

## Nonlinear optical properties of graphene-based materials

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Graphene, a two-dimensional carbon atom sheet, has attracted tremendous attention and research interest because of its exceptional physical properties. Graphene has high mobility and optical transparency, in addition to flexibility, robustness and environmental stability. The main focus so far has been on fundamental physics and electronic devices. However, because the linear dispersion of the Dirac electrons enables ultrawideband tunability, we believe its true potential lies in photonics and optoelectronics. In this review, we introduce recent advances in the nonlinear optical properties of graphene-based materials. The rise of graphene in nonlinear optics is shown by several recent results, ranging from saturable absorbers and the four-wave mixing effect to giant two-photon absorption, reverse saturable absorption and optical limiting. The relevant forms of the graphene-based materials include pure graphene, graphene oxide and graphene hybrids.

**graphene, nonlinear optical properties, optical limiting, saturable absorber, graphene oxide**

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Graphene is a two-dimensional single layer of carbon atoms with a hexagonal packed structure. Electrons propagating through graphene behave as massless Dirac fermions because of the linear relation between their energy and their momentum [1]. Graphene has thus shown many unique properties, such as the quantum Hall effect, high carrier mobility at room temperature, a large theoretical specific surface area, good optical transparency, and excellent thermal conductivity. Some remarkable optical properties have also been observed in graphene. For example, it can be optically visualized, despite being only a single atom thick [2]. Its transmittance can be expressed in terms of its fine-structure constant [3]. Broadband saturable absorption was also observed as a consequence of Pauli blocking caused by the linear dispersion of the Dirac electrons in graphene, which makes it suitable for application to ultrafast mode-locked lasers [4–7]. Also, nonequilibrium carriers and chem-

ical or physical treatment of graphene can lead to luminescence [8,9]. These properties make it an ideal photonic and optoelectronic material. Consequently, there is growing interest in graphene optoelectronics and initial demonstrations of graphene-based photodetectors [10,11], optical modulators [12], plasmonic devices [13,14] and ultrafast lasers [4–7] have been reported.

Recently, it has been predicted that graphene's linear dispersion properties should lead to strongly nonlinear optical (NLO) behavior at microwave and terahertz frequencies [15]. At higher optical frequencies, one can also expect enhanced optical nonlinearity because of the graphene band structure, because interband optical transitions occur at all photon energies. Materials with excellent photophysical properties and large optical nonlinearities have many potential applications including fast optical communications, all-optical switching, and optical limiting. Graphene shows remarkable optical nonlinearities with ultrafast response times and a broadband spectral range. For pristine graphene,

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strong saturable absorption (SA) and four-wave mixing (FWM) have been found because of the large absorption and Pauli blocking [5,16]. Apart from pristine graphene, a number of its derivatives have been synthesized and other NLO effects have been observed, including two-photon absorption (TPA) [17], reverse saturable absorption (RSA) [18], and optical limiting [19,20]. In the following, we will focus on the NLO properties of graphene-based materials, the exploration of their properties, and studies of their applications.

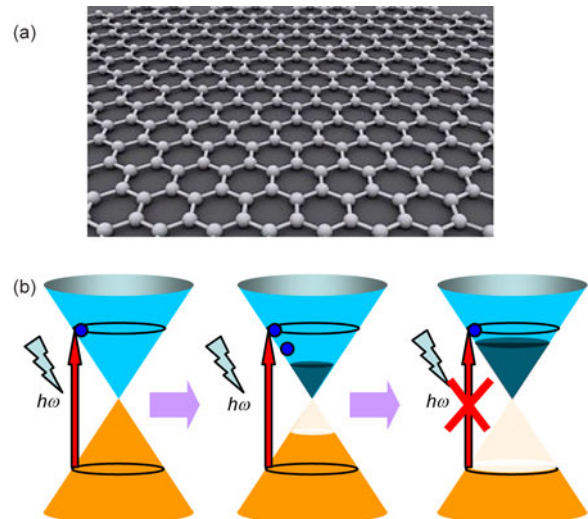
## 1 Graphene-based materials

Pristine graphene is a hydrophobic material, and has no appreciable solubility in most solvents. However, it is known that solubility and processability are the first issues for many prospective applications of graphene-based materials. To improve the solubility and change the physical properties of graphene, different functional groups have been attached to the carbon backbone by covalent or noncovalent chemical modification. Other forms of graphene-related materials, including graphene oxide (GO), reduced GO, and exfoliated graphite, have been reliably produced on a large scale. Their promising properties together with their ease of processability and functionalization make graphene-based materials ideal candidates for incorporation into a variety of functional materials. These graphene-based materials with their different forms have different nonlinear properties and photophysical processes. In particular, manipulation of the structure of graphene provides opportunities to tailor its optoelectronic properties.

### 1.1 Pristine graphene

The electronic and optical properties of pristine graphene, a single atomic layer of  $sp^2$ -hybridized carbon forming a honeycomb crystal lattice (Figure 1(a)), can be described in terms of massless Dirac fermions with linear dispersion near the Fermi energy. Pristine graphene can be obtained from the mechanical exfoliation of graphite using adhesive tapes [21], chemical vapor deposition (CVD) growth on metal surfaces [22], and carbon segregation on SiC [23].

The linear dispersion of Dirac electrons means that the optical interband transitions are expected to be frequency independent and are solely determined by the optical conductance over a broad range of photon energies. On the other hand, the remarkably large absorption of atomic-layer graphene implies a lower saturation intensity or a higher photocarrier density compared to traditional semiconductor materials such as gallium arsenide. A schematic of the excitation process responsible for absorption of light in graphene is shown in Figure 1(b). The arrow indicates the optical interband transition. The photogenerated carriers thermalize and cool down within sub-picosecond time scales to



**Figure 1** (Color online) Graphene structure (a) and absorption of light in graphene (b). Electrons from the valence band are excited into the conduction band in (b).

form a hot Fermi-Dirac distribution, meaning that an equilibrium electron and hole distribution could be finally approached through intraband phonon scattering and electron-hole recombination. At high excitation intensities, the photogenerated carriers cause the states near the edge of the conduction and valence bands to fill, blocking further absorption. Thus, broadband SA is the main NLO property of graphene, which has relevance for fiber laser mode locking [4–7,24–26].

