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$Ti_3C_2T_x$ thin film as a saturable absorber for passively generating Q-switched pulses in thulium-doped fiber laser cavity

M. A. Buntat[1], A. H. A. Rosol[2], M. F. M. Rusdi[2], A. A. Latif[1], M. Yasin[3], S. W. Harun[2]

[1]Fakulti Kejuruteraan Elektronik dan Kejuruteraan Komputer, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia, Malaysia

[2]Photonics Engineering Laboratory, Department of Electrical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

[3]Department of Physics, Faculty of Science and Technology, Airlangga University, Surabaya, Indonesia

yasin@fst.unair.ac.id, swharun@um.edu.my

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We demonstrated a Q-switched thulium-doped fiber laser (TDFL) based on Mxene $Ti_3C_2T_x$ saturable absorber (SA) as Q-switcher. $Ti_3C_2T_x$ was obtained using selective etching and embedded into polyvinyl alcohol (PVA) film. As the film was added into a TDFL cavity, a stable Q-switched pulse train operating at 1996 nm was produced within a single mode 1552 nm pump power range from 161.8 to 237.1 mW. When the pump power was varied within this range, the repetition rate increased from 19.6 to 33.3 kHz while the pulse width decreases from 6.71 to 3.55 μs. To the best of our knowledge, this is the first report of a $Ti_3C_2T_x$ SA for passively generating Q-switched pulses in the 2 μm wavelength region.

Keywords: MXene $Ti_3C_2T_x$, Q-switching, thulium doped fiber, energy efficiency.

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1. Introduction

Mid-infrared light sources operating at around 2 μm have drawn a great deal of interest in recent years due to their potential applications in various areas, including biomedical diagnostic [1], atmospheric gas analysis [2], free-space communication [3], and THz generation [4]. To date, many laser sources have proposed and developed for operation in 2 μm region, including the quantum cascaded based solid-state lasers and thulium or holmium doped fiber lasers. In this regard, fiber-based laser systems are preferable, due to their numerous advantages: they are compact, alignment free, compact, low maintenance cost, and featuring excellent heat dissipation etc.

Thulium doped fiber (TDF) has a broad gain bandwidth, ranging from 1800 nm to 2100 nm, and thus, it offers opportunities for short pulse generation and wide tuneability. For instance, Q-switched TDF lasers (TDFLs) were widely proposed and demonstrated for various industrial and scientific applications, such as LIDAR [5], nonlinear frequency conversion [6] and supercontinuum generation in mid-infrared region [7]. They could be achieved passively by using an external controller such as modulator as Q-switcher to provide variability of laser performance including repetition rate and pulse duration. However, the modulator is a bulky component with complex electronics and thus would be a barrier towards robust and portable systems design. Therefore, the passive technique utilizing physical saturable absorber (SA) is preferable for Q-switching. This technique is more desirable due to its flexible design, inexpensiveness and less complexity.

Many SAs have been reported for use in pulse generation via Q-switching such as semiconductor saturable absorber mirror (SESAM) [8], carbon nanotube (CNT) [9, 10] and graphene [11, 12]. SESAM offers high stability during the high intensity of light but operating in narrow bandwidth regime. Due to this limitation, more research has focused on CNT and graphene, that can be fabricated in lower cost and operated in broad bandwidth regime. Recently, the groups of topological insulators, transition metal dichalcogenide, noble metal nanoparticle [13] and black phosphorus [14] have also been used as a Q-switcher.

Recently, a ternary metal carbide/nitride so-called MXene has also gained interest as a new member for 2D nanomaterial class [15]. It has a general formula of $M_{n+1}X_nT_x$, where M, X and T is a transition metal, carbon or nitrogen (with $n = 1, 2, 3\dots$), and face-termination group likes oxygen or fluorine, respectively. MXene can be produced by selectively etching of MAX layer [16, 17]. The MXene has been previously utilized in various photonic and nanoscience applications due to its excellent optical, thermal and physical properties [18]. It has a small band gap size, excellent metallic conductivity, and hydrophilic nature of its surface, which are advantages for many applications. Mxene also has an excellent saturable absorption characteristic, which is suitable for photonic diodes [19]. It is also reported that the MXene also exhibits the zero-bandgap structure, which has the potential to be used for the broadband optical device [20]. Here, we proposed the use of Mxene $Ti_3C_2T_x$ film for realizing Q-switching operation in Thulium-doped fiber laser (TDFL). The Mxene $Ti_3C_2T_x$ obtained by a simple selective etching technique was mixed with polyvinyl alcohol (PVA) solution to fabricate the SA thin film. The film was slot in between two ferrules and inserted into a ring TDFL cavity to function as a Q-switcher.

