168 fs pulse generation from graphene-chitosan mode-locked fiber laser

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Abstract: We propose new graphene-chitosan solution as a saturable absorber for a mode-locked Erbium-doped fiber laser. We demonstrate stable, mode-locked operation with pulse as short as 168 fs, which are the shortest pulses generated from an Er-doped fiber laser with the use of graphene so far. Graphene-chitosan solution was obtained in soluble forms by the addition of the acetic acid. The ring laser is able to generate optical solitons centered at 1554 nm wavelength with 15.2 nm bandwidth and 63 MHz repetition rate.

OCIS codes: (140.4050) Mode-locked lasers; (140.3510) Lasers, fiber; (140.3500) Lasers, erbium.

References and links

1. U. Keller, "Recent developments in compact ultrafast lasers," Nature **424**(6950), 831–838 (2003).
2. U. Keller, "Ultrafast solid-state laser oscillators: a success story for the last 20 years with no end in sight," Appl. Phys. B **100**(1), 15–28 (2010).
3. S. Yamashita, Y. Inoue, S. Maruyama, Y. Murakami, H. Yaguchi, M. Jablonski, and S. Y. Set, "Saturable absorbers incorporating carbon nanotubes directly synthesized onto substrates and fibers and their application to mode-locked fiber lasers," Opt. Lett. **29**(14), 1581–1583 (2004).
4. A. Martinez, K. Fuse, and S. Yamashita, "Enhanced stability of nitrogen-sealed carbon nanotube saturable absorbers under high-intensity irradiation," Opt. Express **21**(4), 4665–4670 (2013).
5. Q. L. Bao, H. Zhang, Y. Wang, Z. H. Ni, Z. X. Shen, K. P. Loh, and D. Y. Tang, "Atomic layer graphene as saturable absorber for ultrafast pulsed laser," Adv. Funct. Mater. **19**(19), 3077–3083 (2009).
6. H. Zhang, D. Y. Tang, L. M. Zhao, Q. L. Bao, and K. P. Loh, "Large energy mode locking of an erbium-doped fiber laser with atomic layer graphene," Opt. Express **17**(20), 17630–17635 (2009).
7. G. Sobon, J. Sotor, I. Pasternak, A. Krajewska, W. Strupinski, and K. M. Abramski, "Thulium-doped all-fiber laser mode-locked by CVD-graphene/PMMA saturable absorber," Opt. Express **21**(10), 12797–12802 (2013).
8. J. Sotor, G. Sobon, I. Pasternak, A. Krajewska, W. Strupinski, and K. M. Abramski, "Simultaneous mode-locking at 1565 nm and 1944 nm in fiber laser based on common graphene saturable absorber," Opt. Express **21**(16), 18994–19002 (2013).
9. P. L. Huang, S.-C. Lin, C.-Y. Yeh, H.-H. Kuo, S.-H. Huang, G.-R. Lin, L.-J. Li, C.-Y. Su, and W.-H. Cheng, "Stable mode-locked fiber laser based on CVD fabricated graphene saturable absorber," Opt. Express **20**(3), 2460–2465 (2012).
10. T. Hasan, Z. Sun, F. Wang, F. Bonaccorso, P. H. Tan, A. G. Rozhin, and A. C. Ferrari, "Nanotube–polymer composites for ultrafast photonics," Adv. Mater. **21**(3839), 3874–3899 (2009).
11. D. Popa, Z. Sun, F. Torrisi, T. Hasan, F. Wang, and A. C. Ferrari, "Sub 200 fs pulse generation from a graphene mode-locked fiber laser," Appl. Phys. Lett. **97**(20), 203106 (2010).
12. Z. Sun, D. Popa, T. Hasan, F. Torrisi, F. Wang, E. J. Kelleher, J. C. Travers, V. Nicolosi, and A. C. Ferrari, "A stable, wideband tunable, near transform-limited, graphene-mode-locked, ultrafast laser," Nano Res. **3**(9), 653–660 (2010).
13. A. Martinez, K. Fuse, B. Xu, and S. Yamashita, "Optical deposition of graphene and carbon nanotubes in a fiber ferrule for passive mode-locked lasing," Opt. Express **18**(22), 23054–23061 (2010).
14. Y.-H. Lin, C.-Y. Yang, J.-H. Liou, C.-P. Yu, and G.-R. Lin, "Using graphene nano-particle embedded in photonic crystal fiber for evanescent wave mode-locking of fiber laser," Opt. Express **21**(14), 16763–16776 (2013).
15. A. Martinez, K. Fuse, and S. Yamashita, "Mechanical exfoliation of graphene for the passive mode-locking of fiber lasers," Appl. Phys. Lett. **99**(12), 121107 (2011).

