

# Polymer-Free Carbon Nanotubes Saturable Absorbers for Nanosecond Pulse Generation

A V Zasedatelev<sup>1,2</sup>, V I Krasovskii<sup>2,4</sup>, O Reynaud<sup>3</sup>, Yu G Gladush<sup>1</sup>, D S Kopylova<sup>1</sup>, E A Komochkina<sup>4</sup>, E I Kauppinen<sup>3</sup> and A G Nasibulin<sup>1,3,5</sup>

<sup>1</sup>Skolkovo Institute of Science and Technology, Moscow, Russia

<sup>2</sup>Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, Russia

<sup>3</sup>Department of Applied Physics, Aalto University School of Science, Espoo, Finland

<sup>4</sup>National Research Nuclear University «MEPhI», Moscow, Russia

<sup>5</sup>St.Petersburg State Polytechnical University, St. Petersburg, Russia

E-mail: anton.zasedatelev@gmail.com

**Abstract.** Hereby we present the results of investigations of nonlinear optical properties of single-walled carbon nanotube (CNT) thin-film saturable absorbers without binding polymers. Developed CNT-based polymer-free saturable absorbers exhibit high third-order nonlinear susceptibility:  $\chi^{(3)} \sim 10^{-8}$  esu, low absorption saturation intensity:  $I_s \sim 30$  mW/cm<sup>2</sup>, and high photostability. Using CNT-based polymer-free saturable absorbers for passive Q-switching mode of Nd:YAG laser, 25 ns laser pulses have been obtained.

## 1. Introduction

Carbon nanostructures are potentially promising nonlinear optical materials in laser physics. Due to a significant absorption saturation effect, graphene and CNTs are widely used as passive saturable absorbers for generation of ultrashort laser pulses both in fiber and solid-state laser systems [1,2]. Extremely high relaxation rate of the nonlinear response and large modulation depth of the absorption along with simple, flexible and low cost production of CNT-based materials are the main reasons of their rapid development in laser physics. Moreover, CNTs can be directly deposited on the optical fiber end or mirror, allowing their implementation in both classical and ring linear resonators [3]. Due to their high non-saturable losses, CNT-based saturable absorbers (CNT SA) become widely used in fiber lasers rather than in solid state systems. The elements, typically formed by deposition of CNT incorporated polymer suspension directly on the fiber end or quartz substrate, have several drawbacks. The dominant one is irreversible degradation of the polymer host of CNT SA, which caused by high intensity of laser radiation in the cavity. In order to prevent degradation processes in CNT SA polymer-free preparation methods have been developed [4].

The paper examines saturable absorption effect in polymer-free thin films of CNTs. Nonlinear optical measurements were carried out using open-aperture Z-scan technique, where 10 ns Nd:YAG laser (1064 nm) was used as a light source. We found out two mechanisms of nonlinear absorption, which related to fraction of CNT showing semiconductor and metallic properties. Nonlinearity of semiconductor CNTs can be described in two-level approximation, whereas nonlinearity of metallic CNTs is well described using third-order nonlinear susceptibility (Kerr nonlinearity). Here we