After SA, the third-order optical susceptibility is found to be large in both single and multi-layer graphene [16]. This large optical nonlinearity originates from the interband electron transitions and is 8 orders of magnitude larger than the nonlinearities observed in dielectric materials without such transitions. In contrast to carbon nanotubes, the optical nonlinearities in graphene do not show resonant behavior as a function of excitation wavelength. Giant TPA has also been reported for bilayer graphene [27]. It was found that TPA is significantly different and greater in Bernal-stacked bilayer graphene structures than in monolayer graphene.

### 1.2 Graphene oxide

GO is synthesized by the oxidation of graphene, and its unique atomic and electronic structure has been revealed to show small  $sp^2$  carbon clusters that are isolated by the  $sp^3$  matrix [28,29]. In contrast to pristine graphene, the graphene-derived sheets in GO are heavily oxygenated, bearing hydroxyl and epoxide functional groups on their basal planes, with carbonyl and carboxyl groups located at the sheet edges. The presence of these functional groups makes the GO sheets strongly hydrophilic, which allows GO to readily swell and disperse in water.

Initially, GO traditionally served as a precursor for

graphene. However, GO is increasingly attracting chemists and researchers from other disciplines for its own characteristics. A pristine graphene sheet consists entirely of  $sp^2$ -hybridized carbon atoms. In contrast to the well-established electronic structure of graphene as a zero-gap semiconductor with  $sp^2$  hybridized carbon atoms, GO is a two-dimensional network consisting of  $sp^2$  and  $sp^3$  hybridized regions, resulting in a heterogeneous electronic structure that features both  $\pi$ -states from the  $sp^2$  carbon sites and a large energy gap between the  $\sigma$ -states of the  $sp^3$  bonded carbons. Tuning of the  $sp^2$  fraction by careful and controllable removal of specific oxygen groups presents possibilities for tailoring of the electrical, optical and chemical properties of GO.

Based on Gaussian and density functional theory calculations, the  $sp^2$  clusters with diameters of  $\sim 3$  nm have energy gaps of approximately 0.5 eV [9]. There is a large energy gap (carrier transport gap) between the  $\sigma$ -states of the  $sp^3$ -bonded carbons in GO, similar to that of amorphous carbon, in which a large energy gap ranging from 2.7 to 3.1 eV for  $sp^3$ -bonded carbons has been reported [30]. From this, a heterogeneous optical transition and a nonlinear dynamic are expected in GO, as shown in Figure 2(b). The ultrafast relaxation dynamics and NLO study show that the unique atomic and electronic structure of GO leads to the emergence of variable absorption processes under different input intensities, and the different absorption processes are distributed between the  $sp^2$  clusters and the  $sp^3$  domains of GO [31]. Consequently, the NLO properties of GO are determined by the combined action of the  $sp^2$  and the  $sp^3$  domains. Under the excitation of a near-infrared laser, it is found that the charge carriers with SA from the  $sp^2$ -hybridized domains dominate the nonlinear response at low pump intensities, while the influence of the TPA from the  $sp^3$ -hybridized domains on the transient absorption signal

becomes increasingly strong with increasing pump intensity [31]. Thus far, SA, TPA and excited state absorption have been observed in GO under the excitation of nanosecond to femtosecond pulse lasers. This concept suggests new possibilities for engineering of the linear and NLO properties of a nonstoichiometric macromolecule by manipulating the size, shape, and relative fraction of the different absorption domains [29].

Also, to improve the solubility and simultaneously preserve some of the unique properties of the pristine graphene, it is necessary to retain the large fraction of  $sp^2$  domains in GO. Using the arc-discharge method, few-layer GO was synthesized and has fast carrier relaxation combined with good solution processing capability, which arises from the large fraction of  $sp^2$  carbon atoms together with the oxidation that mainly exists at the edge areas [32,33].

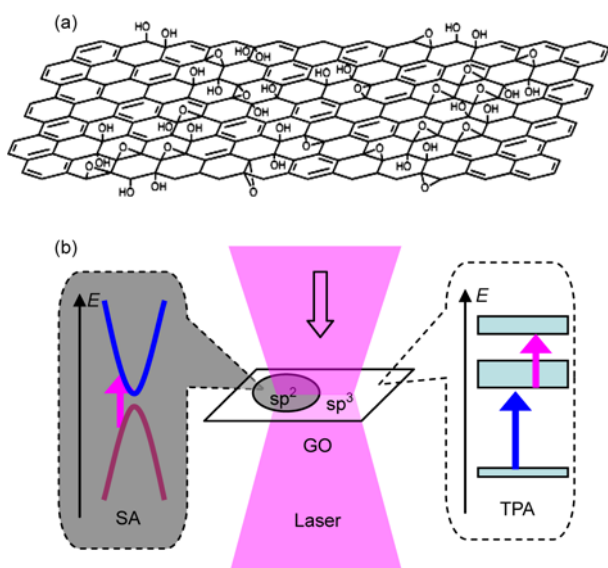
### 1.3 Graphene hybrid materials

Functionalization of graphene or GO surfaces is one of the most important ways to further expand the potential of these materials and to improve their solubility and processability. It is expected that the combination of electron-donor molecules such as porphyrins, fullerenes, polythiophenes or oligothiophenes with the electron-acceptor molecules of graphene would generate an interesting push-pull hybrid, potentially with good optoelectronic properties. Solution-processable multifunctional graphene hybrid materials that combine the advantages of the superior properties of both graphene and the functionalizing materials have been largely unexplored. The enhanced NLO properties are caused by a combination of multiple NLO mechanisms from graphene and other NLO materials, and the proposed photoinduced electron or energy transfer in the hybrid materials, which provides a good approach to obtain materials with high value NLO properties [34].

