

Third-order Optical Nonlinearities of Singlewall Carbon Nanotubes for Nonlinear Transmission Limiting Application

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Abstract. Third-order nonlinear susceptibility of single wall carbon nanotubes thin film was measured to be $\sim 1.4 \times 10^{-16} \text{ m}^2/\text{V}^2$. The nonlinear transmission limiting threshold of carbon SWNT was $\sim 20 \text{ MW}/\text{cm}^2$ with visible and nanosecond laser excitation.

1. Introduction

Carbon singlewall nanotubes (SWNTs) are of great interest for possible nonlinear optical applications in battlefield enhancement and homeland security from various types of laser threats. The development of nonlinear transmission limiters for photonic device protection in visible spectra region and the nanosecond time scale is of current interest.

The carbon nanotube is a very promising material for new nonlinear optical devices since it has very large electronic optical nonlinearity with a fast response time due to the delocalized π -electron cloud along the tube axis. In addition, carbon nanotubes also show striking stability under high light flux. Ultrafast nonlinear optical responses [1,2], resonant saturable absorption [3,4], and off-resonant nonlinear optical response [2,5] of carbon SWNTs in suspensions and in films have been investigated extensively recently. The nonlinear transmission limiting properties of carbon SWNTS in water-surfactant suspensions were also demonstrated by excitation with 532 and 1064 nm lasers in seven nanoseconds temporal pulse width [6]. The dominant mechanisms of optical power limiting by the carbon SWNT in water-surfactant suspensions were nonlinear scattering and nonlinear refraction. In this work, we investigated the third-order nonlinearity and the mechanism of nonlinear transmission limiting properties of a carbon SWNT thin film using both Z-scan and degenerate four-wave mixing techniques by 532 nm laser in eight nanosecond temporal pulse width.

2. Linear Optical Properties

The SWNT thin film was prepared with HIPCO SWNTs (Carbon Nanotechnologies Inc.). The median diameter of HIPCO SWNTs was $\sim 1 \text{ nm}$. The tube lengths were largely distributed between $\sim 300 \text{ nm}$ and $\sim 1 \text{ }\mu\text{m}$. The as-produced SWNTs contained $\sim 30 - 35 \text{ wt. \%}$ Fe and $\sim 5\%$ of non-SWNTs. For all optical characterization, the SWNTs were stacked on a glass plate with $10\text{-}\mu\text{m}$ thickness.

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The linear transmittance spectrum of the SWNT thin film was recorded in the visible and near infrared range using a Cary 5E spectrophotometer. The linear transmittance has colorless and broadband transparency with multiple weak absorption bands (~ 0.84 , 0.93 , and 1.03 eV) at the near-infrared region as shown in figure 1. The transparency at the visible spectral region is almost that of a sunglass polarizer level.

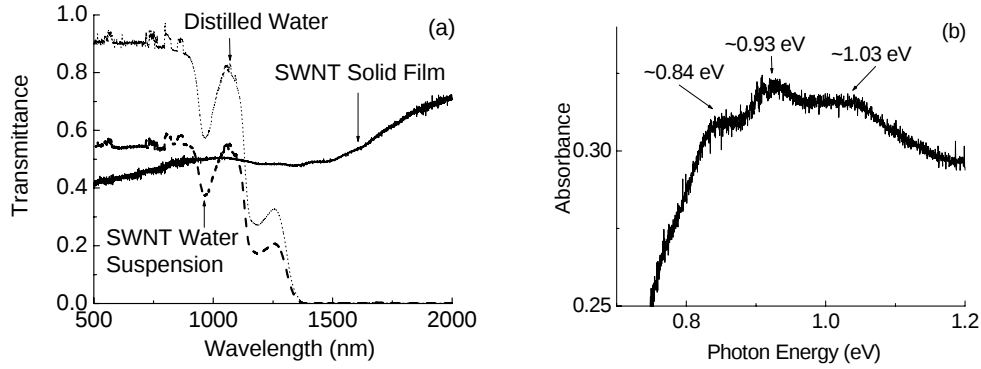


Fig. 1. Linear transmittance of SWNT thin film.

