Chapter 2

Porphyrin and Phthalocyanine Covalently Functionalized Graphene and Carbon Nanotube Nanohybrids for Optical Limiting

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.69587

Abstract

Optical limiters are smart materials that follow passive approaches to provide laser protection, which are useful for the protection of human eyes, optical elements, and optical sensors from intense laser pulses. Many functional materials have been widely investigated with the view to realize practical passive optical limiting application. However, preparation of the required nonlinear optical active materials for optical limiters still presents a significant chemical challenge. In particular, this chapter gives emphasis to the nonlinear properties modulation of porphyrin and phthalocyanine covalently functionalized graphene and carbon nanotubes nanohybrids for the function of optical power limiting aiming the achievement of effective systems through the appropriate combination and modulation of several structural components. The nonlinear optical mechanisms observed in inorganic-organic nanohybrids, i.e., nonlinear scattering, nonlinear absorption, nonlinear refraction, and others, are discussed in conjunction with the influence of the materials properties and the laser source on the optical limiting performances.

Keywords: porphyrin, phthalocyanine, graphene, carbon nanotubes, optical limiting

1. Introduction

Nonlinear optics, which investigates the interaction of intense pulse field with materials, is a relatively promising field in photoelectronics and photonics with many fundamental scientific and technological potential [1–3]. Select the topic "nonlinear optics" in the ISI Web of Science and I found 44,486 papers in January, 2017 (**Figure 1**). This is because nonlinear optics impacts a wide range of technical fields, including X-rays, quantum optics,

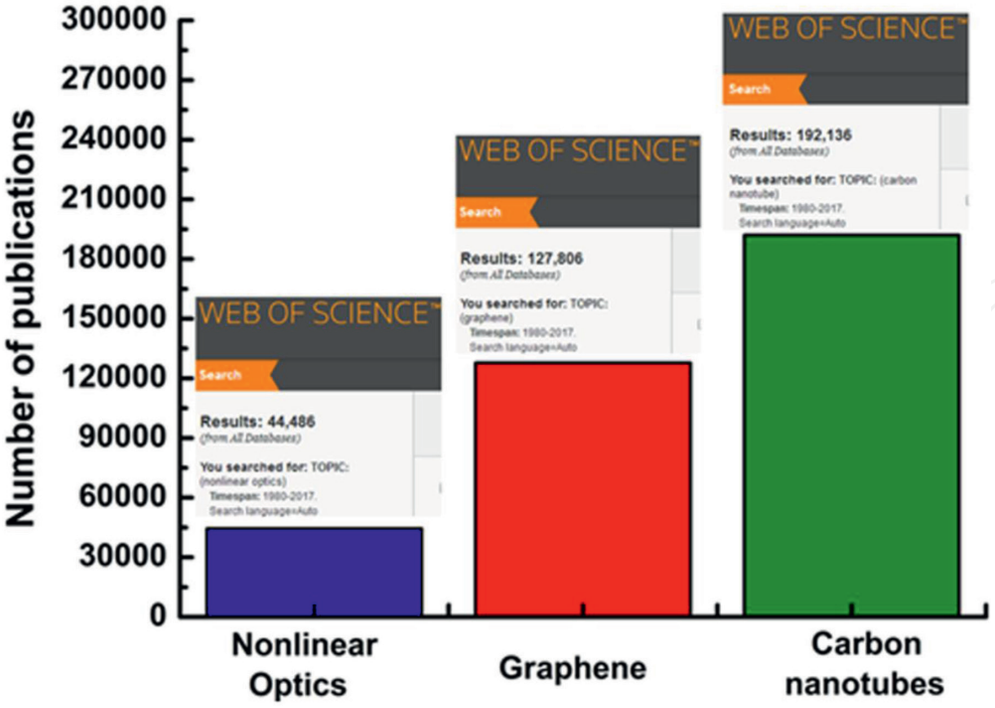

Figure 1. Publications statistics about nonlinear optics, graphene, and carbon nanotubes from Web of Science (Thomson-Reuters) database.

optical communications, fiber optics, ultrafast lasers, spectroscopy, photorefractivity, liquid crystals, polymers, semiconductors, organics, switching, ultraviolet, telecommunications, and signal processing [4, 5]. To further advance the performance of optical materials and devices, researchers have sought for lots of novel materials with improved nonlinear optical properties, including inorganic semiconductors, organic molecules, polymeric systems, and other nanomaterials [6, 7]. The latter, specifically, are of great interest because they present high nonlinear optical properties combined with versatility of available routes of synthesis, used to alter and optimize nanostructure to maximize nonlinear responses and other properties [8]. The rapid development of nanoscience and nanotechnology provides many unique opportunities for nonlinear optics. A growing number of nanomaterials, including graphene, carbon nanotubes, and their derivatives have been shown to possess remarkable nonlinear optical properties [9, 10], which promotes the design and fabrication of nanoscale optoelectronic and photonic materials. Materials that exhibit nonlinear optical performances are useful because they allow manipulation of the fundamental properties of laser light beams, and are hence of great technological importance in areas such as photonic switching, optical computing, and other optical data processing systems. It is thus of critical importance to explore innovative nonlinear optical materials required for the practical applications.

