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Saturable absorption and nonlinear refraction in free-standing carbon nanotube film: Theory and experiment

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The nonlinear absorption and refraction of free-standing films made of single-walled carbon nanotubes (SWNTs) have been investigated experimentally and theoretically. By solving the quantum kinetic equations that take into account both the intra- and interband transitions, we obtain the analytical expression for the SWNT nonlinear conductivity. The nonlinear absorption coefficient and saturation intensity of the film comprising randomly orientated SWNTs have been calculated in a broad spectral range spanning over M11, S11, and S22 absorption bands. The effects of the laser pulse duration and dynamic Burstein–Moss shift on the saturation intensity have been revealed. We demonstrate in the experiment that, under irradiation with femtosecond laser pulses, the absorption modulation depth of SWNT film at resonance wavelength 1375 nm is as high as 30%. The observed saturation intensity minimum is red-shifted with respect to the absorption maximum due to the dynamic Burstein–Moss shift. The saturation intensity within the S22 band is 26–fold lower than that out of the band at 795 nm. The closed-aperture z-scan measurements reveal the negative nonlinear refractive index n2 = −3.1 × 10−12 cm2/W at 795 nm.

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1. Introduction

Free-standing single-walled carbon nanotube films (FSCNFs) offer a unique opportunity to explore the electronic ensemble of individual single-walled carbon nanotubes (SWNTs) [1]. Aerosol synthesis [2] allows one to obtain FSCNFs composed of virtually non-electromagnetically interacting SWNTs having prescribed diameters [3,4]. The advantageous electronic and optical properties of such FSCNFs enable transparent capacitive touch sensors, thin-film transistors, electrochemical sensors, bright organic light-emitting diodes, incident light polarization analyzers, and terahertz modulators [3,5–7]. In future, the films made SWNTs can be employed as transparent flexible electrodes for different applications, e.g. for solar cells, and in flexible electronics, e.g. for flexible touch screens and keyboards. Moreover, they can be used as an active material for the field effect transistors. In photonics, one of the most promising applications of FSCNFs is low-cost broadband mode-locking for compact yet powerful femtosecond lasers [8]. FSCNFs have reduced nonsaturable absorption which inevitably increases when carbon nanotubes are embedded into a polymer matrix or deposited onto a substrate [4,9]. They have demonstrated high performance and robustness in passive mode-locking of fiber lasers at the wavelengths of 1.05, 1.32, 1.56, 1.9, and 1.99 μm [3,4,10–12]. Moreover, FSCNFs can be applied to vary the light pulse duration at the telecom wavelengths from the femtosecond to the microsecond [13]. Very recently, we have also shown that the linear and nonlinear optical properties of FSCNFs [14] can be drastically improved by the combined acid and laser treatment. Specifically, the enhancement of linear transmittance across the visible range [14,15] and by 26% increase in the saturable absorption (SA) coefficient at the wavelength of 795 nm have been demonstrated.

The SA theory based on the numerical solution of the quantum
kinetic equations for individual SWNT has been presented in Refs. [16,17]. Such an approach is convenient if one considers a single interband transition between two sub-bands. However, when many electron interband transitions occur between different sub-bands in SWNTs comprising the film, obtaining the intensity-dependent absorption coefficient of the FSCNF requires knowledge of the analytical solution of the kinetic equations. The efficiency of such an approach has been recently demonstrated neglecting the intraband transitions [18], however, the frequency dependence of the absorption coefficient of the FSCNF has not been studied yet. Also, only a few papers report on the measurements of the nonlinear refraction in free-standing SWNT films [19–21] and not covering 795–1500 nm although.

In the present work, we combine the experiment and the theoretical modeling to quantitatively describe the SA in the FSCNF neglecting the intraband transitions [18], however, the frequency efficiency of such an approach has been recently demonstrated when many electron interband transitions occur between different single interband transition between two sub-bands. However, the numerical solution of equations (4) and (5) is stable only in the steady-state approximation, we will present the temporal evolution of the density matrix elements is governed by the following system of kinetic equations [16,17].

\[
\frac{\partial \rho_{nn}}{\partial t} + e E_z \frac{\partial \rho_{nn}}{\partial p_z} = \frac{2ie}{\hbar} E_r R_{cv}(\rho_{cv}^* - \rho_{cv}) - \frac{\rho_{nn} - \rho_{nn}}{\tau_1},
\]

(4)

\[
\frac{\partial \rho_{cv}}{\partial t} + e E_z \frac{\partial \rho_{cv}}{\partial p_z} = \frac{ie}{\hbar} E_r R_{cv}\rho_{nn} - i\omega_{cv}\rho_{cv} - \frac{\rho_{cv}}{\tau_2},
\]

(5)

where \(\tau_1\) and \(\tau_2\) are the longitudinal and transverse electron relaxation times, respectively; \(\rho_{nn} = \rho_{cc} - \rho_{rr} = 2\rho_{cv} - 1\) is the population inversion; \(\omega_{cv}(p_z,s) = 2\epsilon_c(p_z,s)/\rho_{nn}(p_z,s)\).

Equations (4) and (5) should be supplemented by periodic boundary conditions in quasi-momentum space, \(\rho_{cv}(t, p_z = p_b, s) = \rho_{cv}(t, p_z = -p_b, s)\) and \(\rho_{nn}(t, p_z = p_b, s) = \rho_{nn}(t, p_z = -p_b, s)\), and initial conditions \(\rho_{nn}(t = 0, p_b, s) = \rho_{nn}(p_b, s)\) and \(\rho_{cv}(t = 0, p_z, s) = 0\).

Numerical solution of Eqs. (4) and (5) allows us to calculate the inter- and interband currents densities introduced in Eqs. (1) and (2) for any \(E_z(t)\).

