Length Dependence of Ultrafast Optical Nonlinearities in Vertically Aligned Multiwalled Carbon Nanotube Films

Hendry Izaac Elim, Yan Wu Zhu, and Chorng Haur Sow

J. Phys. Chem. C, Just Accepted Manuscript • DOI: 10.1021/acs.jpcc.6b03651 • Publication Date (Web): 18 Jun 2016

Downloaded from http://pubs.acs.org on July 24, 2016

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
Length Dependence of Ultrafast Optical Nonlinearities in Vertically Aligned Multiwalled Carbon Nanotube Films

Hendry Izaac Elim (Elim Heaven),¹,² Yanwu Zhu,³ and Chorng-Haur Sow⁴

¹Nanomaterials for Photonics Nanotechnology Laboratory (Lab. N4PN), Physics Department, Faculty of Mathematics and Natural Sciences,
²Research Center of Nanotechnology and Innovative Creation (PPNRI-LEMLIT), Pattimura University, Ambon, Indonesia 97233
³Department of Materials Science and Engineering, University of Science and Technology of China, 96 Jin Zhai Rd., Hefei 230026
⁴Department of Physics, National University of Singapore 2 Science Drive 3, Singapore 117542, Republic of Singapore

#Email: hendry.elim@fmipa.unpatti.ac.id; elimheaven@outlook.com

Telp. (+62-81247524158)

Abstract

Tube-length-dependent optical nonlinearities of vertically aligned multiwalled carbon nanotube (MWNT) films have been investigated by Z-scan and transient absorption measurements with femtosecond laser pulses in the near-IR spectral range from 780 to 1550 nm. Both saturable absorption and optical Kerr nonlinearity are found to be dependent on excitation wavelength and tube length, indicating that band-filling in semiconducting tubes and longitudinal surface plasmon resonance in metallic tubes play an important role, respectively. The 1-ps relaxation time for the nonlinear response of the MWNT films, however, is independent of tube length, as evidence from dissipation of excited energy in the radial direction. Such ultrafast vertically length-dependent in CNT can significantly contribute to fabricate vertically nanochip in various types of integrated nanodevice just like a creation of living 3D fish bone (a kind of cowfish).
**Introduction**

Recently, ultrafast nonlinear-optical (NLO) responses of single-wall carbon nanotubes (SWNTs) in suspensions and films have received increasing attention.\(^1\)\(^-\)\(^6\) At resonant band (0.8-1.1 eV) of the lowest inter-band transitions of semiconducting SWNTs, a strong transient photo-bleaching has been observed with femtosecond laser pulses. The strongest imaginary part of the third-order NLO susceptibility, $\chi^{(3)}$ has been determined as large as $10^{-7}$ to $10^{-6}$ esu.\(^5\)\(^,\)\(^7\) Moreover, at the second lowest inter-band transitions (~1.6 eV) of semiconducting electronic structure in SWNTs, saturable absorption has also been detected using femtosecond laser pulses. In contrast, photo-induced absorption has been measured under off-resonant conditions of SWNTs. The band-filling effects have been identified as the mechanism responsible for the resonant saturable absorption, while the off-resonant photo-induced absorption is attributed to a global red-shift of the $\pi$-plasmon resonance.\(^3\) These investigations have been so far focused on the ultrafast NLO responses of SWNTs.

It is interesting to note that the tube-length dependence of quantum electrical conductance has been theoretically studied\(^8\) for carbon nanotubes with various nanotube structures such as straight tubes and nanotube multitapers. The tube-length dependence has been attributed to an intrinsic feature of the nanotubes and verified by the experimental findings of de Pablo \textit{et al.}\(^9\) which pointed out that the electronic transport through SWNTs is not Ohmic. Their observation\(^9\) showed that the electrical resistance increases with increasing nanotube length or diameter. Furthermore, they suggested that such a mechanism is due to the presence of nondissipative scattering centers. This effect
is strong evidence for coherent electron transport along the nanotubes, even for those with high intrinsic resistances.

Here, we report the first observation of both wavelength-scaling and tube-length \((L)\) dependence of NLO properties in vertically aligned multiwalled carbon nanotube (MWNT) films. By employing Z-scan and transient absorption measurements with 180-fs laser pulses at wavelengths ranging from 780 to 1550 nm, we have found from our samples with three different tube lengths of 4, 7, and 12 µm that the shorter the tube length of MWNTs is, the stronger the NLO properties are, which is attributed to the longitudinal surface plasmons in metallic nanotubes. The wavelength-scaling of NLO properties demonstrate that the semiconducting part of MWNTs plays an important role. The relaxation time of the nonlinearities is, however, determined to be independent of wavelength and tube length. This finding can significantly contribute to make the vertically nanochip consisted of a nanotube such as this CNT in an integrated nanodevice. The contribution of this idea can significantly enrich the development and fabrication of vertically nanochip in various types of integrated nanodevice just like a creation of living 3D fish bone (a kind of cowfish).

