering the nonlinear absorption, the third-order nonlinear susceptibility is now considered to be a complex quantity:

$$\chi^{(3)} = \chi_R^{(3)} + i\chi_I^{(3)} \quad (2)$$

where the imaginary part is related to β through

$$\chi_I^{(3)} = \frac{n^2 \epsilon_0 c \lambda \beta}{2\pi} \quad (3)$$

where n is the linear refractive index, ϵ_0 is the permittivity of free space, c is the speed of light, and λ is the wavelength of the incident light in vacuum.

The open-aperture Z-scan technique^{28,29} can be used to determine the nonlinear absorption coefficient. The nonlinear absorption arises from either direct multiphoton absorption, saturation of the single photon absorption, or dynamic free-carrier absorption. Under the thin

sample approximation, the open-aperture Z-scan is sensitive to nonlinear absorption, the normalized transmittance $T_{\text{Norm}}(z)$, as a function of z , is given by^{28,29}

$$T_{\text{Norm}}(z) = \frac{\ln \left[1 + \frac{\beta I_0 L_{\text{eff}}}{1 + (z/z_0)^2} \right]}{\frac{\beta I_0 L_{\text{eff}}}{1 + (z/z_0)^2}} \quad (4)$$

where z_0 is the diffraction length of the beam, I_0 is the intensity of the laser beam at focus, and L_{eff} is known as the effective length of the sample. If one can obtain $T_{\text{Norm}}(z)$ experimentally, using eqs 3 and 4, one can calculate the nonlinear absorption coefficient β and $\chi_1^{(3)}$. If $\chi_1^{(3)} > 0$, the open Z-scan will result in a valley when the sample is near the focus (RSA). If $\chi_1^{(3)} < 0$, then the Z-scan will produce a peak near the focus, indicating induced transparency (SA).

Measurements and Discussion

The measurement of the nonlinear optical absorption of the samples was carried out by using a Continuum Surelite-I laser system with a pulse width of 5–7 ns. To exclude the thermal effect, a repetition rate of 1 Hz was maintained. The standard Z-scan setup is shown in Figure 4. The laser beam was focused to about 30 μm at the focal point. A quartz cuvette with 1 mm length of optical path was used to contain the SWNT–ssDNA solution that is driven by a translation stage with a resolution of 10 μm . In order to prevent heat damage to the cuvette, we limited the energy per pulse at 1.5 mJ. For each point, the ratio between the transmission and the reference was measured for 100 pulses and the average value was taken for normalization.

Figure 5 shows the nonlinear absorption coefficient as a function of the concentration of H_2O_2 . Except for the sample without H_2O_2 , the measurement started 5 h after H_2O_2 was added to the samples unless otherwise noted. One can see that the SWNT–ssDNA sample without H_2O_2 exhibits SA ($\circ$). The theoretical fit gives a negative nonlinear absorption coefficient $\beta = -1.64 \times 10^{-15}$ m/W. After the sample reacts with a 10 ppm concentration of H_2O_2 for 5 h, SA is decreased but can still be observed (Δ). The theoretical fit shows the nonlinear optical coefficient decreases to $\beta = -6.11 \times 10^{-16}$ m/W. At a 20 ppm concentration of H_2O_2 , the nonlinear optical coefficient is about 0 (∇). With increasing concentration of H_2O_2 , the solution now starts to exhibit RSA. $\diamond$ shows the result for 30 ppm, and $\square$ displays the result for 100 ppm. Theoretical fits give $\beta = 5.47 \times 10^{-16}$ m/W and $\beta = 7.99 \times 10^{-16}$ m/W for 30 and 100 ppm, respectively. The results of continuing to increase the concentration of H_2O_2 to 150 ppm (Δ) and 200 ppm (∇) are shown in Figure 6. For comparison purposes, the result of 100 ppm is also repeatedly shown here ($\circ$). One can see that the nonlinear absorption coefficient decreases for these two high concentrations. The fitted results are $\beta = 4.76 \times 10^{-16}$ m/W and $\beta = 4.02 \times 10^{-16}$ m/W for 150 and 200 ppm, respectively. Figure 7 shows RSA as a function of time for the solution with 50 ppm of H_2O_2 . One can see that the nonlinear optical absorption coefficient decreases with time. For clarity, the measured result for the reaction time of 2 h is shown in Figure 8. The fitted result of this curve gives $\beta = 4.94 \times 10^{-16}$ m/W.