The performed numerical simulation (see Section 2.2) showed that the second term in the left-hand side of (3) can be ignored because its contribution to the current density is less than 1%.

The numerical solution of equations (4) and (5) is stable only in the vicinity of the interband transitions and the calculation time increases as the field amplitude increases. In order to reveal the main features of the nonlinear response of the FSCNF, we solve Eqs. (4) and (5) for the monochromatic light wave at frequency \(\omega\) by assuming

\[
E_z(t) = E_0 \exp(-i\omega t) + E_0^\prime \exp(i\omega t),
\]

(6)

where \(E_0\) is the wave amplitude.

In the steady-state approximation, we will present \(\rho_{nn}(t, p_z, s)\) and \(\rho_{cv}(t, p_z, s)\) in the following form:

\[
\rho_{cv}(t, p_z, s) = \rho_{cv}^{(+)}(p_z, s) E_0 \exp(-i\omega t) + \rho_{cv}^{(+)}(p_z, s),
\]

(7)

\[
\rho_{nn}(t, p_z, s) = \rho_0(p_z, s) + \rho_1(p_z, s) E_0 \exp(-i\omega t) + \rho_1^*(p_z, s) E_0^\prime \exp(i\omega t).
\]

(8)

Substitution of Eqs. (6) and (7) in Eq. (5) yields

\[
\rho_{cv}(p_z, s) = \frac{e E_r R_{cv}(p_z, s)}{\hbar (\omega - \omega_{cv} + i/\tau_2)}
\]

After substitution of Eqs. (6), (8) and (9) in Eq. (4) and taking into account only resonance terms (rotating-wave approximation) we arrive at
\[ \rho_0(p_z, s) = \frac{1 + \tau_s^2(\omega - \omega_{cv})^2}{1 + \tau_e^2(\omega - \omega_{cv})^2 + 2 \sqrt{\mu_0/\epsilon_0} e^2 h \tau_e R_{2s}(p_z, s) \tau_s I} \] \tag{10}

\[ \rho_1(p_z, s) = -\frac{ie}{\omega + i/\tau_1} \frac{dp_0(p_z, s)}{dp_z}. \] \tag{11}

where \( I = 2 \sqrt{\epsilon_0/\mu_0} E_0^2 \) is the intensity of the light pulse.

The obtained solution of kinetic equations allows us to present the SWNT current density in the following form

\[ j(t) = \sigma(\omega, I) E_0 \exp(-i\omega t) + c.c. \] \tag{12}

where \( \sigma(\omega, I) = \sigma_{\text{intra}}(\omega, I) + \sigma_{\text{inter}}(\omega, I) \) is the nonlinear conductivity comprising intra- and interband contributions

\[ \sigma_{\text{intra}}(\omega, I) = -\frac{ie^2}{2\pi^2 \hbar a} \frac{1}{\omega + i/\tau_1} \sum_{s=1}^p \frac{\partial \epsilon_c(p_z, s)}{\partial p_z} \frac{\partial \rho_0(p_z, s)}{\partial p_z} dp_z, \] \tag{13}

\[ \sigma_{\text{inter}}(\omega, I) = \frac{ie^2(\omega + i/\tau_2)}{2\pi^2 \hbar a} \times \sum_{s=1}^p \frac{p_s \omega_{cv}(p_z, s) R_{2s}(p_z, s) \rho_0(p_z, s)}{\omega_{cv} - (\omega + i/\tau_2)^2} dp_z. \] \tag{14}

One can observe from Eqs. 13 and 14 that for a weak light wave \( \rho_0(p_z, s) = \rho_{\text{in}}(p_z, s) \) and \( \sigma(\omega, I) \) reduces to the linear conductivity [25]. In such a low-intensity regime, longitudinal and transverse relaxation times \( \tau_1 \) and \( \tau_2 \) are associated with relaxation times of the intra- and interband transitions, respectively.

We will consider a FSCNF having a thickness much smaller than the typical length of SWNTs. In-plane conductivity of the film comprising identical randomly oriented SWNTs can be obtained by averaging \( \sigma(\omega, I) \) over random orientation of the nanotubes in the plane of the film

\[ \sigma_{\text{eff}}(\omega, I) = \frac{2F_0}{\pi a} \int_0^\pi \int_{-\pi/2}^{\pi/2} \sigma(\omega, I) \cos^2(\varphi) \cos^2(\varphi) d\varphi . \] \tag{15}

\( F_0 \) is a volume fraction occupied by SWNTs. Our analysis shows that \( \sigma_{\text{eff}}(\omega, I) \approx F_0(\sigma_{\text{in}})^{-1} \sigma(\omega, I) \) at the moderate intensities of the incident light. Equation (15) can be easily generalized for the case of the film comprising a mixture of SWNTs having different radii and structures.

At normal incidence, the intensity-dependent absorption coefficient \( a \) of the film can be introduced as

\[ a(\omega, I) = \sqrt{\frac{\mu_0}{\epsilon_0}} \Re \left[ \sigma_{\text{eff}}(\omega, I) \right]. \] \tag{16}

Saturation intensity \( I_s \) for the FSCNF can be found from the following equation

\[ a(\omega, I_s) = \frac{1}{2} a(\omega, 0). \] \tag{17}

Our calculations show that the saturation intensity is 50% higher for the film with random orientations of SWNTs than for the film with SWNTs aligned along the light polarization direction.

