Broadband Saturable Absorption of Graphene Oxide Thin Film and Its Application in Pulsed Fiber Lasers

Xiaohui Li, Yulong Tang, Zhiyu Yan, Yue Wang, Bo Meng, Guozhen Liang, Handong Sun, Xia Yu, Ying Zhang, Xueping Cheng, and Qi Jie Wang

Abstract—Graphene oxide (GO) has been used for optical intensity manipulation and short pulse shaping. Most interestingly, it can be used as a broadband light absorber. Such property has been systematically investigated in this paper, in a broad wavelength range from 1 to 2-μm. We fabricated one type of GO/polyvinyl alcohol (GO/PVA) film and use it as a saturable absorber (SA) in Er-, Yb-, and Tm-doped fiber ring lasers, respectively, to build pulsed fiber lasers. It is demonstrated that broad range of mode-locking in the 1-μm and 1.5-μm regions can be obtained. In addition, Q-switching around wavelength of 1870 nm can be obtained in a Tm-doped fiber ring lasers. To the best our knowledge, this is the broadest wavelength regime in which one type of GO SA film can be used to build all-fiber pulsed ring lasers.

Index Terms—Fiber lasers, graphene oxide, mode-locking, Q-switching, modulation depth.

I. INTRODUCTION

VARIous carbon based materials, due to their unique and outstanding optical, magnetic, electronic and structural properties, have been intensively studied and applied in many fields, such as ultrafast optics [1]–[7], biosensing [8], optical modulator [9], and photodetector [10]–[12]. Single walled carbon nanotube (SWNT) and graphene have been applied in ultrafast optics [12]–[24]. SWNT has also been used in the broadband technology by combining SWNTs with diameter distribution [15]. Through tuning the extra components such as stretching CFBG, the wavelength tunability can be also achieved [23]. Very recently, single-layer graphene has been validated the intrinsic broadband operation property [25]. Among carbon based materials, graphene oxide (GO), as an excellent nonlinear optical material, can be employed for optical intensity manipulation and short pulse shaping [26]–[28]. These two characteristics are developed as optical limiters (OLs) and saturable absorbers (SAs) [28]. OL allows a low transmission at high light densities, which can be used for light protection and in sensor focal-plane. While SA gives a low absorption at high light densities, which can be used to achieve ultrashort pulses in solid state lasers, waveguide lasers, fiber lasers and even semiconductor lasers [29]–[34]. GO can be considered as an insulating and disordered analogue of a highly conducting crystalline graphene [26]. However, the fast carrier relaxation and large saturable absorption of few-layered GO indicate that oxidation mainly exists at the edge areas and has negligible effects on ultrafast dynamics and optical nonlinearities [35].

GO, as a cheap carbon material which can be mass produced, has been widely utilized in passively mode-locked lasers as a SA. Recently, GO-based passively mode-locked fiber lasers have been demonstrated in Er-doped, Yb-doped, and Tm-doped fiber lasers, respectively [31], [36]–[39]. We have reported GO wall paper absorber that was applied in the Yb-doped passively mode-locked fiber laser operating in the all-normal-dispersion (ANDI) regimes [31]. Liu et al. demonstrated Er-doped fiber lasers mode-locked by using a hollow-core photonics crystal fiber filled with GO solution [36]. Recently, Jung et al. investigated the GO SA implemented on a side-polished fiber for femtosecond pulse generation in the 2-μm region [38]. However, all the aforementioned results are reported only in one particular operation wavelength region. It is not clear whether one type of GO SA film can perform in a wide spectral range as a SA, e.g. from the 1-μm region for Yb-doped fiber (YDF) laser, to the 1.5-μm region for Er-doped fiber (EDF) laser, and up to the 1.9-μm region for Tm-doped fiber (TDF) laser. In addition, even it can operate in different wavelength regions, what would be the performance of those pulsed fiber lasers? All these questions should be answered in order to better understand the saturable absorption properties of GO so as to apply it to the implementation of high performance pulsed fiber lasers in a broadband wavelength range.

