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Citation: Chin. Phys. B . 2018, 27(11): 114214. **doi:** 10.1088/1674-1056/27/11/114214

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Chin. Phys. B . 2018, 27(8): 084206. **doi:** 10.1088/1674-1056/27/8/084206

Carboxyl graphene oxide solution saturable absorber for femtosecond mode-locked erbium-doped fiber laser*

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(Received Receivd 15 May 2018; revised manuscript received 6 August 2018; published online 25 October 2018)

The carboxyl-functionalized graphene oxide (GO-COOH) is a kind of unique two-dimensional (2D) material and possesses excellent nonlinear saturable absorption property and high water-solubility. In this paper, we prepare saturable absorber (SA) device by depositing GO-COOH nanosheets aqueous solution on a D-shaped fiber. The modulation depth (MD) and saturable intensity of the SA are measured to be 9.6% and 19 MW/cm^2, respectively. By inserting the SA into the erbium-doped fiber (EDF) laser, a passively mode-locked EDF laser has been achieved with the spectrum center wavelength of 1562.76 nm. The pulse duration, repetition rate, and the signal-to-noise ratio (SNR) are 500 fs, 14.79 MHz, and 80 dB, respectively. The maximum average output power is measured to be 3.85 mW. These results indicate that the GO-COOH nanosheets SA can be used as a promising mode locker for the generation of ultrashort pulses.

Keywords: fiber lasers, mode-locked pulse, nonlinear optical materials, carboxyl graphene oxide

PACS: 42.55.Wd, 42.60.Fc, 42.70.Nq **DOI:** 10.1088/1674-1056/27/11/114214

1. Introduction

Passive mode-locked fiber lasers are widely applied in the fields of optical communication, industrial material processing, optical sensing, and biomedical diagnostics due to the advantages of compact structure, stable performance, flexibility, and excellent beam quality.[1–4] It is reported that the passive mode locking technology of fiber lasers mainly depends on nonlinear polarization evolution (NPE) or saturable absorbers (SAs).[5,6] Although, the pulsed fiber lasers based on NPE technique have the advantages of ultrashort pulse duration and simple structure,[5,7] they can be easily influenced by the external environment and have the relatively high mode-locked laser starting threshold.[8,9] By contrast, the passive mode locking technique based on semiconductor saturable absorber mirrors (SESAMs) or broadband nonlinear materials can be used to overcome those disadvantages. The process of fabricating SESAMs is complex and costly. And the fabricated SESAMs have a narrow bandwidth.[10] Apart from the traditional SESAMs, some nanomaterials like single-walled carbon nanotubes (SWCNTs),[11–13] graphene,[14,15] topological insulators (TIs),[16,17] transition metal dichalcogenides (TMDs),[18,19] and black phosphorus[20] have been widely investigated for ultrashort pulse generation owing to their advantages of ultrafast broadband photon-response, easy fabrication, and low cost. Although the above nonlinear materials can be used to modulate laser systems, the nonlinear materials with a broadband nonlinear modulation effect, low saturation intensity, and good stability are objective pursued by many researchers, such as Mxene,[21] Antimonene,[22] and so on.

Compared with other two-dimensional (2D) materials, the graphene has been earlier applied to prepare SAs. The graphene as an excellent SA possesses a variety of specific electronic and photonic properties, including zero band-gap, high damage threshold, ultrashort recovery time, and ultra-broadband absorption.[23–25] In 2009, Bao *et al.*[8] and Hasan *et al.*[26] demonstrated ultrashort pulses from passively mode-locked fiber lasers by incorporating graphene as SAs. Since then, based on graphene SAs, researchers have obtained mode-locked pulses at 1 μm, 1.5 μm, 2 μm, and 2.5 μm.[27–29] In general, the graphene SAs can be grown on various substrates and then easily transferred to fiber connectors, and also directly grown on D-shaped fiber or taper-fiber by chemical vapor deposition (CVD).[30] However, the yield of the graphene is very low. The graphene can be obtained by exfoliating graphite in aqueous solutions with surfactant. And then, the graphene is wrapped into organic polymer composites or be directly coated on D-shaped fiber.[31,32] Graphene is usually hydrophobic because of the symmetrical structure and the high cohesive van der Waals force between graphitic nanosheets, which result in the difficulty of dissolution of

*Project supported by the Central University Special Fund Basic Research and Operating Expenses, China (Grant No. GK201702005), the Natural Science Foundation of Shaanxi Province, China (Grant No. 2017JM6091), the National Natural Science Foundation of China (Grant No. 61705183), and the Fundamental Research Funds for the Central Universities, China (Grant No. 2017TS011).