Basically, optical limiting, an important application of nonlinear optics, is useful for the protection of human eyes, optical elements, and optical sensors from intense laser pulses and is of great interest to the private industry and military [11]. As shown in **Figure 2**, ideal optical limiters have a linear transmittance at low input fluence, while above the threshold intensity the transmittance becomes constant. Over the past several decades, a huge pile of scientific reports

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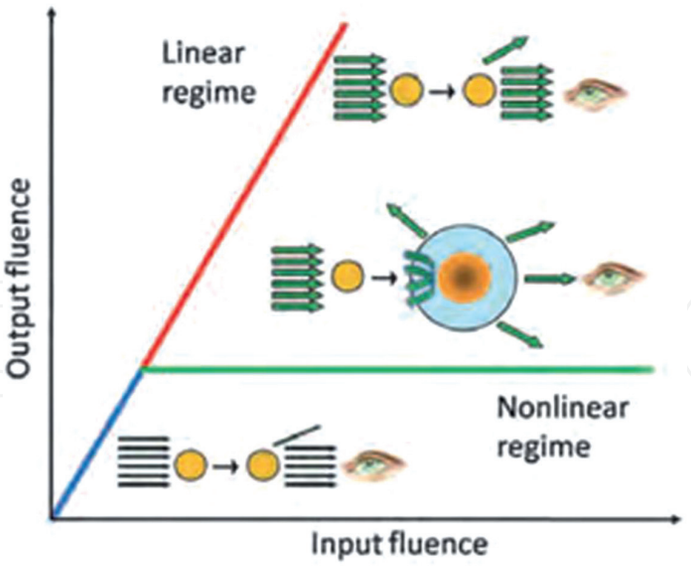

Figure 2. Trend of the light intensity (output fluence) transmitted by an ideal optical limiter versus the incoming light intensity (input fluence) [9].

has been published related to the study of these novel forms of carbon-based nanomaterials as highlighted in some prestigious reviews of graphene and carbon nanotubes with the view to realize practical passive optical limiting application [12–14]. The data about carbon nanomaterials have been swelled up so quickly that a single word of graphene and carbon nanotubes on web of science has resulted in thousands of publications statistics; the results are shown in **Figure 1**, which can help spur on the rapid development of carbon-based nanoscience. Porphyrins and phthalocyanines are attractive target materials for optical limiting applications due to the fact that they have a highly conjugated two-dimensional 18π-electron system resulting in a small HOMO-LUMO energy difference [15]. They also exhibit other additional advantages, i.e., exceptional stability, versatility, and processability features. The architectural flexibility of porphyrins and phthalocyanines can alter the electronic structure of the macrocyclic core, and thus, they allow the fine-tuning of the nonlinear optical performances [16]. Novel nonlinear optical materials may not be obtained from simple monomeric porphyrins or phthalocyanines, but be produced when strong electronic interactions between the highly delocalized π-electron systems and graphene/carbon nanotubes are induced by connecting them in a single system. Over times, the number of publications concerning the investigations and applications of porphyrins and phthalocyanines-functionalized graphene/carbon nanotubes has been an interesting observation. While phthalocyanine-functionalized graphene/carbon nanotubes have elicited wide interest in this area, porphyrins-functionalized graphene/carbon nanotubes have also increasingly attracted more attention (**Figure 3**). However, preparation of the required nonlinear optical active materials for optical limiters still presents a significant chemical challenge. Far from giving an exhaustive description of all the work that have been done in this area. This chapter will not explore application in detail, but only lay special stress on describing the recent achievements on the optical limiting properties of porphyrin and phthalocyanine covalently functionalized graphene/carbon nanotube nanohybrids. A great deal of information about nonlinear optics is now available on the ISI Web of Science.

