

Research Article

Saturable Absorption and Modulation Characteristics of Laser with Graphene Oxide Spin Coated on ITO Substrate

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The graphene oxide (GO) thin film has been obtained by mixture of GO spin coated on substrate of indium tin oxide (ITO). The experiment has shown that continuous-wave laser is modulated when the graphene oxide saturable absorber (GO-SA) is employed in the 1064 nm laser cavity. The shortest pulse width is 108 ns at the pump power of 5.04 W. Other output laser characteristics, such as the threshold pump power, the repetition rate, and the peak power, have also been measured. The results have demonstrated that graphene oxide is an available saturable absorber for 1064 nm passive Q-switching laser.

1. Introduction

For recent years, graphene has attracted significant attention for its remarkable mechanical and physical properties [1, 2]. It is the building block nanomaterial of carbon nanotubes and graphite, a two-dimensional layer with carbon atoms arranged in a honey-comb lattice [3]. This feature has resulted in diverse applications in real world, such as plasmon wave guiding [4] and photodetectors [5]. Moreover, it is a potential candidate to enhance or enable the biomedical, chemical, and industrial processes [6, 7]. The very important application is that it can provide the nonlinear saturable absorption covering a wide wavelength range [8, 9], due to its point band gap structures [10] combined with Pauli blocking [11]. There already have been some researches on nanosecond and picosecond lasers employing graphene as the saturable absorber [12-15]. The distribution of graphene sheet and its derivatives into polymers has been widely considered for the fabrication of nanocomposites with enhanced properties [16, 17]. It can enhance the strength of the parent material. Compared with the pure polymer, the graphene polymer has better mechanical, thermal, electrical, gas barrier, and flame retardant properties.

Although the graphene has so many advantages and applications, the distribution of graphene sheets in the polymer matrix, as well as the relatively weak interfacial bonding with the polymer chain, limits the improvement of the physicochemical properties for the nanocomposite materials [18]. Moreover, the point band gap structure in graphene restricts it to application in nanoelectronics. As a potential alternative to graphene, graphene oxide (GO), an atomic sheet of carbon by analogy to graphene, has been discovered recently [19]. It is significantly more compatible with polymers. It has carboxylic groups at its edges and phenol and epoxide groups on its basal plane. The adsorption of oxygen opens up the band gap in the graphene. It is possible that mass of graphene and some of the graphene saturable absorbers can be obtained by reducing the stable GO [20, 21]. Indium tin oxide (ITO) is a practical coated substrate for graphene in addition to the usual used quartz or SiC [22]. This substrate is a solid solution of indium oxide (In_2O_3) and tin oxide (SnO_2) , and it is widely employed in transparent conducting oxides due to the electrical conductivity and optical transparency.

For the above-mentioned reasons, we have prepared the graphene oxide thin films by mixture of GO spin coated on substrate of indium tin oxide (ITO). The transmissivity has



FIGURE 1: The experimental setup.

been measured, and it is around 76% at 1064 nm wavelength. We locate the GO-SA in the laser cavity and realize the Q-switched modulation. The output laser characteristics, such as the threshold pump power, the pulse width, the repetition rate, and the peak power, have been measured. The shortest pulse width of 108 ns has been obtained at the pump power of 5.04 W. In this paper, the results have demonstrated that graphene oxide is an available saturable absorber for 1064 nm wavelength and it can effectively obtain the passive Q-switching pulse laser. The passively Q-switched laser performance of GO-SA is comparable with that obtained by graphene saturable absorber.

2. Materials and Methods

2.1. Preparation of the Graphene Oxide Saturable Absorber. The graphene oxide saturable absorber is obtained by spin coated mixture of GO on ITO substrate. The first step is to prepare the mixture of GO. The graphite and NaNO₃ were mixed with the ratio of 2/1, and then H_2SO_4 with the concentration of 95% was mixed together. 300 g KMnO₄ was subsequently injected into the suspension by inches. The injection should be together with nonstop agitation. The processes above were carried out in a flask and cooled in ice bath to avoid overheating. Then, the suspension was stirred at room temperature by machine lasting for two hours. With the distilled water being slowly added in the suspension, the bright brown suspension was observed to become yellow in color, caused by the temperature increasing to 90°C. Then, the suspension should be sequentially stirred for twelve hours and treated with 30% H_2O_2 to reduce the KMnO₄ and MnO₂. After that, the suspension was washed with hydrochloric of low concentration, then with distilled water. The last step was to centrifuge the suspension and then dry it under vacuum condition. The vital procedure of graphene oxide preparation is purification. There are still some salts and acids residues in GO powders, so they have a brown dispersion when the black synthesized graphene oxides (GOs) powders were suspended in water. Ultrapure Milli-Q water was used in order to effectively dialyze in all experiments. The GO in the brown dispersion was exfoliated and centrifuged. After powerful shaking, the dispersion in the vial was put in a high-temperature water bath. Finally, the brown-colored dispersion turned black.