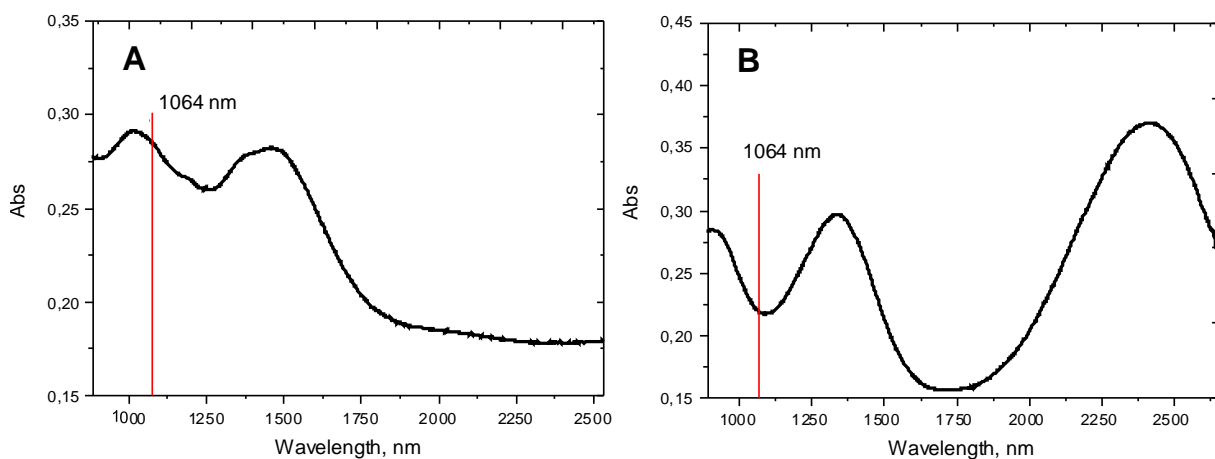


estimated saturation intensity and nonlinear susceptibility through the numerical fitting of Z-scan data. As a result of high nonlinear optical properties and photostability of polymer-free CNT SA, 25 ns laser generation in Nd:YAG laser was obtained.

## 2. Formation of thin-film saturable absorbers

The CNTs were synthesized by an aerosol (floating catalyst) CVD method by two various approaches. The first one is based on thermal vapor decomposition of ferrocene in carbon monoxide atmosphere at the temperature of 875 °C [4]. Hereinafter, the product, single-walled CNTs produced by this method, will be named as Sample 1. In the second approach the feedstock solution contained ferrocene as a catalyst particle precursor, toluene and ethylene as carbon sources and thiophene as a promoter was introduced in the reactor in a hydrogen atmosphere and heated up in the reactor. The CNTs synthesized at 1100 °C with a 17 sccm ethylene flow and a molar ratio of sulfur and iron of 1:1 (ferrocene and thiophene concentrations of 0.5 % wt.) were a mixture of single-walled and double-walled CNTs (Sample 2) [5]. In both cases the product was collected downstream of the reactor by filtering the flow in the form of thin films with adjustable thicknesses (transmittance) and subsequently transferred on a desirable substrate by a dry transfer technique [6]. A piece of a nitrocellulose membrane filter with a CNT-film was placed on a quartz substrate with the CNT-film upside down. Then, the substrate and the filter were pressed together at the pressure of 1000 Pa. After the pressing procedure, the membrane filter was peeled off and the CNT- film was strongly adhered to the mirror surface. It is worth noting that the CNT-film was utilized as-deposited and no purification or dispersion steps were required. When compared to standard wet deposition methods, which may require several time-consuming stages, such as purification, dispersion and filtering, the approach of the CNT-film preparation demonstrated here is simple and easily scalable [7].

Following the abovementioned procedure two types of CNT thin films have been prepared. Sample 1 exhibits resonant absorption at 1050 nm, whereas Sample 2 has minimum in absorption at this spectral region (figure 1A and 1B respectively). Thus, the irradiation of Nd:YAG laser ( $\lambda=1064$  nm) is reputed to be resonant and nonresonant with regard to absorption of Sample 1 and 2, respectively. The absorption spectra of both samples are shown in figure 1.



