SCIENCE CHINA
Chemistry

• MINI REVIEWS •

December 2015 Vol.58 No.12: 1782–1791
doi: 10.1007/s11426-015-5480-0

Carbon-based optical limiting materials

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Received June 11, 2015; accepted July 9, 2015; published online October 22, 2015

In this mini-review, special attention has been paid to carbon-based optical limiting materials. After a brief introduction to optical limiting mechanisms of carbon-based optical materials and their characterization technique, this mini-review presents the recent progress of carbon-based optical limiting materials including carbon black suspensions (CBS), carbon nanotubes (CNTs), fullerenes, graphene and detonation nanodiamond. Finally, perspectives on carbon-based optical limiting are given.

carbon black suspensions (CBS), carbon nanotubes (CNTs), fullerenes, graphene, optical limiting, composite materials

1 Introduction

Optical limiting materials exhibit high transmission under low input intensity, accompanying with constant output intensity if the incident radiation is higher than their threshold. One of the most important features of optical limiting materials is that they are capable of protecting the sensors of optical systems and our naked eyes from laser damage. For this application, several materials with large optical limiting responses have been proposed and developed [1–9]. Among them, carbon-based materials, such as carbon black suspensions (CBS) [2,3], single-walled and multi-walled carbon nanotubes (CNTs) [4–6], fullerenes [7] and graphene [8,9], have been considered as promising candidates for the limiting of the laser radiation intensity due to their large nonlinearities, fast response time, and broadband spectral response [10]. To optimize and enhance the optical limiting performance of carbon-based materials, much effort has been devoted to the investigation of influence factors of optical limiting, the establishment of relationship between the structures of materials and their optical limiting performance, and the development of composite materials with excellent optical limiting properties. In this mini-review, we summarize the recent developments of carbon-based materials for optical limiting. We briefly discuss optical limiting mechanisms for carbon-based materials including nonlinear absorption and nonlinear scattering, and characterization technique. Then, we focus on the progress of carbon-based optical limiting materials based on CBS, CNTs, fullerenes, graphene and detonation nanodiamond, in particular.

2 Optical limiting mechanisms of carbon-based materials

Every optical limiting material exhibits at least one nonlinear optical mechanism. In many cases, optical limiting materials exhibit multiple nonlinear optical mechanisms with one as primary mechanism. Nonlinear optical mechanisms include nonlinear absorption, nonlinear scattering, nonlinear refraction, and phase transitions. For carbon-based materials, nonlinear absorption and nonlinear scattering are two

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dominating mechanisms, which will be discussed separately.

2.1 Nonlinear absorption

Reverse saturable absorption (RSA) and two-photon absorption (TPA) are two main nonlinear absorption mechanisms in carbon-based materials. Generally, RSA takes place on a laser irradiation of nano-second or longer timescale, owing to the relatively long excited state lifetimes of materials, while optical limiting materials based on TPA can work under the laser irradiation of pico-second or shorter timescale [11].

2.1.1 Reverse saturable absorption

For a material, if its excited state absorption cross section is larger than the ground state cross section, RSA will play a key role for optical limiting. The absorption cross section of the ground state is supposed to be σ_1, and absorption cross section of the excited state is σ_2. When the material absorbs light, the excited state begins to be populated. If σ_2 is smaller than σ_1, then the material becomes more transparent with the increase of incident light intensity. This material is known as saturable absorber. If σ_2 is larger than σ_1, then the total absorption increases with the increase of incident light intensity, and the material with this behavior is known as a reverse saturable absorber. If z is assumed to be the beam propagation direction, then the change of light intensity can be written as follows:

$$\mathrm{d}I/\mathrm{d}z = -\left[\omega_\Gamma\sigma_1 + \omega_2(\sigma_2 - \sigma_1)\right]I \quad (1)$$

where ω_Γ is the total number of molecules per unit area in the slice dz, ω_2 is the number of molecules of the excited state per unit area. The number of the ground state per unit area is:

$$\omega_1 = \omega_\Gamma - \omega_2 \quad (2)$$

Eq. (2) is substituted into Eq. (1), the following equation is then obtained:

$$\mathrm{d}I/\mathrm{d}z = -\left(\omega_1\sigma_1 + \omega_2\sigma_2\right)I \quad (3)$$

If L is the length of the material along beam propagation direction, the output intensity is

$$I = I_0 \mathrm{e}^{-\omega_1\sigma_1 L}\mathrm{e}^{-\omega_2\sigma_2 L} \quad (4)$$

where I_0 is the input laser intensity. At a low input fluence, the excited state is unpopulated, and the output intensity increases with the increase of incident fluence, and the process is linear initially and deviates from linear gradually. When the input fluence reaches a certain value, the excited state becomes substantially populated due to the large σ_2, the optical nonlinearity becomes dominant and the change of light intensity becomes very slow with increasing incident fluence. The RSA behavior is shown in Figure 1(a). The larger the ratio of σ_2/σ_1 is, the lower the transmission of optical limiting material will be at incident intensity.

