Passively Q-Switched Mode-Locked Tm, Ho:CaYAlO\(_4\) Laser Based on Double-Walled Carbon Nanotube Saturable Absorber

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A passively Q-switched mode-locked (QML) operation in Tm, Ho:CaYAlO\(_4\) bulk laser was demonstrated experimentally by employing double-walled carbon nanotubes (DWCNTs) as a saturable absorber. The laser is pumped by a self-made wavelength tunable Ti:sapphire laser, and the pump threshold of Tm, Ho:CaYAlO\(_4\) laser was measured at 677 mW using transmittance of 1.5% output coupler. A stable QML operation state was achieved when the absorption pumping power reached 1,958 mW. When the pumping power reached 2.6 W, the maximum output power was 64 mw with a central wavelength of 2,085 nm, the corresponding repetition frequency of mode-locked pulse was 98.04 MHz, and the modulation depth in Q-switching envelopes is close to 100%.

Keywords: Tm, Ho:CaYAlO\(_4\) laser, passively Q-switched mode-locked, double-walled carbon nanotube, saturable absorber, resonant cavity

OCIS codes: 140.3580 (Lasers, solid-state), 140.3070 (Infrared and far-infrared lasers), 140.3380 (Laser materials), 140.4050 (Mode-locked lasers), 140.3410 (Laser resonators)

INTRODUCTION

Recently, thanks to the rapid development of laser technology, a variety of lasers, including medium infrared ultrafast lasers [1, 2], ultrafast fiber lasers [3, 4] are playing an important role in more and more fields [5, 6]. Among them, ultrafast solid-state lasers emitting around eye-safe 2 µm exhibits the potential applications in LIDAR, biomedicine, time-resolved spectroscopy, atmospheric remote sensing, nonlinear frequency conversion, optical communications, etc. [7-9]. Crystal, ceramic, and glass materials doped with thulium (Tm\(^{3+}\)), holmium (Ho\(^{3+}\)) ions [10], or Tm\(^{3+}\), Ho\(^{3+}\) co-doped are currently the most promising candidates for 2-µm mid-infrared laser sources. The passive mode-locking technique with saturable absorber (SA) [11-13] is the most widely convenient and low-cost method to obtain ultrafast lasers at 2-µm wavelength. Up to now, SAs such as semiconductor saturable absorber mirrors (SESAMs) [14-16], carbon nanotubes [17-19], graphene [20-22], and transition metal dichalcogenides (TMDs) [23, 24] have been adopted for passive Q-switching or mode-locking operations. However, SESAMs have the disadvantage of having narrow bandwidth, complex fabrication, and high cost to limit the application and development of mid-infrared ultrafast lasers. Therefore, it is very important to develop 2-µm wavelength ultrafast lasers based on new materials.

In recent years, a batch of new 2D nanomaterials with unique properties has received widespread attention. Among them, carbon nanotubes are favored as new SA in the field of ultrashort pulse laser due to their excellent electrical, optical, and mechanical properties. According to the number...
of graphite layers, carbon nanotubes are divided into single-walled carbon nanotubes (SWCNT) and multiwalled carbon nanotubes [25]. It has been reported that SWCNT-SAs can passively mode lock in 0.8–2.0 μm laser [26–28]. As the simplest multiwalled carbon nanotubes, double-walled carbon nanotubes (DWCNTs) are made of two layers of graphite, which are coiled according to a certain helix angle. The diameters of the inner and outer walls are 0.8–1.1 and 1.6–1.8 nm, respectively, and the spacing between the inner and outer layers is 0.34–0.39 nm [29]. Under the same irradiation condition, DWCNT conductivity is better due to its higher chemical stability and smaller energy gap than SWCNT [30]. Meanwhile, DWCNT has the characteristics of relatively low cost, relatively short relaxation time, and the advantages for mass production. Therefore, DWCNT-SAs has ultra-short recovery time, wider absorption band, and higher damage threshold in a 1–2-μm band [31]. Now, the reports on mode-locked DWCNT-SAs are mainly focused on the solid-state and fiber lasers at 1-μm band [32, 33], while the reports on mode-locked DWCNT-SAs at 2-μm band are few, and the output power is lower than 200 mW [34–36]. For example, Wang et al. [37] achieved a mode-locked operation of 0.98 ps in Tm3+-doped silica fiber, and Qu et al. [38] achieved a mode-locked operation in Tm:YAP laser. Over the years, our group has been devoted to the research of ultrafast laser technology in the mid-infrared band. In 2018, our group realized the Q-switched and mode-locked simultaneous operation with low threshold based on the DWCNTs in the Tm, Ho:LLF laser, and the maximum output power was 234 mW [39].

