Graphdiyne as a saturable absorber for 2- μm all-solid-state Q-switched laser

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ABSTRACT As a novel one-atom-thick carbon allotrope, graphdiyne (GDY) has attracted wide interest in two-dimensional materials owing to its unique feature with a planar layer comprising sp^2 - and sp -hybridized carbon atoms and a direct natural bandgap. A high-quality saturable absorber (SA) based on GDY was successfully fabricated, and the nonlinear saturable absorption properties were investigated. A compact diode-pumped solid-state passively Q-switched laser based on the as-prepared GDY-SA could be operated at 2 μm . The Q-switched laser delivered a maximum average output power of 1.29 W at a central wavelength of 1908.41 nm with up to 54.8% slope efficiency. A repetition rate of 91.58 kHz and single pulse energy of 23.08 μJ were obtained. This work is the first application of GDY as an SA to generate all-solid-state pulsed lasers. These results indicate that GDY is a promising SA for solid-state pulsed lasers and has further application potential for ultrafast photonic devices in the 2- μm region.

Keywords: graphdiyne, saturable absorber, all-solid-state laser, passively Q-switched, two-dimensional materials

INTRODUCTION

All-solid-state eye-safe pulsed lasers operating at approximately 2 μm have potential in a wide range of applications, such as gas monitoring, material processing, medical treatment, laser radar systems, and pumping sources for mid-infrared optical parametric oscillators [1–4]. The passively Q-switched mechanism with non-negligible advantages of compactness, flexibility, and reliability

is an expected technique to achieve nanosecond or millisecond pulsed laser operations. In previous years, the semiconductor saturable absorber (SA) mirrors and Cr: ZnS and Cr: ZnSe crystals were commonly used as modulators [5,6]. However, they have disadvantages, such as preparation complexity, high cost, and narrow absorption bandwidths, which restrict their further development and application at 2 μm [7,8]. Hence, a novel SA with broadband absorption, unique optical properties, easy fabrication, and low cost has been explored. In 2004, graphene (G) (sp^2) was successfully fabricated and used as SA for Q-switched or mode-locked regimes, thereby facilitating new opportunities for the development of pulsed lasers [9–12]. Since then, different kinds of two-dimensional (2D) materials, such as topological insulators, transition metal dichalcogenides, black phosphorus, and MXenes, have been uninterruptedly discovered and widely used for generating pulsed lasers at spectral wavebands ranging from visible to mid-infrared [13–21]. The application of 2D materials based on SA is attributed to their excellent nonlinear optical absorption characteristics, such as ultrafast recovery time, controllable modulation depth and low nonsaturable loss, convenience, and low budget.

Graphdiyne (GDY), a novel one-atom-thick carbon allotrope, was successfully synthesized by Li *et al.* [22] in 2010. It is a new generation of full-carbon nanomaterials that emerged after the discoveries of fullerenes (0D, 1985) [23], carbon nanotubes (1D, 1991) [24], and G (2D, 2004) [9]. Moreover, it has been widely used in different sci-