In this paper, we systematically investigated the GO SA properties by using a Ti:sapphire femtosecond laser at different wavelengths tuned by optical parametric oscillator (OPO) technique and a home-made passively mode-locked EDF laser. The optical SA property has been studied in three different wavelength...
II. GO Absorber Preparation and Its Optical Property

In the experiments, the GO sheets, fabricated by ultrasonic agitation after chemical oxidation of graphite, consist of few atomic layers with a thickness of 0.1–5 μm (typically from 1 to 3 layers). GO wall paper absorber is prepared by using vertical evaporation method [29], [31]. The fabrication process of the GO is free of surfactant such as sodium dodecyl sulfate. GO/polyvinyl alcohol (GO/PVA) dispersion is mixed with 0.6 g PVA powder and 0.25 mg GO aqueous solution at 90 °C for 3 h. Then, the GO/PVA dispersion is poured into a polystyrene cell to evaporate for several days. After evaporation the GO/PVA SA is formed. The average thickness of GO/PVA membrane is about 30 μm. We use a small piece of the GO SA film in the passively mode-locked fiber lasers by inserting the film between two fiber connectors. In addition, the graphene oxide can also be fabricated by liquid phase exfoliation method, which is cheap and easily scalable method [40], [41].

Fig. 1(a) shows the linear transmission spectrum of GO/PVA film and PVA thin film measured by using the UV-VIS-NIR spectrometer. The GO/PVA film experiences higher losses at the wavelength regime below 500 nm. The linear transmissions at 1060, 1550, and 1900 nm are 78.1%, 83.7%, and 85.8%, respectively.

Fig. 1(b) shows the Raman spectrum of the GO/PVA SA film excited by a 532 nm laser. The spectrum shows two prominent peaks (i.e., D band at 1336 cm\(^{-1}\), and G band at 1612.4 cm\(^{-1}\)). D band can be interpreted as the structural imperfections induced by the attachment of hydroxyl and epoxide groups on the carbon basal plane. The G band is related to the first-order scattering from the E\(_{2g}\) mode. Only a tiny 2-D band is found, indicating that the GO films of considerable thickness were coated. There are some other peaks as well as the background as seen in the Raman spectrum. They are caused by some acrylic or some other polymers in the SA films, induced in the fabrication processes.

The nonlinear SA property of GO as a function of light intensity can be expressed as [3], [42]

\[
\alpha(I) = \frac{\alpha_S}{1 + I/I_s} + \alpha_{NS}
\]

where \(I_s\), \(\alpha_S\) and \(\alpha_{NS}\) are the saturation intensity, saturable, and nonsaturable absorption, respectively.

The nonlinear SA properties of GO absorber are studied by power-dependent measurements at different wavelengths with a Ti:sapphire femtosecond lasers and an OPO system. SA properties can be obviously observed with the increase of the incident light intensity. The corresponding nonlinear transmission spectrum of the GO SA is shown in Fig. 2. The nonlinear transmission of the GO absorber has been measured at three different wavelengths (i.e., 1.06, 1.5, 1.9 μm), respectively. Due to the material scattering losses and the fiber connector-induced losses, the measured minimum nonlinear transmission at low power intensity are 65.8%, 70.6%, and 72.1%, respectively. The measured values are smaller than the linear transmissions at the corresponding wavelengths as shown in Fig. 2. The modulation depths of GO SA (i.e., \(\alpha_S\)) are 20.6% at 1.06 μm, 16.1% at 1.5 μm, and 12.8% at 1.9 μm. As seen in Fig. 2, we can calculate that the saturation intensities (i.e., \(I_s\)) of the GO SA at different wavelengths are about 1.41, 1.32, and 0.90 MW/cm\(^2\), respectively.

III. Experimental Setup

The GO sheet was mixed with the PVA as the SA film. A piece of GO SA with size of 2 mm\(^2\) is placed into the fiber connectors to form a mode locker. Fig. 3 shows the general experimental setup for the GO SA film applied in different rear-earth doped fiber ring lasers. The GO SA film is inserted into three different fiber ring cavities, which uses 0.8-m YDF (CorActive YB164 with core diameter of around 6 μm, cladding diameter of 125 μm, Numerical Aperture of 0.14, and Core Absorption of about 500 dB/m at 976 nm. The group velocity dispersion (GVD) is about \(-43.33 \text{ ps/nm/km at 1030 nm}\)., 0.8-EDF (Liekk Er80-8/125 with Mode Field Diameter of about
Fig. 2. Nonlinear transmissions of GO SA flake at the (a) 1060 nm, (b) 1550 nm, and (c) 1900 nm regimes, respectively.