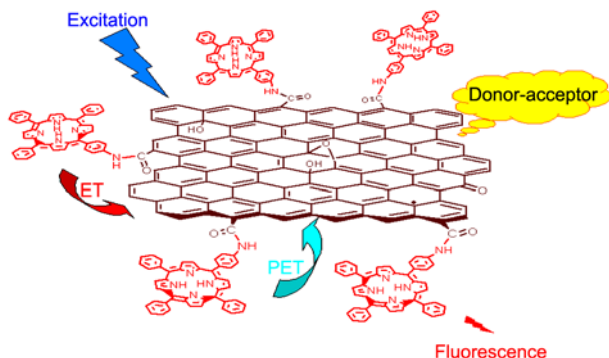
Graphene is covalently functionalized by materials with large optical nonlinearities, including porphyrins [35], fullerenes [36], oligothiophenes [37],  $Fe_3O_4$  nanoparticles [38], and phthalocyanine [39]. Covalently linking two materials with large optical nonlinearities will cause greater enhancement of the optical nonlinearities of this system compared to those of the individual components and the blended system because of the combination of the nonlinear mechanism and the strong interaction between the two components, such as the photoinduced electron or energy transfer as shown in Figure 3.

## 2 Nonlinear optical properties

Nonlinear optics is a revolutionary extension of linear optics promoted by laser technology. This area deals mainly with various new optical effects and phenomena that arise from the interactions of intense coherent radiation with matter.



**Figure 2** (Color online) GO structure (a) and absorption of light in GO (b).



**Figure 3** (Color online) Graphene hybrid material covalently functionalized with porphyrin. Reprinted with permission from [35], Copyright 2009, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The nonlinearity is typically only observed at very high light intensities, such as that provided by lasers. Materials with excellent photophysical properties and large optical nonlinearities have many potential applications including fast optical communications, all-optical switching, and optical limiting. As a novel carbon-based material, pristine graphene shows remarkable optoelectronic properties and optical nonlinearities with ultrafast response times and a broad spectral range. Graphene-based compounds also offer the advantage of tailorability: fine-tuning of the NLO properties can be achieved by rational modification of the chemical structure. Many NLO effects such as SA, TPA, RSA, FWM and optical limiting can be observed in graphene-based materials. All of these chemical variations, including oxidation and functionalization, can alter the electronic structure of the graphene, and therefore they allow fine-tuning of the nonlinear response and make more extensive applications easier because of the multiple NLO mechanisms.

## 2.1 Saturable absorption

SA is a property of materials where the absorption of light decreases with increasing light intensity. At a sufficiently high incident intensity, atoms in the ground state of a saturable absorber material are excited into an upper energy state, while the rate at which they decay back to the ground state is insufficient for them to decay before the ground state becomes depleted, and the absorption subsequently saturates. Under low excitation intensity, the linear optical transition results in the equilibrium of the electron and hole distribution being reached by electron-hole recombination shortly after photo-excitation. As the excitation increases to a higher intensity, the photogenerated carriers increase in concentration (much larger than the intrinsic electron and hole carrier densities in graphene at room temperature [40]) and cause the states near the edges of the conduction and valence bands to fill, blocking further absorption and imparting transparency to light at photon energies just above the band-edge. If the incident light intensity becomes strong enough, because of the Pauli blocking principle, the gene-

rated carriers fill the valence bands, preventing further excitation of electrons at the valence band and allowing photons to be transmitted without loss, as shown in Figure 1(b). Thus, SA or absorption bleaching can be achieved because of this Pauli blocking process.

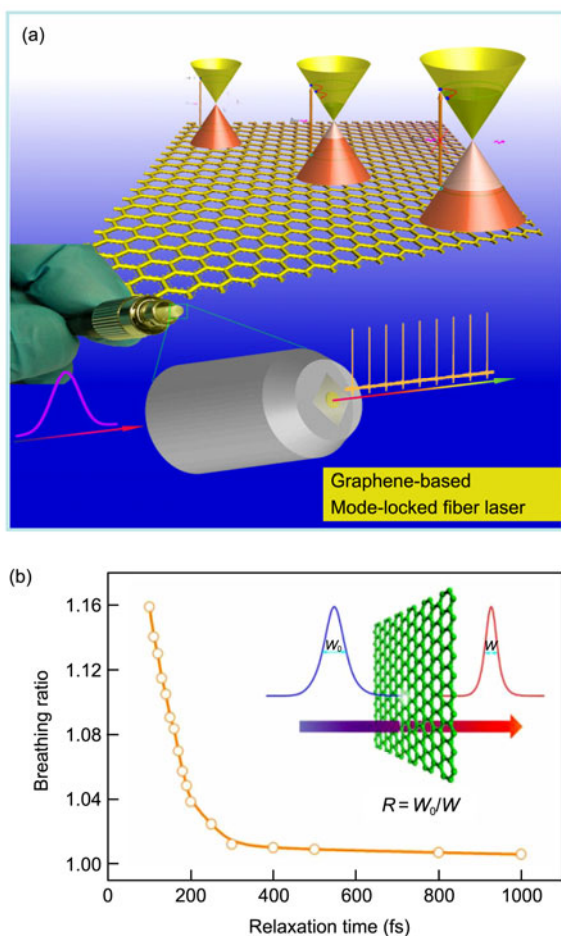
Unlike conventional semiconductor materials, the valence band and conduction band in graphene are smooth-sided cones that meet at a point, called the Dirac point, and graphene has no energy band-gap and readily absorbs all photons at any wavelength. As the high frequency dynamic conductivity for Dirac fermions is constant, the optical absorption of graphene is independent of the wavelength. This is an indication that graphene could potentially be used as a saturable absorber with wide optical response to cover all telecommunications bandwidths and also the mid- and far-infrared.

Apart from broadband operation, high-speed processing is also an important feature of graphene as a saturable absorber. The ultrafast dynamics of charge carriers in graphene have been reported using an ultrafast pump-probe technique, and fast decay times from tens to hundreds of femtoseconds were assigned to carrier-carrier scattering and carrier-phonon scattering [41–44]. The speed limiting processes in pristine graphene, such as photocarrier generation and relaxation, therefore operate on the picosecond timescale.

Fast response times, strong nonlinearity, and a broad wavelength range make graphene an ideal saturable absorber that is a key mode-locking element in an ultrafast laser system (Figure 4(a)). Graphene as a saturable absorber can turn continuous-wave (CW) output into a train of ultrafast optical pulses. Under stable mode locking operating conditions, the pulse durations before and after the graphene were compared, as shown in Figure 4(b). Accordingly, the ratio of pulse width variation was adopted to describe graphene's pulse shaping ability. Until now, various strategies have been proposed to integrate graphene saturable absorbers (GSA) in laser cavities for ultrafast pulse generation. The most common strategy is to sandwich a GSA between two fiber connectors with a fiber adaptor at  $\sim 1.5 \mu\text{m}$  [4,5]. A sub-200 fs pulse has been generated from a graphene mode-locked fiber laser using the sandwich structure [24]. Graphene on a side-polished fiber has also been reported, with the aim of high power generation by evanescent field interaction [25]. A quartz substrate coated with graphene has been used for free-space solid-state lasers to generate ultrafast pulses at  $\sim 1 \mu\text{m}$  [46]. Few-layer GO and functionalized graphene have also been used as saturable absorbers for ultrafast lasers because of the retention of the  $sp^2$  domains in these graphene-based materials [47].

