Graphene-Molybdenum Disulphide Chitin Nanocomposite Based Passive Q-switcher

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Received March 03, 2022; accepted March 31, 2022; published March 31, 2022

Abstract—A simple fabrication of graphene-MoS_2 nanocomposite, as well as individual graphene and molybdenum disulphide (MoS_2) film has been done through a liquid phase exfoliation method using chitin as a binder. All of the developed films are integrated as a passive Q-switcher in an Erbium doped fiber laser. The graphene-MoS_2 nanocomposite based passive Q-switcher is generated by a pulsed fiber laser with the shortest width of 1.63 μs and the highest signal to noise ratio of 51.01 dB. The graphene-MoS_2 nanocomposite films show a better saturable absorption response compared to an individual graphene-chitin and MoS_2-chitin based passive Q-switcher.

A Q-switched laser has gained strong commercial interest and wide photonic application. A passive Q-switching technique with a saturable absorber (SA) offers a more compact, simple and low-cost route to generating a pulsed laser as compared to its bulky, complex and costly active counterpart [1]. An ideal SA must possess several qualities such as low optical loss, strong nonlinear optical properties, tunable energy band gap, broadband wavelength range, and easy integration into an optical system [2]. In recent years, numerous studies have been carried out implementing quite a number of SA's materials such as carbon nanotubes, graphene, black phosphorous, transition metal dichalcogenide (TMDC), topological insulator (TI) and most recent MXene [3]. Drifted by the gapless nature of energy band gap structure with Dirac cones characteristic, graphene has shown a ultrashort-pulse fiber lasers to be of extremely wide broadband wavelength range from ultraviolet (UV) to mid-infrared [4]. In addition to graphene, a 2D layered material TMDCs compound has demonstrated excellent characteristic based on the *d*-electron number of the transition metal [5]. These TMDCs material exhibits a layer dependent tunable and indirect energy gap properties ranging from 1.6 eV for a monolayer to 0.65 eV for a bulk material which allowed implementing SA from mid to near infrared region wavelength.

The interesting properties of an individual 2D material have aroused considerable interest for realization of a hybrid SA consisting of two or more low-dimensional material groups. In recent years, 2D heterostructures such as WSe_2/MoS_2 and graphene-Bi_2Te_3 have been studied via chemical vapor deposition (CVD) and showed properties with improved performance. The studies by [6] have shown that some pulsed laser parameters of a graphene-$BiTe_3$ heterostructure can be tuned depending on the Bi_2Te_3 coverage and demonstrate better Q-switching pulse generation.

In parallel with research on material's properties, rapid progress has been made in synthesizing 2D materials. The scotch-tape method [7] produces high quality 2D nanoflakes but offers a rather small production scale. Later, a large production scale material with a high structural quality via CVD was demonstrated, but its drawback was high initial cost and operation at high temperature involving complex procedures. Alternative to that, a liquid-phase exfoliation (LPE) approach can provide a low-cost route while preserving high-quality material production in scalable conditions at room temperature. Although it shows high dependency of obtaining 2D flakes to its bulk crystal form, an LPE method becomes a favorable choice among researchers. In this paper, liquid-phase exfoliation, as a very convenient and cost-effective approach, was adopted to synthesize a graphene-MoS_2 hybrid material.

A bio-host polymer, chitin, is also introduced in this work for the fabrication of SA film. As an alternative to synthetic polymer usage, this will contribute to a greener pathway.

A graphene filament is one of the newly established starting materials for graphene flakes as reported in [8]. In order to fabricate the SA, a graphene suspension was first prepared by extruding a graphene-polylactic acid (PLA) filament (Conductive Graphene Composites, Black Magic 3D) through a 3D printer nozzle of 0.4 mm in order to reduce the diameter to 400 μm for further process. The filament is composed of graphene platelets (30-40 %), polylactic acid (25-35 %), Tris(nonylphenyl)phosphite (5-10 %) and carbon fibers (5-10 %). The extruded filament weighed around 25 mg and was mixed with 10 ml of tetrahydrofuran (THF) to dissolve the PLA and produce graphene slurry in THF. The graphene-PLA-THF suspension was then ultra-sonicated for 10 minutes by using an ultrasonic bath. To produce an MoS_2 suspension, 5 mg of MoS_2 powder (Sigma Aldrich, purity 99 %, particles diameter ~ 100 nm) was added into 5 mL of the THF solution and stirred using a magnetic stirrer at 1200 rpm and ambient temperature for two hours. The chitin