In some molecular systems, there are two excited states, single excited state and triplet excited state, and the signification intersystem crossing from single excited state to triplet excited state usually occurs. If the lifetime of the triplet state and the intersystem crossing rate are large, the triplet state will also be populated, resulting in an improved absorption capability and hence optical limiting to incident fluence. In this case, the transmission of optical limiting materials will be dramatically reduced.

2.1.2 Two-photon absorption

TPA occurs in the interaction between high power laser and material. In a TPA process, the molecule absorbs two photons continuously to promote an electron from the initial

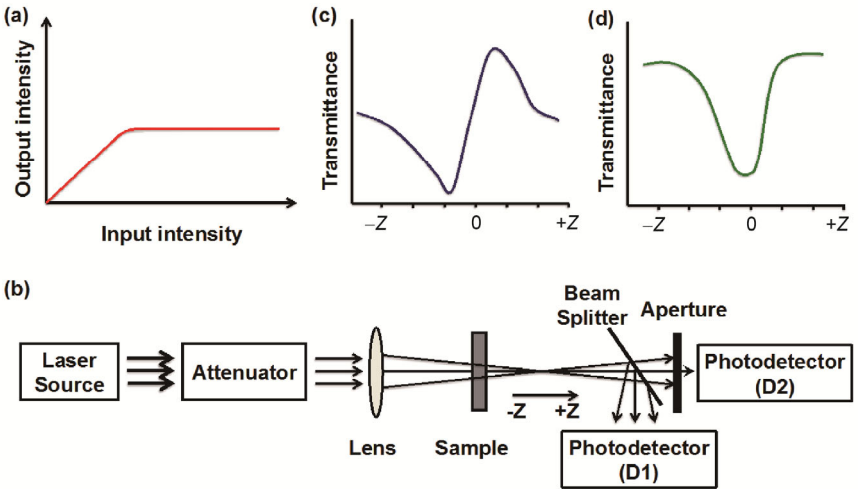

Figure 1 (a) Plot of the incident intensity versus the output intensity in a typical RSA material; (b) schematic representation of Z-scan measurement system and typical Z-scan curve in self-focusing (c) and absorption (d).

state to its final state. This process is one of the three order nonlinear optical effect, and the intensity of the beam along the beam propagation direction (z) is

$$\mathrm{d}I / \mathrm{d}z = -\left(\alpha I + \beta I^2\right) \tag{5}$$

where α is the linear absorption coefficient and β is the TPA coefficient which is related to the imaginary part of $\chi^{(3)}$ by the following equations:

$$\beta = \sigma_2 N_\mathrm{A} C_0 \times 10^{-3} \tag{6}$$

$$\sigma_2 = \frac{8\pi^2 \hbar \omega^2}{n^2 c^2} \mathrm{Im}\left[\chi^{(3)}\right] \tag{7}$$

where N_A is the Avogadro constant, C_0 is the molar concentration, σ_2 is the absorption cross section of the excited state of TPA (cm^4 s/photon), $\hbar$ is the Planck constant, ω is the circular frequency of the optical field, n is the linear refraction index, and c is the speed of light in vacuum. For transparent material at low intensities, $\alpha \ll 1$, thus the solution of the propagation equation is given by

$$I = \frac{I_0}{1 + \beta L I_0} \tag{8}$$

where I_0 is the input intensity and L is the length of the sample. This clearly demonstrates that the output intensity decreases with the increase of input intensity, which results in optical limiting. This equation also demonstrates that the strength of optical limiting depends on the TPA coefficient, the incident intensity, and the sample thickness, which means that TPA materials are more effective for shorter incident pulses since the laser intensity of shorter pulses (fs) is much higher than that of longer pulses (ns).

2.2 Nonlinear scattering

Scattering is caused by light interacting with small centers that can be physical particles or simple interfaces. If scattering occurs, the transmission measured in a given solid angle, will decrease. In a given solution, molecules in solution can reduce the transmittance by nonlinear absorption or by acting as induced scattering centers themselves. Meanwhile, the absorbed optical energy by molecules can be transferred to surrounding solvents. If the accumulated energy is high enough to boil the solvents, a large number of microbubbles are formed. The vapor-liquid interface of bubbles can scatter the optical energy effectively because the refractive index discontinuity is large. This further reduces the transmittance of input laser fluence. These processes in liquid media are often reversible because the liquid in light path can be refreshed by either diffusion or circulation. For organic optical limiting materials, nonlinear scattering is one of the most popular optical limiting mechanisms because most of the optical limiting behaviors of organic materials are observed in liquid media.

