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# Mode-locked Nd: GdVO<sub>4</sub> laser with graphene oxide/polyvinyl alcohol composite material absorber as well as an output coupler

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## ABSTRACT

Graphene oxide/polyvinyl alcohol (GO/PVA) composite material saturable absorbers were fabricated. Sandwich structured GO/PVA absorber was used as an absorber as well as an output coupler in mode-locked Nd: GdVO<sub>4</sub> laser. The laser pulses with the duration of 12 ps, repetition rate of 120 MHz and the maximum average output power of 680 mW were produced.

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## Introduction

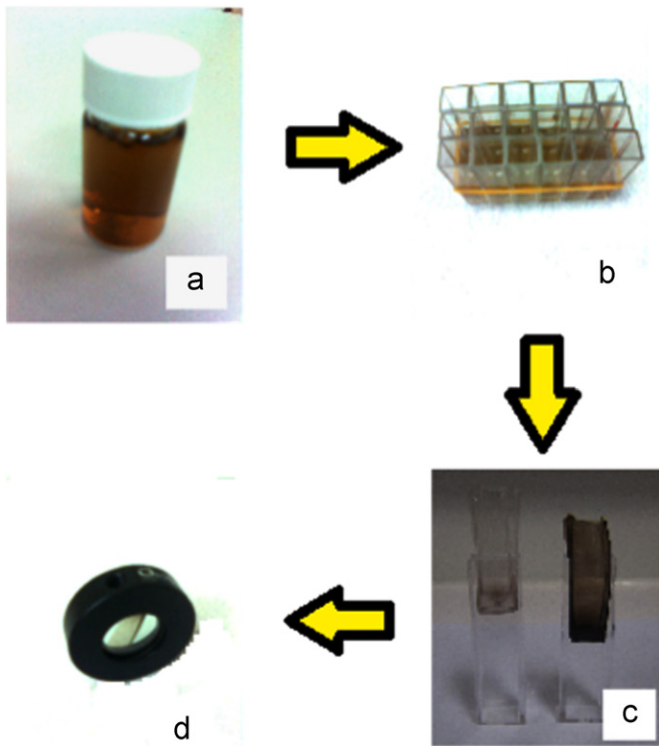
Carbon nanotube (CNT) was first demonstrated to have fast saturable absorption in 2003 [1] and it is attractive because of its application in mode locked fiber lasers [2–4]. Graphene was found to have very similar saturable absorption properties to the CNT, and was applied to fiber laser mode locking, which were developed independently by Bao [5] and by Sun [6–9]. Carbon nanotube and graphene possess some virtues compared to SESAMs [10–12] such as short recovery time, broad operational wavelength range, low cost and easy to be fabricated. However, there existed the problem that the average output power of ultrafast fiber lasers mode locked with CNT or graphene absorber is too low for many applications. In order to get higher output power, mode locked solid-state lasers with CNT [13–15] or graphene [16,17] are required. Generally graphene oxide (GO) is used as a precursor for the industrial mass production of graphene by modified Hummers' method because of its very low cost and simple fabrication method [18]. Graphene oxide nanosheets can be directly dissolved in water without surface modification for its carboxyl and hydroxyl group. Therefore, graphene oxide can be mixed with polyvinyl alcohol (PVA) evenly in aqueous solution. The graphene absorber has a broad

operational wavelength range because of its cone-shaped band structure. The graphene oxide has similar characteristics to that of graphene [19–24]. In this letter, a sandwich structured GO/PVA composite absorber was successfully fabricated. Using this absorber as well as an output coupler, stable and high power mode-locked Nd: GdVO<sub>4</sub> laser were obtained. The output pulses and performance were characterized. The maximum average output power achieved was 680 mW with slope efficiency of 13%. The obtained pulses width and repetition rates are 12 ps and 120 MHz, respectively.