To understand the origin of the nonlinear optical response in the SWNTs and ssDNA hybrids, we measured the suspensions of the pure SWNTs and pure ssDNA. The results are shown in Figure 9. From the two curves, one can see that the pure SWNT suspension could have a very small negative β and the pure ssDNA solution could have a very small positive β . However, the values of for both samples are near zero. The reason is that pure SWNTs easily form bundles due to van der Waals forces and therefore have very poor solubility in water.^{8,17} The ssDNA does not have strong linear and nonlinear absorptions at 1064 nm.¹²

On the basis of the experimental measurements and using eqs 3 and 4, one can compute the values of β and $\chi_1^{(3)}$. The theoretically fitted results of β and $\chi_1^{(3)}$ are shown in Figure 10. The maximum SA coefficient obtained is $\beta = -1.64 \times 10^{-15}$ m/W and RSA coefficient is $\beta = 7.99 \times 10^{-16}$ m/W.

In order to confirm the change of nonlinear optical coefficient is due to the redox reaction of H_2O_2 , we demonstrate regenerating the SA property of SWNT-ssDNA solutions by removing H_2O_2 using the dialysis technique. To remove H_2O_2 from the samples, the H_2O_2 -reacted SWNT-ssDNA samples were placed in a dialysis membrane (6000–8000 MWCO, Spectrum Laboratories, Inc.), which was kept in TE buffer with a pH value of 7. The buffer solution was stirred constantly during dialysis and was replaced by fresh solution every hour. The two samples with 100 and 200 ppm of H_2O_2 were used as examples of removal of H_2O_2 by this method. First, the two samples reacted for 5 h and Z-scan measurements were performed, as shown in Figure 6. Then, the dialysis technique was used to remove H_2O_2 . After 16 h of dialysis, we conducted the Z-scan measurement again and the results are shown in Figure 11. The theoretical results as shown by the solid curves give $\beta = -6.68 \times 10^{-16}$ m/W and $\beta = -6.61 \times 10^{-16}$ m/W for the 100 and 200 ppm samples, respectively. Compared with the top curve shown in Figure 5, one can see that the SA property of the two samples is partially regenerated.

The quantum mechanical density-functional tight-binding (DFTB) theory predicts that the electronic orbital hybridization of semiconducting carbon nanotubes and ssDNA can form the energy band gap (E_{11}) between LUMO and HOMO ranging from 1.38 eV (900 nm) to 0.96 eV (1300 nm) depending on the diameter and length of the semiconducting carbon nanotubes.^{12,23,30} The experimental measurement of I - V characteristics for DNA indicates that poly (G) and poly (C) DNA chains have a band gap of around 2 eV.^{12,31,32} The research work on semiconducting carbon nanotubes infers that (7,3), (7,5), (10,5), (10,2), (10,0), (9,4), (12,1), and (11,3) carbon nanotubes have a band gap (E_{11}) in the range of 1.1 eV (1130 nm) to 1.2 eV (1035 nm).^{30,33} The hybridization system has a smaller band gap than 2 eV because several unoccupied states from the carbon nanotubes fall within the band gap of DNA. According to the calculation in ref 12 in the combined system, the HOMO electronic states mainly locate on the DNA component and the LUMO electronic states are from carbon nanotubes. The theoretical computation in ref 23 predicts that (7,3) carbon nanotubes can establish the band gap E_{11} between 1.1 eV (1130 nm) and 1.2 eV (1035 nm) with poly (A) and poly (C) DNAs. This model also computes that the density of electronic states (DOS) in the LUMO is much less than the DOS in the HOMO. On the basis of these theoretical results, we propose a three-level diagram as shown in Figure 12 to qualitatively explain the SA and RSA observed. Process 1 describes that laser illumination excites the electrons from the HOMO to the LUMO. Process 2 represents the excited electrons returning to the HOMO. Process 2 is normally slower than process 1 that makes the LUMO more populated while illuminating. Because the DOS of the LUMO is smaller than that of the HOMO, due to the limit of the Pauli exclusion principle, as long as the LUMO is fully populated, no electrons can be further excited to the LUMO by absorbing energy from the laser beam that leads the sample to transparency at high intensity illumination. After one adds H_2O_2 to the sample, H_2O_2 withdraws electrons from the LUMO,^{30,34,35} which makes the LUMO less populated. The sample can still exhibit SA at a low concentration of H_2O_2 . As the concentration of H_2O_2 increases, more electrons can be withdrawn from the LUMO and more electronic states will be vacated on the LUMO so that process 1 will be strengthened, which makes the sample exhibit RSA at higher concentrations of H_2O_2 . While withdrawing electrons from the LUMO and HOMO, H_2O_2 can react with SWNTs and DNA to form covalent endoperoxides and carbocations on the surfaces of SWNTs and

