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Graphene oxide mode-locked Yb:GAGG bulk laser operating in the femtosecond regime

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ABSTRACT

High-quality graphene oxide saturable absorber (SA) is successfully fabricated with 1–2 layer graphene oxide. By employing this SA, we have demonstrated femtosecond pulse generation from a graphene oxide passively mode locked bulk laser for the first time to our best knowledge. With two Gires–Tournois interferometer mirrors for dispersion compensation, pulses as short as 493 fs with an average power of 500 mW are obtained at the central wavelength of 1035.5 nm. These results presented here indicate the great potential of GO for generating femtosecond mode-locked pulses in the bulk laser.

1. Introduction

Graphene is a new carbon material with two-dimensional (2D) monoatomic-layer structure which possesses fascinating electronic and mechanical properties, such as high intrinsic electrical conductivity, excellent elasticity, and stiffness [1]. These unique structure and outstanding properties make graphene a promising material in various application area, such as supercapacitors [2], biosensors [3], organic photovoltaics [4–6], field emission cathodes [7] and touch panels [8]. Graphene's conjugated hydrophobic structure also leads to a low solubility in common solvents and the absence of groups makes it difficult to be processed. Therefore, graphene oxide (GO) and reduced graphene oxide (RGO) are the mostly common used graphene derivatives due to the hydrophilic groups [9].

In recent years, graphene has been successfully used as the optical modulator to generate ultrashort pulses [10–15]. The optical absorption of graphene is considered to be wavelength independent but proportional to the number of layers (2.3% per layer) [16,17]. Due to the universal optical absorption property and zero bandgap, graphene can be saturated readily under strong excitation from the visible to near-infrared region. Moreover, its thermal conductivity is higher than any other known materials, which implies the great thermal-induced damage resistance [18]. These excellent properties offer graphene the potential for demolishing the remaining barriers to the development of ultrafast lasers caused by traditional semiconductor saturable absorber mirrors (SESAMs). The fabrication of SESAM requires very complex and costly epitaxial grow processes. In addition, the saturable absorption band is limited by the reflectivity of the Bragg mirror [10]. Besides, GO has been also proved to be the promising saturable absorption material for the pulsed laser [19–24]. The ultrafast dynamics of charge carriers in few-layered GO has been investigated using ultrafast pump–probe technique, and the fast decay time of 0.17 ps is found to be associated with carrier–carrier scattering which is crucial for stabilizing femtosecond pulses [25]. Although the structure model of GO is still elusive today due to its amorphousness and nonstoichiometry (including sample to sample variability), a consensus is that GO is decorated by epoxies and hydroxyls, which are randomly distributed across the carbon backbone [26]. In comparison with pure graphene, GO displays some different properties due to the presence of functional groups. For example, the thermal stability of pure graphene is better than that of GO [27,28], and GO induces a larger non-saturable loss, especially for the shorter wavelengths [24,29]. Nevertheless, GO shows several advantages compared with pure graphene. First, GO can be fabricated by the modified Hummer's method which has the advantages of low cost and mass producing, avoiding the use of any expensive or sophisticated technique [30]. Second, GO can be directly dissolved in water due to the presence of carboxyl

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and hydroxyl groups., which means that GO can be easily transferred to any substrate by redispersing into water. These characteristics facilitate its application greatly.

Most studies have been performed on GO based saturable absorbers (SAs) for all-fiber mode-locked lasers and impressive results have been obtained [21–23]. For the bulk lasers, the mode-locking operation lasers based on GO could generate mode-locked pulses at 1 μm with a power scale of Watt-level [19,20]. However, these mode-locked lasers can only produce picosecond pulses, mainly limited by the gain bandwidth of the Nd^{3+}-doped crystals. At 2 μm spectral region, GO has also been successfully employed to achieve mode-locking operation using a Tm:AlO_3 crystal, while the pulse duration are still in ps-regime due to the claim that the intracavity normal dispersion are not compensated [24]. Up to now, there is no report about the GO operation performance in the femtosecond bulk laser.

In this letter, we demonstrate a passively mode-locked femtosecond bulk laser based on GO for the first time to our best knowledge. By using a novel Yb-doped $Gd_3Al_{0.5}Ga_{4.5}O_{12}$ (GAGG) crystal, stable mode-locked pulses as short as 493 fs are obtained with an average output power of 500 mW and a repetition rate of 46 MHz centered at 1035.5 nm. The results present here indicate that GO is a promising SA for femtosecond bulk lasers.