host polymer which is derived from oyster mushroom (*Pleurotus Ostreatus*) was reported elsewhere by Wan Nawawi *et al.* [9]. Individual graphene-chitin based film SA was developed by mixing homogenous graphene-PLA-THF and chitin in a one-to-one ratio, undergoing an ultrasonic process for two hours before being poured in a petri dish, to remain for two days. The same process was repeated to produce an MoS_2-chitin based SA ~~was developed~~ by mixing a homogenous MoS_2-THF suspension with chitin in a one-to-one ration ~~to produce~~. Meanwhile, the processed solution of graphene-MoS_2 nanocomposite was obtained by mixing graphene-THF, MoS_2-THF and chitin in a controlled ratio with chitin, at least, of 50% volume to ensure the peeling ability of a developed film. The mixed solution will undergo an ultrasonication process for three hours. A large amount of ratio and time for the sonication process ensured a well-homogenized dispersion form and allowed exfoliation of bulk crystal into nanosheets, which involved weakening the van der Waals interaction from the shockwaves and microjets production. The prepared mixed solutions were poured into 35 mm × 35 mm circular shape petri dishes full to the brim. Slow evaporation at room temperature for 36 hours resulted in free-standing SA films of graphene-chitin, MoS_2-chitin and graphene-MoS_2-chitin.

Figure 1 shows materials characterization of the developed individual film of graphene-chitin, MoS_2-chitin and graphene-MoS_2-chitin.

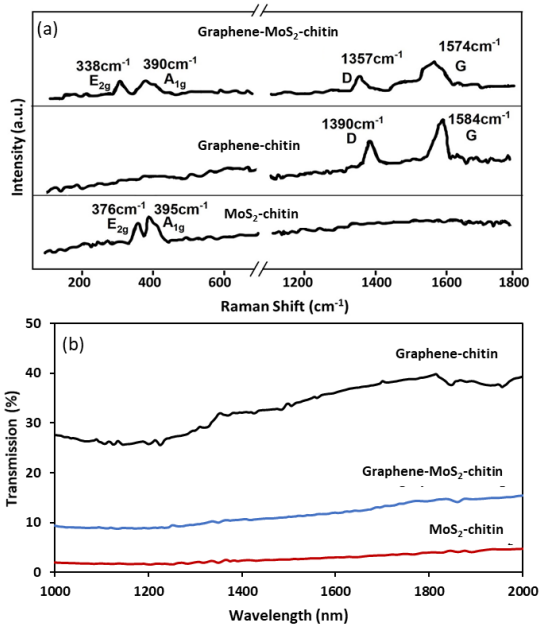

Fig. 1. Material characterization (a) Raman spectroscopy and (b) transmission properties.

A typical Raman spectrum of 532 nm laser excitation was performed and illustrated in Fig. 1(a). The Raman peaks of graphene are located at high frequency range with two characteristic peaks of G-band (1574 cm^{-1}) and 2D band (1357 cm^{-1}) which corresponded to the stretching of C-C bonding and sp^2 carbon hybridization respectively. Meanwhile, a lower frequency range from 200 cm^{-1} to 600 cm^{-1} is observed for Raman peaks of MoS_2. The characteristic peaks of MoS_2 at two points 338 and 390 cm^{-1} are consistent with the A_{1g} and E_{2g} vibrational modes respectively. In comparison to pure graphene, the G peak and 2D peak have obvious shifts which suggest the formation of hybrid interlayer interaction between graphene and other materials. The co-existence of these Raman peaks in the prepared sample are direct evidence of successful formation of a graphene hybrid composite. The transmission spectrum of the SA films as measured by using a UV-Vis-NIR spectrophotometer was shown in Fig. 1(b). linear optical transmission is observed from 1000 nm to 2000 nm with an average transmission of 10 % for graphene-MoS_2-chitin SA.

Figure 2 illustrates the schematic Erbium doped fiber laser in a ring cavity and the integration of the developed film as a passive Q-switcher for pulsed laser generation. A 980 nm laser diode (LD) was used to pump the 2.4 m Erbium-doped fiber through a 980/1550 wavelength division multiplexer (WDM). To ensure unidirectional light propagation, an isolator was equipped into the cavity.

The signal was passed through an 80/20 coupler for output servation where 80% of the signal was retained throughout the cavity while another 20% was tapped out as output for data collection. The developed saturable absorber was sandwiched between two fiber ferrules, aided by index matching gel before being integrated within the cavity as passive Q-switcher. For data collection, the propagated light was observed using a Yokogawa AQ6370B Optical spectrum Analyzer (OSA), optical power meter (OPM) (Thorlab PM100D), Thorlabs DET01CFC 460 kHz bandwidth photodetector connected to a digital oscilloscope (GW INSTEK GDS-3352) for the pulse train and a radio-frequency spectrum analyser (RFSA; Anritsu, MS2683A) for a signal to noise ratio (SNR).

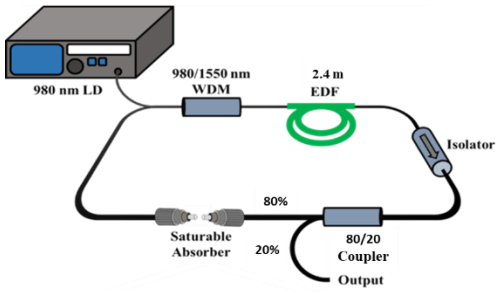

Fig. 2. Erbium doped fiber laser in ring cavity with saturable absorber.