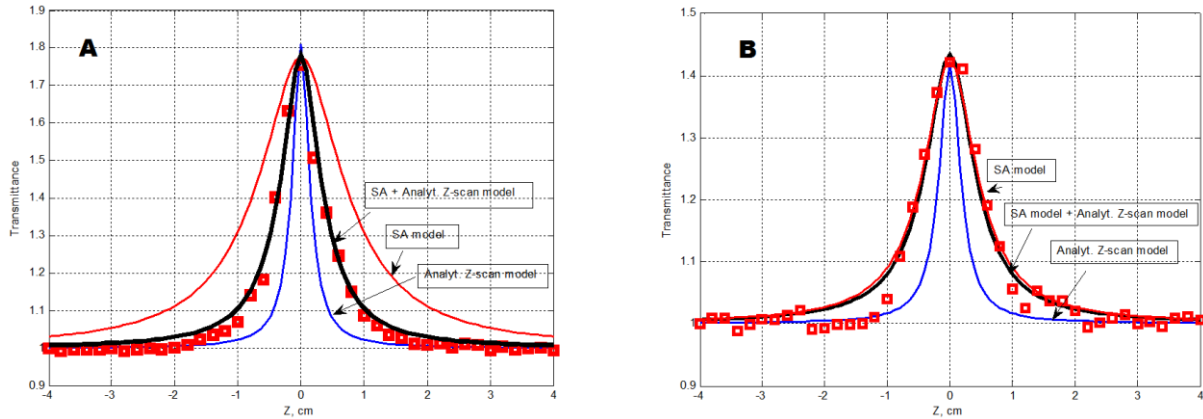
**Figure 1.** Absorbance spectra of Sample 1 – A and Sample 2 – B.

Absorption maxima of the samples are the result of interband (in case of semiconductor CNTs) and intraband (in case of metallic CNTs) transitions.

## 3. Nonlinear optical properties

Experimental studying of nonlinear optical absorption was carried out using open-aperture single beam Z-scan technique [8]. We utilised the first harmonic generation light of mode-locked Nd:YAG

laser (1064 nm) operated in TEM<sub>00</sub> mode with the pulse duration of 10 ns at a low repetition rate of 4 Hz (to prevent heating processes). The beam was tightly focused by a lens, the beam waist was 30 μm with the pulse energy 85 μJ. The peak intensity in the focus ( $I_0$ ) was 340 MW/cm<sup>2</sup>. Z-scan curves are shown in figure 2.



**Figure 2.** Open-aperture Z-scan curves of Sample 1 (A) and Sample 2 (B). Experimental data – red dots, model curves based on two-level saturable absorber approach (SA model) – red lines, model curves based on common used Sheik-Bahae formalism (Analyt. Z-scan model.) – blue lines, model curves based on both approaches (SA + Analyt. Z-scan model) – black lines.

As can be seen in figure 2, both samples exhibit considerable absorption saturation effect. In order to interpret experimental results we applied several fitting approaches. Well-known analytic model based on Sheik-Bahae formalism [8], numerical model of saturable absorber based on two-level approximation [9] and joint numerical model based on both approaches were considered [10]. The latter one is appropriate for nonlinear media having complicated mechanisms of the nonlinearity, such as ensembles of CNTs, and gives an opportunity to determine saturation intensity and third-order nonlinear susceptibility as well. A number of studies have shown the effectiveness of this approach to determine the nonlinear optical properties of SWCNTs and graphene by fitting Z-Scan curves [11,12].

Analytic Z-scan model (Analyt. Z-scan model) is derived from the solution of nonlinear wave equation in the paraxial approximation, where the beam profile is assumed to be Gaussian [8]. Therefore, the model is not appropriate for fitting Z-scans of thick samples and samples with a high phase nonlinearity. The resultant normalized transmittance for a pulse with a Gaussian profile can be written as:

$$T(Z) = \sum_{m=0}^{\infty} \frac{(-\beta_{eff} I_{00} L_{eff})^m}{(1 + (\frac{Z}{Z_0})^2)^m (m+1)^{3/2}} \quad (1)$$

where  $I_{00} = I(Z=0, r=0, t=0) = \frac{4E_p}{3\pi \cdot \tau_p \cdot \varpi_0^2}$  is the on-axis intensity at focus ( $Z=0$ ) at  $r=0$ ,  $t=0$ ,

$E_p$  is the pulse energy,  $\tau_p$  is the pulse duration,  $\varpi_0$  is the beam waist,  $\beta_{eff}$  is the effective third-order nonlinear absorption coefficient,  $L_{eff} = (1 - e^{-\alpha_0 L})/\alpha_0$  is the effective sample thickness,  $\alpha_0$  is the

linear absorption coefficient,  $L$  is the actual sample thickness,  $Z_0 = \frac{\pi \varpi_0^2}{\lambda}$  is the Rayleigh length,  $\lambda$  is the laser wavelength.