2.2. Numerical simulation of the SWNT nonlinear response

In this Section, we shall solve Eqs. (4) and (5) numerically to describe the interaction of the SWNT with an intense Gaussian light pulse with

\[ E_x(t) = 2E_0 \exp \left( -\ln \left( \frac{2t}{\tau_0} \right)^2 \right) \sin(\omega t), \] \tag{18}

where \( \tau_0 \) is the full width at half maximum of light intensity. Such a pulse is shown in Fig. 1a at \( \omega = 1.3 \times 10^{15} \text{ s}^{-1} \) and \( \tau_0 = 160 \text{ fs} \).

In our further calculations, we will use \( \tau_1 = 100 \text{ fs} \) [25] and \( \tau_2 = 10 \text{ fs} \) [26] and consider achiral zigzag and armchair SWNTs having chiral indexes \((m, 0)\) and \((m, m)\), respectively. Table 1 shows the dependence of parameters of these SWNTs on the transverse quasi-momentum \( p_z \) and subband index \( s \).

Fig. 1c shows the time dependence of the population inversion \( \rho_m = \rho_{\text{cc}} - \rho_{\text{nn}} \) at several quasi-momenta \( p_z \) for zigzag (23,0) SWNT. Pulse frequency coincides with bandgap energy, i.e. \( \hbar \omega_0 = 2\epsilon_z(p_z = 0, s = 16) \) (transition number 1 in Fig. 1b). One can see in Fig. 1c that the temporal evolution of the population inversion depends on the quasi-momentum \( p_z \); the smaller the difference \( 2\epsilon_z(p_z, 16) - \hbar \omega_0 \), the stronger the deviation of the inversion from -1. Interband transitions at all \( p_z \) contribute to the nonlinear response of the carbon nanotube.

For quasi-monochromatic incident pulse, the conductivity of SWNT at frequency \( \Omega \) can be defined as \( \sigma(\Omega) = j(\Omega)/E(\Omega) \), where \( j(\Omega) \) and \( E(\Omega) \) are the relevant Fourier components of the current density \( j_z(\Omega) \) and an incident field \( E_z(t) \) introduced in Eqs. (1) and (2) and Eq. (18), respectively.

In Fig. 2, we demonstrate how the transitions between two sub-bands \( \pm e_z(p_z, 16) \) shown in Fig. 1b contribute to the conductivity of the (23,0) zigzag SWNT. Fig. 2a presents this contribution \( \sigma_{\text{int}} \) in the linear regime and for the light pulse peak intensity of \( I_0 = 640 \text{ MW/cm}^2 \) at \( \tau_p = 400 \text{ fs} \). Here, we use \( \tau_p \gg \tau_{1,2} \) in order to satisfy the condition of the steady-state incident field. The relevant inter- and intraband conductivities, \( \sigma_{\text{int}}^{(\text{inter})} \) and \( \sigma_{\text{intra}}^{(\text{inter})} \), are shown in

---

**Fig. 1.** (a) Time dependence of the electric field \( E_x(t) \) of the incident light pulse at the frequency \( \omega = 1.3 \times 10^{15} \text{ s}^{-1} \) and \( \tau_0 = 160 \text{ fs} \); (b) Two sub-bands \( \pm \epsilon_z(p_z, 16) \) and 5 electron transitions \( S_{22} \) (shown by arrows) at \( p_z/h = 0 \) and 0.03; (c) Dependence of the population inversion \( \rho_m = \rho_{\text{cc}} - \rho_{\text{nn}} \) at normalized axial quasi-momentum \( p_z/h \) for (23,0) SWNT exposed to the light pulse shown in (a). (A colour version of this figure can be viewed online.)
In the linear regime, the interband electron transitions $S_{22}$ manifest themselves as a broad resonance in the conductivity $\sigma_{22}$ centered at about 1450 nm (see Fig. 2a). At the light pulse intensity of $I_0 = 640$ MW/cm$^2$, the absorption maximum is suppressed and the resonance frequency increases. Such a blue shift known as a dynamic Burstein–Moss shift [27] originates from the saturation of the absorption just above the band edge. This phenomenon has not been studied in SWNTs before. At low intensity, the contribution of the interband transitions dominates over the intraband transitions. In the saturation regime, the intraband transitions significantly contribute to the imaginary part of the conductivity; whereas their contribution into the real part of the conductivity remains small (see Fig. 2b). It is worth noting that the results presented in Fig. 2 consider only transitions within two sub-bands of a single SWNT shown in Fig. 1b.

### 2.3. Nonlinear conductivity of the FSCNF

In order to describe the nonlinear response of the model film comprising 5 semiconducting zigzag SWNTs with indexes (20,0), (22,0), (23,0), (25,0) and (26,0) and 4 metallic SWNTs (21,0), (24,0), (13,13) and (14,14), we shall use the steady-state solution of the kinetic equations assuming that the SWNTs are randomly oriented (13,13) and (14,14). For the SWNTs shown in Fig. 1b. At $I_0 = 640$ MW/cm$^2$, the absorption maximum is suppressed and the resonance frequency increases. Such a blue shift known as a dynamic Burstein–Moss shift [27] originates from the saturation of the absorption just above the band edge. This phenomenon has not been studied in SWNTs before. At low intensity, the contribution of the interband transitions dominates over the intraband transitions. In the saturation regime, the intraband transitions significantly contribute to the imaginary part of the conductivity; whereas their contribution into the real part of the conductivity remains small (see Fig. 2b). It is worth noting that the results presented in Fig. 2 consider only transitions within two sub-bands of a single SWNT shown in Fig. 1b.