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entific and industrial fields due to its distinctive structure and physical and chemical characteristics [25–27]. GDY is a member of the graphyne (GY) family, which features a planar layer that comprises sp^2 - and sp -hybridized carbon atoms [28]. As reported [29], GDY is the most easily synthetic and stable carbon allotrope in the GY family because of a heat of formation of $919.2 \text{ kJ mol}^{-1}$. In addition, GDY possesses high electron mobility (as high as $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) at room temperature, whereas the value of G is $15,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [30,9]. The electronic conductivity of GDY is $2.516 \times 10^{-4} \text{ S m}^{-1}$ at room temperature [31]. GDY possesses a direct natural bandgap with Dirac cones structure, in contrast to the zero bandgap of G [32]. Theoretically, using different methods and exchange-correlation functions, the bandgap of GDY is in the range of 0.44–1.22 eV [33]. sp -Hybridized carbon-carbon triple bond structure simplifies the doping and modification of GDY, resulting in a flexible energy bandgap, which enables novel nonlinear optical properties that can be applied to optical and electronic devices with different demands [34]. Recently, Guo *et al.* [35] reported the saturable absorption properties of the GDY for the first time. The large nonlinear absorption coefficient ($> -1 \text{ cm GW}^{-1}$), low saturation intensity ($< 13 \text{ GW cm}^{-2}$), broadband Kerr nonlinearity, large nonlinear refractive index ($\sim 10^{-5} \text{ cm}^2 \text{ W}^{-1}$), and ultrafast relaxation time ($< 30 \text{ ps}$) have all confirmed that GDY is a promising 2D material in pulsed laser generation as SA. Zhang *et al.* [36] investigated the broadband nonlinear absorption properties (ultraviolet–infrared waveband) of the GDY nanosheets, indicating that the GDY nanosheets are veritable ultraviolet nonlinear absorption materials. However, GDY as SA was only used to generate mode-locked fiber lasers at wavebands of 1 and $1.5 \mu\text{m}$ [35]. The output power of fiber laser is low and only in the order of milliwatts. All-solid-state laser could supply high output power and compact structure. Unfortunately, the saturable absorption properties of GDY and its applications in all-solid-state lasers have not yet been reported. In 2019, the broadband γ -GY used as SA for Q-switched solid-state laser was reported [37,38]. The results of these experiments demonstrated that the members of the GY family have outstanding broadband saturable absorption properties and show potential for the implementation of Q-switched or mode-locked bulk laser operations.

In this study, we first report the experimental realization of GDY as SA for all-solid-state $2 \mu\text{m}$ pulsed laser generation. The obtained Q-switched laser shows watt-level output power, 54.8% slope efficiency, and 91.58 kHz repetition rate. This research is the first to explore the

nonlinear saturable absorption characteristics of GDY-SA in all-solid-state pulsed lasers. The experimental result proves that GDY is a promising optical modulator in the field of $2\text{-}\mu\text{m}$ bulk pulsed lasers.

EXPERIMENTAL SECTION

Preparation and characterization of GDY-SA

The liquid/liquid interface method was used to synthesize the 2D GDY film in this study [39]. The upper aqueous layer was used as a catalyst for acetylenic homocoupling, including copper (II) acetate and pyridine. The lower liquid layer was the dichloromethane solution of the hexaethynylbenzene (HEB) monomer. To circumvent a random encounter between the HEB monomer and the catalyst, we added dual water between the two layers. After the successive catalytic coupling reaction for 24 h, the GDY film was generated at the liquid/liquid interface. We used a nylon membrane with a pore size of 100 nm to filter the collected film, washed it with HCl (1 mol L^{-1}) and pure water, and then dispersed the treated GDY film in ethanol. Next, the GDY/ethanol solution was transferred on the quartz plate by spin-coating. Two drops of GDY solution were placed on the quartz plate, controlling the spin coater at a speed of 150 r min^{-1} to guarantee that the GDY can be evenly adhered on the quartz plate. Afterward, the sample was dried at room temperature. Lastly, the GDY-SA used in our experiment was successfully prepared, as shown in Fig. 1a.

Using atomic force microscopy (AFM), we recorded the morphology of the 2D GDY film, as shown in Fig. 1b, c. Along with the direction of A and B, the average thickness of the GDY nanosheet was approximately 2.6 nm. The high-resolution transmission electron microscopy (HRTEM) image of the GDY film is shown in Fig. 1d. A clear crystalline lattice spacing of 0.44 nm is the same as the reported characteristics of GDY [40]. The Raman spectrum verified Raman-active carbon-carbon triple bonds of GDY, as shown in Fig. 1e. The D band peaked at 1370.2 cm^{-1} is assigned to the breathing vibration of sp^2 carbon domains in aromatic rings. The peak at 1576.5 cm^{-1} (G band) corresponds to the first-order scattering of the E_{2g} mode for the in-phase stretching vibration of sp^2 carbon lattice in aromatic rings. Additionally, two bands derived from the vibration of the conjugated diyne linkage shifted at 1943.4 and 2130.8 cm^{-1} . Terminal alkyne stretching near $2100\text{--}2120 \text{ cm}^{-1}$ was not observed, indicating that all the terminal alkyne residues of HEB formed the π -conjugated butadiynyl linkage. Fig. 1f demonstrates the high-re-

Figure 1 (a) GDY film prepared on quartz substrate. (b) AFM image, (c) typical height profiles, (d) HRTEM image, (e) Raman spectrum and (f) high-resolution XPS spectrum of GDY.

solution asymmetric C 1s X-ray photoelectron spectroscopy (XPS), presenting the elementary composition of the GDY. The figure shows that the area ratio of the sp/sp^2 hybridized carbon bond is approximately 2, which conforms to the chemical composition of GDY.