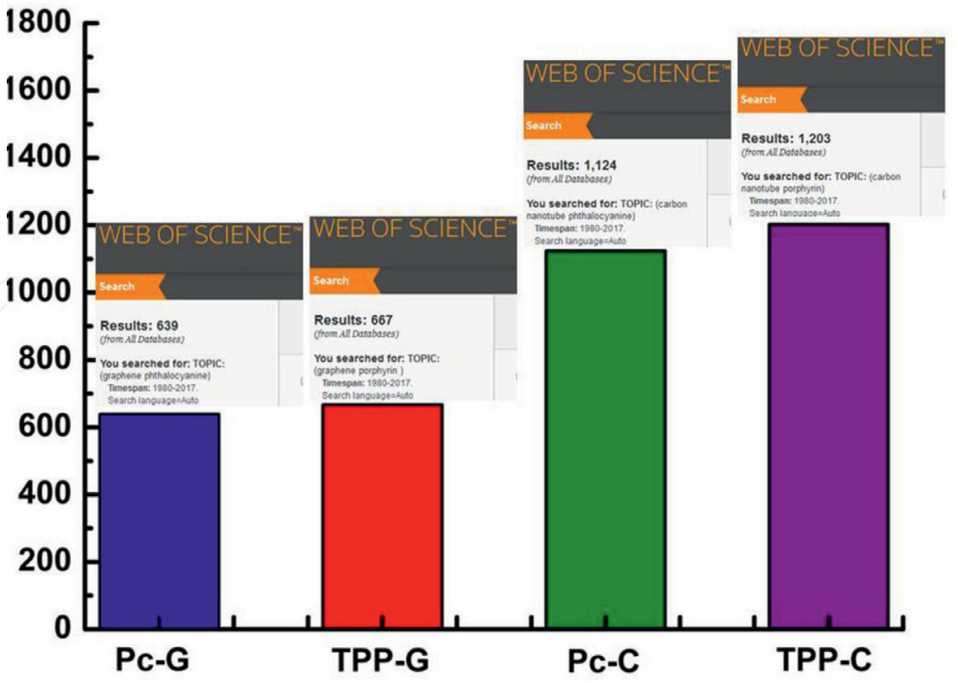

Figure 3. Publications statistics about phthalocyanine-functionalized graphene (Pc-G), porphyrin-functionalized graphene (TPP-G), phthalocyanine-functionalized carbon nanotubes (Pc-C), and porphyrin-functionalized carbon nanotubes (TPP-C) from Web of Science (Thomson-Reuters) database.

2. Experimental setup

With the aim to characterize the nonlinear optical absorption and optical limiting properties of a sample, the Z-can technique, developed by Sheik-Bahae et al. [17, 18], can be used, which is widely used in optical nonlinearity, mainly due to the simplicity of the experimental setup and the easy interpretation of the results. The major advantage of this technique is that the magnitude and the sign of the nonlinearity can be provided simultaneously. The Z-scan is a nonlinear optical experiment in which the irradiance (or fluence) is continuously varied from the linear regime of the sample to an irradiance high enough to induce nonlinear effects and then back to the linear regime. Because of the light-induced lens-like effect, the sample has a tendency to recollimate or defocus the incident beam, depending on its z position with respect to the focal plane. This can be accomplished by translating the sample along the z-axis of a focused Gaussian beam, the results being shown in **Figure 4**. In order to avoid cumulative thermal effects, data were collected in single shot mode.

In the Z-scan experiment, a laser pulse is focused to a minimum waist at the focal point along the propagation direction (z-axis) of this pulse. By moving the sample along the z-axis, the input pulse intensity is varied in the sample. When the sample is placed at the focal point, nonlinear process can be observed because the pulse intensity is high. The pulse intensity within the sample is decreased when the sample is moved away from the focal point, producing no nonlinear process. The consecutive recording of the relative pulse intensity transmitted

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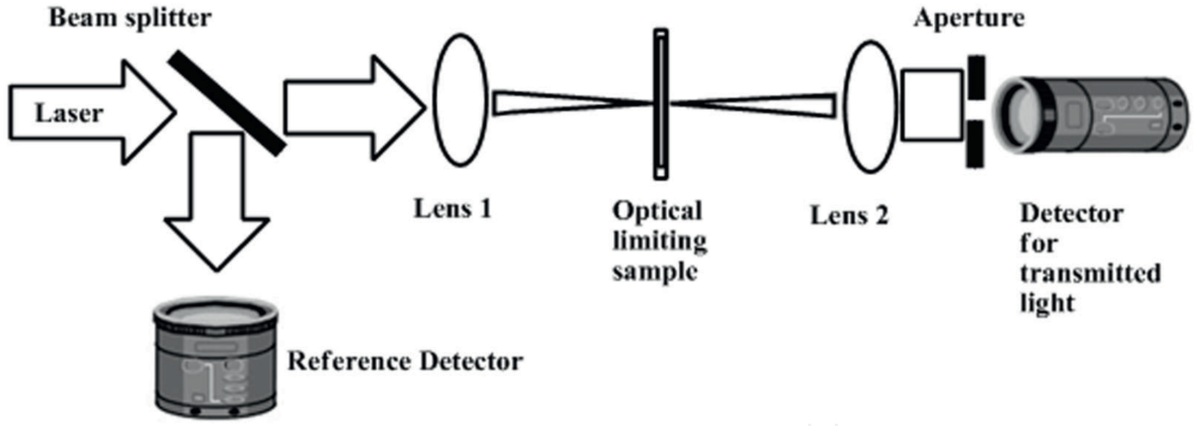

Figure 4. Experimental setup of the Z-scan technique with pulse trains, used to characterize the sample's nonlinear optical response [3].

through the samples as a function of the sample position along the axis provides important information about the imaginary part (the intensity-dependent absorption coefficient) and the real part (change in refractive index) of the third-order nonlinear susceptibility. Since the sample experiences different incident laser energy at each position as it moves along the z direction, any nonlinearity in transmission can be revealed by this measurement. The energy of the input (laser energy reaching the sample) and output (laser energy exiting the sample) laser pulses was monitored simultaneously by two energy detectors (Rjp-765 energy probe), which were linked to a computer by a general-purpose interface bus (GPIB) interface. To measure the nonlinear absorption of the samples, the Z-dependent transmittance was measured by using the open-aperture Z-scan method. In this technique, the aperture is absent, and so the total transmitted energy is detected, from which the nature of the absorptive optical nonlinearity can be determined alone. Division of the Z-scan curve obtained with an aperture by that without an aperture gives a curve with nonlinear absorption effectively eliminated and affords the nonlinear refraction response. The optical limiting measurements were performed when the sample was located at focal point by varying the input energy and recording the output energy. Both the incident and the transmitted energies were measured simultaneously by two pyroelectric detectors with Laser Probe Rjp-765 Energy Ratio meter.