#215252 - $15.00 USD Received 2 Jul 2014; revised 21 Aug 2014; accepted 21 Aug 2014; published 2 Sep 2014

16. Y. Chang, H. Kim, J. Lee, and Y. Song, "Multilayered graphene efficiently formed by mechanical exfoliation for nonlinear saturable absorbers in fiber mode-locked lasers," Appl. Phys. Lett. **97**(21), 211102 (2010).
17. G. Sobon, J. Sotor, J. Jagiello, R. Kozinski, K. Librant, M. Zdrojek, L. Lipinska, and K. M. Abramski, "Linearly polarized, Q-switched Er-doped fiber laser based on reduced graphene oxide saturable absorber," Appl. Phys. Lett. **101**(24), 241106 (2012).
18. M. N. Cizmeciyan, J. W. Kim, S. Bae, B. H. Hong, F. Rotermund, and A. Sennaroglu, "Graphene mode-locked femtosecond Cr:ZnSe laser at 2500 nm," Opt. Lett. **38**(3), 341–343 (2013).
19. I. Baek, H. W. Lee, S. Bae, B. H. Hong, Y. H. Ahn, D.-I. Yeom, and F. Rotermund, "Efficient Mode-Locking of Sub-70-fs Ti:Sapphire Laser by Graphene Saturable Absorber," Appl. Phys. Express **5**(3), 032701 (2012).
20. W. B. Cho, J. W. Kim, H. W. Lee, S. Bae, B. H. Hong, S. Y. Choi, I. H. Baek, K. Kim, D. I. Yeom, and F. Rotermund, "High-quality, large-area monolayer graphene for efficient bulk laser mode-locking near 1.25 μm," Opt. Lett. **36**(20), 4089–4091 (2011).
21. J. Sotor, G. Sobon, J. Tarka, I. Pasternak, A. Krajewska, W. Strupinski, and K. M. Abramski, "Passive synchronization of erbium and thulium doped fiber mode-locked lasers enhanced by common graphene saturable absorber," Opt. Express **22**(5), 5536–5543 (2014).
22. H. Zhang, C. X. Liu, X. L. Qi, X. Dai, Z. Fang, and S. C. Zhang, "Topological insulators in Bi2Se3, Bi2Te3 and Sb_2Te_3 with a single Dirac cone on the surface," Nat. Phys. **5**(6), 438–442 (2009).
23. M. Buzaglo, M. Shtein, S. Kober, R. Lovrinčić, A. Vilan, and O. Regev, "Critical parameters in exfoliating graphite into graphene," Phys. Chem. Chem. Phys. **15**(12), 4428–4435 (2013).
24. M. Cai, D. Thorpe, D. H. Adamson, and H. C. Schniepp, "Methods of graphite exfoliation," J. Mater. Chem. **22**(48), 24992–25002 (2012).
25. H. Fan, L. Wang, K. Zhao, N. Li, Z. Shi, Z. Ge, and Z. Jin, "Fabrication, Mechanical Properties, and Biocompatibility of Graphene-Reinforced Chitosan Composites," Biomacromolecules **11**(9), 2345–2351 (2010).
26. J. Zou and F. Kim, "Self-assembly of two-dimensional nanosheets induced by interfacial polyionic complexation," ACS Nano **6**(12), 10606–10613 (2012).
27. X. Kang, J. Wang, H. Wu, I. A. Aksay, J. Liu, and Y. Lin, "Glucose Oxidase-graphene-chitosan modified electrode for direct electrochemistry and glucose sensing," Biosens. Bioelectron. **25**(4), 901–905 (2009).
28. A. C. Ferrari and J. Robertson, "Interpretation of Raman spectra of disordered and amorphous carbon," Phys. Rev. B **61**(20), 14095–14107 (2000).
29. D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, and L. Wirtz, "Spatially Resolved Raman Spectroscopy of Single- and Few-Layer Graphene," Nano Lett. **7**(2), 238–242 (2007).
30. A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim, "Raman spectrum of graphene and graphene layers," Phys. Rev. Lett. **97**(18), 187401 (2006).