According to the two-level saturable absorber model (SA model), the absorption coefficient is determined by the following expression:

$$\alpha = \frac{\alpha_0}{1 + I/I_s} \quad (2)$$

where  $I_s$  is the saturation intensity,  $\alpha_0$  is the linear absorption coefficient.

The output intensity is determined by numerical solution of the following differential equation:

$$\frac{dI}{dL} = I \cdot \exp[-\alpha \cdot L] \quad (3)$$

Normalized transmittance can be obtained by numerical spatial and temporal integration of the input and output intensities:

$$T(z) = \frac{\int_{-\infty}^{\infty} dt \int_0^{\infty} I_{out} r dr}{\int_{-\infty}^{\infty} dt \int_0^{\infty} I_{in} r dr} \quad (4)$$

where  $I_{out}(Z, r, t)$  is output intensity (which is determined from equation 3),  $I_{in}(Z, r, t)$  is the input intensity.

The joint model (SA + Analyt. Z-scan model) involves properties of both two-level saturable absorber, and a Kerr-like nonlinear medium. According to the model, the absorption coefficient consists of slow term related to two-level saturable absorber and fast third-order nonlinear contributions:

$$\alpha = \frac{\alpha_0}{1 + I/I_s} + \beta_{eff} \cdot I \quad (5)$$

In that case normalized transmission is also determined by numerical integration of the intensities (in accordance with equation 4), where the output intensity can be obtained by solving the differential equation 3.

Fitting was performed with least-square method where the nonlinear absorption coefficient  $\beta_{eff}$  and the saturation intensity  $I_s$  were considered as variable parameters.

The fitting results are presented in figure 2. As can be seen, the joined model provides the best coincidence with experimental data. Especially it gives the best fit for Z-scan of Sample 1 (figure 2A), the analytic and the two-level saturable absorber model are not able to fit the data. We suppose that Sample 1 consists of both types of CNTs exhibiting semiconductor and metallic properties, which provide slow and fast nonlinearity respectively. Slow nonlinearity is associated with the saturation of interband transition in the semiconductor fraction, meanwhile the fast is related to excitation of hot electrons in the metallic fraction. Since the Z-scan data of Sample 2 can be well fitted by two-level saturable absorber model, the fraction of CNTs with its metallic properties is negligible, i.e. nonlinear response in that case is attributed only to semiconductor CNTs. The best fit nonlinear optical parameters for both samples are listed in table 1.

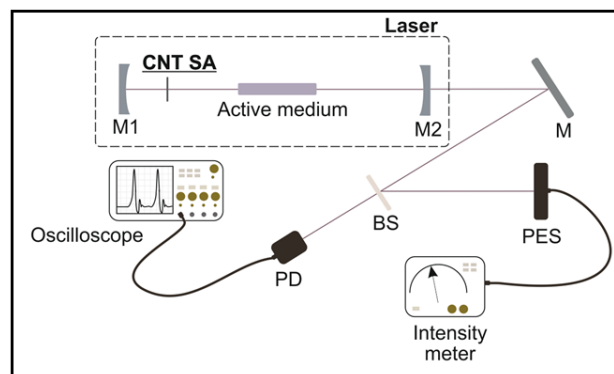
**Table 1.** Nonlinear optical properties of polymer-free CNT SA

	$I_s$ [mW/cm <sup>2</sup> ]	$\beta_{eff}$ [m/W]	$\chi^{(3)}$ [esu]
Sample 1	30	$-6 \cdot 10^7$	$-1,3 \cdot 10^{-8}$
Sample 2	35	$-1,2 \cdot 10^7$	$-3,4 \cdot 10^{-9}$