As shown in Fig. 2a, the transmission spectrum of GDY-SA ranging from 300 to 2100 nm was also measured, demonstrating that the GDY-SA has potential for broadband optical modulation. Fig. 2b shows an enlarged transmission curve ranging from 1880 to 1940 nm, indicating that the transmittance of GDY-SA is higher than 52%. An open-aperture Z-scan technique was used to investigate the nonlinear saturable absorption capability of GDY-SA at 2 μm . The pump source was a Ti:sapphire oscillator (800 nm, 100 fs, 1 kHz) and an optical parametric amplifier system operated at the 1800 nm wavelength region. The measured nonlinear transmittance and open-aperture Z-scan curves of the GDY-SA are shown in Fig. 2c and d, which indicate the highly sensitive saturated absorption response of GDY-SA. The saturable intensity of 2.15 GW cm^{-2} and modulation depth of 62.5% were fitted.

Experimental setup

To study the saturable absorption properties of GDY-SA, a compact linear plane-concave resonator was constructed to investigate the passively Q-switched Tm:YLF

Figure 2 (a, b) Transmission spectra, and (c) nonlinear transmittance and (d) Z-scan curves of GDY-SA.

laser performance, as schematically shown in Fig. 3. The pump source applied was a 792-nm fiber-coupled laser diode with a core diameter of $105 \mu\text{m}$ and a numerical aperture of 0.22. A 1:2 imaging module was adopted to focus the pump light into the crystal. The gain medium was a *c*-cut Tm:YLF crystal with a 3 at% thulium-doped concentration and a size of $3 \times 3 \times 8 \text{ mm}^3$. Both end faces were anti-reflection coated from 790 nm to 795 nm and

Figure 3 Scheme of the Q-switched Tm:YLF laser based on the GDY-SA.

1910 nm. To remove the generated heat while pumping, the crystal was wrapped with indium foil and tightly mounted in a water-cooled copper block at the temperature of 12.5°C. The input mirror (IM) was a plane mirror, which was coated for high-transmission at 790–810 nm and high-reflection at 1900–2000 nm. The output coupler (OC) had a curvature radius of 100 nm and gave partial transmissions (T) of 2%, 5%, and 10% in the range of 1900–2000 nm. The prepared GDY-SA was inserted into the laser resonator close to the IM to obtain the large power density.

RESULTS AND DISCUSSION

The output performance of the continuous-wave (CW) and Q-switched Tm:YLF laser is displayed in Fig. 4a–d.

The output power was measured by a 30 A-SH-V1 (Israel) laser power meter. When the transmissions of OCs were 2%, 5%, and 10%, the CW maximum output power were 1.71, 1.98, and 1.88 W, corresponding to slope efficiencies of 72.6%, 81.5% and 80.9%, respectively, as shown in Fig. 4a. Theoretically, Tm^{3+} ions exhibit a cross-relaxation cooperative mechanism indicated as ${}^3\text{H}_4 + {}^3\text{H}_6 \rightarrow 2 \times {}^3\text{F}_4$. Efficiency was significantly enhanced and became close to twice the quantum efficiency of the laser due to the strong cross-relaxation process. In $\eta = \lambda_p/\lambda_l$, η is the Stokes factor, λ_p is the pump wavelength, and λ_l is the laser emission wavelength [41]. For $T = 5\%$ OC, $\eta = 792 \text{ nm}/1925 \text{ nm} \approx 41.14\%$, the CW laser efficiency was almost twice the quantum efficiency, indicating that the CW laser operation is efficient. The laser emission spectra were recorded by an optical spectrum analyzer with a wavelength resolution of 0.34 nm (MS3504i). In the CW operation, the emission spectra (Fig. 4b) exhibited a dual-wavelength for different OCs. Under the absorbed pump power of 2.62 W, the central wavelengths of $T = 2\%$, 5%, and 10% OCs were 1939.88 and 1934.76 nm, 1925.74 and 1927.13 nm, and 1909.34 and 1907.48 nm, respectively.