**Experimental Method**

MWNTs studied in our experiment were grown on quartz substrate. The MWNTs were prepared by a method of plasma-enhanced chemical vapor deposition. The details on the preparation were reported elsewhere.\(^{10-11}\) Figures 1(a)-(e) show high magnification scanning electron microscopy (SEM) images of the films with three different lengths of MWNTs. As shown by these images, the nanotubes were grown mainly in the direction
perpendicular to the surface of the quartz substrate. As the MWNTs were grown longer, the higher order in alignment could be evident. There was no significant difference in the outer-layer diameter (~20 nm) of nanotubes for the three films. Both linear optical and NLO properties of the MWNT films were examined as the light propagates in the axis perpendicular to the quartz substrate (or normal incidence on the film) at room temperature. In Fig. 1(d), the near-IR spectra of the MWNT films with \( L = 4 \mu m, 7 \mu m \) and 12 \( \mu m \) show a feature centered at \( \sim 1100 \) nm, which is assigned to the second lowest interband transitions in semiconducting MWNTs. It unambiguously indicates the existence of semiconducting nanotubes in the films, though they are predominated by metallic nanotubes. The feature decreases to a minimum at \( \sim 1400 \) nm, where the appearance of complex transitions is noticeable, reflecting the complex interplay of various chiral indices \((n, m)\) for different sizes and structures of nanotubes. As the wavelength increases further, the absorbance arises due to be resonant with the lowest interband transitions.

In the UV region, the absorption spectrum of MWNT film with \( L = 4 \mu m \) is dominated by a broadband centered at 5.4 eV, which is attributed to the \( \pi \)-plasmon resonance, and blue shifted by \( \sim 0.4 \) eV in comparison to that of SWNTs measured by Lauret et al.\(^3\). The blue shift is anticipated since there are more \( \pi \)-electrons in MWNTs than SWNTs. This \( \pi \)-plasmon resonance covers the entire visible spectral region and extends to the near-infrared region. As for MWNT films with \( L = 7 \mu m \) and \( L = 12 \mu m \), similar blue-shifts also occur but they are slightly smaller than that of the MWNT film with \( L = 4 \mu m \).
Our Z-scans and degenerate pump-probe experiments were performed at wavelengths ranging from 780 to 1550 nm. Accumulative thermal effects were minimized by employing lower average power of 180-fs laser pulses at 1-kHz repetition rate. The laser pulses were generated by a mode-locked Ti: Sapphire laser, which seeded a Ti: Sapphire regenerative amplifier (Quantronix). The laser wavelengths were tunable as the laser pulses passed through an optical parametric amplifier (Quantronix, TOPAS), whose output was focused onto the film by a lens. The incident and transmitted laser powers in the Z-scans were monitored as the MWNT film was moved (or Z-scanned) along the propagation direction of the laser pulses.

**Results and Discussions**

Figure 2(a) illustrates a relationship inspiration of a 3D bone of fish called as “poro bibi” fish (a type of cowfish living in east Africa) in Ambon, Indonesia with an interaction of elastically graphene like structure associated with man-made interaction between 3D vertically aligned MWNTs and laser beams with two different beam waists. We thought in our opinion as the aim of such good illustration was that the created 3D structure of living creature had been there in nature before the MWCNT structure was discovered by man (Ijima, ~1991 at NEC company, Japan). Moreover, this illustration is necessary to open the insight of many different physicist or multidisciplinary scientists to elaborate and extend their work in the near future as an integrated research.

The Z-scan data in Fig. 2(b) demonstrate that the nonlinear absorption coefficient ($\alpha_2$) in the MWNT films should be dependent on beam waist. The larger the beam waist is, the greater the $\alpha_2$ is. Under laser beam with larger beam waist, more MWNTs interact
with the laser beam and contribute to the measured nonlinearity, suggesting that not only the intrinsic process of individual tubes but also inter-tube interactions make contribution to the observed nonlinearities. The inter-tube interaction should be anticipated by taking imperfect nanotube alignment into account, as revealed by our SEM studies. It is also consistent with the findings of enhanced photoluminescence signals from bundled SWNTs in comparison to isolated SWNTs.\textsuperscript{12}

Figure 2(b) shows a negative $\alpha_2$, indicating photo-bleaching or optically induced transparency, typical behavior resulting from saturation of absorption. It is partially due to band-filling effects in the semiconducting nanotubes. In this process, charge carriers from the states in the valence band are excited by absorbing photons to fill the states in the conduction band, and thus the sample absorption becomes quenched. The similar observation was reported for isolated semiconducting SWNTs by Ostojic \textit{et al.}\textsuperscript{6} Such saturation of absorption in the isolated SWNTs was observed at laser fluence of $\sim 1 \text{ mJ/cm}^2 (\sim 7 \text{ GW/cm}^2)$ due to the resonance condition.