2. Fabrication and characterization of SA

The MAX Ti_3AlC_2 and hydrofluoric acid were obtained respectively from Shanghai Winfay Industry Ltd and Merck KGaA while the PVA powder was purchased from Sigma Aldrich. We performed selective etching of $Ti_3C_2T_x$ with hydrofluoric acid to fabricate MXene $Ti_3C_2T_x$. The etching process was conducted at room temperature for six hours. Then, we obtained the sample of $Ti_3C_2T_x$ through vacuum-assisted filtration by polyvinyl difluoride filter membrane. It was dried with a vacuum oven at 80 °C for 24 hours for formation of clay. The powder was collected and put into a clean beaker. Next, 20 mg of $Ti_3C_2T_x$ powder was mixed with 10 mg of PVA powder and 40 ml of distilled water. The mixture was then agitated at room temperature for 24 hours. We used the ultrasonic bath for 2 hours to separate the agglomerate of $Ti_3C_2T_x$ particles by cavitation. Consequently, about 5 mL of the $Ti_3C_2T_x$ solution was placed inside a clean petri dish and left for 48 hours to dry. Finally, the dried MXene $Ti_3C_2T_x$-film was peeled out for use as Q-switcher.

Figures 1(a) and (b) show the actual and FESEM images of the prepared $Ti_3C_2T_x$ PVA film, respectively. The FESEM image reveals that the $Ti_3C_2T_x$ elements are uniformly distributed in the polymer composite. The prepared $Ti_3C_2T_x$ thin film was then cut to a tiny piece and placed onto a fiber ferrule after depositing index-matching gel onto the fiber end as shown in Fig. 1(c). The ferrule was then linked to another clean ferrule via a fiber adaptor to assemble a transmissive type of SA as shown in Fig. 1(d). The nonlinear absorption of the MXene $Ti_3C_2T_x$ film was also characterized by utilizing a twin balance detection approach. It is worthy to note that the saturable intensity, saturable absorption, and non-saturable absorption of the film were measured to be about 20 MW/cm^2, 4.8 and 3.6 %, respectively.

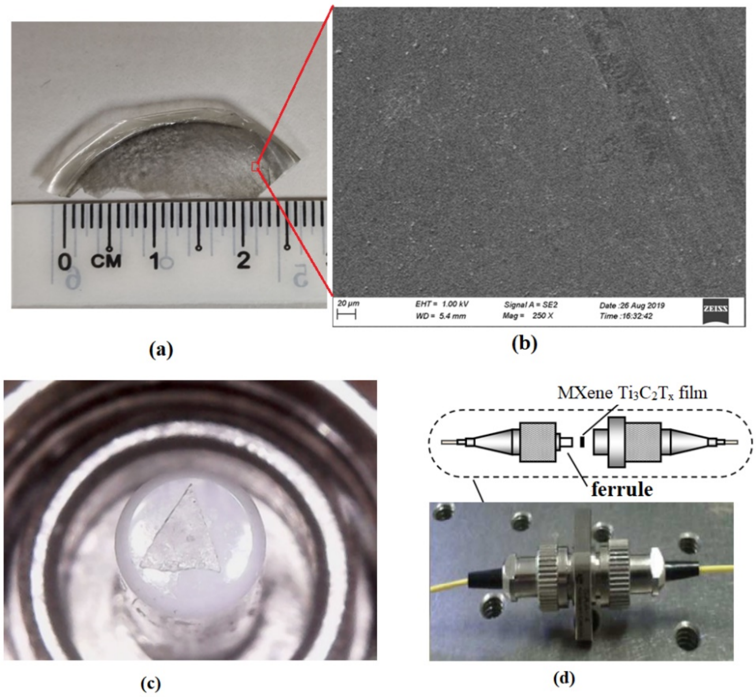


FIG. 1. $Ti_3C_2T_x$ PVA film (a) real image (b) FESEM image (c) the attachment of the film on the fiber ferrule, (b) construction of transmissive type SA