CaYAlO4(CYA) crystal belongs to the perovskite structure, which is an excellent laser medium matrix material fabricated by the Czochralski method [40]. Tm:Ho:CaYAlO4 crystals have higher absorption efficiency and wider tuning width, and their main absorption peaks are 691, 797, 1,212, and 1,694 nm [41]. Currently, there are few researches on related mode locking of this crystal. In 2018, only Zhao et al. realized continuous mode-locking operation in Tm, Ho:CaYAlO4 laser based on SESAM [10].

In this paper, a stable simultaneously Q-switched mode-locking (QML) operation was experimentally demonstrated for the first time in Tm, Ho:CaYAlO4 crystal by using DWCNTs-SA. The pump source was a self-made wavelength-tunable Ti:sapphire solid laser. With 1.5% output coupler, the maximum output power of QML is 64 mw at the central wavelength of 2,085 nm, the repetition frequency of mode-locked pulse in Q-switched envelope is 98.04 MHz, and the modulation depth was close to 100%.

**EXPERIMENTAL SYSTEM**

The experimental setup of the passive mode-locking Tm, Ho:CaYAlO4 laser is shown in Figure 1 [9]. A typical X-type five-mirror cavity structure is adopted to obtain better pattern matching effect, which is composed of a typical X-type four-mirror folded cavity and focused concave mirror. The laser is pumped by a self-made Ti:sapphire solid-state laser with an output wavelength of 798 nm. The laser crystal of Tm:Ho:CaYAlO4 with 6% Tm3+ and 0.5% Ho3+-doped was cut at the angle of Brewster. Its size is 3 × 3 × 4 mm, and the strongest absorption peak is 798 nm. In order to reduce the thermal lensing effect of crystal and mitigate the thermal load, it is necessary to cool the laser crystal to ensure the stable operation of the laser. Here, the laser crystal is wrapped in indium foil and mounted in a copper heat sink, which is cooled by circulating water at a constant temperature of 12°C [42]. The standard X-folded cavity consisted of M1, M2, M3, M4, and an output coupler (M5). In Figure 1, M1 and M2 are 2-μm pump mirrors produced by Layertec company with curvature radii of 100 and 75 mm, respectively, whose transmittance are higher than 95% in the wavelength range from 770 to 1,050 nm, and reflectivity is higher than 99.9% at 2-μm wave bands. M3 is a plane-concave reflector with the curvature radius of concave surface of 100 mm, and M4 is a planar reflector. The reflectivity of both flat concave mirror M3 and flat reflector M4 is >99.9% for oscillating light at 2-μm wave bands. M5 is an output coupler with partial transmission for oscillating light. In the experiment, the output mirror with a transmittance of 1.5% was selected to obtain a high intracavity power density. DWCNTs were inserted before the M4 plane mirror as SA. The collimated pump light is incident into the Tm:Ho:CaYAlO4 crystal by a focusing lens (f = 150 mm) with higher than 95% transmittance for 798 nm. The laser beam diameter is 54 μm on the surface of SA, which

![Figure 1](image-url)
EXPERIMENTAL RESULTS AND DISCUSSION

The absorption and output characteristics of the laser are shown in Figure 2. First, the absorption efficiency of the laser crystal of Tm,Ho:CaYAlO$_4$ is shown in Figure 2A [43]. It can be seen that the absorption efficiency of laser crystal to the pump light at 798 nm is 89.7% due to a large amount of pump light that is absorbed by the crystal when there is no laser running in the cavity. When continuous wave (CW) operation in the cavity is realized, the absorption efficiency of the laser crystal increases to about 91.6% due to the large number of upper-level particles returning to the lower level under stimulated radiation. After inserting the DWCNT-SA into the cavity, the operating state of QML is achieved, and the absorption efficiency of the laser crystal did not change significantly and still remained around 91.6%.

