Current Applied Physics 16 (2016) 985–988

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

The nonlinear absorption of graphene oxide water solution in femtosecond regime

Lingling Ran, Zhijun Chai, Yachen Gao, Wenzhi Wu, Qing Chang, Degui Kong*

College of Electronic Engineering, Heilongjiang University, Harbin 150080, PR China

ARTICLE INFO

Article history:
Received 7 March 2016
Received in revised form
10 May 2016
Accepted 24 May 2016
Available online 26 May 2016

Keywords:
Two-photon absorption
Excited state absorption
Excited state lifetime

ABSTRACT

The nonlinear absorption properties of graphene oxide water solution were investigated with femtosecond pulses using Z-scan and pump-probe techniques at 800 nm wavelength. The researching results indicated that the nonlinear absorption of graphene oxide water solution include three parts: two-photon absorption of bound electrons from valence band, excited state absorption of electrons from the low energy state in conduction band and the excited state absorption of electrons from the bottom of conduction band. By theoretically fitting the experimental results, we got the two-photon absorption coefficient about $\beta = 3 \times 10^{-14}$ m/W, and the two excited state absorption cross section in the order of 10^{-20} m^2 and 10^{-21} m^2 respectively. In addition, the excited state lifetime of electron on the low energy state of conduction band was obtained. The investigation indicated that graphene oxide water solution is a good nonlinear optical material.

1. Introduction

In the recent decade, as a new star nanomaterial, graphene has received tremendous interest owing to its variously remarkable properties and applications in the fields of modern electronics and photonics [1,2]. But the applications of graphene have been hindered by its poor processability which is mainly caused by the high inter-layer attraction energies [3]. Graphene oxide (GO) is an atomically thin sheet of graphene which is used as precursor of graphene traditionally, and GO has oxygen-containing functional groups on the basal plane or at the edges [4]. GO is also an electronically hybrid material consisting of π-states of sp^2 and σ-states of sp^3 carbon, and the ratio of sp^2 and sp^3 can be tuned [4,5]. The electrical, optical and chemical properties of GO can be controlled because of its tunable energy gap. GO has better hydrophilicity and water solubility than that of pure graphene [2]. So GO was often decorated by noble metal atom, phthalocyanine, porphyrin, or covalent functionalization groups to improve their optical properties [6–12]. In addition, GO itself is a good nonlinear optical material, and its optical nonlinearity was investigated intensively [13–18], [10]. For example, Manish Chhowalla investigated the nonlinear absorption of GO using open aperture Z-scan technique with 5 ns pulses at 532 nm wavelength, and the superior optical limiting effects of GO were also observed [4]. Liu investigated the nonlinear optical properties of GO in nanosecond and picosecond regimes at 532 nm wavelength. The results indicated that the nonlinear absorption of GO came from two-photon absorption (TPA) for picosecond pulses at 532 nm, while the nonlinear absorption came from excited state absorption (ESA) for nanosecond pulses at 532 nm [13]. Feng investigated the nonlinear optical and optical limiting properties of GO nanosheets with 8 ns pulses at 532 nm and 1064 nm wavelength in 2010. The researching results indicated that the graphene families are good optical limiting candidates at 532 nm and 1064 nm [14]. Couris investigated the optical limiting property of GO in different solvent with 4 ns pulses at 532 nm wavelength [19]. Fang investigated the nonlinear absorption, dynamic excitation and relaxation, and optical limiting properties of GO in ethanol with femtosecond pulse at 1.5 μm wavelength. They found GO has ultrafast recovery time in ethanol [20]. Reji Philip investigated the nonlinear absorption of GO nanosheets in the 400–700 nm region with ultrafast laser pulses, and found that the nonlinear absorption came from the nondegenerate TPA [21]. Liaros investigated the transient nonlinear optical response of few layers GO dispersed in different organic solvent with nanosecond pulses excitation under visible and infrared wavelength [22].

To sum up, the reports of GO's optical nonlinearity were almost investigated with nanosecond and picosecond pulses at 532 nm, 1064 nm or 1.5 μm wavelength. To our best knowledge, the reports

* Corresponding author.
E-mail address: victorkonghu@hotmail.com (D. Kong).

http://dx.doi.org/10.1016/j.cap.2016.05.019
1567-1739/

of GO's nonlinear optical properties were very few in the femtosecond regime, and the ultrafast dynamic processes of GO remains unclear. In this paper, we investigated the nonlinear absorption of GO water solution with 130 fs pulses using Z-scan technique and pump-probe technique at 800 nm wavelength. We found that the nonlinear absorption of GO water solution includes TPA and two parts of ESA of electrons from conduction band. We got the TPA coefficient, ESA cross section and lifetime of electrons on the low energy state and the bottom of conduction band respectively.

2. Experiment

In this study, the femtosecond pulses were generated from a self mode-locked Ti sapphire laser (Coherent Mira 900) with a regenerative amplifier (Coherent Legend- F). The pulses are linearly polarized, 130 fs width (full width of the half maximum) and 800 nm wavelength. The frequency of pulses was adjusted to 10 Hz for avoiding thermal effect. The spatial profile of the laser pulses is Gaussian distribution. The details of the Z-scan experimental setup were described in our previously published paper [23]. For investigating the nonlinear absorption of graphene oxide water solution, we conducted the open aperture Z-scan experiment in this paper. Briefly, the collimated beams were focused by a lens with focal length f = 40 cm, and the beam waist radius was about $\omega_0 = 32$ μm at focal position. The sample (GO water solution) was filled into a 2 mm thick glass cell which was fixed on a translating stage. The sample was moved along the propagation direction of the laser pulses with 0.5 mm distance per step. The energy was measured with an energy meter (Coherent J3S-10) after the sample at each sample position z. Normalized transmittances with one in the linear regime, we obtained the open aperture Z-scan experimental results as a function of position z.