During the insertion of the GDY-SA into the laser cavity near the IM, a stable passively Q-switched Tm:YLF

Figure 4 Output performance of the Tm:YLF laser with different OCs. (a) CW output power vs. absorbed pump power. (b) CW laser spectrum. (c) Q-switched output power vs. absorbed pump power. (d) Q-switched laser spectrum.

laser operation was easily implemented. Under the absorbed pump power of 2.62 W, the maximum output power of 1.15 W at 1908.88 nm, 1.29 W at 1908.41 nm, and 1.19 W at 1887.79 nm were obtained for $T = 2\%$, $T = 5\%$, and $T = 10\%$ OCs, respectively, corresponding to the slope efficiencies of 47.4%, 54.8%, and 52.9%, as shown in Fig. 4c, d. The laser threshold pump power (absorbed pump power) was 0.28 W for $T = 2\%$, 0.28 W for $T = 5\%$, and 0.44 W for $T = 10\%$. The Q-switched laser spectra were blue-shifted, which could be attributed to the insertion loss introduced by the GDY-SA [16].

The pulse width, repetition rate, single pulse energy, and peak power of the Q-switched Tm:YLF laser based on GDY-SA *versus* the absorbed pump power are summarized in Fig. 5. The pulse width gradually became narrower with the augmentation of the absorbed pump power, whereas the repetition rate maintained an upward trend.

These phenomena were demonstrated in previous studies on Q-switched lasers. From Fig. 5a, b, no saturation tendency was observed for different OCs with incident pump power augmentation. Under the absorbed pump power of 2.62 W, the shortest pulse durations for $T = 2\%$, $T = 5\%$, and $T = 10\%$ OCs were 3.340, 2.207, and 2.035 μs with a maximum repetition rate of 66.45, 91.58, and 105 kHz, respectively. The relationship of the calculated single pulse energy and peak power *versus* the absorbed pump power is revealed in Fig. 5c, d. Single pulse energy and peak power show an upward trend with an enlargement of absorbed pump power. Under the highest absorbed pump power of 2.62 W, the maximum single pulse energy and peak power were calculated to be 23.08 μJ and 10.46 W for $T = 5\%$ OC. Experimental results are presented in detail in Table 1, demonstrating that optimal results were achieved by using the OC with transmission

Figure 5 (a) Pulse width, (b) repetition rate, (c) single pulse energy, and (d) peak power as functions of absorbed pump power with different OCs.

Table 1 Experimental results of the Q-switched Tm:YLF laser based on GDY-SA

OC	Max. output power (W)	Pulse width (μs)	Repetition rate (kHz)	Single pulse energy (μJ)	Peak power (W)
$T = 2\%$	1.15	3.340	66.45	17.26	5.17
$T = 5\%$	1.29	2.207	91.58	23.08	10.46
$T = 10\%$	1.19	2.035	105	11.30	5.55

of 5% under the same experimental conditions.

A 1-GHz digital oscilloscope (Tektronix DPO4104) and a fast photodiode detector (ET-5000, 250-ps rising time) were used to record the Q-switched pulse trains. For the optimal transmission of 5% under the absorbed pump power of 2.62 W, the shortest pulse profile and stable pulse trains at different timescales are shown in Fig. 6a. The neat pulse trains demonstrated that the Q-switched Tm:YLF laser based on GDY-SA was considerably stable. Fig. 6b shows the typical pulse trains recorded at 10 $\mu\text{s}/\text{div}$ under different absorbed pump power, exhibiting the feature of Q-switched laser.