3. Cavity setup for Q-switched TDFL

A ring cavity TDFL was built to examine the performance of the proposed $Ti_3C_2T_x$ based SA as a Q-switcher, as illustrated in Fig. 2. The total cavity length was estimated to be around 13 m. In the experiment, a 5 m thulium-doped fiber (produced by Nufern) with a nominal absorption of about 27 and 9.3 dB/m at 793 and 1180 nm, respectively, was used as the active medium. The TDF was pumped via wavelength division multiplexer (WDM) by a homemade erbium-ytterbium co-doped fiber laser (EYDFL) operating at 1552 nm up to a maximum power of 1.8 W. 10 % of the oscillating laser was coupled out from the laser cavity by a 10 dB output coupler. 90 % of the oscillating laser was retained within the ring cavity. The spectral and temporal characteristics of the Q-switched laser were analyzed utilizing a mid-infrared spectrometer (Miriad Technologies) and a 7.8 GHz photodetector (ELECTRO-OPTICS TECHNOLOGY, INC., ET-3500F) followed by a 350 MHz digital oscilloscope (GWINSTEK, GDS-3352), respectively. The electrical spectrum of the Q-switched TDFL was measured by a RF spectrum analyzer.

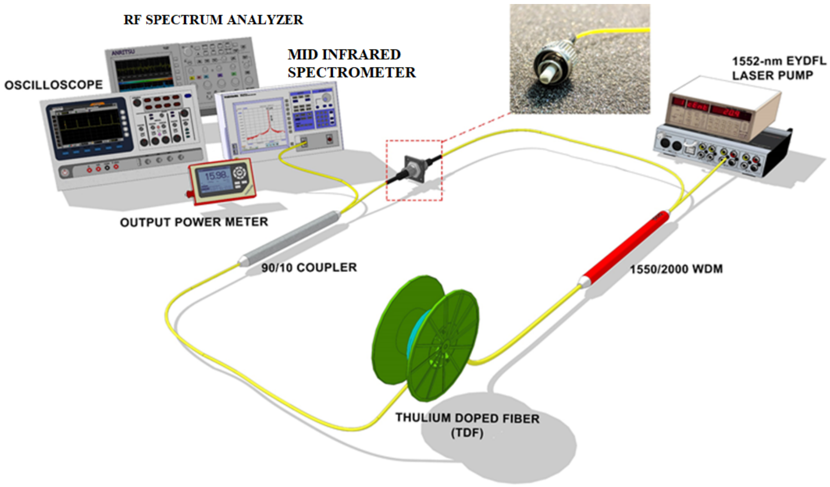


FIG. 2. Configuration of the proposed $Ti_3C_2T_x$ based Q-switched TDFL

4. Result and discussion

To prove that the Q-switching operation here was induced by $Ti_3C_2T_x$ thin film, we intentionally removed the thin film from the TDFL cavity. No Q-switching operation could be observed by the current laser setup even though the pump power was varied across the entire range and the cavity arrangement was manipulated. With the $Ti_3C_2T_x$, the Q-switching behavior was started in the laser as we tuned power of the 1552 nm pump power within a range from 161.8 to 237.1 mW. The characteristics of the Q-switching operation of the fiber laser is summarized in Fig. 3. Fig. 3(a) shows the spectral characteristic of the laser. The laser operated at 1996 nm due to the transition of thulium ions from $^3F_4$ to $^3H_6$ energy level as the TDF was pumped at a wavelength of approximately 1552 nm. Fig. 3(b) shows the measured oscilloscope trace within 1000 μs time scale when 1552 nm pump was fixed at the threshold of 161.8 mW. It shows a peak-to-peak period of 51 μs, which can be translated to the repetition rate of 19.6 kHz. It is observed that the pulse period reduces with the increase of pump power, corresponding to typical pulse behavior of Q-switched laser. Fig. 3(c) illustrates the RF spectrum of the Q-switched pulse train at the maximum pump power of 237.1 mW. The fundamental peak was obtained at 33.3 kHz, which corresponds to the repetition rate of the laser at 237.1 mW pump power. The signal to noise ratio (SNR) of the fundamental frequency is measured to be about 31 dB above the noise level, which indicates that stable Q-switched pulses were being produced. The stability of the Q-switching operation by $Ti_3C_2T_x$ film was further confirmed by the observation of many harmonics within a wideband RF spectrum.