For the pump-probe experiment, each pulse was split into two parts with an energy ratio of 7:3 using a thin-film splitter. The intense and weak beams were used as the pump and probe beam respectively. A half wave plate and a Glan-Taylor polarizer were inserted into the probe beam to attenuate the probe pulse energy, and the energy ratio of pump beam to the probe beam was adjusted to 10:1. The polarizer was placed in such a way that the polarization of the probe beam is perpendicular to that of the pump beam. Two lenses with focal length of 40 cm and 20 cm were used to focus the pump and the probe beam at the same position on the sample with a small angle (less than 5°) respectively. The beam radius of the pump and the probe beam are about 32 μm and 16 μm respectively. After transmitting through the sample, the pump beam was blocked, while the probe beam was accepted by a detector. In this experiment, we used a prism mounted on a translating stage to introduce the time delay into the pump beam with respect to the probe beam. Finally, the energy of probe beam was recorded by a digital lock-in amplifier as a function of the delay time of the probe beam with respect to the pump beam. A computer was used to control the motion of the delay stage and recorded the probe pulse energy. The GO water solution was filled into a glass cell with 2.0 mm in thickness.

The GO water solution was prepared by Institute of Coal Chemistry Chinese Academy of Science. The synthesis method of GO water solution was reported in Chen's papers [24,25]. The concentration of GO water solution is 2 mg/ml. Fig. 1 showed the scanning electron microscope image of GO water solution. From the figure, it can be seen that the lateral distribution size of GO is about several micrometers. In the wavelength region of 500–1100 nm, GO water solution has very weak linear absorption and has no obvious linear absorption peak. In the region of 300–500 nm, the absorption enhances with the wavelength get shorten gradually. The linear absorption spectra were shown as Fig. 2 from 300 nm to 1100 nm.

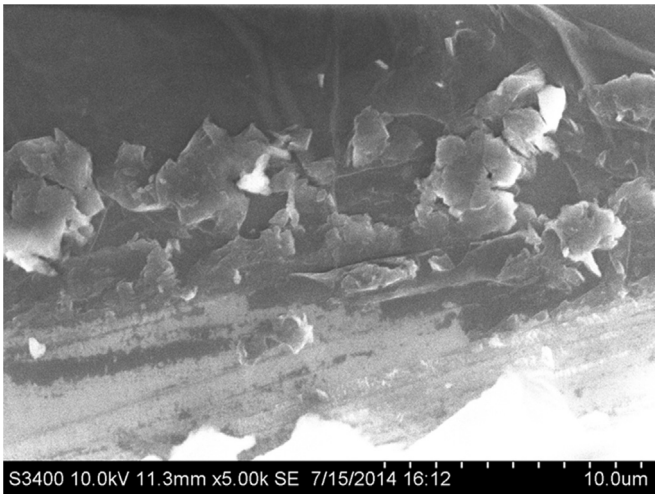

Fig. 1. The scanning electron microscope image of GO water solution.

3. Results and analysis

We conducted the open aperture Z-scan experiment for GO water solution under incident pulse intensity of 1.5×10^{15} W/m^2, 2.0×10^{15} W/m^2, and 3.2×10^{15} W/m^2 respectively. The experimental results are shown as Fig. 3. The triangles, circles and squares are experimental results of GO water solution, and the solid curves are theoretically fitting results under the three different incident intensities.

From the figure, it can be seen that the GO water solution displays reverse saturable absorption at 800 nm wavelength. The depth of valley enhanced with the incident intensity increasing in the open aperture Z-scan experimental results. The experimental results were well fitted with TPA and ESA theories [26]. The used TPA and ESA theoretical expresses were described in the following.

In order to investigate the mechanism of the reverse saturable absorption for GO water solution, we conducted the pump-probe experiment for GO water solution with the same laser pulses as used in the Z-scan experiment. The pump-probe experimental results are shown in Fig. 4 under excitation intensity of 2.0×10^{15} W/m^2. The circles are experimental results, and solid curves are the

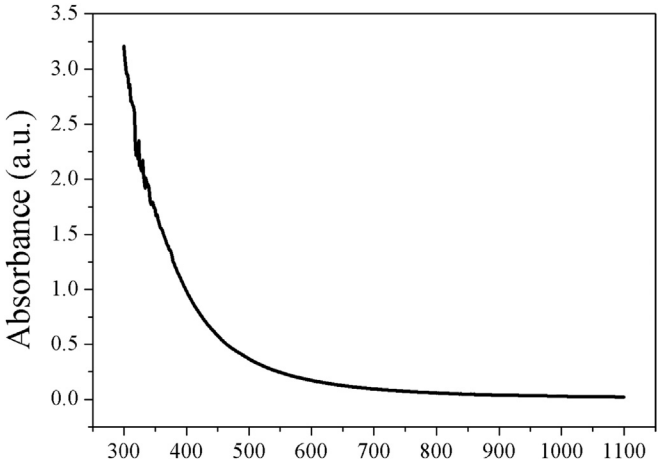

Fig. 2. The linear absorption spectra of GO water solution.