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“Measurement of the third-order nonlinear susceptibility of graphene and its derivatives”

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14. ABSTRACT In this project, saturable absorption and optical Kerr nonlinearity of the atomic layer graphene and CdSe quantum dot doped graphene samples were experimentally measured using the Z-scan method. In addition to measurement of third-order nonlinear optical coefficients of the atomic layer graphene and derivatives, benchmark nonlinear refractive index measurements were performed on carbon disulfide (CS₂). Measurements show, in addition of the large saturable absorption, that graphene also has a large nonlinear refractive index, which is several orders of magnitude larger than conventional dielectric nonlinear materials. Enhancement of nonlinear optical response property of graphene-quantum dots (QDs) may be correlated to the charge transfer effect between graphene and QDs. The research findings show that 1) saturable absorption of graphene is strongly enhanced through doping CdSe QDs, and that maximum transmittance change due to saturable absorption can reach up to 70%; 2) depending on concentration, doping can induce large differences in photoluminescence behavior; and 3) by doping, saturable absorber devices can be tailored to the desired nonlinear optics properties.			
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Abstract

The saturable absorption and optical Kerr nonlinearity of the atomic layer graphene and one of its derivatives, the CdSe quantum dot doped graphene samples, were experimentally measured using the Z-scan method. Our measurement results show that apart from the saturable absorption, graphene also has a very large nonlinear refractive index n_2 , which can be potentially exploited for the nonlinear optical devices applications. Moreover, doping of the CdSe quantum dots in the graphene could enhance its nonlinear saturable absorption.

Research objective

The project is concerned with the experimental measurement of the third-order nonlinear optical coefficients of the atomic layer graphene and its derivatives, and furthermore to investigate the possible applications of atomic layer graphene in nonlinear optical devices. An optical Z-scan setup is constructed to study the optical Kerr effect of graphene and its derivatives. If time is available, the possible applications of the graphene nonlinear optical Kerr effect in nonlinear nano-optical devices, such as nonlinear optical switcher, supercontinuum generation, and Optical Parametric Oscillators (OPO) will be explored.

Research progress and results obtained

a) Construction of the Z-scan setup

A Z-scan experimental setup as shown in Fig. 1 is established. Either a home-made passively mode locked erbium-doped fiber laser or a commercial femtosecond Ti:Sapphire laser (Coherent company, center wavelength: 800 nm, pulse duration: 100 fs, 3 dB spectral width: 15 nm, and pulse repetition rate: 1 kHz) is used as the ultrashort pulse source for the measurement. An optical attenuator is used to control the average power to ensure that the beam intensity is below the optical damage threshold of the sample, and the multiple-photon effect is significantly suppressed. The laser beam is focused by an objective lens and then incident onto the samples. The graphene sample is set perpendicular to the beam axis. A linear translation stage is used to shift the sample position along the Z-axis. A computer controlled dual-detector power meters are used to simultaneously measure the optical power.

Measurements are performed in two regimes, an open-aperture regime wherein all light transmitted through the sample is collected, and a closed-aperture regime wherein only the on-axis transmitted beam is collected by the power-detector. The open-aperture regime enables one to measure the nonlinear absorption, while within the closed aperture regime; the change of optical transmittance is a combined consequence of the nonlinear absorption and the nonlinear phase effect induced by the optical Kerr nonlinearity. The division of the closed-aperture measurement by the open-aperture measurement results in the separation of these two effects.

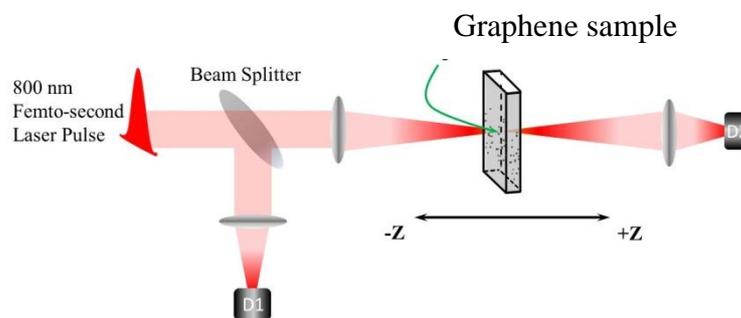


Figure 1: Experimental setup for the z-scan measurements.