Fig. 3. Experimental setup for the three different-wavelength (1, 1.5, and 1.9 \(\mu m\)) pulsed fiber laser based on GO SAs.

When the GO SA film is inserted into the YDF ring cavities, mode-locking can be self-started at the center wavelength of 1029.5 nm in the Yb-doped fiber laser when the pump power is about 50 mW. The mode-locked fiber laser can be self-started at the pump power of 50 mW. With the increase of the pump power, single pulse mode-locking are still obtained in the experiments. Fig. 4 shows the experimental result when the pump power is about 78 mW. The spectral width is about 0.9 nm with a steep edge as shown in Fig. 4(a). The corresponding pulse trains are shown in Fig. 4(b). The pulses operated in normal-dispersion regimes have large chirps, and dissipative soliton can be formed in the fiber cavity [43]. The corresponding pulse width is about 190 ps measured with a high-speed oscilloscope as shown in
Fig. 4. Passively mode-locked Yb-doped fiber laser based on GO film at a pump power of 78 mW. (a) Spectrum, (b) the corresponding pulse train, (c) single pulse durations with measured result and Gaussian fit result. (The center wavelength is 1029.5 nm).

Fig. 4(c). The time-bandwidth product (TBP) of the pulse is about 51, which is much larger than the transform-limited value. By changing the polarization state, the center wavelength of the mode-locking laser can be tuned accordingly which is due to the birefringence of the fiber cavities.

Then we apply the GO SA film in Er-doped passively mode-locked fiber lasers. The EDF laser operates in the wavelength of 1560 nm with pulse duration of 750.5 fs as shown in Fig. 5(a). The spectra width is about 3.8 nm, corresponding to a TBP of 0.352, which is close to the transform-limited values. The EDF laser can be self-started at pump power of 80 mW. Since the cavity operates in anomalous dispersion regime, the conventional soliton is formed in the fiber laser cavity. The suppression of the Kelly sideband is mainly due to the periodic perturbations such as gain, filtering, and loss in the fiber resonator [44].

We also applied the GO SA thin film in the Tm-doped fiber ring lasers. In the experiment, Q-switching phenomena were obtained. The results were measured by using an OSA and an InGaAs photodetector together with an Agilent oscilloscope. The rise time is only about 25 ns. We used a laser diode at 1570 nm as a seed laser (with an optical power of about 10 mW) and an EDFA to amplify the seed laser, and then use it as a pump laser source. When the power of EDFA reaches 330 mW, Q-switching can be obtained as observed from the oscilloscope. Fig. 6(a) and

Fig. 5. Passively mode-locked Er-doped fiber laser based on the GO film at a pump power of 80 mW. (a) Spectrum (The center wavelength is 1559.6 nm), (b) corresponding pulse train, (c) autocorrelation (AC) trace of the pulse. If a $\text{Sech}^2$ profile is assumed for fitting, the pulse duration is the width of AC trace divided by a factor of 1.54.

Fig. 6. Passively Q-switched Tm-doped fiber laser based on the GO SA at a pump power of 330 mW. (a) spectrum, (b) corresponding pulse train. The center wavelength is $\sim$1870 nm.
The center wavelength is 1871 nm and only the substrate of the spectrum becomes broadened when Q-switching are observed in the temporal domain. The pulse width is about 35 μs, and the output power is about 20 mW.

With further increasing the power of the EDFA, the repetition rate of the Tm-doped Q-switched fiber laser increases from 12.5 to 33 kHz and the pulse width decreases from 20.5 to 12.5 μs. Fig. 7(a) shows the corresponding pulse trains observed from the oscilloscope. The variations of the pulse duration and the repetition rate are summarized in Fig. 7(b). As the pump power increases further, Q-switching operation changes to CW operation in the experiments, which may be due to the reason that it is near the damage threshold of the GO SA. We anticipate that the mode locking can be achieved by further control of the fiber cavity parameters and suitable pump power.