In accordance with the obtained nonlinear optical parameters, the saturation intensity is nearly the same for both samples, but imaginary part of third-order susceptibility is about 5-times larger in case of Sample 1. It means a higher nonlinearity of Sample 1 at high input intensities. In fact, the fraction of CNTs having metallic properties provides larger modulation depth  $\Delta T$  of Sample 1 (76%) in comparison with the depth of Sample 2 (42%) at the focus (intensity at the focus equals  $340 \text{ MW/cm}^2$ ). The modulation depth at lower intensities ( $33 \text{ MW/cm}^2$ ) is nearly the same for both samples: 14.5% and 11.5% for Sample 1 and Sample 2 respectively. Therefore, we can conclude that both samples with resonant and nonresonant absorption are equally applicable for utilizing in low- and medium-power laser systems, whereas the Sample 1 exhibiting resonant optical absorption is more appropriate for high power systems than Sample 2.

#### 4. Generation of nanosecond pulses

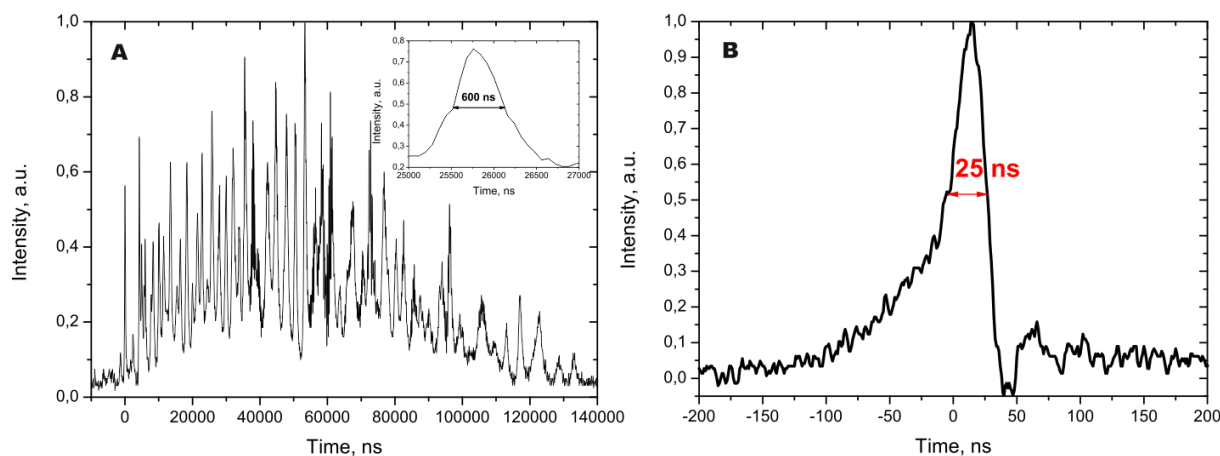
In order to examine a potential of using polymer-free CNT SA for passive Q-switching in solid state lasers with high pulse energy, we built up the following experimental setup based on Nd:YAG laser (figure3).



**Figure 3.** The scheme of experimental setup for laser generation with usage of polymer-free CNT SA.

Silicon photodetector with integrated signal amplifier (HFBR-25X6Z Series Avago Technologies) with a rise time of 3.3 ns, Rigol DS12048 oscilloscope with a bandwidth of 200 MHz and Ophir PE25-C pyroelectric energy sensor (PES) within the Pulsar power meter interface were used to measure the laser output performances. We employed 35 cm linear cavity and flash-pumped Nd:YAG active medium. Without CNT SA laser was operated in free-running mode (figure 4A), where an average duration of the overall pulse train and individual pulse spikes are equal to  $100 \mu\text{s}$  and  $600 \text{ ns}$  respectively.

Considerable pulse narrowing effect and enhancement of the pulse intensity were obtained when Sample 1 was placed into the cavity (figure 4B). It clearly indicates the transition in the regime of laser generation: from free-running to Q-switching mode.



**Figure 4.** Oscilloscope trace of laser output in free-running mode (without CNT SA) – A. Inset: Oscilloscope trace of single pulse spike in free-running mode. Oscilloscope trace of laser output in Q-switching mode with usage of polymer-free CNT SA – B.