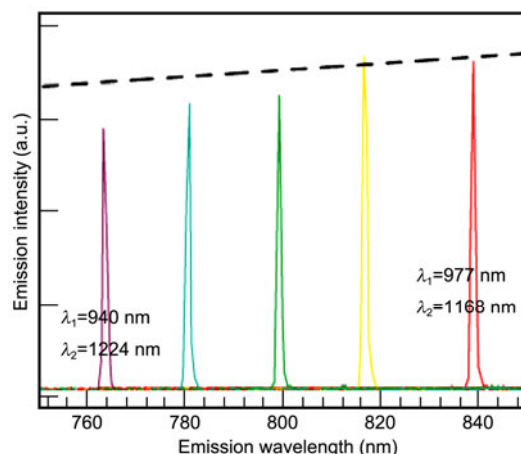
## 2.2 Four-wave mixing

Surprising results have recently been reported on the coherent NLO properties of graphene using FWM. Hendry et al. [16] used FWM to measure the NLO properties of graphene



**Figure 4** (Color online) (a) Schematic of excitation process responsible for SA of light in graphene and schematic of operating principle of graphene-based saturable absorber which locked modes and turned CW into pulses. Reprinted with permission from [5], Copyright 2009, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Breathing ratio of graphene as a function of relaxation time. Inset indicates pulse shaping by graphene and definition of the breathing ratio  $R=W_0/W$ , where  $W_0$  is the pulse width before graphene shaping and  $W$  is the pulse width after graphene shaping. Reprinted with permission from [45], Copyright 2011, Springer Science+Business Media.

flakes (fabricated using the mechanical exfoliation method and deposited on a glass cover slip). The dependence of the nonlinear signal of monolayer graphene on the emission wavelength  $\lambda_c$  is shown in Figure 5 for different combinations of the pump wavelengths  $\lambda_1$  and  $\lambda_2$ . By comparing the emission signal of graphene to that of a well-characterized quasi-2D material under the same experimental conditions, the third-order nonlinear susceptibility value of monolayer graphene could be determined. The third-order nonlinear susceptibility of monolayer graphene in the near-infrared spectral region is determined to be  $1.5 \times 10^{-7}$  esu, which is in good agreement with theoretical calculations based on the nonlinear quantum response. Interband electron transitions result in the large nonlinear optical properties of graphene. The susceptibility value of monolayer graphene is eight orders of magnitude higher than the same nonlinearity in



**Figure 5** (Color online) Emission spectra of a graphene flake excited with pump pulses of different wavelengths, ( $\lambda_1$ ,  $\lambda_2$ ): from left to right, the wavelength pairs are (940, 1224 nm), (950, 1210 nm), (958, 1196 nm), (967, 1183 nm), and (977, 1168 nm). The dashed line represents the wavelength dependence predicted by the theory. Reprinted with permission from [16], Copyright 2010, American Physical Society.

normal dielectric materials. Thus, the large nonlinearity of graphene can be used as a tool in FWM imaging and the visibility of the graphene flakes can be greatly enhanced.

The susceptibility is weakly dependent on the wavelength in the near-infrared frequency range. The dispersion properties are quite different to those of semiconducting nanotubes, which also possess interband transitions. This property makes graphene a candidate material for broadband nonlinear applications. It is believed that stronger nonlinearities could be obtained at lower frequencies, such as far-infrared and terahertz frequencies.

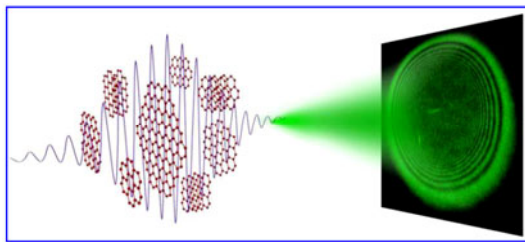
For solution dispersions of graphene sheets, Wu et al. [27] studied the purely coherent NLO response by using near-infrared, visible, and ultraviolet CW and ultrafast laser beams. In their measurements, a laser beam was focused on the graphene suspension, which was contained in a 1 cm-thick quartz cuvette; diffraction rings could then be observed on a white screen placed 430 cm away behind the sample. The number of rings increased nearly linearly with the incident intensity when the intensity was below  $100 \text{ W/cm}^2$ . The intensity threshold for the diffraction rings is about  $12.5 \text{ W/cm}^2$  for a 532 nm CW laser. The threshold could be reduced to  $0.6 \text{ W/cm}^2$  by removing the lens. This reduction of the intensity threshold could be understood in that there were more graphene sheets inside the active illuminated area when the incident beam was unfocused. The diffraction rings originate from a third-order nonlinearity of the graphene sheets, i.e. spatial self-phase modulation. From a theoretical analysis of the diffraction rings, the effective third-order nonlinear susceptibility of single-layer graphene was estimated to be the order of  $1 \times 10^{-7}$  esu, which is in good agreement with Hendry's results. The physical mechanism of the nonlinearity may be attributed to the reorientation and alignment of the graphene sheets induced by the

electromagnetic field, as interpreted by Wu et al. When the incident light passes through the graphene sheets, the electron in the valence band absorbs one incident photon and is excited to the conduction band through an inter-band transition. The generated electrons and holes move in different directions, anti-parallel and parallel to the electric field, respectively. Thus, the graphene sheets are polarized. To minimize the interaction energy between the polarized graphene sheet and the electric field, the graphene sheets will align themselves. On the other hand, alignment caused by plasmonic interaction between the graphene sheets may also occur. The carriers within the different sheets are perfectly in phase in the light field. The diffracted light from the different sheets constructively interferes, as shown in Figure 6. The spatial self-phase modulation diffraction rings could then be observed. The diffraction rings could also be observed by using near-infrared and ultraviolet CW and ultrafast laser beams. Also, nearly equal numbers of rings could be observed, no matter what the wavelength and laser type (CW or pulse) were, at the same average power. This is because the total number of generated free carriers, which affects the observable nonlinearity, and which further determines the spatial self-phase modulation, is the same for different lasers provided that the total average power is identical.