3. Porphyrin and phthalocyanine covalently functionalized graphene and carbon nanotubes nanohybrids for optical limiting

3.1. Porphyrin and phthalocyanine covalently functionalized graphene

Graphene is the name given to a two-dimensional (2D) sheet of sp^2-hybridized carbon packed in a hexagonal lattice, with a carbon-carbon distance of 0.142 nm. Long-range π-conjugation in graphene yields extraordinary thermal, physical, chemical, mechanical, and electrical properties, such as ultrafast carrier dynamics, superlative mechanical strength, large specific surface area, and high electrical and thermal conductivity, among others [19]. Thanks to these

extraordinary and superior properties, graphene has long been the interest of many theoretical studies and more recently became an exciting area for experimentalists with many commercial applications, including gas and energy storage, as well as micro- and optoelectronics [20]. Despite the great application potential, it is worth mentioning that pristine graphene has no appreciable solubility in most solvents. However, the solubility and processability are the primary problems for many prospective applications of graphene-based materials. To improve the dispersibility of graphene in common organic solvents and change its photophysical properties, a variety of methods for the graphene surface modification have been developed [19]. These graphene-based nanohybrids with different forms have different nonlinear optical properties and photophysical processes. In most cases, when organic molecules are covalently attached on the graphene surface, its extended aromatic character is perturbed, providing the opportunities to control its optoelectronic properties. Indeed, it is expected that the combination of graphene and optoelectronically active porphyrin and phthalocyanine molecules would afford species that possess not only the intrinsic properties of porphyrin and phthalocyanine but also some functions arising from the mutual π interaction between graphene and porphyrin/phthalocyanine; multifunctional nanometer-scale materials with enhanced optical limiting responses compared with that of the individual components may thereby be generated. The nonlinear optical properties of graphene-based materials have been extensively investigated, and this area has been reviewed [5, 8, 9, 13, 16]. The discussion here will be limited to selected highlights of our studies and more recent developments.

The electronic structure of porphyrin and phthalocyanine molecules can be tailored by altering the peripheral and axial functionalities or by either metal substitution at the central binding site, thus affording great versatility in controlling their optoelectronic properties [21–23]. For the nonlinear optical and optical limiting applications, Xu et al. designed and synthesized a novel soluble graphene nanohybrid material (TPP-NHCO-SPFGraphene) covalently functionalized with metal-free porphyrin (TPP-NH_2) via an amidation reaction [24]. Attachment of the metal-free porphyrin TPP-NH_2 improves the solubility and dispersion stability of the TPP-NHCO-SPFGraphene nanohybrids in organic solvents. For the donor-acceptor nanohybrids, the fluorescence of the metal free porphyrin TPP-NH_2 was effectively quenched due to a possible electron transfer process. The effective intramolecular energy quenching may also be facilitated by a through-bond mechanism, originating from the direct linkage mode of the two moieties by the amide bond. A superior optical limiting performance, better than the benchmark material C_{60}, the control samples, and the individual components (TPP-NH_2 and graphene oxide (GO)), is observed. Similarly, the preparation and nonlinear optical properties of two novel graphene nanohybrid materials covalently functionalized with porphyrin and C_{60} were reported by Tian et al. [25]. The results displayed that covalently functionalizing graphene with porphyrin and C_{60} can improve the nonlinear optical performance in the nanosecond regime (**Figure 5**).

Very recently, porphyrin-reduced graphene oxide (RGO-TPP) nanohybrids with a push-pull motif have been satisfactorily prepared by our group following the Prato protocol, via a 1,3-dipolar cycloaddition reaction of appropriate formyl derivatives with sarcosine [26]. Stepwise and "one-pot" procedures have been explored (**Scheme 1**): A straightforward Prato reaction (i.e., a 1,3-dipolar cycloaddition) with sarcosine and a formyl-containing porphyrin, and a stepwise