3 Principle of Z-scan

Z-scan has been widely used in nonlinear characterization of materials because nonlinear refraction and nonlinear absorption of samples can be measured simultaneously by this technique. Meanwhile, the third-order nonlinear refractive index, nonlinear absorption coefficient and optical nonlinear susceptibility can be obtained as well [12]. In this technique, two measurement ways are performed: open aperture Z-scan and closed aperture Z-scan. As shown in Figure 1(b), in the open aperture Z-scan, all the light transmitted through the sample is collected on a photodetector (D1), which characters the nonlinear absorption. While in the closed aperture Z-scan, only an on-axis portion of the diffracted beam is collected by photodetector (D2), which is related to nonlinear refraction.

In the closed aperture Z-scan measurement, the sample is moved through the focal point along the z-axis, and the transmittance through an aperture placed in the far field of the focal plane is measured. When the sample is far from the focal plane, self-lensing cannot occur. When the sample is moved from $-Z$ to the focal plane (0), the high intensity of beam induces a lens in the sample. If the nonlinearity of sample is negative, the transmittance through the aperture will be increased. When the sample reaches the focal plane (0), the intensity of beam is the strongest. However, the influence of the induced lens is minimized, which results in minimal effect on transmittance. When the sample is moved farther from the focal plane (0) to $+Z$, the intensity of beam becomes weak again so that the self-lensing is negligible. This process results in a curve of transmittance change versus the position of sample that is anti-symmetric against focus. That is a peak and then a valley as the sample is moved from $-Z$ through focus to $+Z$ (Figure 1(c)). For a positive nonlinearity, a typical curve is consisting of a valley followed by a peak. Thus, Z-scan can provide the sign of the nonlinearity [1].

In the open aperture Z-scan measurement, all the light transmitted through the sample is collected. In this measurement, the nonlinear refraction is usually included since open aperture Z-scan measurement is insensitive to nonlinear refraction. If the sample possesses the property of RSA, the transmittance curve is a symmetrical valley relative to focal plane (Figure 1(d)). It is worth mentioning that nonlinear absorption and induced scattering cannot be distinguished in open aperture Z-scan technique.

4 Carbon-based materials for optical limiting

To understand optical limiting property of carbon-based materials, much attention has been paid to fundamental

studies that help clarify the optical limiting mechanisms in terms of interior and exterior factors. On the other hand, composite materials have been developed recently to optimize the property of carbon-based materials for the purpose of realization in laser protection. In this section, we highlight several carbon-based materials that have been widely investigated in the field of optical limiting.

4.1 Carbon black suspensions

Carbon black suspensions (CBS) is formed by very small carbon particles suspended in a liquid, which is very cheap and easily obtained. When CBS is irradiated, the small carbon particles absorb light, and transfer the energy to break the particles apart and boil the solvent, resulting in microplasma generation and microbubbles formation. Thus, nonlinear scattering is the dominant limiting mechanism for CBS [1,13]. The viscosity of solvents influences greatly on the optical limiting behavior of CBS, when dispersing carbon into different solvents, such as water, ethylene glycol, ethanol, and chloroform, to measure the optical limiting behaviors [14]. In common solvents, such as water and ethanol, the limiting behavior of CBS ceases after a few laser firings and a turnover in the limiting curve appears due to depletion of the carbon black within the focal volume. While for low viscosity liquids, such as carbon disulfide or pentane, the limiting is unaffected by the repetition rate since diffusion of the carbon black particles is quick (Figure 2) [15]. In addition, the optical limiting strength of CBS can be enhanced by the surrounding environment of carbon particles. For example, Tiwari *et al.* [16] compared optical limiting of CBS in pure water and saline water, and found that the optical limiting strength was increased as the salinity of the host liquid increased. The enhanced optical limiting performance was attributed to the increase of carbon particles sizes. Except surrounding environment of carbon particles, the influence from laser pulses on the optical limiting behavior of CBS was also investigated. Vincent *et al.* [17] measured short (0.3 ps, 0.2 ns, and 10 ns) laser pulse transmissions through CBS at 10 mJ of input pulse energy. Limiting was observed with the 10 ns and the 0.2 ns laser pulses, but the 0.3 ps pulses produced white light and underwent the same level of attenuation in the solvent and in the CBS.

4.2 Fullerenes

Since the discovery of fullerenes in 1985 [18], spherical fullerene has been widely investigated in photoelectronic fields. In fullerene molecule, the π-electrons are highly delocalized over its surface; therefore fullerene has been considered as an optical limiting material [7,19–21]. Arbogast and coworkers [22] reported that C_{60} had a higher excited state absorption cross-section than the ground state absorption cross-section, which further implied that fullerene such as C_{60} is RSA material. In 1992, Tutt and Kost [7] first