Next, the average output power as a function of the absorbed pump power under CW and QML is plotted in Figure 2B. In the experiment, 1.5% output coupling mirror is used. When the laser is in CW operation, the laser threshold power is 249 mW, the maximum output power is 301 mW, and the corresponding slope efficiency is 14.97%. When DWCNT-SA was inserted before M4 in the cavity, the laser threshold power increased to 677 mW. When the absorbed pump power reached 1,958 mW, laser entered a stable QML operation, and the maximum output power under the same conditions was 64 mW, which has a corresponding slope efficiency of 4.44%. Here, the main reason why we choose 1.5% output coupler is that it can provide high intracavity power to start QML.

Figure 3 shows the typical spectra of the mode-locked pulse measured with a spectrometer (AvaSpecNIR256-2.5TEC) [9]. As can be seen from Figure 3, the central wavelength of a mode-locked laser pulse is 2,085 nm, and the full width at half-maximum bandwidth is about 13 nm. A 2-µm fast photodiode (ET-5000) was used to connect a 200-MHz digital oscilloscope (RIGOL, DS4024) to detect QML pulse sequences. Figure 4 shows the QML pulse sequences, which is obtained by scanning times of (a) 1 ms, (b) 100 µs, and (c) 10 ns. When the output power reaches the maximum, the pulse width of the Q-switched envelope is 12 µs, the repetition frequency is 83.33 kHz, the frequency of the mode-locked pulse is 98.04 MHz, and the modulation depth of the mode-locked pulse is close to 100%, which is consistent with the theoretical repetition frequency corresponding to the 1.5-m cavity length.

QML is in the transition state from Q-switch to CW mode locking [44–46], Since an autocorrelator is only suitable for measuring the pulse width of a CW mode-locked pulse, a QML pulse cannot obtain autocorrelation envelope because of the envelope modulation of kilohertz, so we can only estimate the pulse duration roughly in theory.

Hence, formula (1) is used to calculate the width of the mode-locked pulse [47].

\[ t_m = \sqrt{t_r^2 + t_p^2 + t_o^2} \] (1)
Here, \( t_m \) is the rising edge time of the measured mode-locked pulse, \( t_r \) is the rising edge time of the actual mode-locked pulse, \( t_p \) is the rising edge time of the photodetector, and \( t_0 \) is the rising edge time of the oscilloscope. In the experiment, the rising edge time of the mode-locked pulse is about 2.1 ns, and the rising edge time of the photodetector is about 35 ps. \( t_0 \) can be estimated as 2,000 ps using formula (2) as follows.

\[
t_0 \times W_b(200 MHz) = 0.35 \sim 0.4
\]

Among them, \( W_b \) is the bandwidth of the oscilloscope, which is 200 MHz in the experiment. Therefore, it can be calculated that the rise time of a mode-locked pulse is about 639.35 ps. Since the actual mode-locked pulse width is about 1.25 times the rising edge time, it is calculated as 799.2 ps.

### CONCLUSION

A passively Q-switched mode locking operation is realized experimentally by using DWCNT-SA in Tm,Ho:CaYAlO\(_4\) all-solid laser for the first time. After DWCNT-SA was added into the resonator cavity, the pump threshold of Tm,Ho:CaYAlO\(_4\) solid-state laser was measured as 677 mW using the transmittance of 1.5% output coupler. When the absorption pumping power reached 1,958 mW, Tm,Ho:CaYAlO\(_4\) solid state laser entered a stable QML operation state. When the pump power was 2.6 W, the maximum output power was 64 mw at the central wavelength of 2,085 nm, the mode-locked pulse repetition frequency is 98.04 MHz, and the modulation depth is close to 100%. The experimental results show that DWCNT-SA can be used as a quick starting element for passively QML solid state laser of 2-\(\mu\)m band, which has an important development and application value.

### DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/supplementary material.

### AUTHOR CONTRIBUTIONS

YZ was the author of the experimental scheme and the general director of the project. WL was the specific guidance for postgraduates during the experiment. DQ, who is a doctoral student, and RS and CC, who are graduate students of the research group, have implemented the experimental scheme.