b) Z-scan measurement of a CS₂ sample

To precisely identify the nonlinear refractive index of the measured samples, we have first measured the nonlinear refractive index of the CS₂ solution contained in a cuvette (1 mm in thick). The result is used as a benchmark for the calibration purpose. The 800 nm femtosecond pulsed laser was used as the light source. Under the illumination of a peak beam intensity of $76 \text{ GW}\cdot\text{cm}^{-2}$ at the focus point, the Z-scan measurement results are shown in Fig. 2. The open aperture measurement shows a typical curve of the optical limiting effect, which indicates existence of two-photon absorption (2PA) effect. Due to the nonlinear absorption, the closed aperture measurement shown in Fig. 2(b) is asymmetric. Dividing by the open aperture curve, the Fig. 2 (c) trace exhibits a typical shape of Z-scan curve. The nonlinear on-axis phase shift $\Delta\Phi$ is fitted to be 1.35 rad and the calculated nonlinear refractive index is about $2.66 \times 10^{-19} \text{ m}^2/\text{W}$, which is in good agreement with $(3 \pm 0.6) \times 10^{-19} \text{ m}^2/\text{W}$ reported. A plot of $\Delta\Phi$ versus peak laser irradiance as measured from various Z-scan on the same CS₂ cell is shown in Fig. 2 (d).

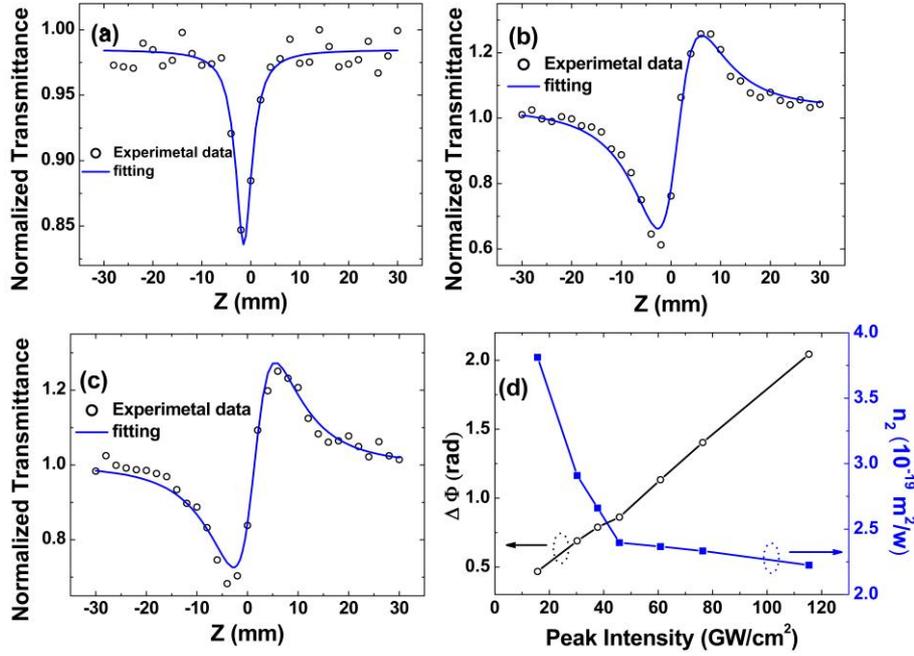


Figure 2: Z-scan traces for 1 mm thickness CS_2 sample at a peak intensity of $76 \text{ GW}\cdot\text{cm}^{-2}$. (a) Near field (open aperture). (b) Far field (closed aperture). Upon dividing by the near field curve one obtains the data of panel (c) which exhibits the typical shape of a Z-scan curve with positive nonlinear phase shift having an on-axis value of $\Delta\Phi = 1.35 \text{ rad}$. (d) The changes of $\Delta\Phi$ and n_2 with increasing peak intensity at the focus.