### 2.3 Two-photon absorption

TPA is the simultaneous absorption of two photons of identical or different frequencies and it is one of the fundamental yet most relevant processes if graphene is to be considered as a candidate material for next-generation photonic and optoelectronic devices. Because of the peculiar band structure of the different layers of graphene, TPA would take place in graphene and varies with the graphene layer numbers.

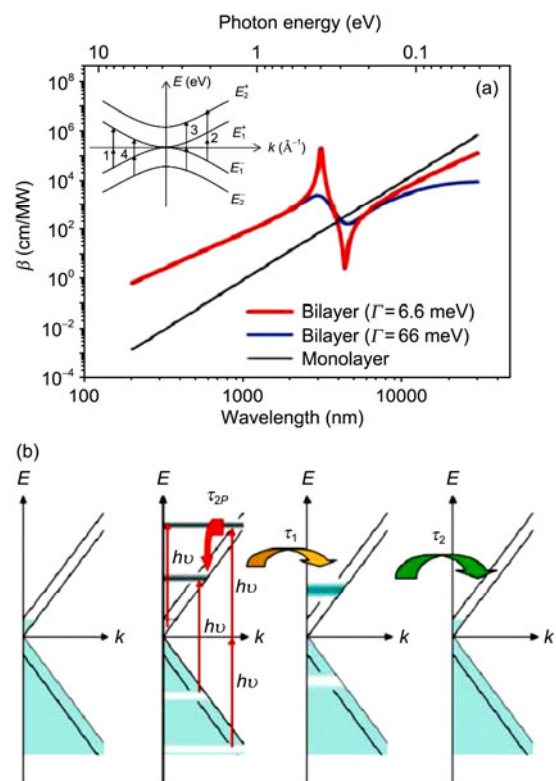
Yang et al. [48] demonstrated that the nonlinear absorption of monolayer graphene is different to that of bilayer graphene (AB-stacked). In 780 and 800 nm open-aperture measurements of nonlinear absorption, SA dominates the nonlinear absorption for monolayer graphene; however, TPA plays an important role in the nonlinear absorption of bilayer graphene at high light intensities beside the SA. The



**Figure 6** (Color online) Micro-mechanism for the observation of spatial self-phase modulation from graphene sheets. Reprinted with permission from [27], Copyright 2011, American Chemical Society.

saturated intensity and TPA coefficients of bilayer graphene were determined to be  $6 \pm 2$  GW/cm<sup>2</sup> and  $10 \pm 2$  cm/MW, and  $1.5 \pm 0.5$  GW/cm<sup>2</sup> and  $20 \pm 4$  cm/MW at wavelengths of 780 and 1100 nm, respectively. The SA is caused by the Pauli blocking of single-photon absorption, and the TPA originates from interband electron transitions. The TPA of bilayer graphene is much greater than that of monolayer graphene in the visible and infrared frequency ranges. TPA dispersion can be calculated based on quantum perturbation theory, as shown in Figure 7(a). The TPA of bilayer graphene depends on  $\omega^{-3}$  in the visible and terahertz regions, while it is proportional to  $\omega^{-4}$  for monolayer graphene at all light frequencies. The TPA coefficient of the AB-stacked bilayer sample is 2 orders of magnitude larger than that of the other stacked bilayer graphene. TPA measurements could be a way of identifying the stacked orders of bilayer graphene. Upon photo-excitation by ultrashort optical pulses, hot carriers (electrons in the conduction bands and holes in the valence bands) are created by both single-photon absorption (including both interband and intraband) and TPA, as shown in Figure 7(b). Subsequently, these nonequilibrium carrier distributions broaden and reach quasi-equilibrium through carrier-carrier scattering.

The NLO properties of GO were also investigated at 532 nm in the picosecond regime [17] and at 800 nm in the femtosecond regime [31]. The results show that TPA



**Figure 7** (Color online) (a) The TPA spectra of monolayer and bilayer graphene. The inset shows four possible transitions in bilayer graphene. (b) Schematic diagrams for photodynamics. Reprinted with permission from [48], Copyright 2011, American Chemical Society.

dominates the nonlinear absorption at high intensities, while SA dominates at low intensities. In contrast to bilayer graphene, TPA in GO arises from the introduction of the  $sp^3$  hybridized domains caused by oxidation. Thus, we can conclude that the heterogeneous nonlinear dynamics of GO are governed by SA in the  $sp^2$  domains and TPA in the  $sp^3$  domains.