1. Introduction

Ultrafast lasers proved to be very valuable and dependable radiation source for various applications, ranging from basic research through material processing ending with medicine applications. In comparison to other lasers, i.e. solid state lasers they distinguish with compact size, efficient heat dissipation and high quality beam. Mode-locking can be achieved in laser system by using non-linear device called saturable absorber (SA). In the last decade various types of SA were extensively investigated. Currently SA technology is dominated by well-known semiconductor saturable absorber mirrors (SESAM), which proved to be very efficient devices, however limited when it comes to their bandwidth [1,2]. Not only limited bandwidth was determining factor to seek for a new kind of SA. Semiconductor based solutions need complicated and expensive molecular beam epitaxy (MBE) manufacturing technology. Novel types of saturable absorber materials such as single-walled carbon nanotubes (SWNT) [3,4] and graphene [5–21] have features which make them almost ideal SA as: fast recovery times, low saturation intensity, low-cost and easy fabrication. Among those Dirac-materials (materials where conduction and valence overlap in finite group of points, so called Dirac points, i.e. Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 [22]) and other novel optical materials such as SWNTs graphene is one of the most promising candidate as a SA. It was the first 2D material that has been used to obtain mode-locking operation [5,10]. Since then a lot of works on graphene based fiber and bulk lasers have been presented. Broadband operation range of graphene saturable absorbers (GSA) has been confirmed with usage of solid states lasers [18–20], tunable erbium-doped laser [12] and simultaneous mode-locking of 1.56 μm and 1.96 μm lasers by a common SA [8,21]. Graphene based SAs are also less complicated and cheaper when it comes to the production processes, ranging from mechanical exfoliation [15–17], chemical vapor deposition (CVD) [7–9,18–21], to chemical exfoliation of graphite [10–14]. Among many methods of production of graphene, the direct graphite exfoliation in liquids seems to be very promising for obtaining good quality and highly conductive graphene

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composites on a large scale, which has been confirmed by a number of studies [23, 24]. Especially interesting is the usage of direct exfoliation of graphite in chitosan solutions as a method of obtaining graphene composite. The main advantage of chitosan, in contrast to many other available solvents, is biocompatibility and atoxicity. Safety of the usage and relatively low cost make chitosan interesting material for many applications. In contrast to other graphene-polymer composites, we obtained the material in a simple, single step processing, where chitosan macromolecules were used as an exfoliating and stabilizing compound. Long chains of chitosan enable to separate graphene layers and prevent them from re-agglomeration after exfoliation of graphite. So far, only prepared graphene oxide (GO) and reduced GO mixed with chitosan has been studied [25–27], with focus on the mechanical and the biological properties of these composites, leaving the optoelectronics properties behind. In this paper we demonstrate an erbium-doped fiber laser mode locked by saturable absorber based on graphene-chitosan solution. Graphene composite layers were deposited onto fiber connector, what allows to build all-fiber system and avoid bulk optics. Laser was capable of generating soliton pulses centered at 1554 nm with 168 fs duration, which to our best knowledge is the shortest pulse obtained from a graphene-based, erbium-doped fiber laser so far.

2. Graphene/Chitosan solution preparation and characterization

The method of preparation of graphene/chitosan composite consists of the following steps. First, acid-washed (intercalated) graphite flakes were inserted into a furnace and expanded at 1050°C to obtain expanded graphite. 0.1 g of chitosan (of low molecular weight) was dissolved in 2.5% acetic acid solution. The structure of chitosan is shown in Fig. 1. Afterwards, 0.1 g of graphite was added to the chitosan and stirred on magnetic stirrer with simultaneous heating at 70°C. The mixture was then sonicated for 1 hour. After this treatment a stable dispersion of carbon material was obtained. Graphene flakes obtained from chitosan dissolved in acetic acid create a compact structure, as it is shown in Fig. 2(a). Typical AFM picture is shown in the Fig. 2(b). Dispersion of the graphene flake solution on the Si/SiO_2 substrate produces a dense coverage, which thickness can be estimated from the depth of the fissures and equals to about 2 nm.