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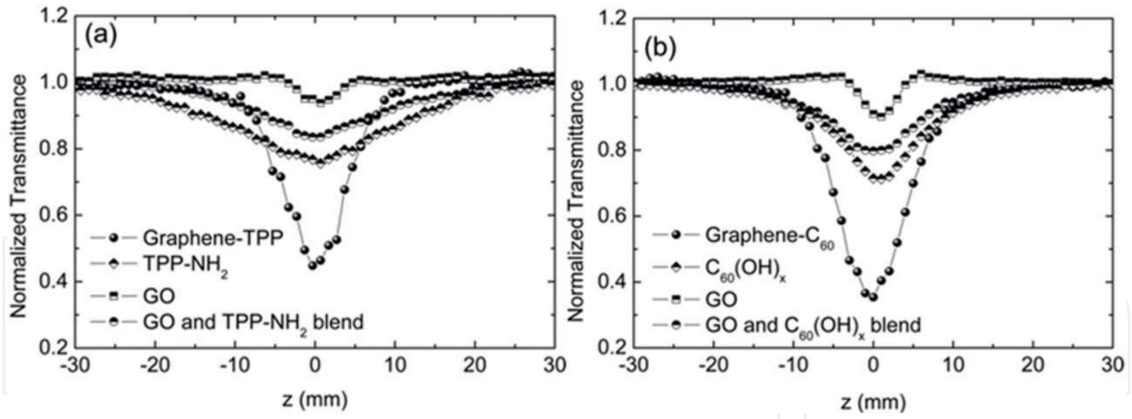
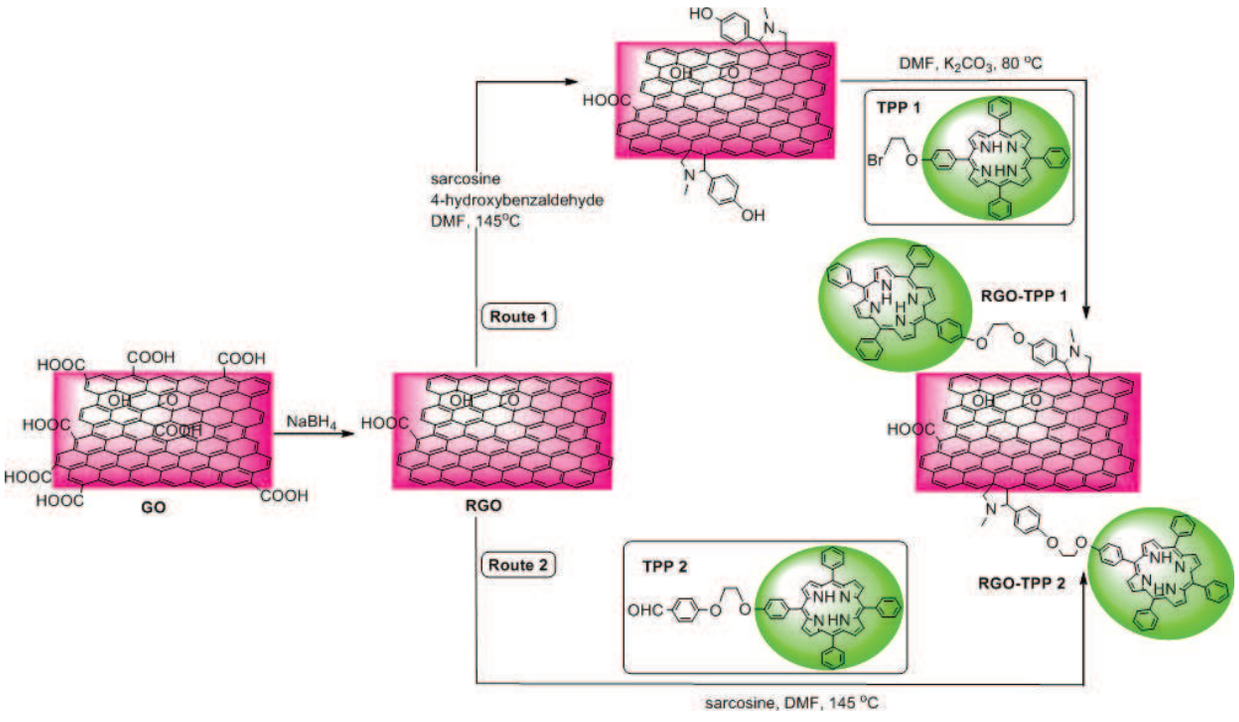


Figure 5. Open-aperture Z-scan curves of (a) Graphene-TPP, TPP-NH_2, GO, and GO and TPP-NH_2 blend, and (b) Graphene-C_{60}, $C_{60}(OH)_x$, GO, and GO and blend $C_{60}(OH)_x$ [25].

method that involves a 1,3-dipolar cycloaddition to the RGO surface using 4-hydroxybenzaldehyde, followed by nucleophilic substitution with an appropriate porphyrin. The interaction between RGO and the porphyrins was followed by fluorescence spectroscopy, and significant fluorescence quenching was observed for both nanohybrids, indicating the presence of efficient electron/energy transfer. When compared to RGO and porphyrins (TPP 1 and TPP 2), both nanohybrids display better nonlinear optical performances (**Figure 6**), implying a synergistic effect between two components due to the covalent linkage. Effective combination of the



Scheme 1. Chemical routes to functionalize RGO with porphyrin molecules: preparation of RGO-TPP 1 (Route 1) and RGO-TPP 2 (Route 2) [26].