## 2.4 Reverse saturable absorption

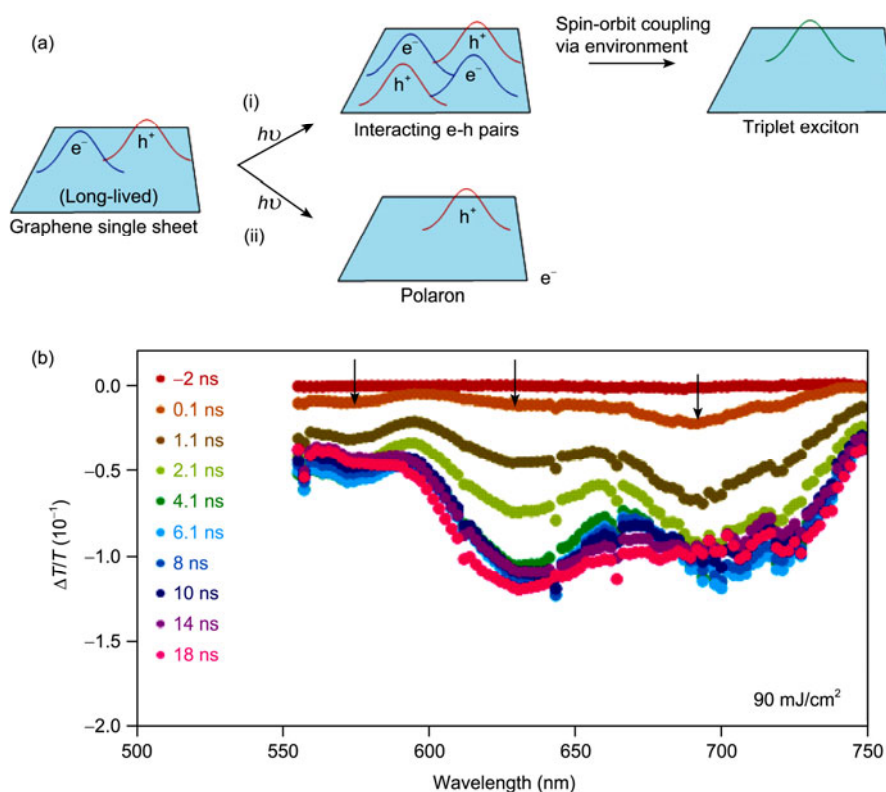
Materials with RSA will be less transmissive when excited. This gives the opposite result to SA and is thus called RSA. In principle, long-lived excited state absorption doses are not exhibited in pristine graphene because of the rapid recombination of the electron-hole gas. However, Lim et al. [18] demonstrated that when graphene is functionalized and dispersed as single sheets in heavy-atom solvents or in certain film matrices, it exhibits a novel excited-state absorption mechanism. Solvent-dispersible graphenes were prepared from sub-stoichiometric graphene oxide (sub- $GO_x$ ) by half-oxidizing graphite and then grafting the sub- $GO_x$  with octadecylamine surface chains to give organic-solvent dispersible sheets in the 300–500 nm range. At a high pump fluence of  $90 \text{ mJ/cm}^2$ , the results of transient absorption spectroscopy show that the transient response is firmly

photo-induced absorption in a wavelength range from 550 to 750 nm, as shown in Figure 8(b). The dynamics are complicated by the presence of slow-rise components (1–3 ns), and multiple decay lifetimes from 6 to 45 ns. This demonstrates that the leading mechanism for photo-induced absorption is excited-state absorption, or RSA.

Because the fluence- and time-dependent crossover from induced transparency to induced absorption is different to the usual behavior of small p-electron systems, these characteristics suggest that the long-lived excitons here are generated not by direct excitation or by the usual singlet  $\rightarrow$  triplet intersystem crossing mechanism, but by interactions within the initial electron-hole gas related to a nonlinear mechanism. This leads us to speculate that the initial electron-hole gas condenses to triplet-like excitons when promoted by spin-orbit coupling with heavy atoms, as schematically illustrated by the path in Figure 8(a).

## 2.5 Optical limiting

Optical limiters are devices that have high transmittance for low incident light intensity, and low transmittance for high incident intensity. There is great interest in these devices for optical sensors and for human eye protection, as retinal damage can occur when intensities exceed a certain threshold.



**Figure 8** (Color online) (a) Photoexcitation of a dispersed graphene single sheet gives long-lived electron-hole pairs. Further excitation causes the appearance of localized states such as (i) excitons (neutral excited state) or (ii) polarons (charged excited state) because of interactions. (b) Normalized transient transmittance  $\Delta T/T$  spectra as a function of pump-probe delay for sub- $GO_x$  dispersed in chlorobenzene at a pump wavelength of 532 nm with pump fluence of  $90 \text{ mJ/cm}^2$ . Reprinted with permission from [18], Copyright 2011, Nature Publishing Group.

Wang et al. [19,49] observed a significant broadband optical limiting response in the liquid-phase exfoliated graphene dispersions for ns pulses at 532 and 1064 nm. As shown in Figure 9, nonlinear scattering (NLS), originating from the thermally induced solvent bubbles and microplasmas, is responsible for this nonlinear behavior. The surface tension of the solvent has a strong influence on the optical limiting performance of each of the graphene dispersions.

Some groups explored the relationship between the microscopic structure of graphene and its macroscopic NLO response. Zhou et al. [50] found that the optical transmittance and limiting properties of GO and graphene are sensitive to oxygen-containing functional groups and structural defects, and demonstrated the tunable optical-limiting performance of GO and graphene. Feng et al. [20] observed the broadband NLO and optical limiting properties of the graphene families, including GO nanosheets, graphene nanosheets (GNS), GO nanoribbons and graphene nanoribbons for nanosecond pulses at 532 and 1064 nm. Reduced graphene samples exhibited stronger NLO and optical limiting responses than their GO precursors because of their increased crystallinity and conjugation. NLS and TPA were

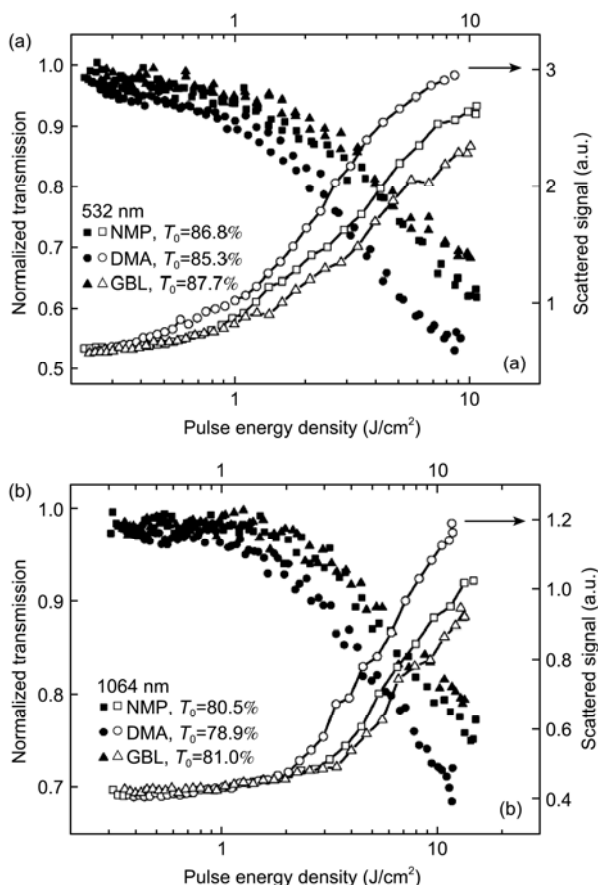
found to have strong effects on the NLO and optical limiting responses of the graphene nanostructures. Zhao et al. [51] found that the presence of  $\pi$  conjugation improves the optical-limiting responses of graphene and the superior limiting performance was retained regardless of the solvent viscosity and polarity. Graphene suspensions in organic solvents can work under 10 Hz laser pulses without losing their excellent limiting performance. More significantly, these outstanding limiting properties are also preserved in a polymer gel matrix.