## 5. Conclusion

We have studied nonlinear optical absorption of polymer-free CNT SA by Z-scan technique using nanosecond 1.06  $\mu\text{m}$  laser irradiation. Complex nonlinear response of the CNT SA was found. Thus, at low input intensities the response can be well described by ordinary saturable absorber model with saturation intensity equal to 30  $\text{MW}/\text{cm}^2$ , but at the high intensity the response is described by third-order Kerr nonlinear susceptibility  $\chi^{(3)} \sim 10^{-8}$  esu. We suppose that such behavior is induced by presence of two types of CNTs in the samples with semiconductor and metallic properties. Developed polymer-free CNT SA demonstrate large saturable absorption effect and high photostability, while retaining their properties during long-term exposure of nanosecond pulses with an average energy  $\sim 100$   $\mu\text{J}$ . In summary, using polymer-free CNT SA we successfully implemented passive Q-switching mode of solid state Nd:YAG laser with a pulse duration of 25 ns.

## Acknowledgements

This work has been supported by the Ministry of Education and Science of Russian Federation (Project No. RFMEFI58114X0006).

## References

- [1] Martinez A and Sun Z 2013 Nanotube and graphene saturable absorbers for fibre lasers *Nature Photon.* **7** 842
- [2] Cho W B, Yim J H, Choi S Y, Lee S, Schmidt A, Steinmeyer G, Griebner U, Petrov V, Yeom D-I, Kim K and Rotermund F 2010 Carbon nanotubes: boosting the non linear optical response of carbon nanotube saturable absorbers for broadband mode-locking of bulk lasers *Adv. Funct. Mater.* **20** 1937
- [3] Set S Y, Yaguchi H, Tanaka Y and Jablonski M 2004 Laser mode locking using a saturable absorber incorporating carbon nanotubes *J. Lightwave Technol.* **22** 51
- [4] Moisala A, Nasibulin A G, Brown D P, Jiang H, Khriachtchev L and Kauppinen E I 2006 Single-walled carbon nanotube synthesis using ferrocene and iron pentacarbonyl in a laminar flow reactor *Chem. Eng. Sci.* **61** 4393
- [5] Reynaud O, Nasibulin A G, Anisimov A S, Anoshkin I V, Jiang H and Kauppinen E I 2014 Aerosol feeding of catalyst precursor for CNT synthesis and highly conductive and transparent film fabrication *Chem. Eng. J.* **255** 134
- [6] Kaskela A *et al* 2010 Aerosol synthesized SWCNT networks with tuneable conductivity and transparency by dry transfer technique *Nano Lett.* **10** 4349

- [7] Zhou Y, Hu L and Grüner G 2006 A method of printing carbon nanotube thin films *Appl. Phys. Lett.* **88** 123109
- [8] Sheik-Bahae M, Said A and Van Stryland E W 1990 Sensitive measurement of optical nonlinearities using a single beam *IEEE J. Quantum. Electron* **26** 760
- [9] Wang F, Rozhin A G, Scardaci V, Sun Z, Hennrich F, White H, Milne W I and Ferrari A C 2008 Wideband-tuneable, nanotube mode-locked, fibre laser *Nat. Nanotechnol.* **3** 738
- [10] Karthikeyan B, Anija M and Philip R 2006 In situ synthesis and nonlinear optical properties of Au:Ag nanocomposite polymer films *Appl. Phys. Lett.* **88** 053104
- [11] Kamaraju N, Kumar S, Sooda A K, Guha S, Krishnamurthy S and Rao C N R 2007 Large nonlinear absorption and refraction coefficients of carbon nanotubes estimated from femtosecond z-scan measurements *Appl. Phys. Lett.* **91** 251103
- [12] Liu Z, Wang Y, Zhang X, Xu Y, Chen Y and Tian J 2009 Nonlinear optical properties of graphene oxide in nanosecond and picosecond regimes *Appl. Phys. Lett.* **94** 021902