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### REFERENCES

1. Hui ZQ, Xu WX, Li XH, Guo PL, Zhang Y, Liu JS. CuO\(_x\)S nanosheets for ultrashort pulse generation in the near-infrared region. *Nanoscale*. (2019) 11:6045–51. doi: 10.1039/C8NR00080A

2. Ma J, Qin ZP, Xie GQ, Qian LJ, Tang DY. Review of mid-infrared mode-locked laser sources in the 2.0 \(\mu\)m–3.5 \(\mu\)m spectral region. *Appl Phys Rev*. (2019) 6:021317. doi: 10.1063/1.5037274

3. Liu X, Han D, Sun Z, Zeng C, Lu H, Mao D, et al. Versatile multi-wavelength ultrafast fiber laser mode-locked by carbon nanotubes. *Sci Rep*. (2013) 3:2718. doi: 10.1038/srep02718

4. Li XH, Wu K, Sun ZP, Meng B, Wang YG, Wang YS, et al. Single-wall carbon nanotubes and graphene oxide-based saturable absorbers for low phase noise mode locked fiber lasers. *Sci Rep*. (2016) 6:25266. doi: 10.1038/srep25266

5. Duan XM, Chen C, Ding Y, Yao BQ, Wang YZ. Widely tunable middle infrared optical parametric oscillator pumped by the q-switched Ho:GdVO\(_4\) laser. *Chin Phys Lett*. (2018) 35:054205. doi: 10.1088/0256-307X/35/5/054205

6. Zhao Y, Guo P, Li X, Jin Z. Ultrafast photonics application of graphene in optical communication region. *Carbon*. (2019) 149:336–41. doi: 10.1016/j.carbon.2019.04.075

7. Wang J, Sramek C, Paulus YM, Lavinsky D, Schuele G, Anderson D, et al. Retinal safety of near-infrared lasers in cataract surgery. *J Biomed Opt*. (2012) 17:959001. doi: 10.1117/1.JBO.17.9.959001

8. Van Leeuwen TG, Jansen ED, Motamedi M, Welch AJ, Borst, C. Excimer laser ablation of soft tissue: a study of the content of rapidly expanding and collapsing bubbles. *IEEE J Quant Electron*. (2002) 38:1339–45. doi: 10.1109/3.303700

9. Keller U, Weingarten KJ, Kartner FX, Kopf D, Braun B, Jung ID, et al. Semiconductor saturable absorber mirrors (SESAMs) for femtosecond to nanosecond pulse generation in solid-state lasers. *IEEE J Sel Top. Quantum Electron*. (1996) 2:435–53. doi: 10.1109/2944.517143

10. Zhao Y, Wang Y, Zhang X, Mateos X, Pan ZB, Loikoet P, et al. 87 fs mode-locked Tm, Ho:CaYAlO\(_4\) laser at \(\sim 2043\) nm. *Opt Lett*. (2018) 43: 915–8. doi: 10.1364/OL.43.000915
11. Ling WJ, Xia T, Dong Z, You LF, Zhang MX, Zuo YY, et al. Passively mode-locked Tm:HeXF laser at 1895 nm. J. Opt. (2019) **48**:209–13. doi: 10.1088/1464-4258/aab5de

12. Kong LC, Xie GQ, Yuan P, Qian LJ, Wang SX, Yu HH, et al. Passive Q-switching and Q-switched mode-locking operations of 2-μm Tm:CLNGG laser with MoS2 saturable absorber mirror. Photon. Res. (2015) **4**(A47–A50. doi: 10.1364/PRJ.3.000A47

13. Liu JS, Li XH, Guo YX, Shi ZJ, Feng TC, et al. SnSe2 nanosheets for sub-picosecond harmonic mode locked pulse generation. Small. (2019) 19:1902811. doi: 10.1002/smll.201902811

14. Li JF, Luo HY, He YL, Liu Y, Zhang L, Zhou KM, et al. Semiconductor saturable absorber mirror passively Q-switched 2.97 μm fluoride fiber laser. Laser Phys. Lett. (2014) **11**:065102. doi: 10.1063/1.4861116

15. Yamashita S, Inoue Y, Maruyama S, Murakami Y, Yaguchi H, Jablonski M, et al. Saturable absorbers incorporating carbon nanotubes directly synthesized onto substrates and fibers and their application to mode-locked fiber lasers. Opt. Lett. (2009) **29**:1581–83. doi: 10.1364/OL.29.001581

16. Liu J, Li YQ, Zheng LH, Su LB, Xu J, Wang YG, Passive Q-switched mode locking of a diode-pumped Tm: SSO laser near 2 μm. Laser Phys. (2013) 10:105812. doi: 10.1088/1612-2011/10/105812

17. Chen XT, Zhao SZ, Zhao J, Yang KJ, Li XH, Guo YX, Qyyum A, Shi ZJ, Feng TC, et al. 2D ductile dimensional nanosheets at 2 μm. Nano Lett. (2013) 13:3518–22. doi: 10.1021/nl401652t

