Two-photon absorption of monolayer graphene suspensions in femtosecond regime

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Nonlinear absorption of monolayer graphene suspension is studied in the wavelength of 800 nm using Z-scan method with 50-fs pulses. Nonlinear absorption property of graphene suspension at different excitation intensities is compared. Large reverse saturable absorptions are found and believed to arise from two-photon absorption.

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Graphene is a two-dimensional (2D) atomic crystal consisting of carbon atoms arranged in a hexagonal lattice. It has attracted considerable interest as a potential new electronic and photonic material owing to its Berry's phase, high conductivity, and localization suppression ability[1,2]. Due to the unique and large 2D π-electron conjugation system, much like that in fullerene (C_{60}) and carbon nanotubes (CNTs), graphene also exhibits good nonlinear absorption (NLA) properties. These highly delocalized π-electrons entrust graphene with high polarizability and fast charge redistribution when they interact with rapidly varying intense electromagnetic fields of laser beams, thereby resulting in strong optical nonlinearities and ultrafast response times. NLA is a phenomenon defined as a nonlinear change (increase or decrease) in absorption with increasing intensity. This can be either of two types: saturable absorption (SA) and reverse saturable absorption (RSA). Recently, nonlinear optical properties of graphene films and suspensions have been studied in great detail due to their potential application in ultrafast optical switching, optical limiting, and optoelectronic devices[3−6]. Using 80-fs laser pulse at 790 nm, SA behavior of graphene in dimethylformamide (DMF) has been observed at an intensity of 16 GW/cm^2[3]. Under intense 3.5-ns laser excitation at 532 nm, a single graphene sheet in heavy-atom solvents exhibits an excited state absorption (ESA)[4].

In this letter, large reverse saturable absorption of monolayer graphene suspension is observed from the Z-scan experiment at 800 nm at different excitation intensities in a femtosecond regime. The mechanism of nonlinear absorption is also discussed. The large RSA is believed to arise from two-photon absorption (TPA) in the femtosecond time domain.

A monolayer graphene sample was dispersed in an alcohol solution. The concentration of the suspension was 1 mg/L. Ultra violet-visible (UV-vis) spectrum was measured at room temperature with a spectrophotometer (Hitachi U-3310) in a wavelength range of 300–900 nm. The incident light propagated normally to the sample, which was taken in a 1-mm optical path length quartz cuvette. The absorption of monolayer graphene is quite flat from 300 to 900 nm, with a peak in the UV region (∼242 nm) (Fig. 1). This is attributed to inter-band electronic transition from the unoccupied states in the conduction band.

The nonlinear optical property of the above sample was detected using the open-aperture Z-scan method[7]. The femtosecond laser system consisting of a mode-locked Ti:sapphire oscillator and a regenerative amplifier (Spitfire, Spectra-Physics, 800 nm, 50 fs, 1 kHz) was used as the excitation source. The sample was scanned along the optical axis (z direction) and focused by a lens with focal length of 200 mm. The radius of the beam waist ω_0 was 30 μm, which was calculated from $\omega(z)^2 = \omega_0^2(1 + z^2/z_0^2)$, where $z_0 = \pi\omega_0^2/\lambda$ represented the Rayleigh length. The value of z_0 was calculated to be 3.5 mm, which was much larger than the thickness of the sample (1 mm). The energy was varied by a combination of a half-wave plate and a polarizer, while the incident and transmitted energies were measured with energy meters. The peak intensities incident on the sample were maintained within a range of 29–117 GW/cm^2 to avoid damage. Under a repetition rate of 1 kHz, the accumulative thermal effects can be neglected.

Figure 2 shows typical open-aperture (OA) Z-scan results for the monolayer graphene suspension at the different incident intensities of 29, 46, 88, and 117 GW/cm^2, respectively. In Fig. 2, the theoretical curves obtained considering the TPA clearly show excellent fit to the experimental data. The observed NLA properties are attributed only to the graphene samples, because the quartz cuvette filled with alcohol does not show any NLA property.

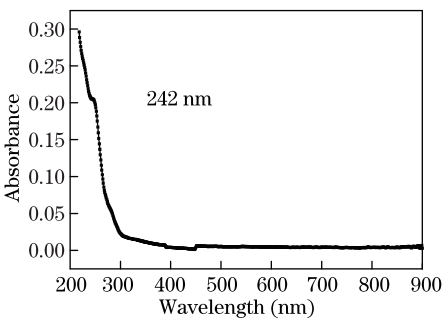

Fig. 1. UV-vis absorption characteristic of monolayer graphene dispersed in alcohol.