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graphene in aqueous solution. Generally, a surfactant is added into graphene aqueous solution, which produces some unsaturated losses and reduces the performance of the mode-locked fiber laser.[33] Usually, graphene oxide (GO) is the intermediate production of the graphene prepared by chemical reduction method. The structure of the GO is similar to that of graphene. There are some oxygen-containing functional groups on the surfaces of two-dimensional carbon atom layer, which makes GO have high solubility compare to that of graphene. However, the water solubility is still limited (< 0.5 mg/mL).[34]

Recently, a kind of water soluble graphene derivative was reported. Carboxyl-functionalized graphene oxide (GO-COOH) possesses more –COOH than GO does. GO-COOH has the nonlinear optical property similar to that of GO. Furthermore, it possesses higher solubility in water than GO, not to say graphene. Recently, Zhao *et al.*[35] and Duan *et al.*[36] have just realized mode locking in erbium-doped fiber (EDF) lasers by using the GO-COOH/PVA SAs. The pulse durations were 1.5 ps and 808 fs, respectively. However, the GO-COOH/PVA film generally shows a low laser damage threshold, which has adverse effects for its application in high power fiber lasers.

In this paper, we prepare the SA device by immersing D-shaped fiber into the GO-COOH nanosheets solution. The modulation depth (MD), saturable intensity, and unsaturated loss are measured to be 9.6%, 19 MW/cm^2, and 35.8%, respectively. Passively mode locked fiber laser with GO-COOH solution absorber is obtained. The center wavelength of the spectrum is 1562.76 nm with a 3-dB spectral bandwidth of 5.80 nm. The pulse duration, repetition rate, and high stability signal-to-noise ratio (SNR) are measured to be 500 fs, 14.79 MHz, and 80 dB, respectively. The mode-locked operation can be maintained with the pump power increasing from 17 mW to 180 mW, and the maximum average output power is 3.84 mW. The experiment results suggest that the GO-COOH SA device is a potential optical modulation material, which can be used in nonlinear optics field.

2. Fabrication of GO-COOH solution SA

In this experiment, we prepare GO-COOH solution by liquid phase exfoliation method, which has been widely used to fabricate high-quality 2D materials because of its simplicity and effectiveness.[37] First, we accurately weigh 10 mg GO-COOH powder, and add it to 10 mL deionized water. In order to disperse the GO-COOH materials in water evenly, the initial dispersions are treated for 8 h by a high-power ultrasonic cleaner. Then the suspension is centrifuged at 7000 r/min for 10 min to remove large agglomerations.

As shown in Fig. 1(a), the GO-COOH Raman spectrum is measured by using a laser source with the center wavelength of 532 nm. The two main peaks of GO-COOH can be observed in Fig. 1(a), the D peak and the G peak located at 1345 cm^{-1} and 1592 cm^{-1}, respectively. The Raman spectral characteristics are basically the same as that of GO. There is no 2D peak in the Raman spectrum, which indicates that there is no graphene sample in GO-COOH. Figure 1(b) is the transmission electron micrograph (TEM) of GO-COOH at the resolution of 100 nm, we can see clearly that the sample presents a multilayer laminar structure.

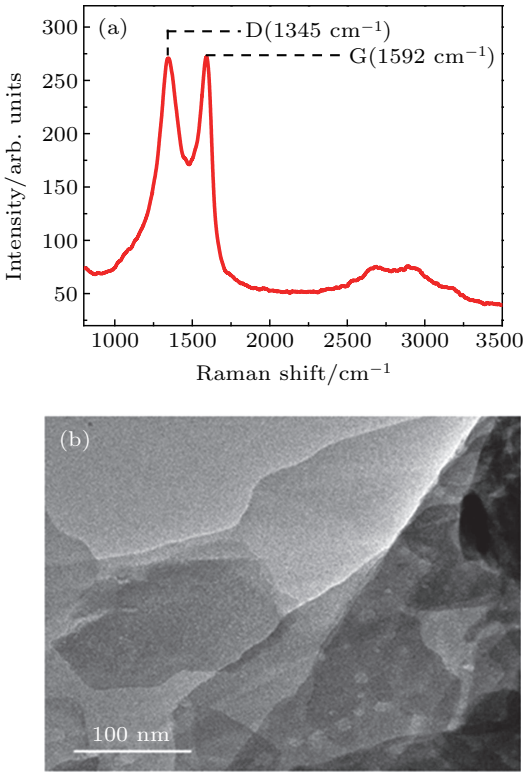


Fig. 1. (color online) (a) Raman spectrum of GO-COOH absorber; (b) TEM image.