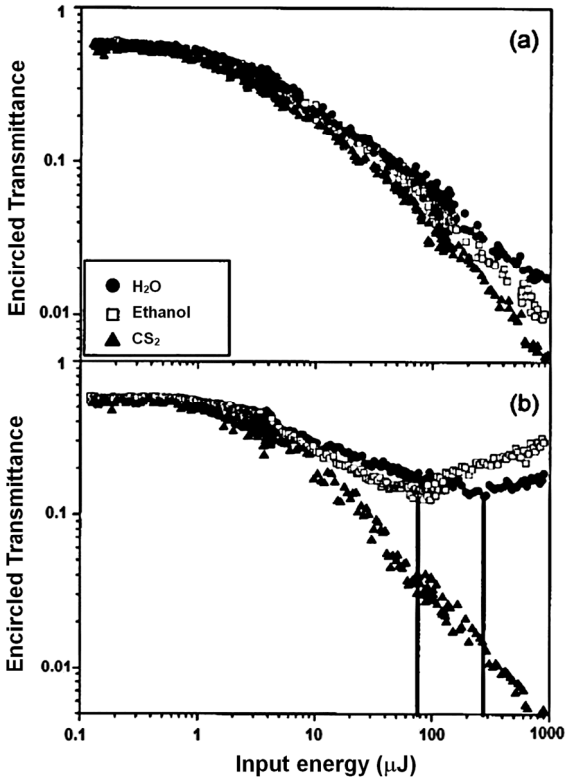

Figure 2 Encircled energy transmittance versus input energy for CBS in three different solvents. (a) Single shot and (b) 10-Hz repetition rate for CS_2 (▲), ethanol (□), and water (●). The linear transmittance of the samples was approximately 60% [15].

reported optical limiting responses of a 63% and an 80% transmitting toluene solution of C_{60} to 8 ns 532 nm optical pulses, and found that the transmittance begins to decrease at an incident intensity of ~100 mJ cm^{-2} and the transmitted fluence effectively becomes clamped at ~65 mJ cm^{-2}. The dominant mechanism is RSA. However, nonlinear scatter might also contribute to the limiting action in solution. The subsequent detailed studies showed that C_{60} exhibits nonlinear absorption properties in a solid, while nonlinear scattering and refraction are main limiting mechanisms in solution [23,24]. Though C_{60} possesses attractive properties for optical limiting, its poor solubility in common solvents is a serious hurdle in the way of practical applications. In order to improve its solubility in common solvents, C_{60} has been installed with some functional groups, such as oxygen-containing functional groups. However, Zhang *et al.* [10] found that C_{60} functionalized with oxygen-containing functional groups exhibited weaker optical limiting properties than that of pristine C_{60} because oxygen-containing functional groups disrupted the conjugation structure of C_{60}. For real application, materials are largely preferred to be in solid states. So, crystalline films of C_{60} were fabricated and their optical limiting properties were studied [25–27]. However, these films were inefficient against pulses longer than tens of ps due to the interaction of neighboring C_{60} molecules in

the crystalline phase, which results in a rapid de-excitation of the laser-created excited state. In order to decrease this interaction between C_{60} molecules, fullerene molecules were smartly dispersed into the pores of SiO_2 sol-gel matrix [28,29]. A similar RSA has been observed in fullerene/SiO_2 as well as in pure C_{60} samples [28].

On the other hand, fullerene is an electron acceptor; charge transfer can occur easily when it interacts with an electron donor via intramolecular or intermolecular interactions. This donor-acceptor interaction will enhance the nonlinear effect of fullerene. Therefore, scientists devoted more and more efforts to the structure modification of fullerene molecules. As shown in Figure 3, a series of C_{70} and C_{60} derivatives have been designed and synthesized, and their optical limiting properties were greatly improved [30–36]. In addition, besides 532 nm nanosecond pulsed laser was applied as the laser source [32–35], optical nonlinearities of some fullerene derivatives were designed to measure under picosecond laser excitation at 532 and 1064 nm [36].

4.3 Carbon nanotubes (CNTs)

Since their discovery in 1991 [37], optical limiting properties of CNTs have been investigated by several research groups [38–43]. Optical limiting behavior of multiwalled carbon nanotube (MWNT) and single-walled carbon nanotube (SWNT) suspensions was reported by Sun and Vivien [38–40], respectively, and it was found that optical limiting effect of CNTs is more effective than both CBS and C_{60}. The Z-scan analysis confirmed that nonlinear scattering from bubble growth and plasma formation is the dominant optical limiting mechanism, but nonlinear refraction from thermal effects also works [41,42]. The thermo-dynamical properties of solvents have big influence on the optical limiting behavior of CNTs. Meanwhile, the structural parameters of CNTs and the measurement parameters, such as bundle size, nanotube length, pulse wavelength and pulse duration of the incident laser, could influence the optical limiting property of CNTs as well [38,43–46]. For example, Xiong and coworkers [47] studied the influence of nonlinear scattering light distributions on the optical limiting properties of CNTs. The results indicated that the optical limiting property of SWNTs dispersion with shorter tube length and smaller bundle size was much better than those with longer length and larger bundles. Recently, Riggs *et al.* [45] compared nonlinear transmittance results for MWNT and SWNT in suspensions and in solutions. They exhibit much weaker optical limiting responses in solutions as compared with that in suspensions. This may be due to the different optical limiting mechanisms between the single tubes in solutions and bundled tubes in suspensions.