C. Z-scan measurement of a three-layer graphene sample

The saturable absorption of a three-layer graphene sample was measured using the open-aperture Z-scan technique. The graphene sample was synthesized by our collaborator Prof. Loh Kian Ping's research group, at National University of Singapore. In this Z-scan measurement a pico-second erbium fiber laser with center wavelength tunable from 1525 nm to 1570 nm was used as the light source. The pulses emitted from the fiber laser were first amplified by an erbium doped fiber amplifier (EDFA), and then focused by a 20 times microscope objective. The beam waist was measured to be $\sim 3 \mu\text{m}$. A portion of the input laser beam is picked off by a beam splitter and measured by the detector D1 as the reference of the incident optical power. The graphene sample was placed perpendicular to the beam axis. By translating the sample through the focal plane with a Newport ESP301 linear motorized stage along its propagation (Z) axis, output power was measured by the detector D2. Dividing the data measured from D2 by the data from D1, a Z-scan curve with a strong peak near the focus point was obtained, as shown in Fig. 3. Fitting this curve yields a saturable intensity of about 74 MW cm^{-2} at the wavelength of 1550 nm.

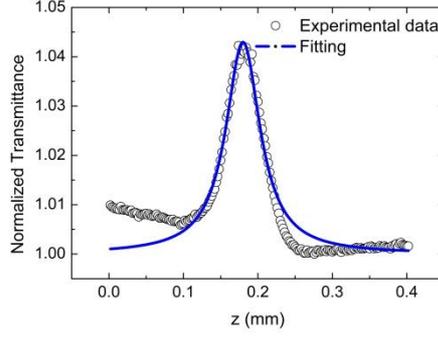


Figure 3: Open-aperture z-scan measurement for three-layer graphene.

D. Open and close aperture measurement of the mono-layer graphene

In order to probe the fundamental nonlinear optics property of graphene, mono-layer graphene, that is only one carbon atom in thickness, was transferred onto a quartz substrate and then preformed under the open and close aperture measurement. Figure 4 shows the open and close aperture measurement of the mono-layer graphene. Under the open aperture measurement, which is a result of the transmittance variation with respect to the distance between the laser focus and the sample, one can find that for mono-layer graphene, the saturation depth that is the transmittance difference between the maximum transmittance at the focus and the minimum transmittance far out of the focus, is about 1.6%. Under the close aperture measurement, which is a combined consequence of both the saturable absorption effect and the nonlinear phase change induced nonlinear transmittance, one can obtain a clearly different z-scan curve from the open aperture measurement as shown in Fig. 4b. Dividing the close aperture measurement by the open aperture measurement, one can eliminate the contribution from the saturable absorption and therefore the nonlinear phase shift can be deduced from the up-down curve as in Fig. 4c. By fitting the results with the classic nonlinear Kerr nonlinearity fitting formula,

$$\begin{aligned}
T(x) = & 1 + \frac{4x\Delta\Phi}{(1+x^2)(9+x^2)} \\
& + \frac{4(3x^2-5)\Delta\Phi^2}{(1+x^2)^2(9+x^2)(25+x^2)} \\
& + \frac{32(3x^2-11)x\Delta\Phi^3}{(1+x^2)^3(9+x^2)(25+x^2)(49+x^2)}
\end{aligned}$$

where $T(x)$ is the normalized transmittance, $x = z/z_R$, $z_R = \pi\omega_0^2/\lambda$, and $\Delta\Phi = kn_2I_0L_{eff}$ is the on-axis nonlinear phase shift at the focus, k is the wavenumber, I_0 is the

irradiance at the focus, L_{eff} is the sample's effective length, one can estimate that the nonlinear refractive index of monolayer graphene is about $n_2=10^{-11} \text{ m}^2/\text{W}$.