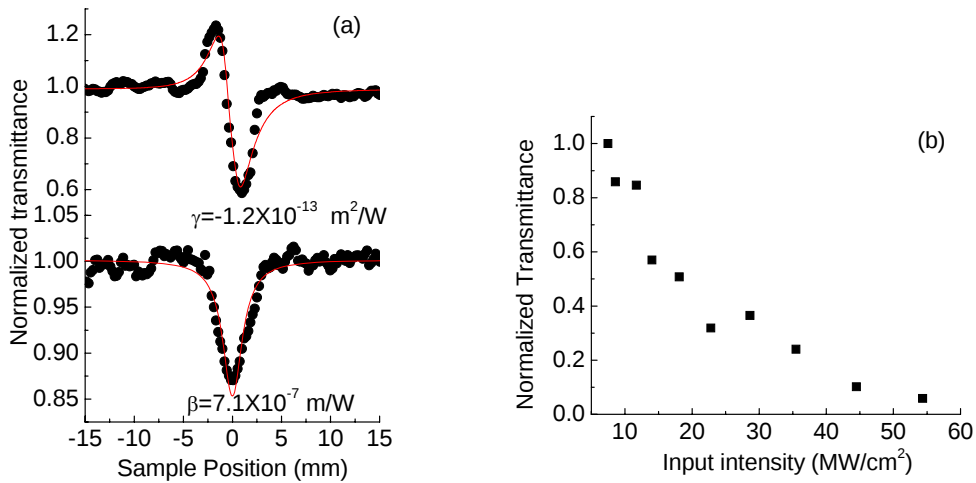


Fig. 2. Normalized transmittance of closed (top of (a)) and open (bottom of (a)) z-scan, and nonlinear transmission limiting properties of SWNT thin film in visible and nanosecond time scale (b).

3. Nonlinear Optical Properties

The nonlinear refraction and absorption of the carbon SWNT in random orientations were measured using both a single beam Z-scan and degenerate four-wave mixing (DFWM) techniques. The sample thickness of the carbon SWNT thin film was ~ 10 μm . The excitation source used was a spatially gaussian shaped, ~ 8 ns pulsed laser (continuum, powerlite) operating at a wavelength of ~ 532 nm with a repetition rate of 10 Hz. The laser beam was focused to a waist radius of ~ 12 μm by a lens with focal length of ~ 8.83 cm.

Normalized nonlinear transmittances of the carbon SWNT thin film by closed and open z-scan are shown in figure 2 (a). A typical peak power density at the focal point of the Z-scan was ~ 1.6 MW/cm^2 . Fitting with the nonlinear transmittance equations in our previous article to the closed and open Z-scan measurements [7], the nonlinear refraction (γ) and nonlinear absorption (β) coefficients of the carbon SWNT thin film were revealed to be $\sim -1.2 \times 10^{-13}$ m^2/W and $\sim 7.1 \times 10^{-7}$ m/W , respectively. The third

order susceptibility of carbon SWNT from Z-scan spectroscopy was estimated to be $\sim 1.8 \times 10^{-15} \text{ m}^2/\text{V}^2$ ($\sim 6.7 \times 10^{-7} \text{ esu}$) using the following equation:

$$\chi^{(3)} = \sqrt{\left(\text{Re}\chi^{(3)}\right)^2 + \left(\text{Im}\chi^{(3)}\right)^2}, \quad (1)$$

where, $\text{Re}\chi^{(3)} = \frac{4}{3}n_o^2\varepsilon_o c\gamma$ is the real part of $\chi^{(3)}$, and $\text{Im}\chi^{(3)} = \frac{1}{3\pi}n_o^2\varepsilon_o c\lambda\beta$ is the imaginary part of $\chi^{(3)}$.

The values of real and imaginary $\chi^{(3)}$ of the carbon SWNT thin film were $\sim 1.4 \times 10^{-15} \text{ m}^2/\text{V}^2$ ($\sim 1.0 \times 10^{-7} \text{ esu}$) and $\sim 4.3 \times 10^{-16} \text{ m}^2/\text{V}^2$ ($\sim 3.0 \times 10^{-8} \text{ esu}$).

Figure 3 (a) shows logarithmic plots of the DFWM signal in carbon SWNTs with excitation of 532 nm and 8-ns temporal pulse width as a function of total pump intensity at around zero delay. The DFWM signal near the zero delay was observed to be $I^{2.96}$, which indicates the dominance of the third-order nonlinearity at the irradiances near and less than $10 \text{ MW}/\text{cm}^2$.