In most solvents, however, CNTs tend to aggregate into bundled tubes because of their high surface energy, which turns out to be a serious obstacle for real applications. Thus, it is of great importance to design and prepare soluble CNTs. By careful design, optical limiting property of soluble CNTs could also be enhanced. For example, by functionalizing CNT with RSA materials, the increased solubility

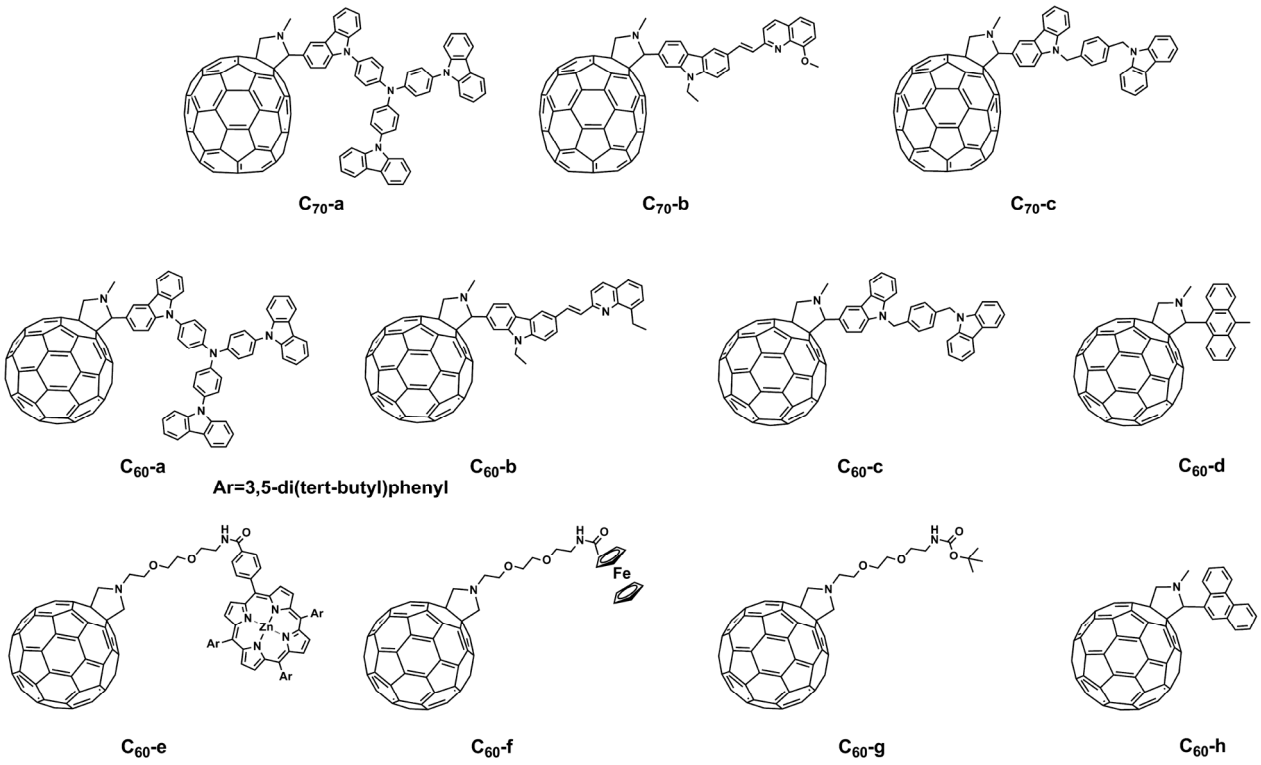

Figure 3 Chemical structures of C_{70} and C_{60} derivatives [30,31,36].

and better optical limiting property are expected in one composite material. These noncovalent and covalent composite materials have been prepared by several groups. For example, MWNTs were noncovalently functionalized with different metal phthalocyanines by π-π stacking method (Figure 4(a)), resulting in composites with stronger optical limiting properties than that of MWNTs or phthalocyanine alone under the same solution concentration [48]. Attachment of the porphyrin moieties to the surface of the MWNTs also significantly improves the solubility and processing of MWNTs, and their nonlinear optical properties under both nanosecond and picosecond laser pulses at 532 nm pulse [49]. Allyloxyporphyrin-functionalized MWNT exhibits enhanced nonlinear optical limiting properties compared to physical blend of MWNTs and porphyrin, as well as to the MWNTs and porphyrin themselves (Figure 4(b)). The mechanism of enhanced optical limiting involves RSA, nonlinear scattering, and photoinduced electron/energy transfer between the MWNTs and the porphyrin [50]. Polyaniline MWNT hybrids demonstrate improved optical limiting property due to electron transfer between polyaniline and MWNT [51]. Considering that materials of liquid and suspensions forms are not suitable for practical optical limiting devices, a versatile solid polymethylmethacrylate (PMMA) composite containing porphyrin-covalently functionalized MWNT was prepared by Zhang and coworkers [52]. Nanosecond and femtosecond pulse Z-scan results show that the solid composite exhibits weaker optical limiting effects than that of the suspension at 532 nm under nanosecond pulse, due to the decrease of nonlinear scattering. Although MWNTs-TPP/PMMA composite shows weak optical limiting properties, it exhibits ultrafast saturable absorption and fast relaxation times at 800 nm under femtosecond pulse.