The D-shaped fiber is fabricated by grinding a single-mode fiber and then fixed on a piece of glass to protect it. The interaction length of the D-shaped area is 10 mm and the distance from the fiber core to the D-shaped surface is 2 μm. The D-shaped fiber section is immersed in the GO-COOH solution. The GO-COOH nanolayers near the surface of the D-shaped fiber interact with the laser evanescent field. The MD of the SA directly determines the performance of passive mode-locked laser, therefore we measure the nonlinear saturable absorption property of the SA device. We use a home-made femtosecond laser with the central wavelength of 1562 nm, repetition rate of 24.93 MHz, and pulse width of 500 fs as a test source. The laser is divided into two beams with a 50:50 coupler. One beam is for power-dependent transmission measurements of the SA device and the other is as reference. The measured results are fitted by function $T = A\exp[-\Delta T/(1 + I/I_{\rm sat})]$ as shown in Fig. 2. Here, A is the normalization constant, ΔT is the MD, I is the incident intensity, and $I_{\rm sat}$ is the saturation intensity. The MD of the GO-

COOH SA is measured to be 9.6%. The unsaturated losses and saturable intensity are 35.8% and 19 MW/cm^2, respectively.

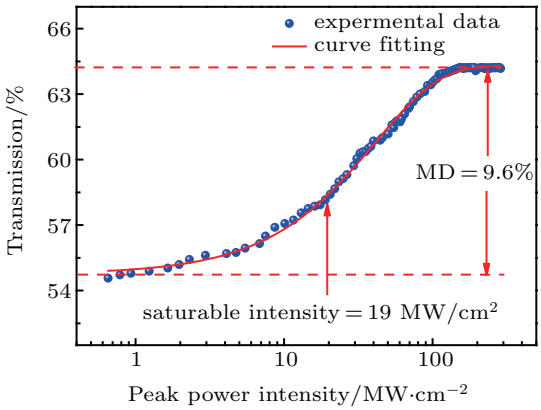


Fig. 2. (color online) The nonlinear saturable absorption curve of SA and the corresponding fitting curve.

3. Experimental setup

Figure 3 shows the schematic of mode-locked fiber laser with our GO-COOH SA device. The pump source is a laser diode (LD) with emission centered at 975 nm, and the maximum output power is 450 mW. A 4 m long Er-doped single-mode fiber is used as the gain medium, which has the absorption coefficient of 3 dB/m at 980 nm. The pump is delivered into Er-doped fiber via a 980/1550 fused wavelength division multiplexer (WDM) coupler. A polarization independent isolator (PI-ISO) is used to ensure the unidirectional transition of laser. Adjusting the PC can set different polarization state in the fiber laser and therefore optimizes the laser performances. The GO-COOH solution SA combined with D-shaped fiber experiences large (small) unsaturated losses under low-intensity (high-intensity) laser, therefore leading to the saturable absorption condition. A fused fiber optical coupler (OC) with an output coupler ratio of 10:90 is used to extract 10% energy from the cavity. The laser resonator cavity length is 14 m. The dispersion parameters D at 1550 nm for EDF and SMF are -16 ps/(nm·km) and 17 ps/(nm·km), respectively. The net cavity dispersion is calculated to be -0.162 ps^2. An optical

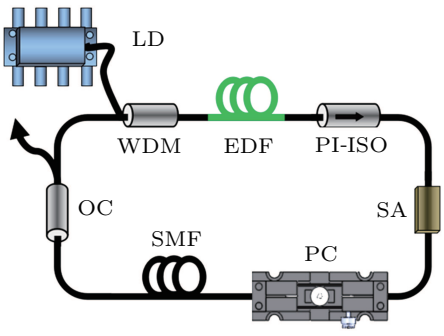


Fig. 3. (color online) Mode-locked fiber laser device diagram.

spectrum analyzer (Yokogawa AQ6370D), a 1 GHz digital oscilloscope (Rohde & Schwarz RTO1014) with a home-made 5 GHz photodiode detector, an autocorrelator (Alnair Laboratories Corporation HAC-200), and a 40 GHz radio-frequency analyzer (Agilent E4447A) are employed to simultaneously monitor the output pulse.