The third-order nonlinear susceptibility of carbon SWNTs were estimated to be $\sim 1.4 \times 10^{-16} \text{ m}^2/\text{V}^2$ ($\sim 1 \times 10^{-8} \text{ esu}$) using the following equation by comparison of the FWM signal beams of carbon SWNTs with that of CS_2 measured under identical conditions [8]:

$$\chi_S^{(3)} = \sqrt{\frac{I_S}{I_R} \left(\frac{n_S}{n_R}\right)^2 \left(\frac{L_R}{L_S}\right) \left(\frac{\alpha L}{e^{-\alpha L/2}(1 - e^{-\alpha L})}\right)} \chi_R^{(3)}, \quad (2)$$

where I is the intensity of the FWM signal beam, n is the refractive index ($n_S = n(\text{SWNT}) \sim 2.0$ [9], $n_R = n(\text{CS}_2) \sim 1.63$ [10]), L is the sample path length ($L_S(\text{SWNT}) \sim 10 \mu\text{m}$, $L_R(\text{CS}_2) \sim 1 \text{ mm}$), α is the linear absorption coefficient ($\sim 8.4 \times 10^4 \text{ m}^{-1}$) of the sample at 532 nm, and S and R indicates sample and reference. The excellent and stable third-order optical response solvent, carbon disulfide (CS_2 , 99+ %, spectrophotometric grade, Aldrich), was selected as reference. It has been assumed that the reference has no linear absorption at the excitation wavelength at 532 nm. The third order nonlinear susceptibility of CS_2 was reported to be $\sim 9.5 \times 10^{-21} \text{ m}^2/\text{V}^2$ ($\sim 6.8 \times 10^{-13} \text{ esu}$) in the nanosecond time-scale [11]. The discrepancy of third-order optical susceptibilities between Z-scan and FWM were due to the scattering effect on the β measurement with Z-scan. However, the scattering in FWM by the SWNT solid film was revealed to be a linear dependence to the pump intensity as shown in figure 3 (b), instead of nonlinear scattering by the SWNT or MWNT suspensions as reported in the previous articles [12-14].

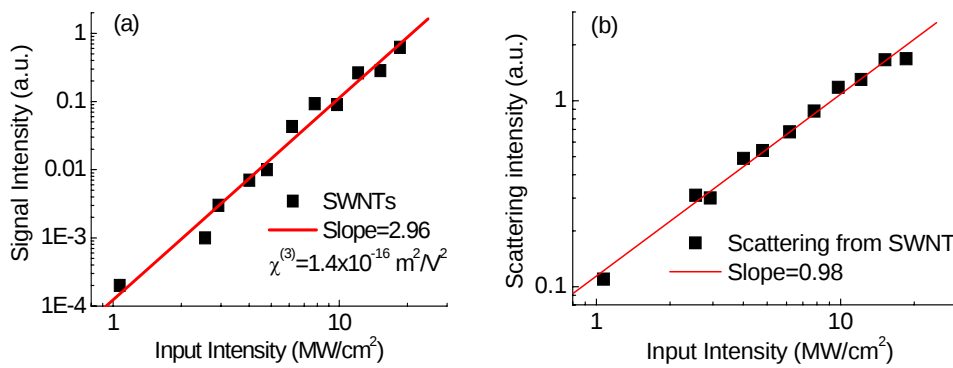


Fig. 3. DFWM signals of the carbon SWNT film (a), and scattering by the carbon SWNT film (b) as a function of input intensity.

Since the peak of the normalized transmittance precedes the valley in the Z-scan measurement, the sign of the refractive nonlinearity of the SWNTs is negative (negative lens effect, or self-defocusing). For self-defocusing materials, the optimum position of materials in the limiter is approximately a Rayleigh range after the focus. For nonlinear transmission limiting experiments, the normalized transmission after the pinhole was measured as a function of input power intensity as shown in Fig. 2

(b). The nonlinear transmission limiting threshold, which is the half of linear transmittance, of carbon SWNT is $\sim 20 \text{ MW/cm}^2$. The carbon SWNT thin film around the valley of z-scan setup is almost opaque for visible and nanosecond laser intensity at $\sim 50 \text{ MW/cm}^2$. The possible mechanism of $\chi^{(3)}$ and nonlinear transmission limiting of solid thin film SWNT is suggested to be nonlinear absorption [12], nonlinear refraction [12], and linear scattering rather than nonlinear scattering [12-14].

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