Figure 3 shows an optical spectrum without SA and with SA at a maximum input pump power of 136.96 mW. The continuous wavelength (CW) without SA operates at

1561 nm and with SA the central wavelength shifted to ~1530 nm for all of the developed film. The CW was obtained at a threshold pump power of 9.76 mW and the threshold pump power for graphene-chitin, MoS_2-chitin and graphene-MoS_2-chitin are 30.12 mW, 14.85 mW and 14.85 mW, respectively.

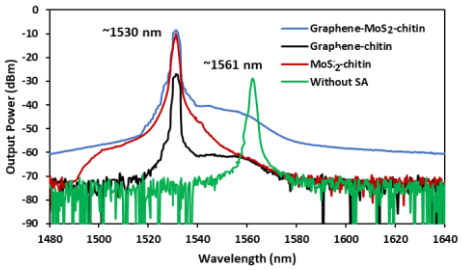

Fig. 3. OSA trace.

The pulse characteristics for graphene-MoS_2-chitin are illustrated in Fig. 4. The pulse train were observed to be quite stable with very little to no amplitude jitters as observed in Figure 4(a). By further increasing the pump power above 136.96 mW, The observed pulses started to fluctuate followed by diminishing pulses which were caused by over-saturation of SA. A stable pulse re-appeared when the SA was tuned from 14.85 mW to 136.96 mW without any significant fluctuations observed in the oscilloscope. This also shows that the SA can sustain the pump power above 136.96 mW without any optical damage. Figure 4(b) shows the variation of the repetition rate and pulse width against pump power where a typical trend of Q-switching graph can be achieved using graphene-MoS_2-chitin films.

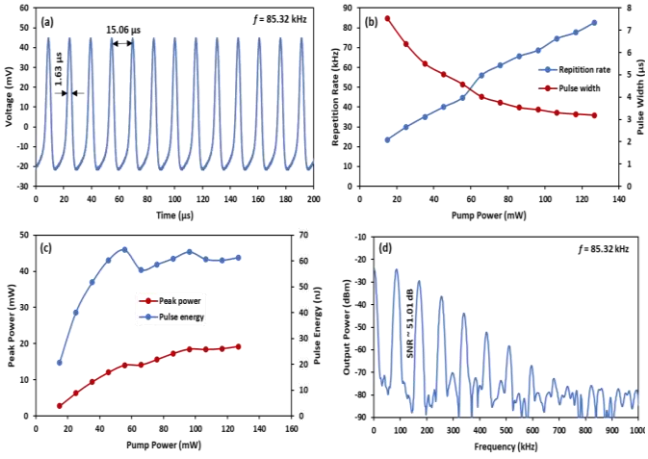

Fig. 4. Characterisation of graphene-MoS_2-chitin SA. (a) Pulse train, (b) Pulse repetition rate and pulse width against pump power, (c) Peak power and pulse energy against pump power, (d) Signal to noise ratio.

The repetition rate increased with an increase in the pump power while the pulse width shows a decreasing trend accordingly. Pulse energy and peak power can be calculated from obtained repetition rate and pulse width. Both parameters typically showed an inclining trend towards maximum pump power as shown in Figure 4(c). Figure 4(d) shows the radio frequency spectrum measurement with the highest SNR value recording an amplitude of 51.01 dB. However, there are slight changes in SNR value after a similar SA was used for Q-Switched pulsed. This is due to the degradation of the fabricated SA.

In comparison to individual graphene and MoS_2 based SAs, Table 1 summarized all the Q-switched parameters obtained. The maximum repetition rate of graphene-chitin and MoS_2-chitin is 96.54 kHz and 82.24 kHz, respectively while the pulse width is recorded at 2.26 µs and 5.40 µs, respectively. Though graphene-chitin records the highest repetition rate, the SNR value shows the lowest at 42.42 dB. Meanwhile, a high pulse energy of 113.57 nJ obtained by MoS_2-chitin SA but low stability can be observed from the SNR result (44.31 dB). This is probably due to the high non-saturable loss of the fabricated SA.

Table 1. Summary of the pulse laser performance.

Material	Repetition rate (kHz)	Pulse width (µs)	Pulse energy(nJ)	SNR (dB)
Graphene-chitin	55.87-96.54	2.26	49.93	42.42
MoS_2-chitin	22.62-82.24	5.40	113.57	44.31
Graphene-MoS_2-chitin	23.42-85.32	1.63	65.05	51.01

In conclusions, the liquid phase exfoliation of graphene-MoS_2-chitin based passive saturable absorber was successfully demonstrated with a repetition rate of 85.32 kHz, shortest pulse width of 1.63 µs and highest SNR of 51 dB at a maximum power of 136.96 mW, respectively, better than that of individual SA of graphene-chitin and MoS_2-chitin.

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