4. Results and discussion

In the experiment, the mode-locked laser can be achieved when the pump power reaches the threshold of 17 mW and the PC is appropriately adjusted. As shown in Fig. 4(a), the stable passive mode-locked operation is obtained with a central wavelength of 1562.76 nm and 3-dB bandwidth of 5.80 nm. Two pairs of Kelly sidebands are symmetrically distributed on both sides of the spectrum, which proves that the fiber laser realizes the output of conventional soliton mode locking operation. The autocorrelation curve is measured as shown in Fig. 4(b), the full width at half maximum (FWHM) of the pulse trace is 770 fs. By using the sech^2 function fitting, the pulse duration is estimated as 500 fs. The time bandwidth product is calculated to be 0.356, indicating that the output pulse is slightly chirped. Furthermore, an autocorrelation trace with a broad scanning range of 50 ps is given in Fig. 4(b). It confirms the singe pulse operation under the highest pump power. It should be noted that no pedestal shown on the autocorrelation trace reveals the excellent quality of mode locking. The mode-locked pulses sequence diagram is demonstrated in Fig. 4(c). The intervals between each two adjacent pulses are always 67.59 ns corresponding to the theoretical value calculated according to the cavity length. Radio-frequency (RF) spectrum of the laser measured with the span of 1 kHz and the resolution bandwidth of 10 Hz is shown in Fig. 4(d). The fundamental repetition rate is 14.79 MHz, which fits well with the cavity length of 14 m. It is demonstrated that the mode-locked pulse state maintains the fundamental repetition rate and there is no harmonic mode-locked state in the fiber laser. SNR is as high as 80 dB and a 500 MHz RF spectrum is also shown as illustration in Fig. 4(d). The high SNR indicates that the mode-locked stability is very good, and implies that the GO-COOH based on D-shaped fiber is an excellent SA.

With the gradually increasing pump power, the mode-locked operation can be maintained until the pump power reaches 180 mW. In the process, the pulse width and repetition rate of the laser do not change, and the spectrum is broadened and has a slight red shift, which implies that the laser operates in the fundamental mode-locked state rather than the Q-switched state.[38] When the pump power exceeds 180 mW, the optical spectrum becomes unstable, and thorn and jitter arise in the pulse. The mode-locked operation disappears when the pump power continues to increase. It should be noted that within the maximum injected pump power of 450 mW, no

harmonic mode locking operation is observed. However, after the pump power is decreased to 180 mW, the stable mode-locking operation is observed again with the same characteristics. This phenomenon indicates that the SA is not destroyed by the thermal accumulation. The relationship between the pump power and the average output power of the laser is shown in Fig. 5(a). We can observe that the average output power almost linearly increases with the pump power. The maximum output power is measured to be 3.85 mW, and the maximum single energy is 0.26 nJ. Compared with the GO-COOH SAs prepared by Zhao *et al.*[36] and Duan *et al.*,[37] our SA device possesses the higher damage threshold and MD. Meanwhile, we obtain shorter pulses and larger output power. The result shows that compared with mixing with polyvinyl alcohol to prepare SAs, the continuous and uniform GO-COOH directly coated on the side of the D-shaped fiber can prevent the material from being affected by combination with other organic matrix polymers. Besides, the effective interaction area between the D-shaped fiber and GO-COOH is large, which improves the modulation ability and facilitates heat dissipation. Further improvement of the system efficiency is possible by high-gain fiber (e.g., double-clad fiber) and further optimizing the cavity parameters (e.g., SA's performance, cavity loss, output ratio of the optical coupler). In addition, in order to evaluate the long term stability of the mode-locked fiber laser, the experiments are performed over 60 h. We record