We used the spin coating method to obtain a uniform thin liquid film composed of graphene oxide. The thickness of membrane depended on speed, rheology of solidifying liquid, and gas conditions. We have prepared the GO-SA by employing the spin coating method. The best films were obtained using spin coating from the graphene oxide colloid (1.0 mg mL^{-1}) at ambient temperature condition and the spin-coating speed was 800 rpm. Then, the graphene oxide saturable absorber spin coated on ITO was obtained. Its transmissivity of different wavelengths is measured using UV-Vis adsorption spectroscopy. UV-Vis adsorption spectroscopy measurement was obtained using a Hitachi U-4100 spectrophotometer. The GO-SA can be used in the wide wavelength range from 1 to 2 μ m. The transmissivity is 76%, 74%, 73%, and 62%, corresponding to the wavelengths of 1.06 μ m, 1.34 μ m, 1.5 μ m, and 2 μ m, respectively.

2.2. Testing Experimental Setup. The saturable absorption characteristics of the graphene oxide have been operated in a laser-diode-pumped Nd:YVO₄ laser cavity at 1064 nm. The arrangement of the experimental equipment is demonstrated in Figure 1. As is shown, a simple flat-concave cavity is employed. The whole length is about 6.5 cm. The laser medium is pumped by a commercially used fiber-coupled laser-diode (FAP-I system, Coherent Inc., USA). Its output beam is 808 nm lasers with the maximum output power of 30 W. The pump beam is focused into the laser crystal by a focusing optical system with a spot size of $400 \,\mu\text{m}$. The laser oscillations operate between two coated mirrors. The input mirror M_{in} is antireflection-coated at 808 nm on the entrance face, high-transmission-coated at 808 nm, and highreflection-coated at 1.06 μ m on the other side, with the curvature radius of 200 mm. The output coupler M_{out} is coated with transmissions (*T*) of 10% and 15% at 1.06 μ m, with two plane end surfaces. The graphene oxide saturable absorber is placed close to the output coupler. An a-cut Nd:YVO4 crystal with 1.0 at.% Nd³⁺-doped is employed as the laser gain medium and located near the input mirror. Its dimensions are $3 \times 3 \times 10 \text{ mm}^3$ and both end sides are high-transmissioncoated at 808 nm and antireflection-coated at 1.06 μ m. The laser crystal is mounted in a copper heat-sink cooled by water, in order to keep its temperature at 20°C and dissipate the heat deposition. The output characteristics are measured by some detection equipment. The generated average output power is measured by the EPM 2000 energy/power meter (Molectron Detector Inc., USA). The pulse width and repetition rate of the laser pulses are measured by a photoelectric detector and a TED 6208 digital oscilloscope (500 MHz bandwidth, Tektronix Inc., USA).

3. Results and Discussion

The experimental setup is a flat-concave laser resonator. We choose T = 10% and 15% because low transmission of



FIGURE 2: Average output power versus pump power.

TABLE 1: The continuous-wave output power.

Pump power (W)	0.235	1.405	2.61	3.8	4.45	5.04	6.2
Output power (W)	0.021	0.442	0.934	1.45	1.69	2.24	2.71

output mirror can hold high photon number density in the resonant, so the laser performance is better expected. Two transmissions are employed for the purpose of comparison. The continuous-wave laser operation at 1064 nm should be operated at first. The incident pump power of 808 nm laser continuously increases. The laser begins to radiate at the pump power of 235 mW, with the output power being 0.021 W, as shown in Table 1. The maximum power is 2.71 W at the pump power of 6.2 W, with the optical-optical conversion efficiency of 43.7%.