The graphene oxide (GO) sheets used in this experiment were fabricated by ultrasonic agitation after chemical oxidation of graphite. The atomic layer of the sheet is one to three and the diameter of the sheet is 0.1 to 5 μm. First, 1 mg of GO sheets were poured into 10 ml aqueous solution. Then the GO aqueous solution was ultrasonically agitated for 12 h. After the ultrasonic process, the dispersed solution of GO was centrifuged to induce sedimentation of large GO clusters. Some PVA powder was poured into the centrifuged solution and dissolved at 90 °C with ultrasonic agitation for 3 h. The GO/PVA solution (Fig.1(a)) was subsequently poured into a polystyrene cell as shown in Fig.1(b), which was put in an oven at 40 or 45 °C for 2 days in order to achieve complete evaporation, after which the wall and the bottom of the cell were coated with a thin plastic film. The strong viscosity of the PVA aqueous solution to the polystyrene cell allows it to adhere to the wall of the cell. When the cell was dry, the GO/PVA film lost the viscosity to the cell so that it can be

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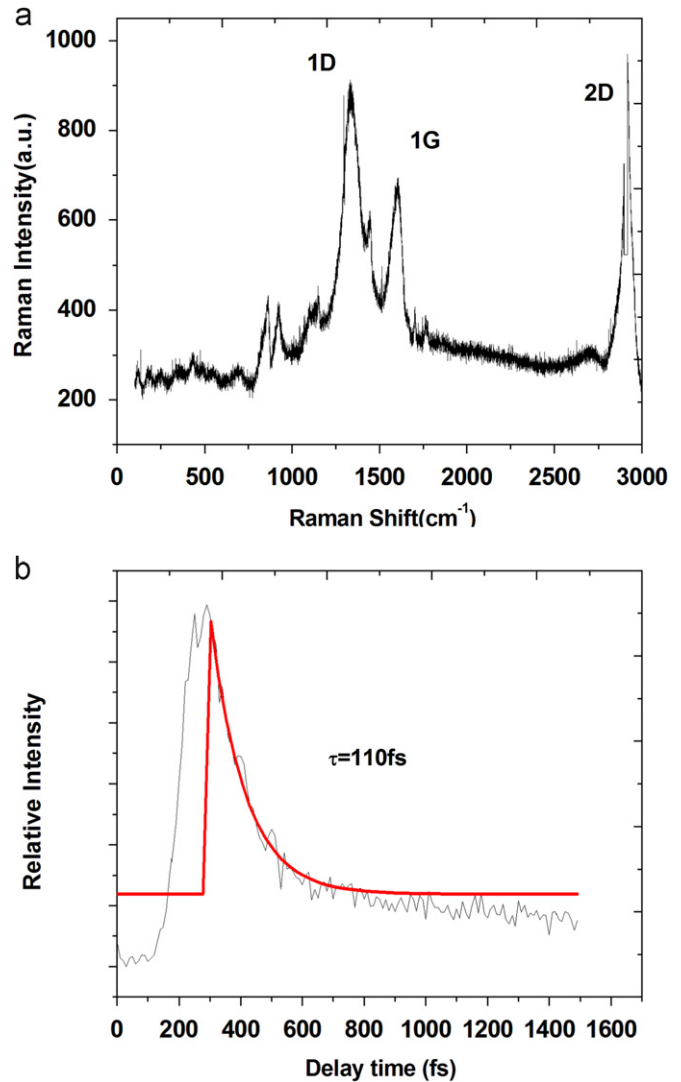
**Fig. 1.** The fabrication procedure of GO absorber: (a) GO/PVA aqueous solution; (b) GO/PVA film deposition cells; (c) the finished GO/PVA film with different concentrations of graphene oxide and (d) combined absorber-quartz/GO/PVA/output coupler.

stripped off the polystyrene cell easily by a pair of tweezers (Fig.1(c)).