By increasing the input intensities, the transmittance valley within the peak becomes deeper. The decreased transmission, along with the increase of incident intensity, implies the optical limiting effect. Similar nonlinear processes have also been previously observed for CNTs and small π-electron conjugation systems, such as C_{60} and phthalocyanines (Pcs). However, the optical limiting mechanisms are totally different. The optical limiting behavior of C_{60} appeared to be dominated by the TPA process in the NIR-IR region[8]. Pcs display limiting effects in specific visible spectral regions due to reverse saturable absorption[9]. Meanwhile, CNTs exhibit prominent optical limiting behavior over a broad wavelength range from the visible to the near-infrared, resulting from effective scattering by laser-induced microbubbles and/or microplasmas[10]. In our experiment, laser pulse fluences are well below the threshold to avoid microbubble or microplasma formation. The closed aperture Z-scan experiments showed that no obvious nonlinear refraction is observed.

To interpret the basic mechanisms responsible for the nonlinear absorption, we pose the nonlinear propagation equation[11]:

$$\mathrm{d}I/\mathrm{d}z' = -\left[\frac{\alpha_0}{(1+I/I_\mathrm{s})} + \beta I\right] I, \tag{1}$$

where α_0 is the linear absorption coefficient for graphene suspension, which is 0.05 cm^{-1} at the excitation wavelength of 800 nm; I and I_S are the laser radiation intensity and saturation intensity, respectively; β is the TPA coefficient. The results under different excitation intensities, and after using a single parameter variation to extract β, show good fit with the proposed model.

To illustrate the mechanism of NLA in a femtosecond regime, we give the value of TPA coefficient β at different excitation intensity I_0 in Table 1. We found that β is weakly dependent on the input optical pulse energy. Moreover, with the increasing excitation intensity, the values of β decreased slightly (Fig. 3), indicating that large two-photon absorption plays an important role in the graphene suspensions in the femtosecond regime.

To understand the origin of the observed TPA and provide its theoretical estimation, we discuss the photoexcited carrier kinetics in graphene. Given that it is a zero band gap semiconductor with a linear dispersion relation $E_\pm(k) = \pm\hbar v_\mathrm{F}|k|$ in the vicinities of the K and K' points

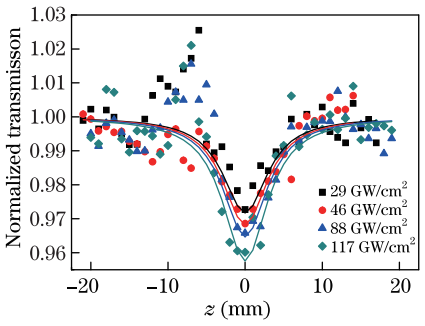

Fig. 2. OA Z-scan results for the graphene suspensions at different excitation intensities at the focal point I_0 = 29 $\mathrm{GW/cm^2}$ (squares), 46 $\mathrm{GW/cm^2}$ (circles), 88 $\mathrm{GW/cm^2}$ (triangles), 117 $\mathrm{GW/cm^2}$ (diamonds). The solid curves show the theoretical fit.

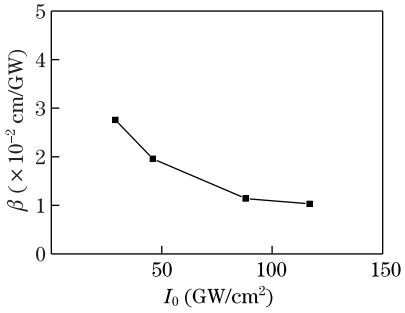

Fig. 3. Variation of the TPA coefficients with the excitation intensity at the focus (I_0).

Table 1. Effective Two Photon Absorption Coefficients β at 800 nm at Different Excitation Intensities I_0

I_0 ($\mathrm{GW/cm^2}$)	29	46	88	117
TPA ($\times 10^{-2}$ cm/GW)	2.76	1.96	1.14	1.03

of the Brillouin zone, where v_F is the electronic group velocity (about 1×10^6 m/s), electrons in the vicinity of the band gap behave as zero mass Dirac fermions. TPA is an interband transition wherein two photons, each with energy $\hbar\omega$, are absorbed simultaneously, thereby creating an electron in the conduction band and a hole in the valence band[12]. Using the quantum perturbation theory TPA coefficient can be analytical expressed as[5]

$$\beta = \frac{4\pi^2}{\varepsilon_\omega \omega^4 \hbar^3}\left(\frac{v_\mathrm{F} e^2}{c}\right)^2, \tag{2}$$

where ε_ω is the dielectric constant. It has been calculated that the TPA value of monolayer graphene is about 10^{-1} cm/GW at a wavelength of 800 nm, which is slightly larger than the experimental data in Table 1.

The higher order nonlinear absorption process described here is expected to be useful in effective optical limiting applications, especially against threats from the increasing availability of ultra-fast pulsed laser systems.

In conclusion, the intensity-dependent nonlinear optical properties of the sample are investigated by Z-scan using femtosecond laser (800 nm, 50 fs). A significant RSA is observed. Given that the TPA coefficients β decrease slightly with increasing the excitation intensity, the large RSA is attributed to an effective TPA mechanism.

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