4.4 Graphene

Graphene is a monatomic sheet of sp^2 hybridized carbon atoms packed tightly into a 2D honeycomb lattice. In the field of nonlinear optical materials, graphene is attractive because of its stable two-dimensional (2D) hexagonally symmetry and the provided large π-π conjugated electrons that can be associated with third nonlinear susceptibility [53]. In 2009, Wang *et al.* [9] observed a significant optical limiting response of graphene dispersions to nanosecond laser pulses at 532 and 1064 nm. The surface tension of solvents has strong influence on the optical limiting performance of graphene dispersions. Nonlinear scattering arising from the formations of solvent bubbles and microplasmas is the principle optical limiting mechanism. Two years later, Lim *et al.* [8] reported that dispersed graphenes exhibited broadband nonlinear optical absorption. For nanosecond visible and near-infrared pulses, a new benchmark for optical energy-limiting onset of 10 mJ cm^{-2} for a linear trans-

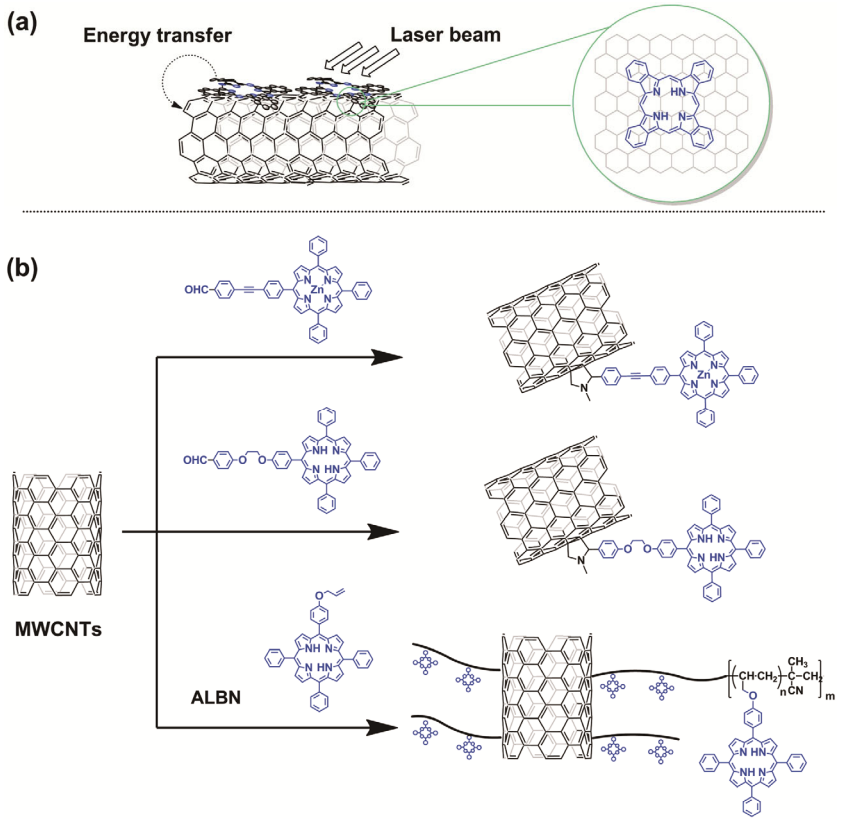

Figure 4 (a) The scheme of composite MWNT/phthalocyanines [48]; (b) the scheme of MWNT and porphyrin hybrid materials [49,50].

mittance of 70%, with excellent output clamping in both heavy-atom solvents and polymer film matrices was obtained. However, same as fullerene and CNT, the large surface energy of graphene imposes restrictions on the formation of single sheet graphene in most solvents. Therefore, graphene oxide (GO), a product of graphene oxidation could be dispersed in water with long-term stability due to the presence of hydrophilic groups, attracts more and more attention [54,55]. And the GO possesses some additional advantages, for example, the structures of GO could be modified by some surface modification methods, and GO could be reduced to graphene easily. More importantly, GO shows optical limiting properties in nanosecond and picosecond regimen for 532 nm pulse laser. TPA dominates nonlinear absorption process of GO in the case of picosecond pulses, while excited state absorption plays an important role in the case of nanosecond pulses [56]. The optical limiting of GO nanomaterials, including GO nanosheets (GONSs) and GO nanoribbons (GONRs), as well as their reduction productors, graphene nanosheets (GNSs), and graphene nanoribbons (GNRs), were also investigated and compared at 532 and 1064 nm by using a nanosecond laser. GNSs, GONRs, and GNRs exhibited broadband optical limiting properties. Reduced graphene samples exhibited stronger optical limiting responses than their GO precursors because of the increase of conjugation [10,57].