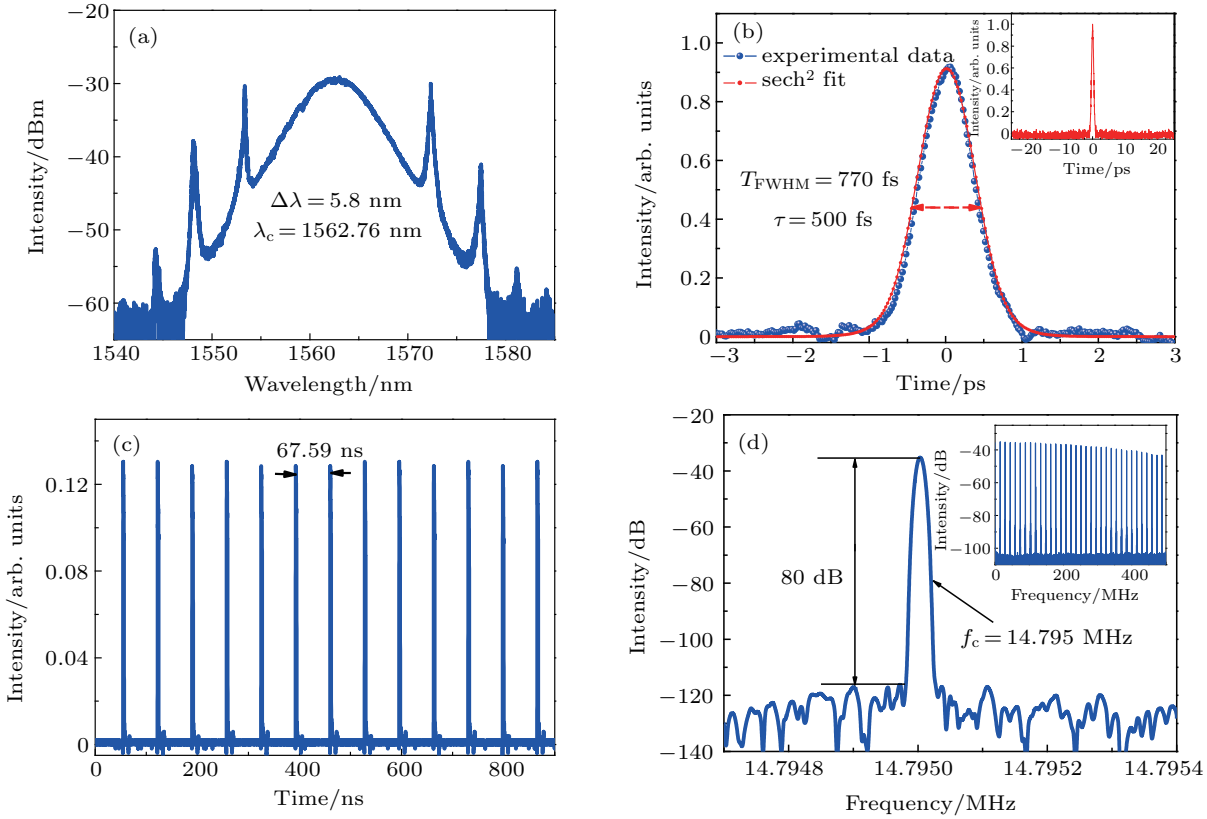


Fig. 4. (color online) Mode-locked pulse state: (a) optical spectrum, (b) autocorrelation traces, (c) pulse trains of oscilloscope, and (d) radio-frequency spectrum.

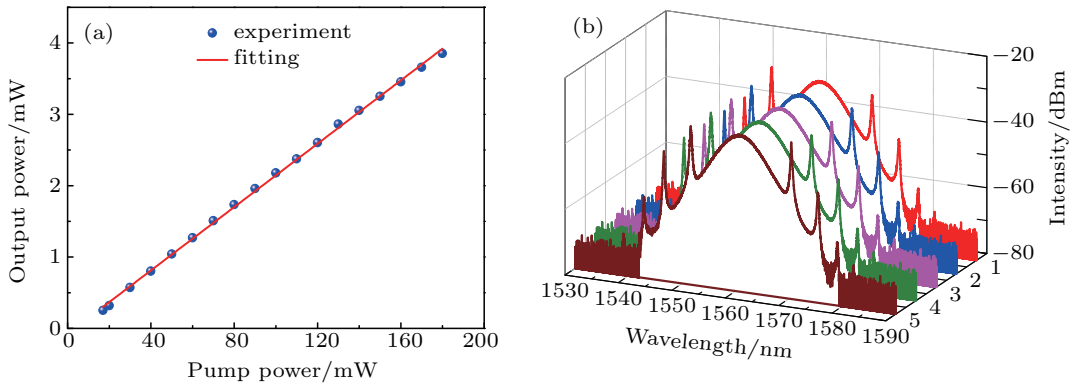


Fig. 5. (color online) (a) Relationship between the pump power and output power. (b) Long term optical spectrum measured over 60 h.

the optical spectrum of the mode-locked fiber every 12 h as shown in Fig. 5(b). There is no significant degradation in the optical spectrum, indicating that the SA has not been damaged after a few days of continuous high-power operation. Finally, we remove SA device from laser cavity to verify whether the mode-locked operation is purely contributed by the GO-COOH based on D-shaped fiber. The mode-locked operation is not observed despite the pump power and PC are tuned over a full range. The results show that the mode-locked operation is indeed contributed by the SA.

5. Conclusion

We measure the morphological characteristics and nonlinear optical property of GO-COOH. The MD, saturable intensity, and nonsaturable loss of GO-COOH SA are measured to be 9.6%, 19 MW/cm^2, and 35.8%, respectively. Moreover, GO-COOH solution combined with D-shaped fiber as SA is applied in ultrafast EDF fiber laser. The pulse width is measured to be 500 fs and the SNR reaches up to 80 dB. The maximum average output power is measured to be 3.85 mW under the pump power of 180 mW. The experimental results show that GO-COOH possesses good saturable absorption property and can be applied in the field of ultrafast optics.

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