Poor fluorinated graphene sheets carboxymethylcellulose polymer composite mode locker for erbium doped fiber laser

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We report poor fluorinated graphene sheets produced by thermal exfoliation embedding in carboxymethylcellulose polymer composite (GCMC) as an efficient mode locker for erbium doped fiber laser. Two GCMC mode lockers with different concentration have been fabricated. The GCMC based mode locked fiber laser shows stable soliton output pulse shaping with repetition rate of 28.5 MHz , output power of 5.5 mW was achieved with the high concentration

GCMC while a slightly higher output power of 6.9 mW was obtained using the low concentration GCMC mode locker.

Ultrafast passively mode locked fiber lasers are light sources with dramatic applications in the areas of optical communication, sensing, metrology, biomedical imaging etc. Owing to the configuration simplicity, versatility and efficient heat dissipation, they are generally regarded as the next generation light sources compared to the bulky solid state lasers. In such a laser, optical pulses with low power and long duration suffers high loss while the optical pulses with high peak power and short duration undergoes low or no loss in a saturable absorber element from which the laser resonator tends to amplify the short pulses. The development of compact ultrafast mode locked fiber lasers strongly relies on the saturable absorber (SA) which induces the mode locking mechanism[1]. Generally, the SA can be either a physical absorber or a mechanism that provides saturable absorption modulating the light within the laser cavity. Currently, major types of saturable absorbers are based on semiconductor saturable absorber mirrors (SESAM)[1], nonlinear polarization rotation (NPR)[2], and recently carbon nanotubes (CNT) based saturable absorbers[3]. NPR is kind of technique that utilizes Kerr effect in optical fiber to achieve short pulse generation. So far the shortest pulses produced directly from an oscillator are generated through such technique[4]. However, one major drawback of such method is the polarization dependency to achieve mode locking. SESAM, as a pure physical absorber, has been the most widely used device in both commercial products and scientific research due to their self-starting properties.

Nevertheless, the SESAM bandwidth limit owing to the Bragg structure restricts the application of mode locked fiber laser. Furthermore, the reflective nature of such device will generally require extra components such as an optical circulator to build the laser. Among these, CNT based SA has drew a lot of attention in the last decade due to their ease of fabrication, low cost, simple installation and polarization independency. Importantly, the saturable absorption properties (saturation intensity, modulation depth, non-saturable loss) can be easily controlled through the wet chemistry fabrication route. The chirality and diameter control of such graphene roll-up structure with bundle engineering has proved to be an efficient mode locker in a very broad optical spectrum from near infrared to infrared [3,5,6]. More importantly, the CNT based SA are very friendly to the optical fiber format which enables highly compact fiber laser source [7]. Very recently, the investigation on 2D materials[8] such as MoS_2 [9], Bi_2Se_3[10] , Bi_2Te_3[11], Sb_2Te_3[12] exhibiting strong nonlinear optical absorption properties offers more opportunities for ultrafast optical pules generation.

Graphene, the wonder material of single atomic layer , has received significant attention over the last ten years since its discovery[13]. Due to its 2D crystal lattice structure with point band gap properties, it has many potential applications in future electronics such as flexible electronics, high frequency [14]and logic transistors[15]. The combination of optical and electronic properties of graphene opens the door for photonic and optoelectronic application such as photodetector[16], broadband polarizer[17] and optical modulator[18] etc. The recent intensive study on graphene - material with a zero energy band gap - shows it exhibits wavelength independent saturable absorption which is ideal for laser mode locking[14,15].