For solubilized graphene with increased optical limiting property, some researches were focused on the combination of different nonlinear effects into one functionalized graphene to obtain optical limiting materials with ideal properties [58,59]. For example, a reduced graphene oxide-zinc phthalocyanine (RGO-ZnPc) hybrid material with good dispersibility has been prepared by covalent functionalization method (Figure 5(a)). The Z-scan technique at 532 nm with 4 ns laser pulses shows that the efficient functionalization and reduction of GO make RGO-ZnPc hybrid much larger optical limiting performance than those of individual GO, ZnPc and the GO-ZnPc hybrid. This is ascribed to the combination of different nonlinear optical absorption mechanisms including TPA, excited state absorption, RSA, and efficient photo-induced electron transfer or energy transfer between ZnPc and RGO into RGO-ZnPc hybrid [60]. A porphyrin functionalized graphene composite was synthesized and the soluble graphene nanohybrid exhibits improved optical limiting performance. RSA, TPA, nonlinear scattering and photo-induced electron transfer were responsible for the enhanced optical limiting response (Figure 5(b)) [59,61]. The solution-processed graphene polymer composites were also designed. For example, the thermally RGO were functionalized with PVK (Figure 5(c)) [62]. The resulting hybrid material RGO-PVK displayed very good broadband optical limiting responses at 532 and 1064 nm due to the effective combination of nonlinear scattering and TPA.

4.5 Detonation nanodiamond

Detonation nanodiamond (DND), the so-called ultradispersed diamond (UDD), is a diamond that originates from a detonation. Same as carbon black and carbon nanotubes, DND can form suspensions. However, compared with other carbon nanomaterials, DND suspension possesses remarkable stability, especially DND with modified surfaces. And the excellent stability can be maintained during and after laser radiation [63]. Recently, the optical limiting mechanisms of DND suspension and the influence factor of its optical limiting, such as concentration and particle size, were investigated in detail. For example, Mikheev *et al.* [64] reported that optical limiting of DND suspensions could be maintained for a long time at laser intensities up to 1 GW cm^{-2}. Vanyukov *et al.* [63] proved experimentally that the optical limiting performance of stable aqueous DND suspensions was a nonmonotonous function of concentration. At an incident intensity of 0.8 GW cm^{-2}, the optimal DND concentration was as low as 0.88%. At this concentration, the linear transmittance of the sample was reduced from 82% to 23%. Josset *et al.* [65] investigated the optical limiting properties of DND, focusing on their optical power limiting efficiency in optronics. They observed that colloidal DND hydrosols were efficient at blocking high energy beams (1064 nm), with linear transmittances over the whole visible and near infrared (Vis-NIR) range at low fluencies. Vanyukov *et al.* [66] studied the optical limiting behavior in stable aqueous suspensions of DND clusters with average sizes of 50, 110, and 320 nm. The nanosecond Z-scan measurements at a wavelength of 532 nm revealed that the larger the cluster size, the better the limiting performance and the higher the ray stability of the DND suspension. The nonlinear scattering and the nonlinear absorption were mainly contributed to the optical limiting mechanisms.

4.6 Other carbon based materials

Besides the above-mentioned materials, some other carbon based materials, such as carbon nano-onions, carbon nanohorns, graphyne may also be explored in optical limiting field. In fact, the optical limiting behavior of carbon nano-onions has been observed and the response of the carbon nano-onions is stronger than that of the nanodiamond particles. This response was mainly related to nonlinear absorption, which resulted in an efficient optical limiting action [67]. In addition, Gao *et al.* [68] grew carbon nano-onions with high crystallinity through the laser resonant excitation of precursor molecules and improved optical limiting effect was obtained. Single-walled carbon nanohorn is about 40–50 nm in length and about 2–3 nm in diameter, consisting of irregular tubules with cone-shaped tip [69–72]. Graphyne is made of sp- and sp^2-hybridized carbon atoms, which was proposed by Baughman *et al.* [73]. In