Table 2 summarizes some recent experimental results obtained from passively Q-switched 2- μm bulk lasers based on different 2D materials, revealing that the Q-switched laser based on GDY-SA could generate pulsed lasers with the highest output power and higher repetition rate compared with the Tm³⁺-doped all-solid-state Q-switched lasers based on SAs (GO, ReSe₂, InSe, SnSe₂,

Ta₂NiS₅, and Ag-NR). In particular, compared with γ -GY, GDY-SA as a modulator can deliver pulses with superior characteristics in terms of output power, repetition rate, single pulse energy, and peak power. GDY-SA possesses excellent nonlinear absorbed saturable properties and is a promising optical modulator in high-output-power and high-repetition-rate pulsed laser generation.

CONCLUSIONS

In summary, GDY-SA as an optical modulator for all-solid-state diode-pumped Q-switched laser operated at 2 μm was achieved for the first time. GDY, an emerging generation of full-carbon nanomaterial, possesses sp- and sp²-hybridized carbon atoms and a direct natural band-gap, which are different from G (sp²-hybridized carbon atom structure and zero bandgap). In this work, GDY was successfully synthesized using the liquid/liquid interface method and the GDY-SA sample was prepared *via* spin-coating. The nonlinear optical response of GDY-SA was

Figure 6 (a) Q-switched temporal pulse profile and trains at different timescales under the maximum absorbed pump power with OC of 5%. (b) Typical Q-switched pulse trains recorded at 10 $\mu\text{s}/\text{div}$ under different absorbed pump powers of $T = 5\%$ OC.

Table 2 Summary of some passively Q-switched laser output performances based on 2D materials

SA	Crystal	Wavelength (nm)	Typical Q-switched laser parameters					Ref.
			Output power (W)	Pulse width (μs)	Repetition rate (kHz)	Pulse energy (μJ)	Peak power (W)	
GO	Tm:YLF	1928.23	0.379	1.038	38.33	9.89	9.53	[42]
ReSe ₂	Tm:YLF	1906.5	0.18	1.61	28.78	6.25	3.88	[43]
InSe	Tm:YLF	1985	0.205	0.21	121	1.7	8.1	[44]
SnSe ₂	Tm:YLF	1871.8	0.113	0.716	54.6	2.07	2.89	[45]
Ta ₂ NiS ₅	Tm:BYF	1910	1.1	0.313	50	22	71	[46]
Ag-NR	Tm:CaF ₂	1935.4	0.385	3.1	9.3	41.4	13.3	[47]
G	Tm:YAP	2013.5	0.362	0.735	42.4	8.5	11.56	[10]
G	Tm:YAG	2011	0.038	2.08	27.9	1.74	0.84	[11]
γ -GY	Tm:YAP	1932	0.354	0.862	76	4.7	5.5	[37]
GDY	Tm:YLF	1908.41	1.29	2.207	91.58	23.08	10.46	This work

investigated using an open-aperture Z-scan technique. Using the as-prepared GDY as SA, a passively Q-switched Tm:YLF bulk laser operation was demonstrated and the performance of pulsed laser was systematically investigated for the first time. The maximum Q-switched laser output power reached up to 1.29 W with a slope efficiency of 54.8% and maximum repetition rate of 91.58 kHz. These results demonstrate that the GDY-SA possesses superior saturable absorption properties and enormous potential for generating all-solid-state pulsed lasers with high performance. Future research will focus on achieving all-solid-state ultrashort pulsed lasers at 2 μm using GDY-SA.

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Conflict of interest The authors declare that they have no conflict of interest.

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石墨炔作为可饱和吸收体的2 μm 全固态调Q激光器

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摘要 作为一种新型单原子层的碳同素异形体, 石墨炔在二维材料领域引起了广泛兴趣, 其独特之处在于: 具有sp²和sp杂化的碳原子组成的平面结构和直接存在的天然带隙能. 本文成功制备了基于石墨炔的高质量可饱和吸收体, 并研究了其非线性可饱和吸收特性. 以石墨炔可饱和吸收体制备的脉冲激光调制器件, 实现了高效、结构紧凑的二极管泵浦全固态2微米被动调Q激光运转. 调Q激光器中心波长位于1908.41 nm处, 最大输出功率1.29 W, 斜效率高达54.8%, 最高重复频率91.58 kHz. 这是首次将石墨炔作为可饱和吸收体应用于全固态脉冲激光器中. 实验结果表明石墨炔可饱和吸收调制器件在高功率全固态脉冲激光器中具有广泛的应用前景.