This is in contrast to a CNT based SA where only selected tubes, failing in resonance with lasers light, will contribute to the specific wavelength while other tubes could merely increase the non-

saturable loss. So far, various types of graphene saturable absorber have been demonstrated including substrate transfer deposition[19], optical deposition[20], evanescent field interaction[21] and polymer matrix composites [22]. Graphene produced by various approaches have also been investigated for fiber laser mode locking including mechanically exfoliation[23], liquid phase exfoliation[24], and chemical vapor deposition[25,26]. Among these, the graphene polymer composites based SA are very attractive because of their simplicity and easy handling. A number of polymer materials have been investigated as a host of graphene to form the graphene SA. This includes polyvinyl alcohol (PVA)[24,26,27], polyvinylidene fluoride (PVDF) [28]. With the sophistication of CNT polymer composite SA [29], it is fundamentally interesting to see functional graphene polymer composites for a range of integrated photonic system. Carboxymethylcellulose (CMC), a derivative of cellulose, has been previously exploited as an efficient matrix for CNT polymer composite mode locker[6,30]. Such material functions as both surfactant with high CNT dispersion activity and polymer matrix. Therefore, the resultant nanomaterial polymer composite contains only polymer and CNT/graphene without any residual surfactant. Very recently, graphene CMC composite has shown efficient saturable absorption which is promising for laser mode locking [31]. In this paper, we present poor fluorinated graphene sheets produced through thermally expanded graphite embedded in carboxymethylcellulose polymer composite (GCMC) as an efficient mode locker in an erbium doped fiber laser.

The procedure for preparing poor fluorinated graphene sheets was conducted in several steps. Firstly, a highly oriented pyrolytic graphite was intercalated with liquid ClF3 at room temperature. Then, the fluorinated graphite intercalation compound was exfoliated using thermal shock process at 750 ^{o}C resulted in production of thermally expanded graphite[32]. Next, the thermally expanded graphite was dispersed in 1 wt. % CMC (CMC sodium salt of averaged

viscosity was purchased from Sigma Chemical Co.) an aqueous solution by ultrasonication (35 kHz, 500 W, 30 min) followed by centrifugation (10,000 g, 30 min) in order to obtain a stable suspension of poor fluorinated graphene sheets enriched with single and few layer graphene[33]. X–ray Photoelectron Spectroscopy shows the elemental composition of the expanded graphite as follows: C, 96.4; F, 2.4; Cl, 0.1; and O, 1.1 at. % (Quantera SXI spectrometer).

Films of optical quality were obtained by pouring the poor fluorinated graphene sheets suspension on a flat substrate followed by slow evaporation of solvent in a thermostat at 40 ºC for 24 hours. Two Graphene-CMC (GCMC) films with a thickness of 15 μm have been fabricated containing 0.27 wt% (GCMC1) and 0.08 wt% (GCMC2) graphene sheets in the polymer matrix. Figure 1 describes the linear absorption of GCMC1 and GCMC2 (Shimadzu UV-3101PC scanning spectrophotometer). It clearly shows that GCMC1 has higher absorption across a broad range of wavelength than GCMC2. The UV absorption peak is the feature of π plasmon[34]. Figure 2 plots a Raman spectrum (Horiba Jobin Yvon T64000 instrument) of highly ordered pyrolytic graphite (HOPG) (curve 1), poor fluorinated graphene sheets on glass (curve 2) and composite GCMC1 (curve 3). The 2D band on the Raman spectrum of the graphene sheets has a single Lorentzian line shape with a maximum intensity at 2691 cm^{-1} and a FWHM of 92 cm^{-1}. For composite GCMC1 and HOPG, these values for a 2D band are 2709 and 84, and 2723 and 32 cm^{-1}, respectively. The number of layers are identified by examining of 2D peak in the graphene sheets Raman spectra (Fig. 2b) and was estimated as 3 – 5 layers[35].

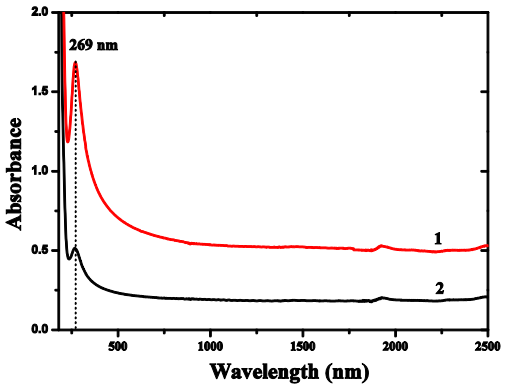

Fig. 1 Optical absorption spectrum of GCMC film composite: 1 – GCMC1, 2 – GCMC2.