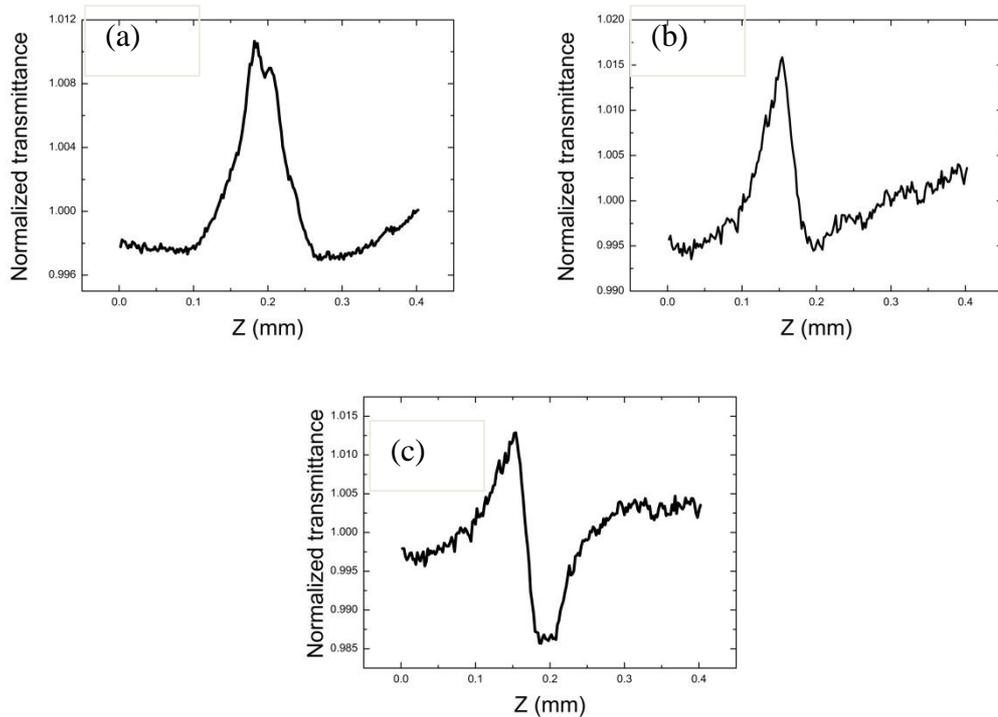


Figure 4: (a) Open-aperture z-scan measurement for mono-layer graphene. (b) Close-aperture z-scan measurement for mono-layer graphene. (c) The division of the close and open aperture measurements for mono-layer graphene.

E. Z-scan measurement of the graphene-CdSe quantum dots samples

Although the atomic layer graphene has a very large n_2 value, in the meantime it also has strong absorption per unit mass (2.3% per atom-layer). Define the figure of merit of a nonlinear optical material as the ratio of nonlinear phase change with respect to the light absorbance. This feature of graphene undermines its use as a nonlinear optical material for some nonlinear optics applications. To improve the figure of merit of graphene it was proposed to heavily dope graphene to shift its Fermi level below the one-photon inter-band transition energy. In this way it might be possible to change graphene to have negligible linear losses but still maintain the high Kerr nonlinearity. To this end we then studied the nonlinear optical properties of graphene doped with different concentrations of the CdSe quantum dots.

The samples were fabricated by our collaborator Prof. Loh Kai Ping's group at National University of Singapore. The linear properties of the CdSe quantum dots doped graphene samples with different CdSe doping concentrations were characterized at first. Fig. 5 shows the linear absorbance of the doped samples under different CdSe doping concentrations.

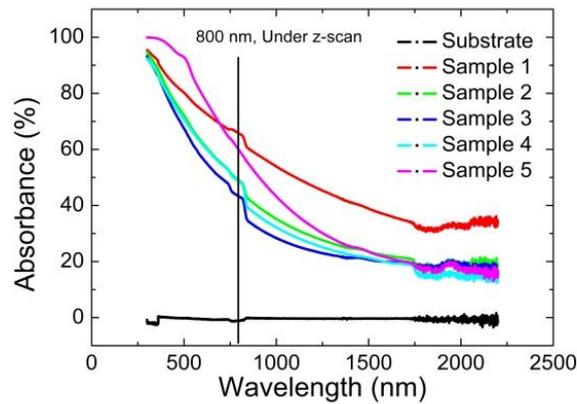


Figure 5: Linear absorbance of the CdSe quantum dots doped graphene samples.

Fig. 6 shows the photo-luminescence of the samples, obtained under the illumination of a laser beam with central wavelength of 532 nm and a power of 2 mW. Experimentally, it was found that graphene samples doped with different CdSe quantum dot concentrations could have different fluorescence spectra. While some samples have a single fluorescence peak, peaked at 670nm, the others have a double-peak structure, peaks at 571 nm and 586 nm. Moreover, no photo-luminescence was observed for graphene oxide-PVA or pure graphene oxide.