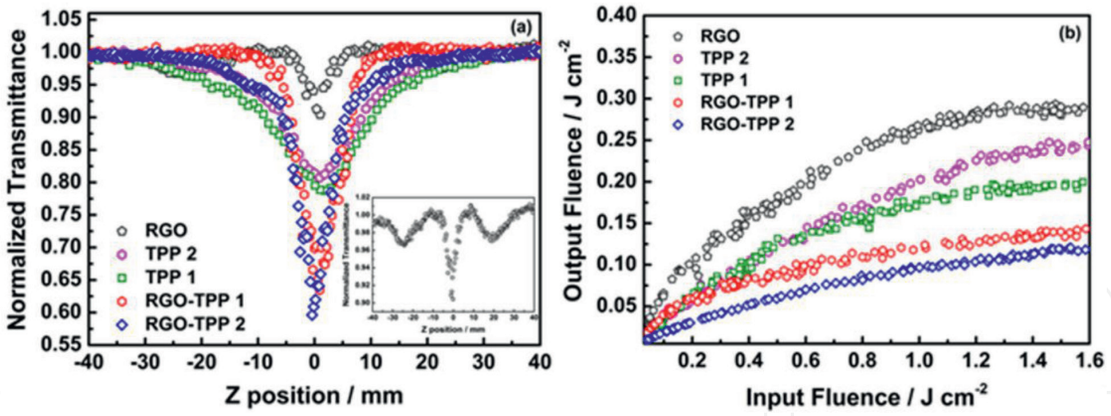


Figure 6. (a) Open-aperture Z-scan curves and (b) Optical limiting performances of RGO, TPP 2, TPP 1, RGO-TPP 1, and RGO-TPP 2 [26].

different nonlinear optical mechanisms, i.e., reverse saturable absorption, saturable absorption, excited absorption, nonlinear scattering, and photo-induced energy/electron transfer in the RGO-TPP nanohybrids leads to the improved nonlinear optical (including optical limiting) performances for 4 ns pulses at 532 nm. In the nanohybrid system, the nonlinear scattering originating from the graphene moieties can largely enhance the damage threshold of the nanohybrids. The similar accumulation effect leading to an increased nonlinear optical performance was also confirmed in RGO-TPP nanohybrid systems prepared by two synthetic routes that involve functionalization of the RGO by means of diazonium chemistry [27].

"Axial-bonding" at porphyrins may provide an approach for the preparation of arrays with tunable photoelectronic properties by changing the π-orbital interactions [28]. Axial substituents in porphyrins can favorably influence the nonlinear optical properties due to the presence of a dipole moment that is perpendicular to the macrocycle in the axially functionalized porphyrins. SnTPP and phosphorus-cored porphyrin (PTPP) (**Figure 7**) are well-known axial-bonding building blocks, the Sn-OH and P-Cl bonds being reactive toward carboxylates and aryloxides, respectively. By using the reactive activity of hydroxyl and carboxyl groups on the basal planes of GO, as shown in **Figure 7**, Wang et al. synthesized two novel graphene nanohybrids incorporating axially functionalized porphyrins (GO-PTPP and GO-SnTPP) [29]. Their nonlinear optical properties and optical limiting performance have been studied by using the Z-scan technique at 532 nm with 4 ns and 21 ps laser pulses. Both nanohybrids exhibited enhanced nonlinear optical and optical limiting properties in comparison to the individual GO and porphyrins in both the nanosecond and picoseconds regimes, due to an effective combination of different nonlinear optical mechanisms, i.e., nonlinear scattering and/or two-photon absorption with reverse saturable absorption, and photo-induced electron or energy transfer from the electron-donor porphyrin moiety to the acceptor graphene.

Very recently, in order to optimize the RGO dispersion and enhance interfacial bonding, we reported two covalent functionalization approaches for the fabrication of RGO-TPP nanohybrid materials (**Scheme 2**) [30]. These are based on the initial covalent introduction of phenol groups onto the RGO surfaces by 1,3-dipolar cycloaddition or a diazotization reaction, and subsequent nucleophilic substitution at dichloro(5,10,15,20-tetraphenylporphyrinato)tin(IV) (SnTPP). The