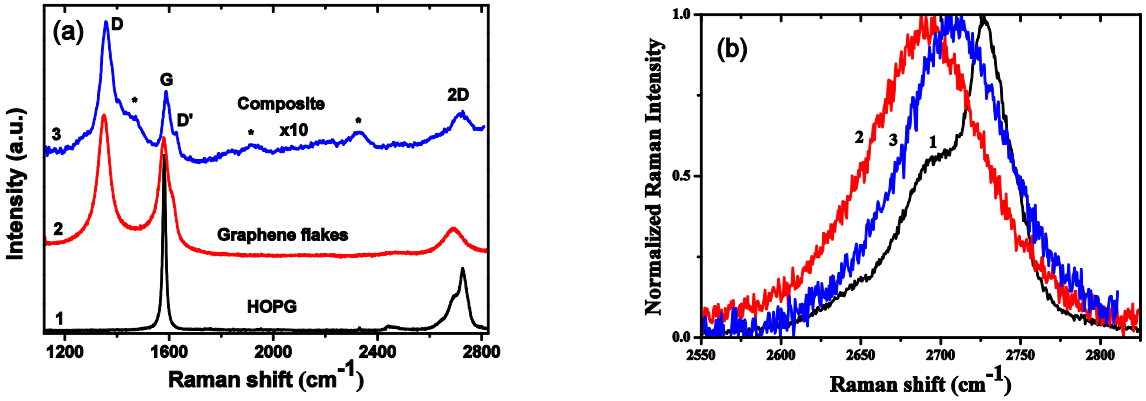

Fig. 2 Measured Raman spectra using 514.5 nm laser excitation for (a) composite GCMC1 (curve 3, blue line), graphene sheets on glass (curve 2, red line), and HOPG crystals (curve 1, black line); (b) zoomed in description of the measured 2D mode. *Bands for CMC polymer.

Fig.3 depicts the schematic setup of the GCMC mode locked erbium doped fiber laser. The laser consists of ~ 0.8 m highly doped erbium fiber (Liekki Er80) as the gain medium. A fiber pigtailed optical isolator (OIS) is employed to ensure single direction oscillation of the laser. The laser is pumped by a grating stabilized 975 nm laser diode through a 980/1550 nm wavelength division multiplexer (WDM). A commercial laser diode controller is used as laser diode driver and temperature stabilizer. A standard fused fiber 50:50 coupler is used to extract 50% optical power out of the laser cavity.

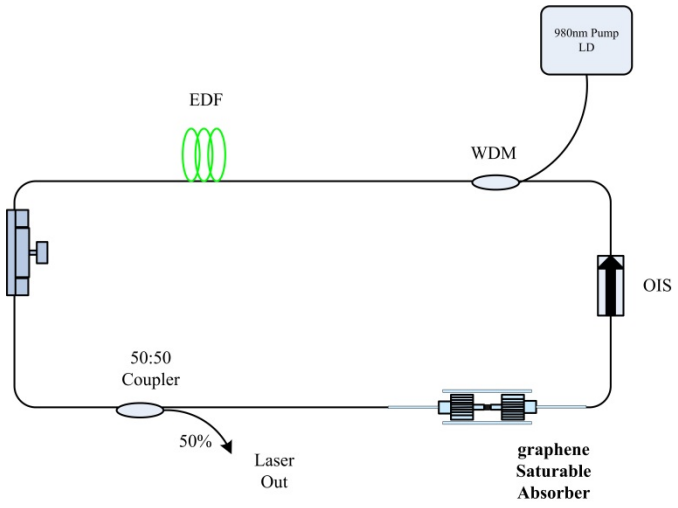

Fig. 3: schematic description of the graphene CMC mode locked erbium doped fiber laser configuration.