#### Table 1

<table>
<thead>
<tr>
<th>p_0</th>
<th>R_{sc}(p_0, s)</th>
<th>\epsilon_v(p_0, s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>zigzag</td>
<td>$\frac{2\pi h}{3b}$</td>
<td>$- \frac{b_0^2}{2c(p_0, s)} \left[ 1 + \cos\left( \frac{3b_0b}{2\pi} \right) \cos\left( \frac{3s}{m} \right) \right] - 2\cos^2\left( \frac{s}{m} \right)$</td>
</tr>
<tr>
<td>armchair</td>
<td>$\frac{2\pi h}{\sqrt{3}b}$</td>
<td>$- \frac{3b_0^2}{2c(p_0, s)} \sin\left( \frac{3b_0b}{2\pi} \right) \sin\left( \frac{s}{m} \right)$</td>
</tr>
</tbody>
</table>

Fig. 2b.

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Fig. 3a shows the measured (see Section 3) and calculated absorbance spectra of the FSCNF. One can observe that the calculated and measured absorbance spectra are well correlated in the range 800–2500 nm. There is no full coincidence between the spectra below 800 nm because the developed theory does not take into account the $\pi - \pi$ plasmon resonance at 215 nm. $\pi - \pi$ plasmon contributes to the nonsaturable absorption, which is described only empirically [28]. It is worth noting that the difference between the
measured and the calculated spectra in the visible spectral range is because the modelling was performed for the film comprising only 9 types of SWNTs, whereas in our experiment, FSCNF is composed of much more types of SWNTs. Overlapping of their electron transitions at \( \lambda < 800 \text{ nm} \) smoothes the absorption spectrum of the FSCNF.

The contributions to the linear absorption from the interband transitions in semiconducting SWNTs (S11 and S22) and metallic SWNTs (M11) are shown by dashed lines in Fig. 3a. It is worth noting that the interband transitions are inhomogeneously broadened due to the presence of SWNTs with different radii. The broadening is the weakest for the S11 peak. Moreover, the interband resonances have a high-frequency tail due to the curvature of the energy bands (see Fig. 1b). This leads to overlapping of the neighbouring resonances and explains the observation of the SA between the peaks [29].

As shown in Fig. 3a, the calculated saturable absorbance of the film at \( \lambda = 0 \) varies slightly near 0.07 in a wide wavelengths range of 400–2500 nm. The absorbance of the film at \( \lambda = 4.8 \text{ GW/cm}^2 \) demonstrates a strong wavelength dependence (see Fig. 3a). The dipole moments of \( \pi \)-electrons are higher for the lower frequency electron transitions resulting in a stronger nonlinear response at lower frequencies. This tendency has been noticed also in e.g. Ref. [30].

Fig. 3b shows the calculated saturation intensity \( I_s \) of the model FSCNF. One can see that \( I_s \) has strong wavelength dependence demonstrating a dip near the transition S11. Due to the dynamic Burstein–Moss shift, the central wavelength of the dip is slightly larger than the central wavelength of the absorption peak. Such behaviour can be seen in the spectra presented in Ref. [29], though the authors did not pay attention to this.

In order to estimate the saturation intensity from experimental data, the measured in the experiment nonlinear absorption coefficient is fitted with [27,31].

\[
\alpha(l) = \alpha_{ns} + \alpha_0 / (1 + I / I_s),
\]

where \( \alpha_0 \) and \( \alpha_{ns} \) are the saturable and nonsaturable absorption coefficients, respectively.

Fig. 4 shows the calculated dependence of the normalized absorption coefficient on the intensity \( I \) for the SWNT film at the peaks S11 and S22 and above M11 peak; calculation was done for the same model film as in Fig. 3 assuming \( \alpha_{ns} = 0 \) (solid lines); for comparison, an approximate formula \( \alpha(I) = \alpha_0 / (1 + I / I_s) \) was also used (dashed lines). One can see that Eq. (19) well corresponds to the result of the numerical solution of Eq. (17) only at low intensities (\( I < I_s \)). At high intensities (\( I > I_s \)), Eq. (19) gives overestimated value of the saturation intensity. Such a departure from the simplified two-level model originates from both the curvature of the energy bands and the inhomogeneous broadening of the absorption bands.

Since the pulse duration used in the experiments (100–150 fs, see Refs. [29,30]) is comparable with the electron relaxation time \( \tau_1 \approx 100 \text{ fs} \), the measured saturation intensity depends on the pulse duration. For example, our calculations made for the SWNT (23.0) at the central frequency of the interband transition S22 (\( \lambda = 1450 \text{ nm} \), see Fig. 2a) gives the saturation intensity of 0.44, 0.37, 0.32, and 0.27 GW/cm² for a pulse duration of 100, 160, 250, and 400 fs, respectively. We also found that in our model film, the inhomogeneous broadening of the S11 band is not strong enough to modify the value of \( I_s \). However, a stronger broadening of the band S22 leads to a 2–fold increase in the saturation intensity. The heating of the SWNT film during the measurements can lead to a decrease in the electron relaxation time resulting in an increase of the saturation intensity. The relaxation time for intraband electron transitions \( \tau_1 \) is proportional to the absolute temperature \( T \) of the sample [25]. The SWNT oxidation starts at \( T > 600 \text{ K} \) that is two times higher than the room temperature. If we assume that \( \tau_1 \propto T \) and \( \tau_2 \propto T \), then one can expect that heating up to 600 K can lead to a 2–fold increase in \( I_s \).

3. Experimental

3.1. FSCNF fabrication

The SWNTs are synthesized by the floating catalyst (aerosol) chemical vapour deposition (CVD) method [2], which is based on the high-temperature decomposition of ferrocene in a CO atmosphere. An advantage of this method is that the nanotubes are downstream from the reactor on membrane filters and by adjusting the collection time and the CO flow rate one can control the film thickness and the diameter of the tubes, respectively [2,5]. At the outlet of the reactor, the SWNTs form a film with randomly oriented networks of metallic and semiconducting tubes. In contrast to SWNTs synthesized by arc-discharge [32,33] or by laser ablation [26,34], which require laborious processes of purification and dispersion in liquids before they can be transferred [35], the obtained network of nanotubes can be easily transferred to almost any material by an easy dry transfer technique [3,5].