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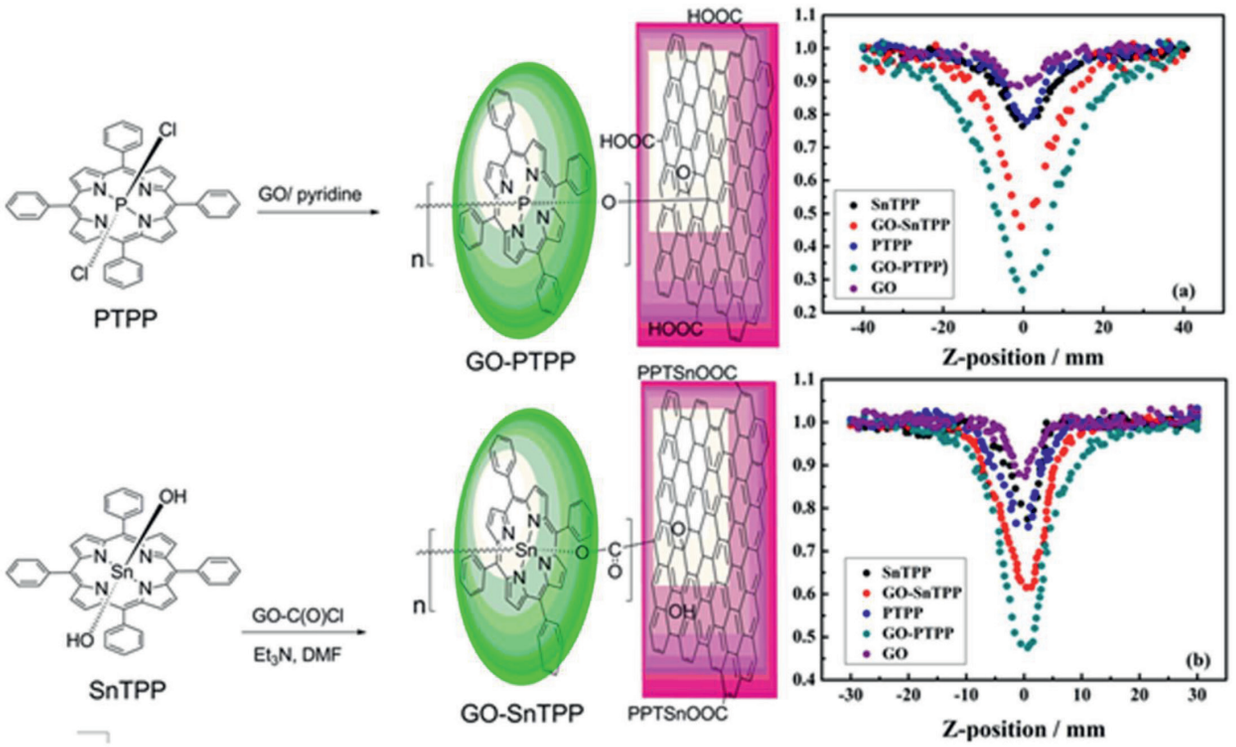
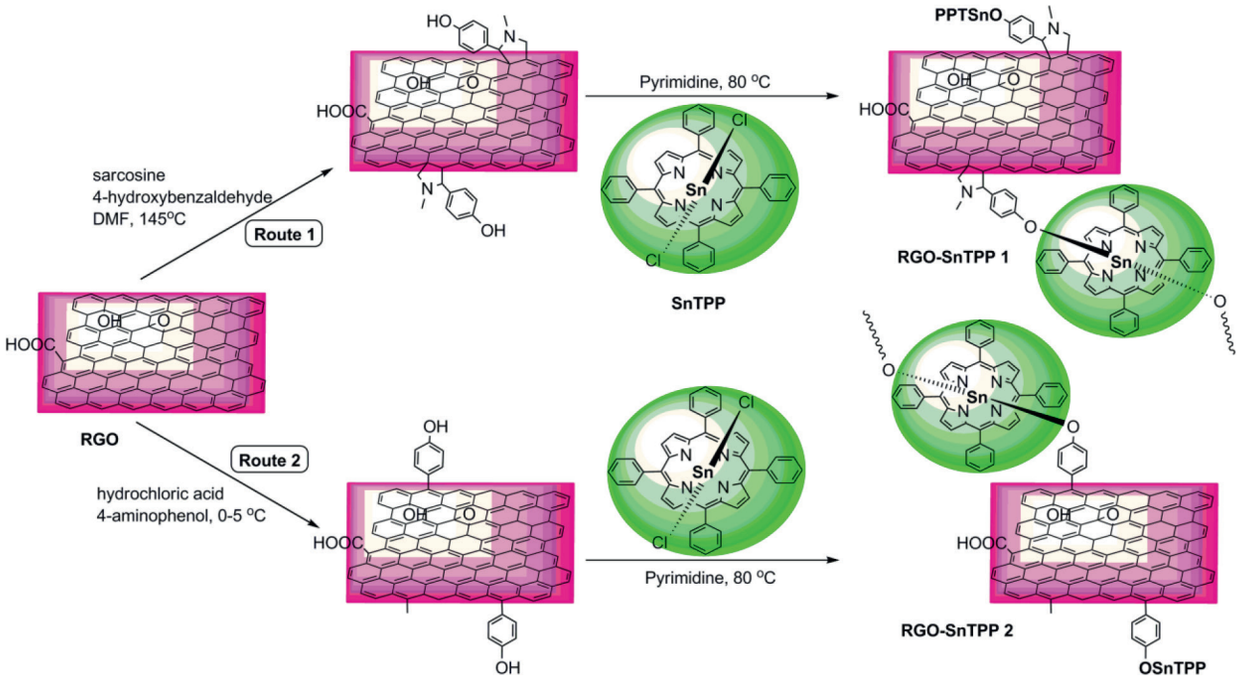


Figure 7. Synthetic routes of GO-PTPP and GO-SnTPP, and open-aperture Z-scan curves of GO, SnTPP, GO-SnTPP, PTPP, and GO-PTPP at 532 nm with (a) 4 ns and (b) 21 ps pulse duration [29].