The repetition rate and pulse width of the $Ti_3C_2T_x$ Q-switched fiber laser can be tuned by varying the 1552 nm pump power as shown in Fig. 4(a). The pulse repetition rate increases almost linearly from 19.6 kHz at threshold pump of 161.8 to 33.3 kHz at the maximum power of 237.1 mW. On the other hand, the pulse width decreases from 6.71 to 3.55 μs with the increase of pump power within the same range. This phenomenon is due to a strong pumping, which induced gain compression effect; a similar trend has been commonly observed in SA-based Q-switched fiber lasers. The relation between the average output power and pump power is presented in Fig. 4(b). The output power rises with pump and the maximum output power of 3.7 mW was obtained at 237.1 mW pump power. The slope efficiency of the laser was 1.84 %. No residual pump was also observed at 1552 nm, which indicates the pump light was fully absorbed by the active TDF. The pulse energy was calculated to be around 111 nJ at 237.1 mW pump power. The performance of the Q-switched laser could be improved by reducing the total cavity loss by optimizing the SA and gain medium parameters. Finally, a performance comparison between the previously demonstrated Q-switched TDFLs with SAs and our laser is presented in the Table 1. Comparatively, the laser generated in this work has lower pulse energy, which is mainly caused by its small output power. However, it is obvious from the table that our laser exhibited better

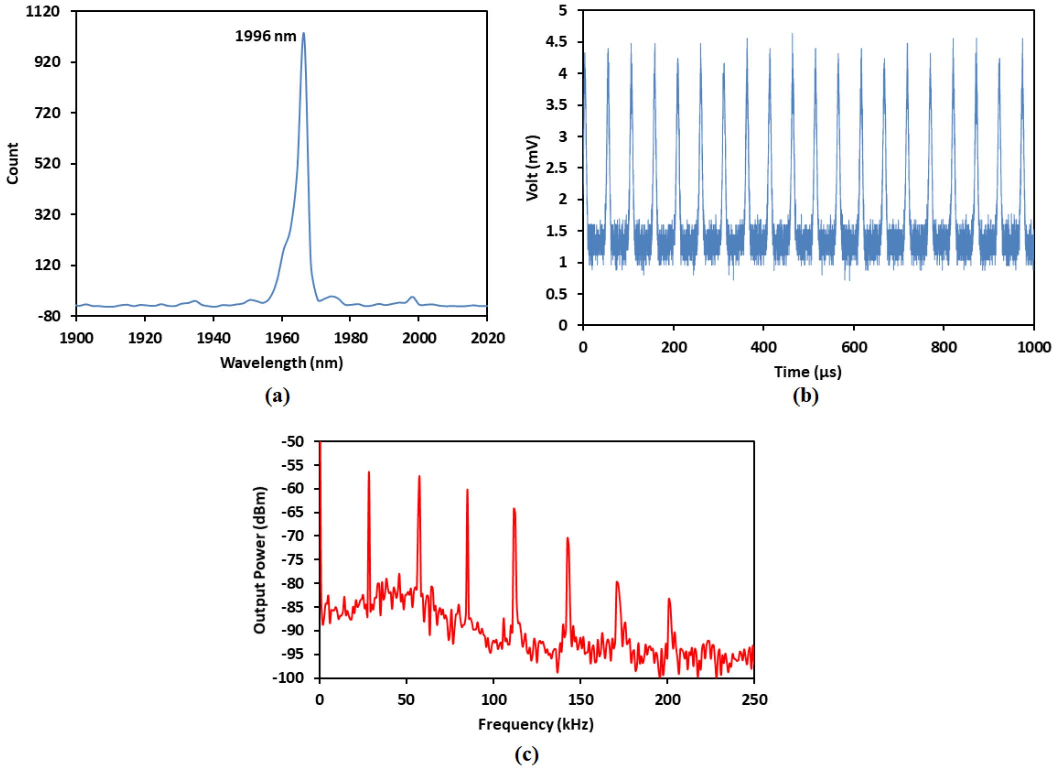


FIG. 3. (a) spectral (b) temporal and (c) frequency characteristics of the Q-switched TDFL with $Ti_3C_2T_x$ SA