In the experiments, the SWNT film is transferred by pressing it towards the surface [5] of a small glass plate with an opening in its middle similar to Ref. [14]. The area of the opening provides a free-standing film of nanotubes for optical measurements. The mean diameter of the tubes is about 1.5 nm so that the second van Hove optical transition S22 covered the telecom range. At the same time, the film is adjusted to have a thickness of \( L = 38 \text{ nm} \) [13] and linear transmittance \( T_0 \approx 80\% \) at 1.5 \( \mu \text{m} \) [10,12] similar to those used in fiber lasers at telecom wavelengths of 1.32 and \(-1.56 \mu\text{m}\). The film thickness is calculated according to an empiric equation \( L \approx 417 \times A_{550nm}^{\text{Abs}} \), where \( A \) is the absorbance at 550 nm [36].

The fabricated FSCNFs are characterized by optical absorption and scanning electron microscopy (Fig. 5). The dashed arrows in Fig. 5 mark the experimental laser excitation wavelength of 795 nm close to the band M11, and the resonance excitation wavelengths of 1200, 1300, 1375, 1440, 1500 nm within the band S22. While the theoretical modeling is performed in the range of 400–5000 nm, the filled area in Fig. 5 marks corresponding available measured spectra data 400–2500 nm (0.5–3.1 eV). The inset in Fig. 5 shows the morphology of the dry transferred network of randomly oriented SWNTs. The Raman spectra of the studied film that have been presented in Ref. [14] are dominated by characteristic for SWNTs' G-, D-, G'–peaks and the “radial breathing” modes. The transmission electron microscopy image of the individual single-walled carbon
nanotube has been presented in Ref. [37]. The atomic force microscopy and the X-ray photoelectron spectroscopy analysis presented in Ref. [15] identifies the morphology of the studied films and the presence of carbon, oxygen, and iron represented by C1s, O1s, Fe2p peaks, respectively.

3.2. Z-scan measurements

In the experiment, we employ the CDP 2017 optical parametrical amplifier (OPA) to get tunable radiation within the telecom range [38]. In the OPA, the pulses of the Ti:sapphire laser with the energy of ~0.3 mJ and pulse duration of τ = 150 fs at a central wavelength of λ = 795 nm generate a femtosecond white-light continuum in a 2-mm thick sapphire slab. The spectrally selected part of the white light is used as a seed pulse to achieve the parametrical amplification in beta barium borate (BBO) crystal. Two passes through BBO crystal allow one to get the required pulse energy and beam quality in the broad spectral range [39]. We use the fundamental mode for OPA pumping as it has less group-velocity dispersion in the IR range than the second harmonic. Considering the low value of group velocity dispersion and the optical path length that the laser pulse travels, we have evaluated the duration of laser pulses at each converted excitation wavelength. In the experiments, the OPA radiation is tuned in the range of 1200–1500 nm. Since the conversion efficiency at each wavelength is different, we have found pulse energy of 40 nJ (~ 8.5 GW/cm² for 1375 nm) as an optimum to provide a comparison of SA amplitudes within the telecom range. In order to define the evolution of SA at the excitation wavelength of 795 nm, the incident pulse energy is varied from 4 nJ up to the damage threshold (~100 nJ) and above.

The linearly polarized laser beam is focused on the FSCNF using a F = 75 mm lens. The beam waist radius measured at 1/e² of the maximal intensity at 795 nm is w₀ = 18.5 μm corresponding to the Rayleigh length of z₀ = πw₀²/λ = 1.35 mm. The Rayleigh length for excitation wavelengths of 1200, 1300, 1375, 1440, 1500 nm (marked in Fig. 5) is 2.03, 2.12, 2.35, 2.41, 2.51 mm, accordingly. The measurements of SA and nonlinear refraction are performed using open- and closed-aperture z-scan setups, respectively, described elsewhere [41–43]. The transmittance $E_{\text{out}}/E_{\text{in}}$, where $E_{\text{in}}$ and $E_{\text{out}}$ are the energies of the incident and transmitted laser pulses, is measured as a function of the distance z between the FSCNF and the laser beam waist. The energies of the incident pulse are measured using Thorlabs S122C 700–1800 nm energy head calibrated with the Ophir PD10-C energy meter.

3.3. Experimental results and discussion

3.3.1. Open-aperture z-scan

We perform open-aperture z-scan measurements in the wavelength range spanning from 1200 to 1500 nm, where the nonlinear response is mainly governed by semiconducting SWNTs (see Fig. 5). The normalized transmittance $T_n$ as a function of the FSCNF position measured at the incident pulse energy of 40 nJ (see Fig. 6 and Fig. S1 in Supplementary) demonstrate a pronounced SA for all resonant wavelengths.