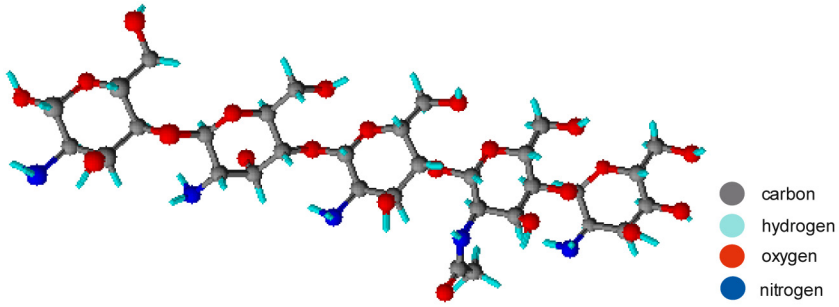

Fig. 1. The structure of chitosan chain fragment.

The quality of carbon-based materials can be easily estimated using Raman spectroscopy. This powerful technique is especially useful in determining the amount of the sp^3 defects in the graphene sp^2 honeycomb structure and yields some information about the number of the graphene layers forming the flake. The first information is taken from the relative intensity of the D mode (about 1350 cm^{-1}) to the G mode (1580 cm^{-1}) and usually is denoted as I_D / I_G [28]. The second information is obtained mainly from the intensity and shape of the 2D mode (about 2700 cm^{-1}) [29]. The G mode stands for the main vibration (tangential stretching) of the graphene two dimensional hexagonal lattice. The D mode, sometimes called “breathing” mode, reflects more complicated Raman scattering process requiring phonons from the boundary of the Brillouin zone and existence of structural defects, that can add a crystal momentum to the energy-momentum balance equation. The overtone of the D mode is called

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2D. This two phonon scattering process does not require defects (taking two phonons with opposite crystal momentum) but fortunately is directly related to the electronic structure details. Particularly, changes in the band structure induced by the interaction between layers forming the flake can be seen straightway in the mode shape and intensity [30].

Morphological properties were investigated with scanning electron microscopy (SEM), using Auriga CrossBeam Workstation (Carl Zeiss). AFM was acquired in tapping mode using Veeco Nanoman V microscope with Bruker MPP-11100-10 silica probe. The microstructure was characterized by Raman spectroscopy (Dilor XY-800 spectrometer), using 514 nm wavelength of an argon-ion laser with low laser power of 1 mW.

Results of the Raman measurements on the graphene flakes are presented in the Fig. 2(c). Apart the main G mode there is 2D mode split into two peaks. Its shape and intensity suggest that studied flakes are multi-layered structures rather than single-layered graphene. This conclusion is supported by the AFM studies. Almost no D mode proves high quality of produced materials.

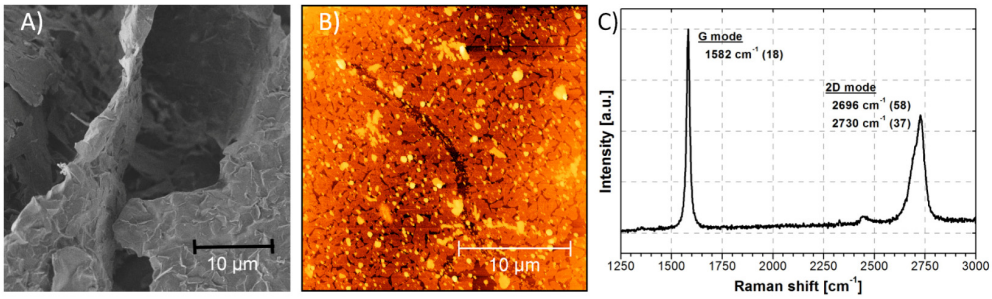

Fig. 2. a) SEM image of graphite flakes exfoliated with chitosan dissolved in acetic acid. b) AFM image of few layer graphene sheets. c) Raman spectra from graphene flakes prepared in chitosan solution.

Such characterized and measured graphene/chitosan solution was used to prepare the GSA. Demonstrated solution was deposited on surface of fiber connector with micropipette, then placed in oven for vaporization. Such prepared GSA was investigated in terms of linear and nonlinear (power-dependent) absorption (Fig. 3). Investigation shows that the prepared GSA is characterized by a flat absorption in the whole C band (1520 – 1620 nm) and introduces about 8 dB loss. Saturable absorption was measured using an all-fiber setup similar to that in [10], with the use of a femtosecond laser with 100 MHz repetition rate. Investigation shows that prepared GSA is quite immune for high fluence (>500 µJ/cm^2). When the peak power intensity was increased, saturable absorption was observed. Under high intensity, the transmission of the sample increases by about 2.6%. Chitosan itself show no saturable absorption. To prove this, we have tested our laser using fiber connectors with deposited chitosan (without graphene). No mode-locking was observed. Thus, we believe it does not affect the saturable absorption of graphene. Moreover, chitosan also exhibits flat absorption in the whole Er-band and introduces low losses. A trace showing the transmission of connectors with deposited pure chitosan is depicted in Fig. 3(b).