An in-line fiber polarization controller is incorporated into the laser cavity to optimize the total cavity birefringence. The GCMC polymer composite is sandwiched between two FC/PC connectors by use of the index matching gel in order to minimize the laser cavity loss. This integrated fiber based GCMC mode locker is then spliced into the cavity forming an all fiber mode locked erbium doped fiber laser configuration. The total cavity length is ~ 7.86 m, corresponding to a net dispersion of ~ - 0.14 ps^2 indicating the laser operates in anomalous dispersion regime from which soliton pulse shaping regime dominates. The output pulse of the fiber laser is fed into an optical spectrum analyzer, a digital oscilloscope and a commercial autocorrelator for diagnostics.

Fig.4(a) shows a typical output optical spectrum of the GCMC1 mode locked fiber laser centered at 1560 nm. The full width half maximum (FWHW) spectral bandwidth is measured to be ~3.52 nm. Clear Kelly side bands indicate soliton pulse shaping as expected. The laser pulse is then

directly fed into the autocorrelator without any amplification. The measured pulse width through the autocorrelator is ~ 1289 fs corresponding to ~ 837 fs pulse duration which is shown in Fig.4(b). A typical pulse train registered by the oscilloscope is shown in Fig.4(c) with ~35 ns pulse interval thus giving a repetition rate of ~28.5 MHz. The measured output power is ~ 5.5 mW at ~100 mW pump rendering pulse energy of ~ 0.19 nJ. Fig.4(d) shows the measured RF spectrum of the laser with a 66 dB signal-to-noise ratio (SNR) indicating stable mode locking. The laser has been operated under the laboratory condition for a couple of hours, no visible damage or degradation of laser performance has been observed.

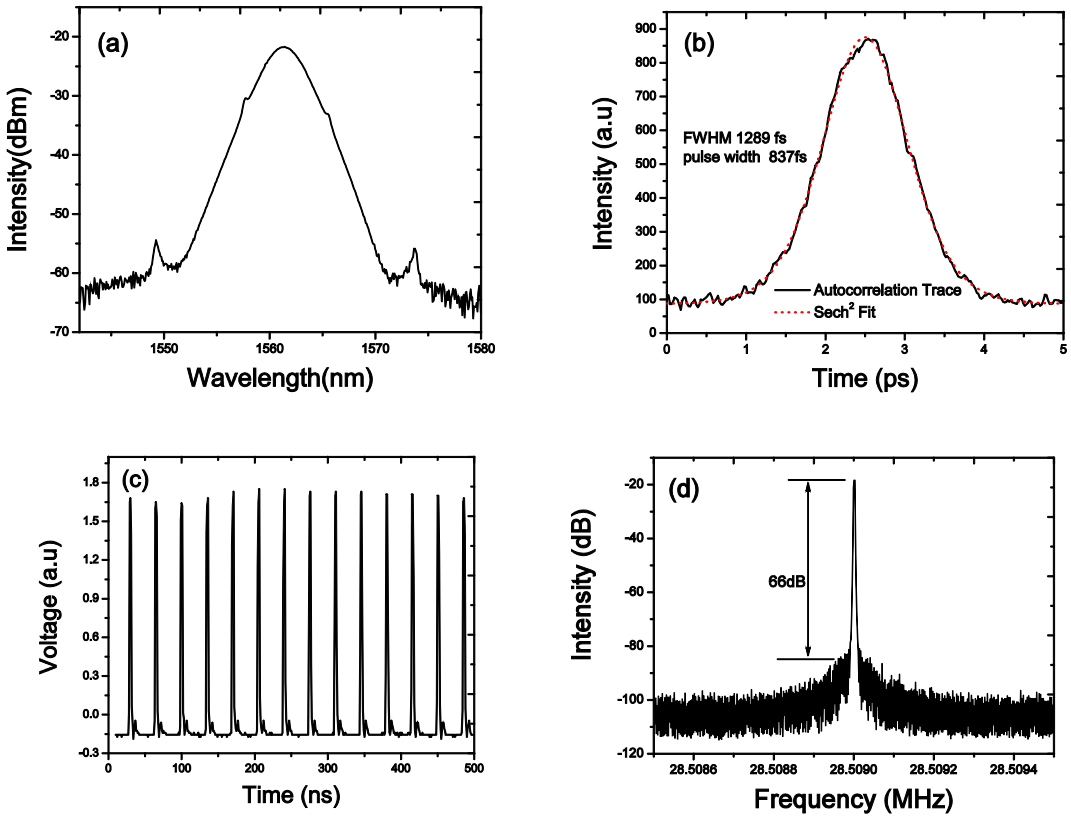

Fig. 4 (a)a typical output optical spectrum with clear Kelly side bands indicating soliton pulse shaping;(b) measured autocorrelation trace of the mode locked laser pulses showing a pulse