In order to explain the z-scan experimental data, we used a conventional two-level model [27,31]. In this model, the evolution of the light intensity $I$ inside the medium is described by the system of Eq. (19) and equation

$$\frac{dt}{dz'} = - \alpha(I) \times I,$$

where $z'$ is the propagation coordinate. A solution to this system yields [44]:

$$T_n = \left[ \frac{I_{\text{out}}/I_s + 1 + \alpha_0/\alpha_{\text{ns}}}{I_{\text{in}}/I_s + 1 + \alpha_0/\alpha_{\text{ns}}} \right]^{-\frac{z_0}{\alpha_0}},$$

where $I_{\text{in}}$ and $I_{\text{out}}$ are the input and output intensities, respectively. The former depends on the FSCNF position z with respect to the beam waist, i.e., $I_{\text{in}} = E_{\text{in}}/(\tau \times \pi w^2 (z))$, $w(z) = w_0(1 + (z/z_0)^2)^{1/2}$ is the beam radius. Considering that $I_{\text{out}} \approx T_0 \times I_{\text{in}}$, we arrive at [14]:

![Fig. 6. Normalized transmittance of FSCNF measured for S22 resonance excitation wavelengths in open-aperture z-scan (symbols) at the incident pulse energy of 40 nJ. For each wavelength, the value of $z_0$ was determined separately. Solid lines correspond to approximations with Eq. (22). (A colour version of this figure can be viewed online.)](image-url)
where \( E_i = \pi w_0^2 L \). The fitting with Eq. (22) matches well with the symmetrical experimental data points indicating a pure SA effect [45]. The fitting returns \( a_0/a_{ns} \) and \( I_s \). By using the obtained value of \( a_0/a_{ns} \) and relation \( \ln I_0 = - (a_{ns} + a_0) \times L \), we get \( a_0, a_{ns}, \) and the modulation depth \( \Delta = a_0/(a_0 + a_{ns}) \) [29]. Large \( \Delta \) at small \( a_0 \) is desirable for a saturable absorber in laser mode-locking [9]. Therefore, the ratio of saturable/non-saturable losses

\[
R = \frac{\exp \left(-a_{ns} \times L\right) - \exp \left[- (a_{ns} + a_0)L\right]}{1 - \exp \left(-a_{ns} \times L\right)} \tag{23}
\]

is an important parameter [9].

The values of \( a_0, a_{ns}, R, \Delta, \) and \( I_s \), which were revealed using Eqs. (22) and (23), are summarized in Table 2. One can observe that within the S22 band, \( a_0, R, \) and \( \Delta \) are enhanced as expected [29] and that maximum values are achieved at 1375 nm. However, the saturation intensity \( I_s \) minimum occurs at wavelength of 1440 nm. Such a red shift with respect to the position of the absorption maximum may be associated with a Burstein–Moss shift of the absorption band. It is worth noting that even within the S22 absorption band \( a_0 \) is lower than \( a_{ns} \).

In Fig. 7, we compare the absorption modulation depth \( \Delta = a_0/(a_0 + a_{ns}) \), the ratio of saturable to non-saturable losses \( R \approx a_0/a_{ns} \), and the saturation intensity \( I_s \) with literature data [29,31,46–51] for the SWNT-based SA at the wavelengths of 1500–1560 nm. It is worth noting that we used larger-diameter SWNTs and exploited the S22 band, whereas authors of [31,47–49] dealt with thinner tubes thus exploiting the S11 band. This explains the higher saturation intensity for our samples (see Fig. 7). The highest (apart from presented in Ref. [46]) values of the modulation depth and ratio of losses are probably inherent to tens of nanometer-thick free-standing film; other authors studied tens of micrometer-thick composite films (except [46] where SWNTs was deposited on silica microtoroids) where the matrix could give an extra contribution to the non-saturable absorption coefficient \( a_{ns} \). The difference between the experimentally obtained \( I_s \) ~ 1 GW/cm² (or saturation fluence of \( F_s = 150 \mu J/cm² \)) and the theoretically estimated \( I_s \) ~ 0.6 GW/cm² (see Fig. 3b) may be partly explained by the usage of high-intensity radiation (\( I > I_s \)) and short pulse duration, as well as possible sample heating (see Sec. 2.2).

The nonlinear optical response of FSCNF at a non-resonance wavelength of 795 nm has been also studied. Similar measurements at the incidence pulse energy of 20 nJ (12.4 GW/cm²) have been recently reported [14]. We performed the measurements at pulse energies varied from 4 nJ (2.5 GW/cm²) up to 130 nJ (80.6 GW/cm²). The damage threshold of SWNT film is observed at the laser pulse energy of 100 nJ, which corresponds to the intensity of ~ 62 GW/cm². Fig. 8 illustrates the data for the pulse energy range of 4–90 nJ, i.e. below the damage threshold. In these energies, the z-scan curves are wave-shaped symmetrical and reproducible indicating an increase in the transmittance \( T_0 \) originating from the saturation of light absorption in the film rather than from the film damage caused by either heating or high peak intensities. At the energies exceeding 100 nJ, the wave-shaped open-aperture z-scan curves are replaced with cone-like ones having a sharp apex \( z_0 \) because a hole with a diameter of ~ 7 μm is formed in the film. Z-scan data for the incident pulse energies of 100–130 nJ (i.e. above the damage threshold) are presented in Fig. S2 (see Supplementary materials).

The fitting of experimental data with (22) gives \( a_0/a_{ns} = 0.39 \) and \( I_s = 25.6 \text{ GW/cm}^2 \) at 795 nm above the absorption band M11 (see Table 2). The theoretical calculations made for the model film predicts the saturation intensity to be about 3.5 GW/cm² just above the M11 band (Fig. 3b). Such a difference can be explained by the