Figures 3(a)-(f) represent only a small portion of our Z-scan data. From the Z-scans,\textsuperscript{13} we obtain the NLO parameters for the MWNT film with $L = 7 \text{ µm}$ as $\alpha_2 = -250 \text{ cm/GW}$ or $\text{Im}\chi^{(3)} = -1.5\times10^{-10} \text{ esu}$, and $n_2 = -0.40\times10^{-2} \text{ cm}^2/\text{GW}$ or $\text{Re}\chi^{(3)} = -1.1\times10^{-10} \text{ esu}$ at 1100 nm. At another wavelength (1550 nm), we find that $\alpha_2 = -260 \text{ cm/GW}$ or $\text{Im}\chi^{(3)} = -1.6\times10^{-10} \text{ esu}$, and $n_2 = -0.40\times10^{-2} \text{ cm}^2/\text{GW}$ or $\text{Re}\chi^{(3)} = -1.1\times10^{-10} \text{ esu}$. The experimental errors in these measurements are 15%. It should be pointed out that the contribution from the substrate is negligible since its $\chi^{(3)}$ values are at least three orders of magnitude smaller. Between these two wavelengths, there is a dip at 1400 nm, see Fig.
3(g) and Fig. 3(h), which give clear evidence that the semiconducting part of MWNTs should play an important role in the measured nonlinearities. In particular, the 2nd-lowest interband transitions result in large nonlinearities covering the range from 900 to 1400 nm. In comparison with SWNTs, the redshift should be expected because of the larger diameters of tubes investigated here. In addition, these nonlinear values are about 2~3 times smaller than the values of $\alpha_2 = -540$ cm/GW and $n_2 = -1.1 \times 10^{-2}$ cm$^2$/GW, reported for the SWNT film (HiPco tube) at 1460 nm.

As shown by Fig. 3(b), Fig. 3(d) and Fig. 3(f), the closed-aperture Z-scans reveal negative signs for the refractive nonlinearities. In our previously reported nanosecond closed-aperture Z-scans on solutions of MWNT/polymer composites, a positive sign of $n_2$ was detected in association with thermally originated nonlinear scattering for optical limiting. The negative $n_2$ (or self-defocusing) observed here leads us to conclude that thermal effects are insignificant in the MWNT films under our experimental conditions.

To evaluate the relaxation time and to gain more understanding of underlying mechanisms for the nonlinearities observed by the Z-scans, we conducted the degenerate pump-probe experiment or transient absorption measurement at laser wavelengths from 900 to 1550 nm. Three typical measurements are shown in Fig. 4(a). From these pump-probe data, we plot the transient transmission signal ($\Delta T/T$ at zero delay) as a function of laser wavelength measured with the same pump irradiance, as shown in Fig. 4(b) where there is a minimum centered around 1400 nm, totally consistent with our Z-scans. Each transient signal shows that there are two components. By using a two-exponential component model, the best fits produce $\tau_1 = \sim 180$ fs and $\tau_2 = \sim 1$ ps. $\tau_1$ is the
autocorrelation of the laser pulses used. The $\tau_2$ component is the recovery time of the excited $\pi$-electrons in the MWNT films and is found to be independent of tube length within our experimental errors. The ratio of slow ($\tau_2$) to fast ($\tau_1$) component is independent of wavelength as well. The $\tau_2$ component is comparable to the findings for SWNTs.$^{3,7,16}$ Its independence of tube length gives evidence that relaxation of excited carriers preferably occur in the radial direction (perpendicular to the tube axis). The nature of this relaxation process is speculated as follows. The relaxation through nonradiative recombination: exciton energy transfer between adjacent tubes which has been observed in SWNT bundles.$^{16}$ It may also be attributed to the excitation and relaxation of surface plasmons in the radial direction, reported recently for SWNT bundles.$^{16}$ In particular, those transverse surface plasmons are independent of tube lengths.