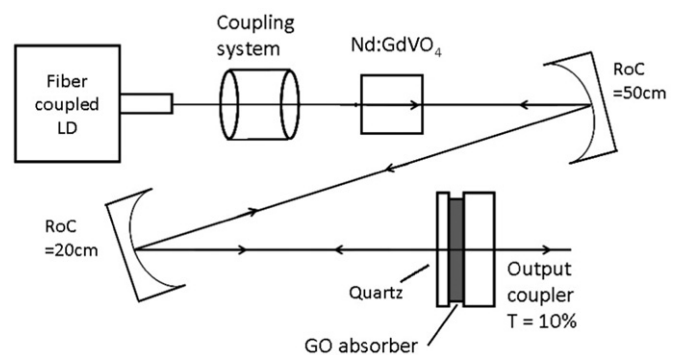
However the film, which is called GO absorber, cannot be directly used as saturable absorber in laser cavity because it is not free-standing. The graphene oxide film was cut into small pieces and one of them was inserted between two mirrors (Fig.1(d)). By this way, a piece of quartz, a piece of GO/PVA film and a piece of output coupler formed the combined sandwich structure, which can be used as an absorber as well as an output coupler in mode-locking system.

Fig. 2(a) shows the Raman spectrum of the graphene oxide absorber excited by a 488 nm Ar ion laser, revealing the two characteristic peaks 1D and 1G of graphene oxide (the 1D peak at  $1330\text{ cm}^{-1}$  and the 1G peak at  $1600\text{ cm}^{-1}$ ). The 1D peak is from the structural imperfections and the 1G peak corresponds to the first-order scattering of the E<sub>2g</sub> mode. Fig. 2(b) shows the fast recovery time of 110 fs measured by 1060 nm pump probe system—a Spectra-Physics ultrafast laser, which proves that the fabricated GO absorber is suitable for the application of the ultrafast laser because of its very short recovery time.

The schematic setup of our laser with folded z-configuration is shown in Fig. 3. A fiber-coupled diode-array laser with center wavelength of 808 nm was used as the pump source. The laser gain media is a  $3 \times 3 \times 8\text{ mm}^3$  a-cut Nd:GdVO<sub>4</sub> crystal (with 0.5-at% Nd<sup>3+</sup> concentration). One side of the laser crystal is high reflection (HR) coated at 1064 nm and anti-reflection (AR) coated at 808 nm for pumping end as well as a resonator reflection mirror; while the other side with 2° wedge is AR coated at 1064 nm. Two curved mirrors with radii of curvatures of 500 mm and 200 mm respectively were used as folding mirrors to conduct the laser through the GO/PVA composite absorber, the latter was as well as an output coupler. The beam diameter at the absorber is estimated to be about 50 μm. Output coupler mirror with reflectivity of 90% at 1064 nm was used to generate mode



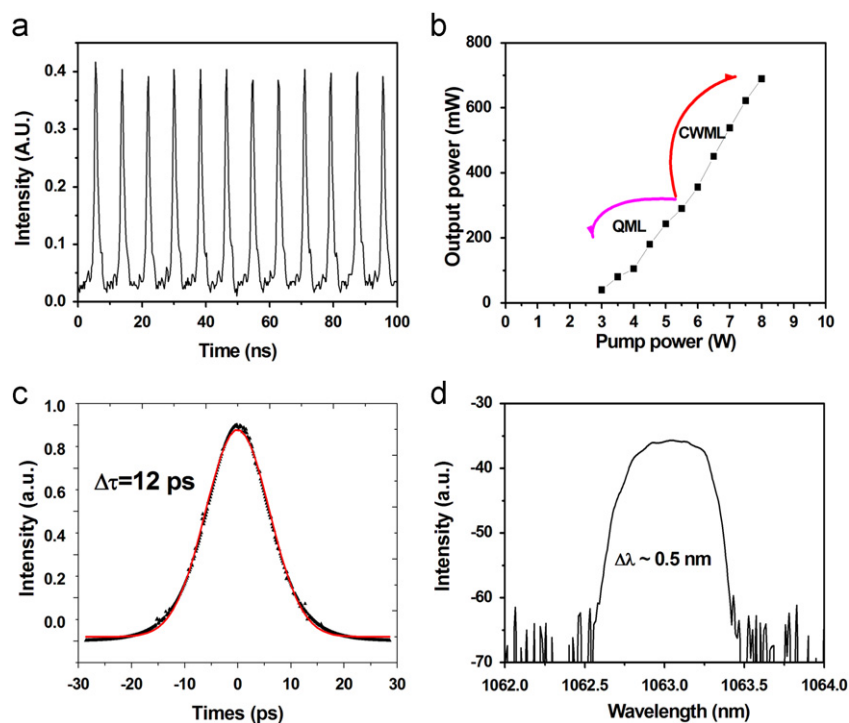
**Fig. 2.** Characteristics of GO absorber: (a) Raman spectrum and (b) recovery time.