In order to detect the saturable absorption characteristics of the GO-SA, it is located near the output mirror in the cavity. Then, the threshold pump powers increase to 1.37 W and 1.62 W corresponding to the output transmissivity of 10% and 15%. The larger threshold pump powers demonstrate the absorption of low power laser. The threshold pump powers are much lower than those of laser passively Q-switched with grapheme saturable absorber (3.14 W with Nd:LuVO₄ [23]). Figure 2 has shown the average output power versus pump power. It is obvious that the largest output power is obtained by T = 10%. It can be seen that the maximum output power is measured to be 180 mW, obtained at the pump power of 5.04 W. The laser average output power of T = 15% is always lower than that obtained by T = 10%.

The passive Q-switched operation has been realized once the pump power reaches the threshold. A typical temporal pulse shape with the pulse width of 108 ns has been depicted in Figure 3.

As is shown in Figure 4, in which the pulse width versus pump power has been demonstrated, the pulse widths



FIGURE 3: Temporal profile of the single pulse with pulse width of 108 ns.



FIGURE 4: Pulse width versus pump power.

monotonously decrease along with the increase of pump power. The shortest pulse width is 108 ns obtained by T = 10%at the pump power of 5.04 W. The data of T = 15% are larger than those of T = 10% at each pump power. The pulse width for T = 15% continuously reduces from 240 ns to 134 ns with the pump power increasing from 2 W to 5.04 W. The passively Q-switched laser performance of GO-SA is comparable with that obtained by graphene saturable absorber. We obtain the shortest pulse width at the pump power of 5.04 W, and the shortest pulse width obtained by graphene SA is 161 ns at the pump power of 12.9 W [14]. Also, the pulse width obtained by GO-SA is shorter than half of that obtained by graphene SA with Nd:YAG (260 ns) [15].

Figure 5, in which the variation of pulse repetition rate versus pump power is displayed, has demonstrated that the repetition rates for T = 10% and T = 15% increase with



FIGURE 5: Pulse repetition rate versus pump power.

the accretion of incident pump power. At the pump power of 2 W, the value for T = 10% and T = 15% is 183 kHz and 156 kHz, respectively. The largest repetition rate is 345 kHz, obtained by T = 10% at the pump power of 5.04 W, while the maximum for T = 15% is 300 kHz. With graphene SA, the repetition rate is 167 kHz when the pulse width reaches the minimum [15].

By mathematical computation, single pulse energy *E* and the peak power P_{peak} can be calculated out ($E = P_{\text{out}}/F$ and $P_{\text{peak}} = E/W$, where P_{out} is the average output power, *F* is the pulse repetition rate, and *W* is the pulse width). Both the pulse energy and the peak power of T = 10% or T =15% monotonously increase along with the pump power. The values for T = 10% are always larger than those of T = 15%. The largest pulse energy of $0.52 \ \mu$ J and the highest peak power of 4.8 W are obtained by T = 10%, while the maximums for T =15% are 0.49 μ J and 3.7 W under the same conditions.

Besides GO-ITO saturable absorber, other GO composite material absorbers also show optical absorption ability. There is report on mode-locked laser operation with grapheme oxide/polyvinyl alcohol composite material, in which the absorber is employed as the output coupler. The average output power of 680 mW and the pulse duration of 12 ps are obtained [24]. Reduced graphene oxide-Pani hybrid has optical absorption in UV-Visible spectrum. The GO exhibits a broad absorption which is continuously decreasing to 800 nm, whereas the hybrid in dimethyl formamide shows an absorption maximum at 325 nm, attributed to the π - π ^{*} transition, and a peak at 618 nm due to the excitonic transition of polyaniline [25].

4. Conclusions

In conclusion, we have prepared the graphene oxide thin films by mixture of GO spin coated on substrate of indium tin oxide (ITO). The transmissivity has been measured and it is around 76% at 1064 nm wavelength. The experiment has shown that once the graphene oxide saturable absorber (GO-SA) is employed in the 1064 nm laser cavity, the continuouswave laser is modulated. The output laser characteristics, such as the threshold pump power, the pulse width, the repetition rate, and the peak power, have been measured. The shortest pulse width of 108 ns is obtained at the pump power at 5.04 W. The results have demonstrated that graphene oxide is an available saturable absorber for 1064 nm wavelength and it can effectively achieve passive Q-switching laser operation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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