Covalent or noncovalent combinations of NLO materials may be a better approach to improve the NLO properties of materials than modification of the individual NLO materials. Figures 3 and 10 shows the structure of a graphene hybrid material that has been covalently functionalized using porphyrin [35,52], fullerenes [36], oligothiophene [53],  $\text{Fe}_3\text{O}_4$  nanoparticles [38], and phthalocyanine [39]. We studied the NLO properties of a GO hybrid that was covalently functionalized with porphyrin for ns pulses at 532 nm. We found that the hybrid material showed enhanced NLO performance compared to that of the individual GO and of porphyrin by the combination of a nonlinear mechanism (RSA, TPA and enhanced NLS) and photoinduced electron or energy transfer between the porphyrin moiety and GO, as shown in Figure 11. Similar enhancement behavior was also observed in a GO hybrid material that was covalently functionalized with fullerenes [36] or oligothiophene [37,53].

Krishna et al. [54] investigated the NLO and optical limiting properties of covalently linked graphene-metal porphyrin composite materials in the nanosecond regime. They observed enhanced NLO and optical limiting properties in the graphene-porphyrin composites in comparison to the individual graphene and porphyrins. The improved optical limiting properties of these composites were attributed to energy transfer between the porphyrins and the graphene, which improved both excited state absorption and NLS.

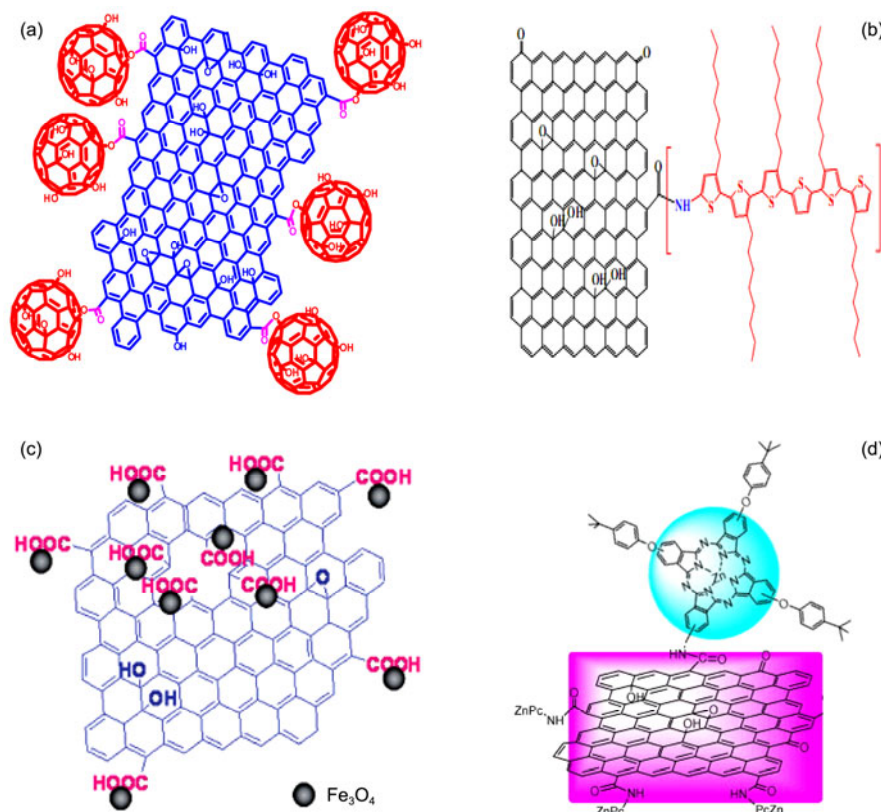
Zhu et al. [39] reported a soluble GO covalently functionalized with zinc phthalocyanine (PcZn), called GO-PcZn. They found that the hybrid material exhibited much larger NLO extinction coefficients and broadband optical limiting performance than GO at both 532 and 1064 nm, indicating a remarkable accumulation effect as a result of the covalent link between the GO and the PcZn. The same group also investigated a hybrid material, rGO-PVK, with excellent broadband optical limiting responses at 532 and 1064 nm because of the effective combination of the different NLO mechanisms, i.e. RSA, NLS, and TPA [55]. Midya et al. [56] synthesized two soluble polymer-grafted reduced GO (rGO) hybrids based on fluorene, thiophene, and benzothiadazole structures using the Suzuki coupling procedure. The donor-acceptor-type polymer-grafted rGO displays enhanced optical limiting properties for the 532 nm laser beam that are superior to those of CNTs, perhaps because of more efficient NLS.

Compared to covalent functionalization, the strategy to

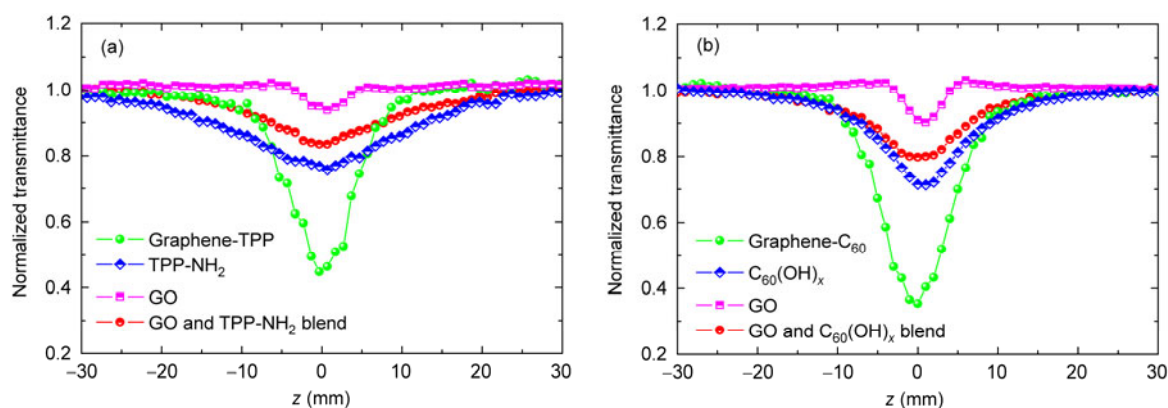


**Figure 9** Nonlinear transmission and scattering for graphene in three solvents under 532 nm (a) and 1064 nm (b) excitations. Linear transmission  $T_0$  is also presented. Reprinted with permission from [19], Copyright 2009, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.