18. Feng JJ, Li XH, Shi ZJ, Zhen C, Li XW, Leng DY, et al. Passively Q-switched Tm:YAlO3 laser based on WS2/MoS2 two-dimensional nanosheets at 2 μm. J. Mod. Opt. (2020) **59**:1825–8. doi: 10.1080/09500340.2012.747633

19. Ma J, Xie GQ, Lv P, Gao WL, Yuan P, Qian LJ, et al. Wavelength versatile graphene-gold film saturable absorber mirror for ultra broadband mode-locking of bulk lasers. Sci. Rep. (2014) **4**:5016. doi: 10.1038/srep05016

20. Li XH, Yu XH, Sun ZP, Yan ZY, Sun B, Cheng YB, et al. High-power graphene mode-locked Tm/Ho co-doped fiber laser with evanescent field interaction. Sci. Rep. (2015) 5:16624. doi: 10.1038/srep16624

21. Ma YE, Sun HY, Ran BF, Zhang SC, Zhang H, Tittel FK, et al. Passively Q-switched Tm:YAO3 laser based on WS2/MoS2 two-dimensional nanosheets at 2 μm. Opt. Laser Technol. (2020) **126**:106084–9. doi: 10.1016/j.optlastec.2020.106084

22. Ling WJ, Xia T, Dong Z, Liu Q, Wang YG, Passively Q-switched mode-locked Tm:Ho:LLF laser with a WS2 saturable absorber. Acta Phys. Sin. (2017) **66**:927–7. doi: 10.7498/aps.66.20177174

23. Feng C, Liu DH, Liu J. Graphene oxide saturable absorber on golden reflective film for Tm:YAP Q-switched mode-locking laser at 2 μm. J. Mod. Opt. (2015) **62**:19624. doi: 10.1080/1050250x.2012.747633

24. Ma J, Xie GQ, Lv P, Gao WL, Yuan P, Qian LJ, et al. Wavelength versatile graphene-gold film saturable absorber mirror for ultra broadband mode-locking of bulk lasers. Sci. Rep. (2014) **4**:5016. doi: 10.1038/srep05016

25. Li XH, Yu XH, Sun ZP, Yan ZY, Sun B, Cheng YB, et al. High-power graphene mode-locked Tm/Ho co-doped fiber laser with evanescent field interaction. Sci. Rep. (2015) 5:16624. doi: 10.1038/srep16624

26. Ma YE, Sun HY, Ran BF, Zhang SC, Zhang H, Tittel FK, et al. Passively Q-switched Tm:YAO3 laser based on WS2/MoS2 two-dimensional nanosheets at 2 μm. Laser Phys. Lett. (2020) **126**:106084–9. doi: 10.1016/j.optlastec.2020.106084

27. Ling WJ, Xia T, Dong Z, Liu Q, Wang YG, Passively Q-switched mode-locked Tm:Ho:LLF laser with a WS2 saturable absorber. Acta Phys. Sin. (2017) **66**:927–7. doi: 10.7498/aps.66.20177174

28. Feng C, Liu DH, Liu J. Graphene oxide saturable absorber on golden reflective film for Tm:YAP Q-switched mode-locking laser at 2 μm. J. Mod. Opt. (2015) **62**:19624. doi: 10.1080/1050250x.2012.747633

29. Ma J, Xie GQ, Lv P, Gao WL, Yuan P, Qian LJ, et al. Wavelength versatile graphene-gold film saturable absorber mirror for ultra broadband mode-locking of bulk lasers. Sci. Rep. (2014) **4**:5016. doi: 10.1038/srep05016

30. Li XH, Yu XH, Sun ZP, Yan ZY, Sun B, Cheng YB, et al. High-power graphene mode-locked Tm/Ho co-doped fiber laser with evanescent field interaction. Sci. Rep. (2015) 5:16624. doi: 10.1038/srep16624

31. Ma J, Xie GQ, Lv P, Gao WL, Yuan P, Qian LJ, et al. Wavelength versatile graphene-gold film saturable absorber mirror for ultra broadband mode-locking of bulk lasers. Sci. Rep. (2014) **4**:5016. doi: 10.1038/srep05016

32. Li XH, Yu XH, Sun ZP, Yan ZY, Sun B, Cheng YB, et al. High-power graphene mode-locked Tm/Ho co-doped fiber laser with evanescent field interaction. Sci. Rep. (2015) 5:16624. doi: 10.1038/srep16624

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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