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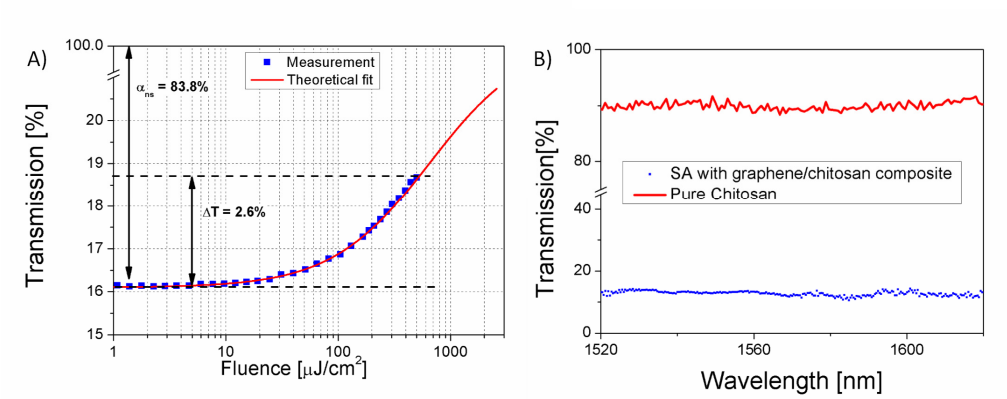

Fig. 3. a) saturable absorption measurements, b) linear absorption.

3. Experimental setup and results

Such prepared connector was spliced into fiber resonator which is depicted in Fig. 4. The all-fiber resonator consist of: a 40 cm long erbium doped fiber (Liekki Er80-4/125), fiber isolator, polarization controller (PC), 20% output coupler and a 980/1550 nm wavelength division multiplexer (WDM). The laser is pumped by 980 nm laser diode through the WDM coupler. Optical isolator impose counter direct oriented pumping. A fiber-based in-line polarization controller placed in the loop allows to adjust the intra-cavity polarization and start the mode-locked operation.

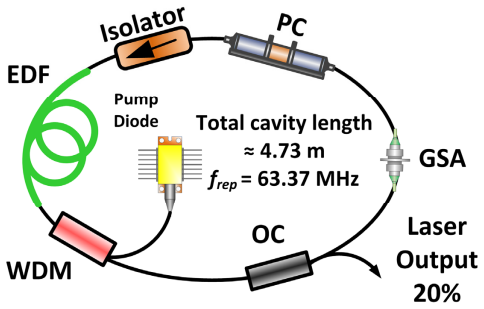

Fig. 4. Experimental setup of the mode-locked fiber laser.

The performance of the laser was observed using an optical spectrum analyzer with scanning range up to 2400 nm (Yokogawa AQ6375), 12 GHz digital oscilloscope (Agilent Infiniium DSO91304A), 3 GHz radio-frequency (RF) spectrum analyzer (Agilent EXA N9000A) coupled with a 12 GHz photodetector (Discovery Semiconductors DSC2-50S), and an optical autocorrelator (APE PulseCheck).

After adjustment of polarization controller laser starts to operate in the mode-locked regime with pomp power of 72 mW. Stable pulsed operation is observed till 106 mW of pumping. The total net cavity dispersion is anomalous, thus, the laser generates pulses which are solitons. Moreover, characteristic Kelly's sidebands visible in the optical spectrum (inset Fig. 5(a)), which are typical for soliton lasers.

In Fig. 5(a) one can see generated spectrum centered at 1554 nm with full-width at half-maximum (FWHM) bandwidth of 15.2 nm. Pulse duration was measured with autocorrelator assuming $sech^2$ pulse shape was 168 fs (Fig. 5(b)), which is to the best of our knowledge the shortest pulse obtained from laser mode-locked with graphene-based saturable absorber. The time-bandwidth product (TBP) of the presented laser is 0.320, in comparison to the 0.315 for $sech^2$ transform-limited pulse. It means, that the pulses are almost transform-limited.