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**Table 2**

<table>
<thead>
<tr>
<th>( \lambda, \text{nm} )</th>
<th>( a_0/a_{ns} )</th>
<th>( a_0 \times 10^4, \text{cm}^{-1} )</th>
<th>( a_0, % )</th>
<th>( a_{ns} \times 10^4, \text{cm}^{-1} )</th>
<th>( a_{ns}, % )</th>
<th>( R = a_0/a_{ns} )</th>
<th>( \Delta = a_0/(a_0 + a_{ns}) )</th>
<th>( I_s, \text{GW/cm}^2 )</th>
<th>( F_s, \mu J/cm² )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>0.34</td>
<td>1.12</td>
<td>26</td>
<td>3.25</td>
<td>74</td>
<td>0.34</td>
<td>0.26</td>
<td>0.95</td>
<td>142.5</td>
</tr>
<tr>
<td>1440</td>
<td>0.39</td>
<td>1.27</td>
<td>28</td>
<td>3.27</td>
<td>72</td>
<td>0.38</td>
<td>0.28</td>
<td>0.86</td>
<td>129</td>
</tr>
<tr>
<td>1375</td>
<td>0.43</td>
<td>1.44</td>
<td>30</td>
<td>3.29</td>
<td>70</td>
<td>0.43</td>
<td>0.30</td>
<td>1.15</td>
<td>172.5</td>
</tr>
<tr>
<td>1300</td>
<td>0.37</td>
<td>1.23</td>
<td>27</td>
<td>3.33</td>
<td>73</td>
<td>0.37</td>
<td>0.27</td>
<td>1.03</td>
<td>154.5</td>
</tr>
<tr>
<td>1200</td>
<td>0.26</td>
<td>0.88</td>
<td>21</td>
<td>3.40</td>
<td>79</td>
<td>0.25</td>
<td>0.21</td>
<td>1.17</td>
<td>175.5</td>
</tr>
<tr>
<td>795</td>
<td>0.36</td>
<td>1.27</td>
<td>27</td>
<td>3.50</td>
<td>73</td>
<td>0.36</td>
<td>0.27</td>
<td>25.6</td>
<td>3840</td>
</tr>
</tbody>
</table>
dependence of the saturation intensity on the carrier relaxation time that can depend on the temperature [25], incident power [52], frequency [53,54], crystalline quality, and chirality of the SWNTs [54]. Since we cannot take into account all these effects, in calculations, we use the same frequency-independent relaxation time for all SWNTs comprising the film in Fig. 3. Another possible explanation is the presence of different impurities including iron nanoparticles. Their oxidation into ferric chloride (FeCl₃) may result in a significant decrease in saturation intensity [14]. One may assume that the vanishing of impurities will further decrease the experimental saturation intensity and the nonsaturable absorption coefficient. The observed modulation depth of 28% is much higher than that obtained for SWNT composite films (~5%) at a non-resonant frequency close to the band M11 [29]. Comparing the experimental results, it is seen that the amplitude of \( T_{o} \) for the resonance band S22 is up to three times bigger compared with that for the non-resonant wavelength 795 nm, which is in good agreement with the reported values for SWNT composites [29,55,56]. Although the modulation depth is relatively constant, the boosted SA for the band S22 is accompanied by ~26-fold lower saturation intensity than that obtained for SWNT composite films (~5%) at a non-resonant wavelength 795 nm (see Table 2). Note that the theory predicts at least a 10–fold difference in the value of \( I_{o} \) (see Fig. 3b).

3.3.2. Closed-aperture z-scan

The results of the closed-aperture z-scan (see Fig. S3a in Supplementary) just above the M11 band are similar to those collected in the open-aperture z-scan (Fig. 8) up to the energies of 50 nJ. This indicates the significant contribution of SA in the nonlinear response. With an increase of the incident pulse energy from 50 to 90 nJ, we record a significant deviation of closed-with the open-aperture data by the presence of two peaks in film transmittance (see Fig. S3b in Supplementary) indicating the strengthening of nonlinear refraction. In order to visualize the contribution of SA and to obtain the nonlinear refraction coefficient, we plot the closed-aperture/open-aperture data ratio [57]. Fig. 9 presents the results obtained for 35 and 90 nJ pulse energy. The results obtained for pulse energies of 50, 55, and 70 nJ are presented in Fig. S3 in Supplementary materials.

The experimental data are normalized to \( T_{o} \) and present the valleys and peaks with the symmetrical amplitudes relative to the \( z/z_{0} = 0 \) [58]. With the relative positions of the peaks and valleys to the scanning direction (from a lens to aperture, from -z to +z [58]) one can evaluate the film negative nonlinear refraction, i.e. the defocusing by the sample [59].

The solid lines in Fig. 9 show fitting of the experimental data with the following equation [60,61]:

\[
T_{n} = 1 + 8 \frac{z/z_{0}}{1 + (z/z_{0})^{2}} \left(9 + (z/z_{0})^{2}\right) - \frac{n_{2}E_{in}L_{eff}}{w_{0}^{2}\lambda\pi} \tag{24}
\]

Here \( n_{2} \) is the nonlinear refractive index, \( L_{eff} \) is the effective length of the sample \( L_{eff} = \left[1 - \exp(-aL)\right]/\alpha \), where \( \alpha \) is the linear absorption coefficient. Visible deviation of the experimental data from the theoretical approximation in Fig. 9 is caused by asymmetries relative to \( z = 0 \) and can be explained by misalignment, which may essentially influence the experimental data at low intensity [62]. The fitting of the nonlinear refractive index gives \( n_{2} = -3.1 \times 10^{-12} \text{ cm}^{2}/\text{W} \). The obtained negative sign of \( n_{2} \) has been also reported for free-standing films of DWNTs [19]. To the best of our knowledge, this is the first-time report on the \( n_{2} \) for FSCNFs for femtosecond pulse at 795 nm. The obtained \( n_{2} \) is the same order of magnitude as for free-standing films of double-walled carbon nanotubes (DWNTs) [19] and is one order of magnitude lower than for SWNT film on substrate [63] and suspended SWNTs [64] and DWNTs [65].

Since the noise in the measurements of \( T_{n} \) within the S22 band is 10 times stronger than that at 795 nm (see Supplementary Fig. S4), we do not record the effect of nonlinear refraction within this band.