**Fig. 3.** Experimental setup of the mode-locked laser with combined GO absorber.

locked laser pulses. It should be noted that high pressure should be added on both sides of the GO absorber to isolate it from the air. Otherwise, the GO absorber could be burned due to oxidation of the graphene oxide under high optical intensity.

Fig. 4(a) shows the mode-locked pulse train under the incident pump power of 8 W. The measured repetition rate of the pulse train is 120 MHz. The average output power as a function of the incident pump power is shown in Fig. 4(b). Q-switched mode



**Fig. 4.** (a) Mode-locked pulse train under the incident pump power of 8 W. (b) Average output power versus incident pump power for mode-locking operation. (c) Autocorrelation trace of the 12 ps pulse and (d) Wavelength spectrum of the mode-locked laser.

locking occurred at the pump power below 5.5 W and continuous mode locking occurred at the pump power above 5.5 W. The laser threshold, maximum output power and slope efficiency are 2.5 W, 680 mW and 13%, respectively. The black squares in Fig. 4(c) shows the measured profile of autocorrelation signal with the width (FWHM) of 12 ps and a Gaussian fitting line. Fig. 4(d) shows the corresponding optical spectrum. The spectral FWHM of the mode locked laser is about 0.5 nm. The time bandwidth product is 1.5, which is larger than the transform-limited value of 0.44 for Gaussian pulses, indicating that the mode-locked pulses are frequency chirped and their duration of the pulses could be further compressed.

Generally, (CNT or graphene)/polymer composite absorbers contain surfactant impurity [25]. The impurity may increase the non-saturable losses and strong scattering in the composite film. Graphene oxide can be dispersed very well into water without surfactant such as SDS (sodium dodecyl sulfate). Therefore, the impurity involved by surfactant can be avoided. The characteristics of the GO/PVA film can be changed by adjusting the content of the GO and PVA in the aqueous solution. The increase of the content of the GO in the solution will lead to the increase of saturable absorption and non-saturable losses of the GO absorber. The increase of the content of PVA in the solution will increase the hardness of the film. Super soft GO absorber under pressure may fracture easily, whereas if it is too hard, it cannot be pressed tightly to isolate from the air in sandwich structure. Therefore, both the content of GO and the content of PVA should be optimized to improve the mechanical and optical properties. Graphene oxide can be mass produced using cheap graphite and PVA is also cheap material. Additionally, the simple fabrication procedure of the saturable absorber is suitable for mass production. Hence, the market price of the GO/PVA absorber can be more competitive compared with other saturable absorber currently available in the market, not to mention its virtue of easy integration with the output coupler or reflective mirror by sandwich structure.

In conclusion, high performance Nd: GdVO<sub>4</sub> mode-locked laser using graphene oxide absorber as well as an output coupler has been successfully demonstrated. The measured average output power is 680 mW and the pulse duration is 12 ps.

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