From Fig. 4(a), it is concluded that the largest signal is obtained from the MWNT film with the shortest length of 4 µm followed by that with the length of 7 and 12 µm, in agreement with our Z-scan data. Such tube-length dependence is observed for the first time. We attribute it to the length dependence of longitudinal surface plasmon resonance (L-SPR). As the films comprise of semiconducting and metallic nanotubes, the measured nonlinearities should result from these two types of nanotubes. If the tubes are perfectly aligned in the vertical direction, L-SPR should not be excited as the laser light propagates along the tube axis. Due to the imperfection of alignment, L-SPR should influence the observation. It is well known that the L-SPR depends on the length of one-dimensional metallic nanosystems, in particular, the resonant wavelength of L-SPR increases as the
tube length increases. Further, as revealed by our TEM studies, the order of alignment is improved as the tube length increases from 4 to 12 µm, suggesting that the extent of L-SPR impact onto the measured nonlinearities is less in the longer tubes than the shorter tubes.

The relaxation times of the three films are the same (~1 ps), extracting from fitting the two-exponential component model. From the Z-scans obtained for the film with the shortest tube length (~ 4 µm), we determine that \( \alpha_2 = -350 \text{ cm/GW} \) and \( n_2 = -0.85 \times 10^{-2} \text{ cm}^2/\text{GW} \), at 1300 nm, one of the important optical communication wavelengths. To assess the material requirements for all-optical switching devices, we compute the following figure of merit (FOM) for the MWNT film with \( L = 4 \mu \text{m} \), \( |\chi^{(3)}|/(\alpha_0 \tau) \), where \( \alpha_0 \) is the linear absorption coefficient. With \( \lambda = 1300 \text{ nm} \) and laser irradiance operating under 0.4 GW/cm², the best FOM is found to be 2.7 esu cm s⁻¹, which is one order smaller than the reported FOM for SWNTs. In comparison with preparation of SWNTs, however, simpler synthesis process involved for MWNTs should facilitate wide applications of vertically aligned MWNT films to large-area planar optical switches.

**Conclusion**

In summary, we have presented, for the first time, the wavelength and tube-length dependence of NLO properties in vertically aligned MWNT films, determined with femtosecond Z-scans and pump-probe measurements. The wavelength and tube-length dependence are attributed to the semiconducting and metallic properties of MWNTs. A large FOM of 2.7 esu cm s⁻¹ is measured for the MWNT film with \( L = 4 \mu \text{m} \) at 1300 nm.
The 1-ps recovery time of the absorptive nonlinearity is independent of wavelength and tube length, indicative of dissipation of excited energy in the radial direction. More significantly, our findings open a new avenue to monitor the amount of semiconducting component or the degree of disorder in vertically aligned carbon nanotube films as well as a system in a future nanodevice working like a living 3D fish bone structure in a kind of cowfish.

**Acknowledgement**

We would like to thank the support of H.I. Elim current research works from a fund granted by “Riset Unggulan Daerah” grant no. 1039/UN13/SK/2015, Pattimura University, Indonesia about superfibers project.
References


Figure Captions:

Fig. 1 (Color online) SEM images of aligned MWNT films with average tube length of (a) 4 µm, (b) 7 µm, and (c) 12 µm. (d) Absorption spectra provided with the whole UV-VIS-NIR spectra.

Fig. 2 (Color online) (a) Illustration of interaction between laser beam and vertically aligned MWNTs in comparison with God’s graphene 3D-like structures in a living 3D fish (a kind of cowfish) bone. (b) Open-aperture Z-scans of MWNT film with $L = 7$ µm measured with different beam waist.

Fig. 3 (Color online) The data in (a), (c) and (e) are typical examples of open-aperture Z-scans; and the data in (b), (d) and (f) are closed-aperture Z-scans for MWNT film with $L = 7$ µm. The solid lines are the best fittings calculated by the Z-scan theory reported in Ref. [12]. (g) and (h) show the wavelength dependence of $\alpha_2$ and $n_2$ measured at the same irradiance of $\sim 2.7$ GW/cm$^2$, respectively.

Fig. 4 (Color online) (a) Pump-probe measurements at 1300 nm on the three MWNT films with different tube lengths. (b) Signal of $\Delta T/T$ at zero delay as a function of wavelength. Inset shows the ratio of slow to fast component as a function of wavelength.
Figure 1
Figure 2
Figure 3
(a) $I = 5.7 \text{ GW/cm}^2$

$\Delta T/T$ (a.u.)

Time Delay (fs)

- $L = 4 \mu\text{m}$
- $L = 7 \mu\text{m}$
- $L = 12 \mu\text{m}$

$\lambda = 1300 \text{ nm}$

(b)

Max. $\Delta T/T$

$\lambda (\text{nm})$

- 1100 nm
- 1550 nm

Inset:

Slow/Fast

$\lambda (\text{nm})$
God's 3D "garden fish" (a kind of weird fish) fish bones with graphene-like structure, found in GMT.

SEM Image of L = ~7 μm Vertically Aligned MWCNTs

(b)

Normalized Transmittance

I = 2.6 GW/cm²

w_x = 30 μm
w_y = 10 μm
w = 1300 nm