DNA.^{30,34,35} This process will then shift the band gap between the LUMO and HUMO and diminish RSA.^{30,34–36} SA partially recovers after H₂O₂ is removed by dialysis.

Conclusions

We have demonstrated that the DNA-wrapped SWNTs have SA and RSA nonlinear optical properties. The SA and RSA coefficients can be controlled by adjusting the concentration of H₂O₂ and the reaction time. A high concentration of H₂O₂ can completely quench the nonlinear optical absorption due to the redox process among H₂O₂, SWNTs, and DNA. After removing H₂O₂, the nonlinear optical absorption can be partially restored.

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Figure 1.

Agarose gel electrophoresis of DNA: (1) low-molecular-weight DNA ladder; (2) single-stranded DNA (3%). One can see the ssDNA used in this work is around 25 bases long (~8.5 nm).

Figure 2.

Raman spectra from ssDNA, SWNTs, and a hybrid of ssDNA and SWNTs. Note the changes of the RBM and G bands after mixing ssDNA and SWNTs. On the spectrum of ssDNA, a sugar band (750–900 cm^{-1}), phosphate symmetric band (1220 cm^{-1}), and base pairing band (1680–1720 cm^{-1}) can be seen. On the spectrum of the hybrid, they cannot be seen due to the high intensity of RBM and G bands.

Figure 3. Absorption spectrum of SWNT–DNA dispersions. Note the first absorption band E_{11} (950–1080 nm) and the second absorption band E_{22} (700–800 nm) of hybridization of semiconducting SWNTs and ssDNA.

Figure 4. Schematic diagram of the experimental arrangement for the open-aperture Z-scan measurements. BS, beamsplitter; D, detector; Ls, lenses; OI, optical isolator.

Figure 5.

Z-scan measurement results for SWNT-DNA dispersions after 5 h of reaction with different concentrations of H₂O₂. From top to bottom: 0, 10, 20, 30, and 100 ppm. Note that negative absorption changes to positive absorption at 30 ppm.

Figure 6. Z-scan measurements for SWNT-ssDNA dispersions after 5 h of reaction with different concentrations of H₂O₂. From top to bottom: 200, 150, and 100 ppm. Note that nonlinear absorption decreases under higher concentrations of H₂O₂.

Figure 7. Dependence of nonlinear absorption on reaction time for SWNT-ssDNA dispersions with 50 ppm of H_2O_2 . Note that, after 15 h of reaction, the nonlinear absorption coefficient is completely quenched.

Figure 8. Z-scan measurement for SWNT-ssDNA dispersions after about 2 h of reaction with a 50 ppm concentration of H₂O₂. The theoretical fit gives $\beta = 4.94 \times 10^{-16} \text{ m/W}$.

Figure 9. Z-scan measurements for pure SWNT and ssDNA suspensions. One can see that both suspensions show near zero nonlinear absorption. For the SWNT suspension, it is because SWNTs have very poor solubility without ssDNA. For the ssDNA suspension, this is because ssDNA does not have absorption in the near IR range.^{12,31,32}

Figure 10. Measured nonlinear optical coefficient and computed imaginary part of the third-order susceptibility $\chi^{(3)}$.

Figure 11. Dialytic recovery of SA property in two SWNT-ssDNA samples. Before doing dialysis, the two samples have reacted for 5 h with 100 ppm ($\diamond$) and 200 ppm ($\circ$) of H_2O_2 , respectively. Note that the two samples exhibit SA again after 16 h of dialysis.

Figure 12.

Three-energy-level diagram to explain the SA and RSA observed. According to the DFTB theory, the LUMO has lower DOS while the HOMO has higher DOS. Without H₂O₂, the sample should exhibit RA. With increasing concentration of H₂O₂, more electrons will be removed from the LUMO by H₂O₂. The sample will exhibit RSA then.