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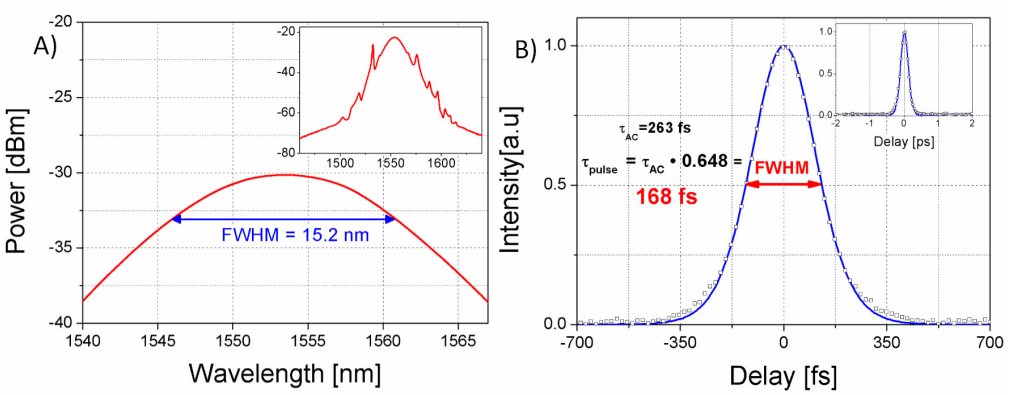

Fig. 5. Generated optical soliton centered at 1554 nm: a) measured optical spectrum with 3 dB bandwidth indicated b) 168 fs pulse autocorrelation.

The RF spectrum of laser is shown in Fig. 6(a). The fundamental repetition rate was equal to 63.37 MHz. The electrical signal to noise ratio (S/N) measured with 100 Hz resolution bandwidth (RBW) at 4 MHz span was higher than 70 dB. The recorded pulse train is depicted in Fig. 6(b). Spacing between pulses were measured to be around 15.7 ns which corresponds to 63.37 MHz repetition frequency and 4.73 m optical resonator length. Measured average output power from presented setup was 3.5 mW, which gives calculated values for pulse energy and peak power 55 pJ and 308 W, respectively.

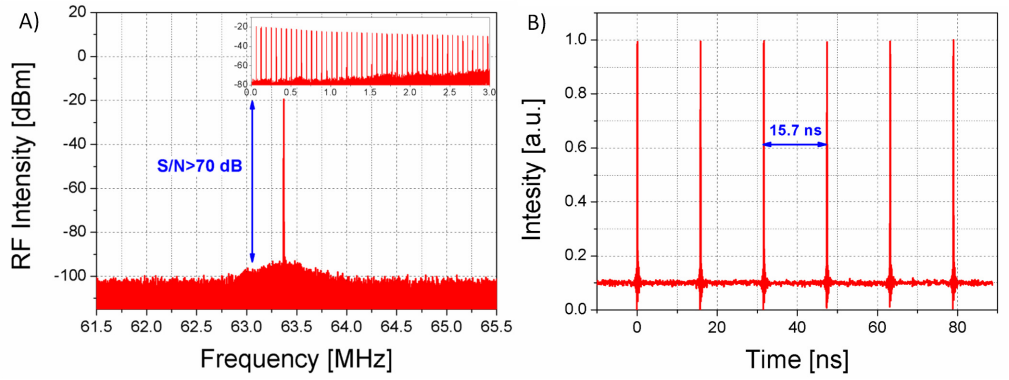

Fig. 6. a) RF spectrum of the mode-locked laser output with 4 MHz span, Inset RF spectrum with 3 GHz span. b) Oscilloscope trace with pulse train.

4. Summary

Concluding, the paper presents for the first time the usage of a graphene/chitosan solution for ultrashort pulse generation from an Er-doped fiber laser. High quality of the graphene flakes dissolved in chitosan with acetic acid was confirmed by Raman spectroscopy. The solution was deposited on a fiber ferrule and used to femtosecond pulse generation. The developed laser was capable of generating nearly transform-limited, 168 fs-short soliton pulses centered at 1554 nm with over 15 nm of bandwidth, which are the shortest pulses generated in a graphene-based Er-doped fiber laser so far.

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