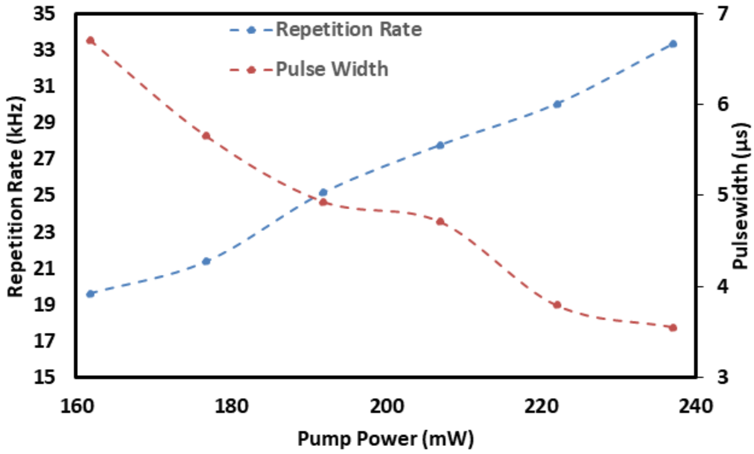
TABLE 1. Comparison of proposed laser performance against other works on Q-switched TDFL

SAs	Center Wavelength (nm)	Max. Repetition Rate (kHz)	Minimum Pulse Width (μs)	Max Pulse Energy (nJ)	Reference
CNT	1890	7.2	3.2	—	[21]
Al_2O_3	1950	40.3	5.3	173.5	[22]
Antimony	1947	23.5	4.9	120.1	[23]
Alcohol	1885	66.7	1.5	930	[24]
$Ti_3C_2T_x$	1996	33.3	3.55	111	This work

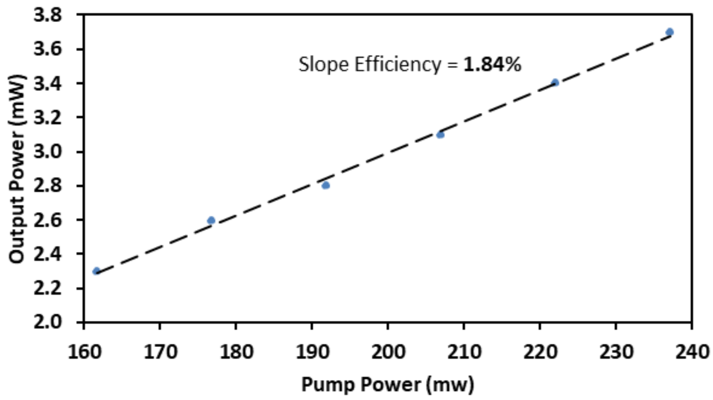
performance than antimony in terms of repetition rate and pulse width. The proposed laser also operated at the longest wavelength in the thulium region at 1996 nm.

5. Conclusion

We have successfully generated a Q-switched pulses train in TDFL cavity using a newly developed Mxene $Ti_3C_2T_x$ based SA. The $Ti_3C_2T_x$ was prepared from MAX Ti_3AlC_2 based on a selective etching technique. It was then embedded into PVA to form a SA film. By incorporated the SA into TDFL cavity, a Q-switched pulse train operating at 1996 nm was produced with a tuneable repetition rate and pulse width. The repetition rate can be tuned from 19.6 to 33.3 kHz by changing the 1552 nm pump power from 161.8 to 237.1 mW. The pulse width decreases from 6.71 to 3.55 μs with the increase of pump power within the same range. This experiment demonstrated the promising potential of $Ti_3C_2T_x$ material as a kind of SA for pulse generation in 2-micron wavelength region.



(a)



(b)

FIG. 4. (a) The repetition rate and pulse width, and (b) average output power performances of the laser at various pump power values

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