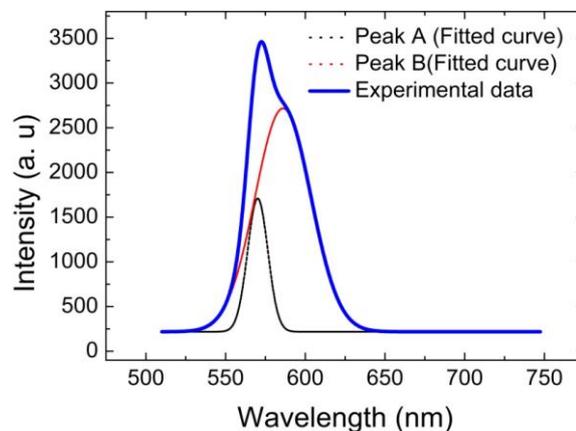


Figure 6: The photo-luminescence spectra of graphene-CdSe quantum dot samples.

Figure 7 is a typical Raman spectrum of the graphene-CdSe quantum dot samples. The D peak and G peak could be seen. However, due to the relatively strong PL effect, these two peaks look very weak now.

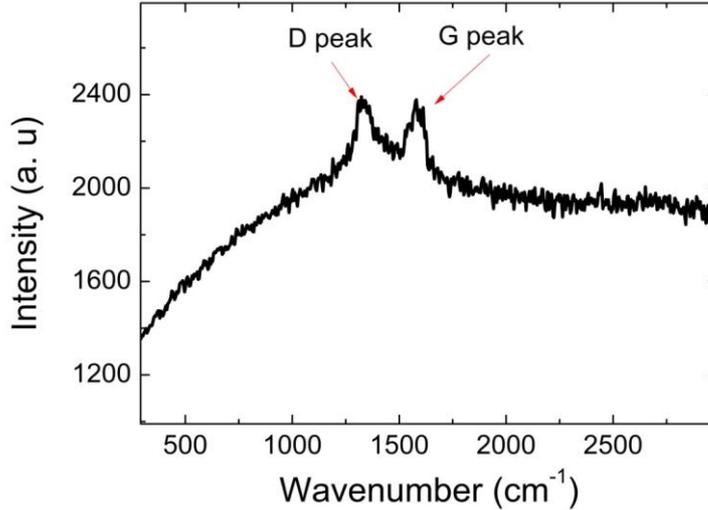


Figure 7: A typical Raman spectrum of the graphene-CdSe quantum dot sample.

The Z-scan was performed at an incident irradiance of 10.4 GW/cm^2 . A typical open aperture trace is shown in Fig. 8(a), when the sample is translated through the beam focus. A sharp and narrow peak located at the beam focus clearly shows the characteristic of nonlinear absorption. Fig. 8(b) shows a typical closed-aperture measurement. In this trace, as the effect of the nonlinear phase is of the same order of magnitude as the effect of the saturable absorption, upon dividing the curve shown in Fig. 8(b) by the curve shown in Fig. 8(a), the nonlinear phase change shown in Fig. 8(c) was obtained. The latter has the typical shape of a Z-scan trace for the Kerr nonlinearity. The pre-focal valley and the post-focal peak suggest the positive sign of the nonlinear refractive index, indicating the self-focusing effect of the sample.

By controlling the incident optical pump power, we are able to characterize the nonlinear optical response of graphene quantum dot under various pump intensities from 0.2 GW/cm^2 to 26.9 GW/cm^2 . By gradually increasing the pump intensity, one could see that the modulation depth of the saturable absorption also increases with the increase of the pump power, as shown in Figure 8. Herein, the

modulation depth is defined to be the intensity difference between the maximum transmittance (when the laser beam is exactly focused onto the sample surface) and the minimum transmittance (when the laser beam size at the sample surface is sufficiently large). The inferred modulation depth increases with the laser pump and then becomes saturated at very high pump power. This value can increase from 42% at a pump power of $0.05 \mu\text{W}$ to 69% at a pump power of $14 \mu\text{W}$. The well match between the relation of modulation depth and the fitted curve in Figure 9, strongly demonstrated the existence of saturable absorption of the graphene-QDs. Moreover, the modulation depth of graphene-QDs (sample 4) is much higher than that of graphene. The enhancement of nonlinear optical response property of graphene-QDs (sample 4) may be correlated to the charge transfer effect between graphene and QDs.