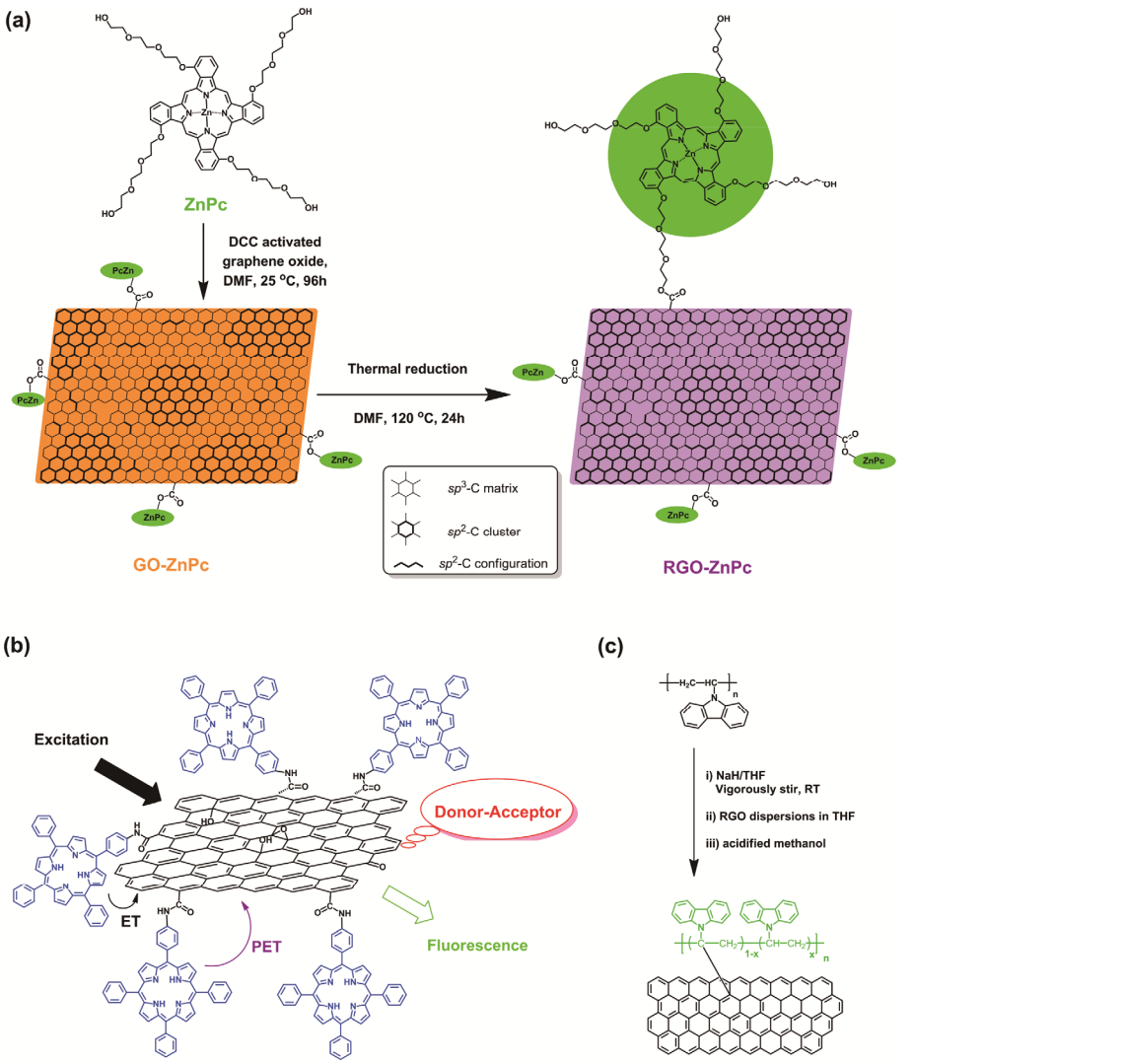

Figure 5 The scheme of RGO-ZnPc (a) [60], porphyrin functionalized graphene (b) [61], and RGO-PVK hybrid material (c) [62] (color online).

graphyne, there are three types of bonds, C(sp^2)–C(sp^2), C(sp)–C(sp^2), and C(sp)–C(sp) [74]. These distinct chemical structures of carbon materials might lead to unique electronic and optical properties with better nonlinear optical properties, considering their imperfect π-conjugated system. We envision these novel carbon-based materials might become a hot topic in the optical limiting research field.

5 Conclusions

Over the past few decades, tremendous progress has been made in the development of carbon-based optical limiting materials. Especially, fullerene, CNTs and graphene, have been taken as the benchmark to evaluate the optical limiting behavior of new materials. Clearly, many factors influence on the optical limiting of carbon-based materials. Therefore, more researches should be focused on the intrinsic of optical limiting of carbon-based materials to obtain materials with high optical limiting performance. On the other hand, in order to improve the solution processability and enhance the optical limiting performance of carbon-based materials, carbon-based composite materials combining different nonlinear effects, becomes a hot topic in this field. In the long run, these composite carbon-based materials with various excellent properties will benefit for the protection of our eyes and the sensors of optical systems from laser with multi-wavelengths, multi-time scales and multi-pulse ranges.

This work was supported by the National Natural Science Foundation of China (51273076, 51473061), and the State Key Laboratory of Laser Interaction with Matter (SKLLIM1403).

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