**Figure 10** (Color online) Structures of the hybrid materials of GO covalently functionalized with (a) fullerenes, (b) oligothiophene, (c) Fe<sub>3</sub>O<sub>4</sub> nanoparticles, and (d) phthalocyanine. Reprinted with permission from [39], Copyright 2011, Elsevier.



**Figure 11** (Color online) (a) Open-aperture Z-scan curves of graphene-TPP, TPP-NH<sub>2</sub>, graphene oxide, and a controlled blend sample of TPP-NH<sub>2</sub> with graphene oxide. (b) Open-aperture Z-scan curves of graphene-C<sub>60</sub>, pyrrolidine fullerene, graphene oxide, and a controlled blend sample of pyrrolidine fullerene with graphene oxide at 532 nm with 5-ns pulses. Reprinted with permission from [52], Copyright 2009, American Chemical Society.

enhance the optical limiting responses in the donor-acceptor complexes by using ionic interactions between the donor and acceptor materials is simple. The donor-acceptor complexes can be prepared by simply mixing oppositely charged donors and acceptors, which offers great advantages over covalent functionalization. Balapanuru et al. [57] synthesized a GO-dye charge-transfer complex using a simple ion-exchange process, and found that this GO-organic dye charge-

transfer complex exhibited enhanced properties for bio-sensing and optical limiting. Mamidala et al. [58] reported the enhanced NLO responses of donor-acceptor ionic complexes in aqueous solutions. The optical limiting performance of a negatively charged GO (acceptor) was shown to improve significantly when it was mixed with a water-soluble, positively-charged porphyrin (donor) derivative because of enhanced nonlinear scattering. In contrast, no enhancement

was observed when mixed with the negatively-charged porphyrin.

Dong et al. [59] reported a carbon nanotube-graphene oxide core-shell structure (SWCNT/GO). The formation of such a hybrid structure is because of the strong  $\pi$ - $\pi$  stacking interaction between the two materials. They found that the optical limiting performance of SWCNT/GO was better than either that of SWCNT or of GO individually for nanosecond pulses at 532 nm. The outstanding optical limiting performance of SWCNT/GO is likely to be a consequence of the ultrafast electron and/or energy transfer between the two components upon photon excitation, which suppresses dissipation of the absorbed energy through photoemission. Also, the generation of light-scattering microplasmas may be synergistically eased by the ionization of both the GO nano-sheets and the SWCNTs upon rapid absorption of the laser energy.

Graphene can also be decorated with nanoparticles. We studied the NLO properties of a hybrid material of GO coordinated with  $\text{Fe}_3\text{O}_4$  nanoparticles [38,60], as shown in Figure 10(c). The results showed that the GO- $\text{Fe}_3\text{O}_4$  hybrid exhibited enhanced NLO and optical limiting properties in comparison to the pristine GO in the nanosecond regime, because of the enhanced NLS combined with TPA and RSA. During the synthesis of GO- $\text{Fe}_3\text{O}_4$ , the epoxide and hydroxyl groups on GO were partially removed by NaOH, which increases the conjugation network of the nanostructure. The implantation and growth of metal nanoparticles on a GNS leads directly to severe damage to the regular structures of the graphene sheets, which disrupts the extended  $\pi$  conjugation and results in impaired device performance. Miao et al. [61] reported a simple approach to achieve lossless formation of graphene composites decorated with cadmium sulfide quantum dots with excellent NLO properties by using benzyl mercaptan as the interlinker. The excellent NLO properties were mainly contributed by NLS and nonlinear absorption at 532 and 1064 nm, respectively, under excitations in the nanosecond laser pulse regime. Zhao et al. [51] also studied the NLO properties of another hybrid material of graphene decorated with Au nanoparticles, but the NLO performance of this hybrid material was not very good.

### 3 Summary and outlook

Graphene exhibits a unique chemical structure, and outstanding electronic and optical properties for optoelectronic and photonic applications. Large optical nonlinearities, including SA, FWM, and TPA have been observed in pristine graphene. Excellent NLO properties combined with a fast response and broad wavelength range make graphene an ideal saturable absorber in mode-locked ultrafast laser systems. Graphene derivatives, e.g. GO and graphene hybrid materials, have been produced with various synthesis methods to meet increasing requirements for thin film pro-

cessing, composite incorporation, and device integration. The NLO properties of these functional hybrid materials depend not only on the individual component materials, but also on the interactions between them. For GO, the unique chemical structure along with the heterogeneous electronic structure caused by the presence of  $\text{sp}^2$  and  $\text{sp}^3$  bonding confers intriguing properties that offer exciting prospects for tailoring of NLO properties. We observed many useful NLO properties in graphene and its derivatives. The derivatives of graphene represent a key branch in optical limiting research. For most graphene hybrids, great importance is attached to electron or energy transfer by functionalizing graphene, which plays an important role in improving limiting performance. In general, covalent functionalization of graphene materials leads to better limiting performance than noncovalent functionalization. This is because the covalent link can more effectively improve energy or electron transfer from the functional moiety to the graphene nanomaterial, which results in enhanced limiting performance.

To progress, researchers from various backgrounds will be required to develop strategies for further tuning of the NLO properties of graphene-based materials. First, enhancement of the NLO properties of graphene-based materials will be an important area for practical applications. For this purpose, the preparation of novel graphene-based composites with excellent NLO properties will be necessary. Second, the monolithic integration of graphene with an effective optical system is very important to obtain strong light-graphene interaction. For example, graphene must be incorporated into a high-performance optical resonator or waveguide to increase absorption and take full advantage of its unique optical and NLO properties. Finally, to make full use of graphene's ultrawide broadband capability in the field of NLO devices, future effort must focus on demonstration devices with high speeds and at different wavelengths.

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