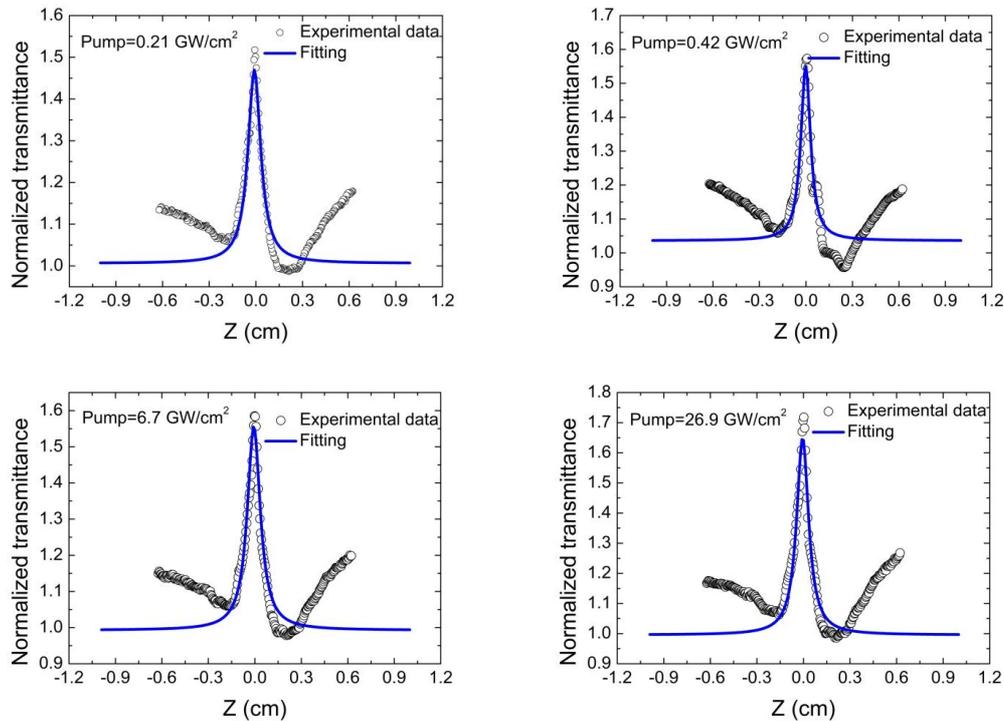


Figure 8. Z-scan measurement of a Graphene-CdSe quantum dots sample under various pump intensity: 0.21 GW/cm^2 , 0.42 GW/cm^2 , 6.7 GW/cm^2 , 26.9 GW/cm^2 , respectively.

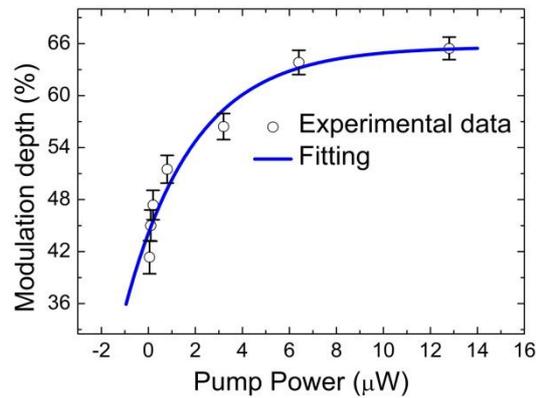


Figure 9. Relation between the derived modulation depth and the input power on the sample.

The experimental measurements show that (1) the saturable absorption of graphene is strongly enhanced through doping CdSe quantum dots. The maximum transmittance change due to saturable absorption can reach up to 70%. (2) Different doping can induce the large differences in the photoluminescence spectra. (3) By doping, the saturable absorber devices can be tailored to the desired nonlinear optics properties.

Suggestions for the future studies

Based on the Z-scan measurements we have experimentally determined the nonlinear saturable absorption and refractive index coefficients of atomic layer graphene. Our measurements show, in addition of the large saturable absorption, graphene also has a large nonlinear refractive index, which is several orders of magnitude large than the conventional dielectric nonlinear materials. Through doping the CdSe quantum dots in the graphene, its nonlinear optical properties could be altered. Depending on the doping concentrations, nonlinear saturable absorption of graphene could be greatly enhanced. For the future research on the topic, we believe it is worth further study on the nonlinear optical properties of graphene under various doping and chemical functionalizations. Research on the nonlinear optical properties of other 2D nanomaterials, such as the various topological insulators, and the MoS₂ nanomaterials etc. and the exploitation of their nonlinear optical properties for the photonic device applications, would also be attractive fields.