duration of 837 fs; (c) measured pulse trains from the mode locked fiber laser with an repetition rate of ~28.5 MHz.

Fig.5 shows optical spectrum of the laser mode locked by GCMC2 sample when GCMC1 has been replaced and the rest of the laser cavity parameter being maintained. The bandwidth of the optical spectrum is ~2.8 nm centered at 1560 nm. One needs to be noticed that the pump power has to be slightly increased to get stable mode locking. The then measured pulse duration is ~1027 fs with the same repetition rate of ~ 28.5 MHz. The measured optical output power is 6.9 mW corresponding a pulse energy of ~0.24 nJ. The measured RF spectrum shows similar behaviour to GCMC1 mode locked laser which has a SNR of 71dB. However, the noise floor level is slightly higher, this could attribute to the lower absorption capability of GCMC2.

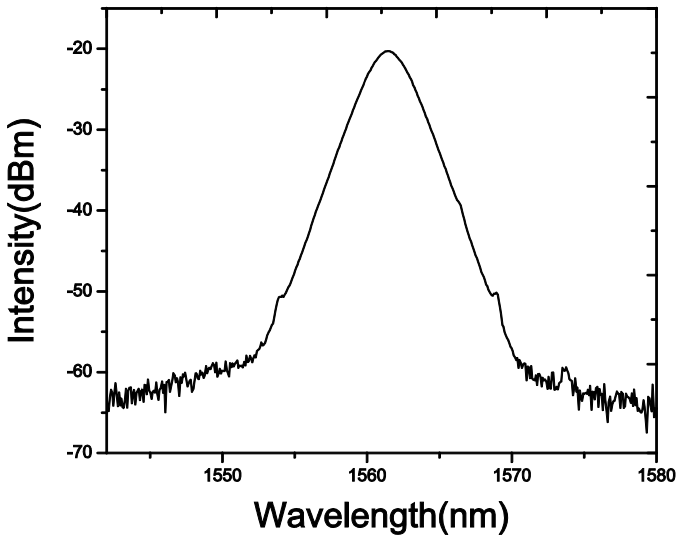

Fig.5 optical spectrum of the GCMC2 mode locked erbium doped fiber laser.

The versatility of graphene polymer composite offers possibilities of robust and compact fiber laser configuration. Due to the inherent broadband absorption, the GCMC could be an ideal broadband absorber for lasers operating in a wide range. Further investigation will focus on achieving broadband ultrafast laser generation in Yb, and Tm fiber laser configuration using

single GCMC SA. Moreover, the polymer format has intrinsic low thermal damage threshold that would not be ideal for high power operation. Irradiation resistance of the GCMC polymer composite depends on optical quality of the film determined by the value of optical density, thermal conductivity of the polymer and photochemical reduction during multi-photon excitation[36]. The polymer composite can be damaged at certain intensities of the incident radiation due to light absorption and subsequent scattering of thermal power in the sample. For similar graphene-containing polymer composite, it was shown the optical destruction occurred when the peak intensity exceed 1.5 GW/cm^2 [31]. For high power operation, other techniques such as microfiber[37] , D-shaped fiber[21] or microchannel[38] are of necessity.

In conclusion, we have demonstrated a GCMC based saturable absorber for efficient soliton laser mode locking in an erbium doped fiber laser. With low concentration GCMC, the laser can give out picosecond pulse duration while with high concentration GCMC, the same laser setup gives out femtosecond soliton pulses. The GCMC based device may find more applications for integrated photonic devices and fiber laser systems under other regimes at other wavelength.

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