The experimental outputs are summarized in Table I. We can see that the cavity lengths of the Er- and Yb-doped fiber laser are almost the same. In the 1 μm regime, the pulses are generated in the dissipative soliton regime in all-normal dispersion regimes, which is due to the combined effects of the gain/loss, all normal dispersion, spectral filtering, and nonlinearity (self-phase modulation) [45]–[47]. While in the 1.5 μm regime, the mode locked fiber laser operates in the conventional soliton regime without dispersion management. This is caused by the interaction of the anomalous dispersion, and the nonlinearity (self-phase modulation). The Q-switching in the TDF ring lasers is due to the relatively high transmission loss in this wavelength regime and the relatively low pump power. Because of the low damaged threshold of the PVA, high pump power cannot be responsible for achieving mode locking with current cavity parameters.

The pulse dynamics for these fiber lasers are different, when the GO SA is applied in different fiber cavities without intentionally managing the dispersion, the nonlinearity, and the pump strength. In order to obtain a transform-limited pulse, the Yb-doped fiber laser can also be designed to work in the conventional soliton regimes by using a piece of anomalous-dispersion component, such as grating pairs, chirped fiber Bragg gratings (CFBG) [48], hollow core photonic crystal fibers (HC-PCF) [49], or high-order-mode fibers (HOMF) [50]. On the other hand, high energy pulses can also be obtained in the 1.5 μm and the 2 μm regimes by inserting normal-dispersion components [51]–[53]. In all the operation wavelength regions, the GO/PVA film acts as a stable SA. In addition, the GO SA can also be potentially applied in the mid-infrared regime (above 3 μm), and even be potentially suitable for the THz and microwave band by controlling the oxidation degree of GO [54], [55]. It is also possible that the ultra-broadband SA will find its application in the external cavity semiconductor lasers as well as solid-state lasers [56].

![Image](image_url)

**Fig. 7.** (a) The oscilloscope trace with different repetition rate under different pump powers. (b) Variations of the pulse duration and repetition rate as a function of the pump powers.

**TABLE I**

<table>
<thead>
<tr>
<th>Gain fiber</th>
<th>The cavity length</th>
<th>Operating state</th>
<th>Period</th>
<th>Pulse duration</th>
<th>TBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb-doped fiber</td>
<td>10.7 μm</td>
<td>Mode-locking</td>
<td>24.4 ns</td>
<td>190 ps</td>
<td>48.4</td>
</tr>
<tr>
<td>Er-doped fiber</td>
<td>10.9 μm</td>
<td>Mode-locking</td>
<td>24.8 ns</td>
<td>750.5 fs</td>
<td>0.352</td>
</tr>
<tr>
<td>Tm-doped fiber</td>
<td>26.2 μm</td>
<td>Q-switching</td>
<td>30-80 μs</td>
<td>12.5-20.5 μs</td>
<td>–</td>
</tr>
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</table>

(b) shows the spectra and the corresponding oscilloscope trace. The center wavelength is 1871 nm and only the substrate of the spectrum becomes broadened when Q-switching are observed in the temporal domain. The pulse width is about 35 μs, and the output power is about 20 mW.

The ultra-broadband SA property of GO/PVA films has been studied in three different wavelength ranges from 1 to 2 μm. This type of GO SA film has been investigated in three-wavelength fiber ring lasers based on Yb-, Er-, and Tm-doped fibers, respectively. The experimental results demonstrated that the modulation depths of the SA vary at different wavelengths. Mode locking of dissipative soliton and conventional soliton can be obtained at 1.06 and 1.56 μm, respectively, whereas Q-switching can be obtained at the wavelength of 1.87 μm. To the best of our knowledge, this is the broadest wavelength regime in which one type of GO SA film can operate in all-fiber pulsed ring lasers.

**V. CONCLUSION**

The ultra-broadband SA property of GO/PVA films has been studied in three different wavelength ranging from 1 to 2 μm. This type of GO SA film has been investigated in threewavelength fiber ring lasers based on Yb-, Er-, and Tm-doped fibers, respectively. The experimental results demonstrated that the modulation depths of the SA vary at different wavelengths. Mode locking of dissipative soliton and conventional soliton can be obtained at 1.06 and 1.56 μm, respectively, whereas Q-switching can be obtained at the wavelength of 1.87 μm. To the best of our knowledge, this is the broadest wavelength regime in which one type of GO SA film can operate in all-fiber pulsed ring lasers.

**REFERENCES**


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