Table 3 summarizes the comparison of the obtained results with the nonlinear optical parameters of some promising saturable absorbers based on perovskites, metal-organic frameworks (MOF), and MXenes. The comparison analysis shows that the studied FSCNFs exhibit relatively higher saturation intensity than, e.g., perovskites, while it is lower than that for the MOFs or MXenes, especially at the wavelength of 1500 nm. The nonlinear refractive index of FSCNFs lies between that of the MOF and MXenes [66–68]. These results suggest that the FSCNF offers a good compromise between modulation depth and saturation intensity and has great application potentials as a saturable absorber. Moreover, further suppression of the unsaturated absorption in
ergies exceeding 50 nJ (31 GW/cm²) up to the damage threshold of (795 nm) and enormously strong within the absorption band S22 shift of the absorbance bands has been shown for the model FSCNF.

To the best of our knowledge, the largest ratio of saturable to nonsaturable losses changing in the wavelength range spanning from 400 to 5000 nm. This study shows that FSCNFs have strong and broad saturable absorption across the 400–5000 nm spectral range and suggesting that they have great application potential in pulse-shaping and optical modulation [76]. These findings together with the double-digit percent improvement of nonlinear optical performance [14] demonstrate that the FSCNF is a nanomaterial with tunable and scalable nonlinearity capable to open new and improve already existing nonlinear optical devices and technologies. Specifically, the obtained results open avenues towards the drastic improvement of the performance of the SWNT-based mode-locked lasers and optical switches operating in the optical communication window.

Table 3: Comparison of the nonlinear parameters of FSCNFs and other promising saturable materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>λ, nm</th>
<th>Tn, %</th>
<th>In, GW/cm²</th>
<th>n2, cm² × W⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimonene and antimonene quantum dots</td>
<td>633</td>
<td>–</td>
<td>–</td>
<td>10⁻⁵</td>
<td>[69]</td>
</tr>
<tr>
<td>Graphdiyne</td>
<td>671</td>
<td>–</td>
<td>–</td>
<td>10⁻⁸-10⁻⁵</td>
<td>[70]</td>
</tr>
<tr>
<td>Free-standing SWCNT film</td>
<td>795</td>
<td>3</td>
<td>25.6</td>
<td>–3.1×10⁻¹²</td>
<td>Current study</td>
</tr>
<tr>
<td>Ni-MOF</td>
<td>800</td>
<td>6.8</td>
<td>30</td>
<td>–4.3×10⁻⁷</td>
<td>[66]</td>
</tr>
<tr>
<td>CH3NH3PbI3, perovskite nanosheet</td>
<td>800</td>
<td>5.7</td>
<td>4.38</td>
<td>–</td>
<td>[67]</td>
</tr>
<tr>
<td>Ti3C2Tx MXene</td>
<td>800</td>
<td>10–35</td>
<td>88.6</td>
<td>–4.66×10⁻¹⁶</td>
<td>[68,71]</td>
</tr>
<tr>
<td>Benzylamine lead (II) bromide perovskite microdisks</td>
<td>800</td>
<td>–</td>
<td>4.85–84.3</td>
<td>–</td>
<td>[72,73]</td>
</tr>
<tr>
<td>Free-standing SWCNT film</td>
<td>1500</td>
<td>5.1</td>
<td>0.95</td>
<td>–</td>
<td>Current study</td>
</tr>
<tr>
<td>Ni-MOF</td>
<td>1550</td>
<td>5.2</td>
<td>19.8</td>
<td>–8.9×10⁻⁷</td>
<td>[66]</td>
</tr>
<tr>
<td>Ti3C2Tx MXene</td>
<td>1550</td>
<td>10–35</td>
<td>39.1</td>
<td>–4.89×10⁻¹⁶</td>
<td>[68,71]</td>
</tr>
</tbody>
</table>

4. Conclusion

In conclusion, we derived the analytical formula for the surface conductivity of SWNT in the presence of an intensive, monochromatic, steady-state field. The developed approach allows obtaining the intensity-dependent absorption coefficient of the film comprising different types of randomly oriented SWNTs.

The nonlinear absorption coefficient and the saturation intensity have been calculated in a wide spectral range (400–5000 nm) for the model FSCNF having linear absorbance spectra similar to that for realistic CVD synthesized SWNT film. Nonsaturable absorption has not been taken into account in calculations. It has been found that the saturation intensity is 1.5–fold higher for the films with random orientations of the nanotubes than for the film with the SWNTs aligned along the incident polarization direction. The inhomogeneous broadening of the absorbance resonance due to distributions of the radius of SWNTs is stronger for S22 than for the S11 band. As a result, for model FSCNF, the broadening practically does not modify the saturation intensity

FSCNFs similar to Ref. [14] can make FSCNFs a champion in terms of the SA performance.

In comparison with nonlinear crystals using in the mode-locking, e.g. LiF with F2– colour centres [74], films made of SWNTs can be easily embedded in the core of fibers similarly to nanodiamond films [75]. Another advantage of the SWNT films is their broad spectral response, which may allow FSCNFs to outperform semiconductor saturable absorber mirrors (SESMs) in femtosecond lasers mode-locking. SESMs enable mode-locking in a narrow wavelength range determined by the semiconductor bandgap and quantum well thickness (5–20 nm). In our work, we demonstrate that the SWNT film is capable to provide absorbance change in the wavelength range spanning from 400 to 5000 nm.

CRediT authorship contribution statement

V.V. Vanyukov: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Validation, Writing – original draft, Writing – review & editing. M.V. Shuba: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Validation, Writing – original draft, Writing – review & editing. A.G. Nasibulin: Resources, Writing – review & editing. Y.P. Svirko: Funding acquisition, Supervision, Writing – review & editing. P.P. Kuzhir: Funding acquisition, Writing – review & editing. G.M. Milchev: Conceptualization, Methodology, Investigation, Data curation, Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