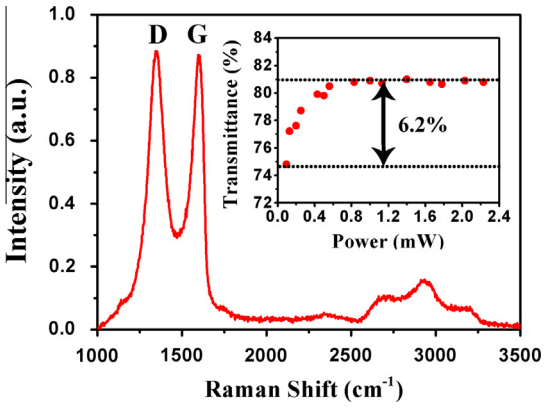

Fig. 1. Raman spectra of GO at room temperature. Inset: Transmittance versus incident pump power on GO SA.

2. The fabrication and characteristics of graphene oxide absorber

In our experiment, GO was synthesized from natural graphite powder by the modified Hummer's method [31]. Exfoliation was achieved by dilution of the GO dispersion with deionized water, followed by 20 min sonication. The resulting homogeneous yellow–brown GO solution was stable for a period of months. In order to fabricate high-quality GO saturable absorber mirrors (SAMs), the most crucial step of our method was the centrifugal pretreatment of the filtered original solution before coated onto the substrate. The large-size atom-thin GO sheets could be separated in the bottom of GO solution. The extracted bottom part of the solution was further diluted to a low concentration of ~0.02 mg/ml to effectively avoid the aggregation of GO. A piece of quartz plate coated for ~4% transmittance at 1035 nm was used as the substrate and output coupler simultaneously. The treated GO solution was spin-coated on this substrate and then dried in vacuum oven at 80 °C for 24 h. After that, the GO based SAM was prepared successfully.

Fig. 1 shows the Raman spectrum of GO sheets on the SAM excited by a 532 nm laser source. The spectrum reveals two main peaks of *D* and *G*. The *D* peak as a breathing mode of sp^2 rings, located at 1349 cm^{-1}, which is attributed to defects and disorders, particularly the defects located at the edges of graphene materials [32]. The *G* peak of 1600 cm^{-1} is generally assigned to the E_{2g} phonon of sp^2 bonds of carbon atoms [32]. The relative intensity ratio of both peaks (I_D/I_G) for GO is smaller than that for RGO. It can be assigned to more graphitization for RGO due to the reduction process [32]. Fig. 1(inset) shows the nonlinear transmittance of GO sheets which are located on a pure quartz measured by a passively mode-locked Yb-doped fiber laser at 1040 nm with a pulse duration of about 500 fs. Considering the Fresnel reflection loss of about 8% for both sides of the pure quartz, the non-saturable loss (NSL) of GO SA is calculated to be 11.5% [33]. The modulation depth (MD) of GO SA is about 6.2% [33]. Fig. 2(a) demonstrates the morphology of GO sheets located on the silicon substrate, which is taken by an atomic force microscope (AFM). The cross-sectional analysis indicates the thickness of our GO sheets is 1–2 nm and the occupied percentage of single-layer structure in GO sample is much larger than that in RGO sample. We attribute this to the good water solubility of GO which can effectively avoid the overlap of GO sheets. Due to the presence of the structural defects and the functional groups, the thickness of single GO layer is about

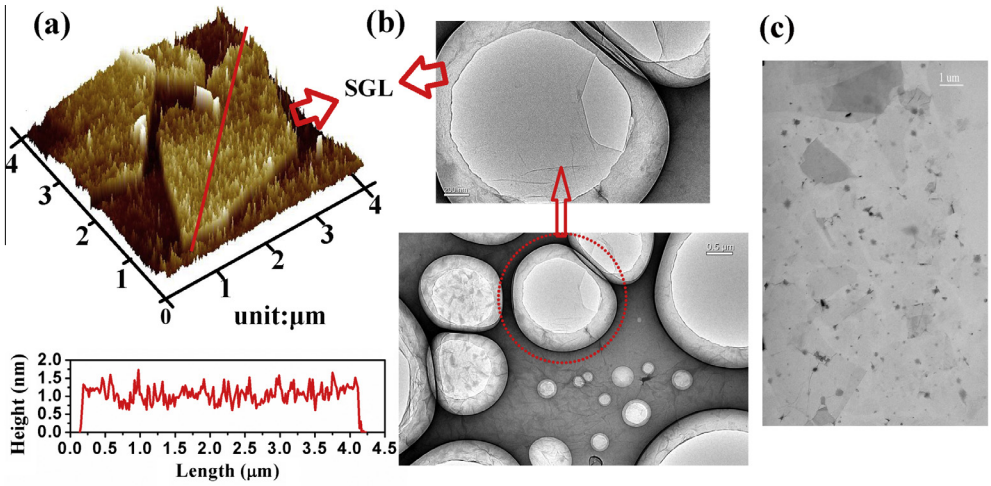

Fig. 2. (a) AFM scan image of the GO surface and the typical height profiles of GO sheets. (b) HRTEM images of single-layer (SGL) GO sheets. (c) TEM images taken over a large area of GO sheets.