Scheme 2. Syntheses of RGO-SnTPP 1 and RGO-SnTPP 2 [30].

porphyrin-functionalized RGO nanohybrids exhibited superior nonlinear optical performance to a RGO suspension at 532 nm under both picosecond and nanosecond regimes (**Figure 8**), due to a combination of mechanisms, while significant differences in their nonlinear optical

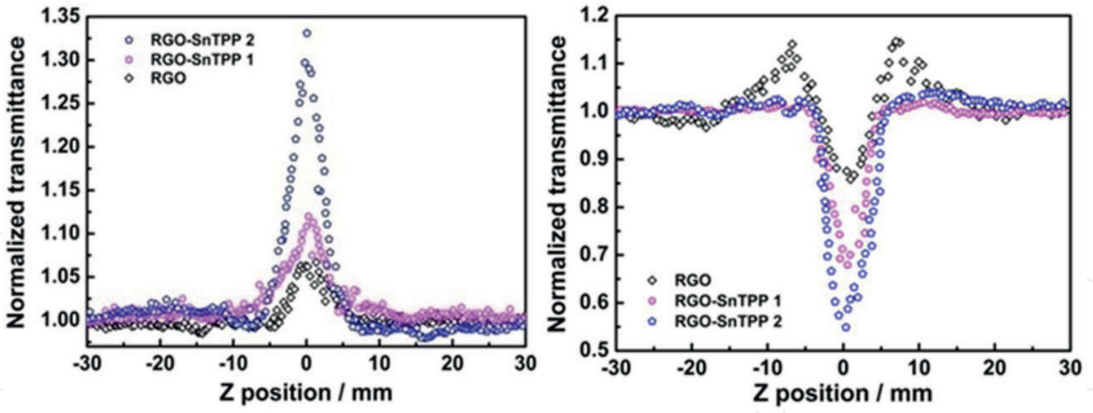


Figure 8. Left: Open-aperture Z-scan traces of RGO, RGO-SnTPP 1, and RGO-SnTPP 2 in dimethylsulfoxide (DMSO), obtained under 21 ps, 532 nm laser excitation. Right: Open-aperture Z-scan traces of RGO, RGO-SnTPP 1, and RGO-SnTPP 2 in DMSO, obtained under 4 ns, 532 nm laser excitation [30].

responses were observed, highlighting the influence on photophysical properties of the degree of functionalization and the synthetic approach employed. We also found that the two-photon absorption coefficients β_2 values increase on proceeding from the components RGO and SnTPP to the nanohybrids, and that the β_2 values of the nanohybrids under ns conditions differ significantly from that of the RGO/SnTPP blend, though being mindful of the errors associated with these measurements. Photo-induced electron or energy transfer mechanisms play an important role in the superior optical limiting performance. While nonlinear scattering dominates the optical limiting response, the photo-induced electron or energy transfer facilitates the deactivation of the nanohybrids, leading to energy dissipation via the nonradiative decay and thus, the effective heat accumulation in the nanohybrids or heat transfer from RGO to the adjacent solvent.

As porphyrin analogs, the structurally similar and biologically phthalocyanine are also effective optical limiters. Zhu et al. reported the synthesis and optical limiting performances of a soluble GO covalently functionalized with zinc phthalocyanine (GO-PcZn) by an amidation reaction [31]. A superior nonlinear optical effect and broadband optical limiting performance, better than GO and PcZn, are observed for GO-PcZn at both 532 and 1064 nm, suggesting a remarkable accumulation effect as a result of the covalent link between GO and PcZn. Similarly, a soluble GO axially substituted gallium phthalocyanine nanohybrid material (GO-PcGa) was prepared and designed by Li et al. [32]. At the same level of concentration of 0.1 g/L, this material displays much better optical limiting than the other three samples (GO, PcGa, and the benchmark optical limiting material C_{60}) at both 532 and 1064 nm. The improved optical limiting performance was assigned to the effective combination of the different optical limiting mechanisms, i.e., reverse saturable absorption in PcGa, and nonlinear scattering and two-photon absorption in GO. For PcGa and C_{60}, only reverse saturable absorption dominates at 532 nm, and no obvious nonlinear scattering was observed. Although the origin of the enhancement of the optical limiting effect for GO-PcGa at 1064 nm is not clear yet, the PcGa should certainly play an important but unknown role in this system due to the fact that GO-PcGa possesses much better broadband nonlinear optical and optical limiting performances than GO and PcGa alone.

Song et al. demonstrated the surface functionalization of RGO with zinc phthalocyanine (ZnPc), based on the initial covalent linkage of ZnPc to GO and subsequent *in situ* reduction of GO moiety to RGO during mild thermal treatment in dimethylformamide solvent [33]. The results display that the new nanohybrids allow the formation of stable colloidal solutions in various polar solvents such as dimethylsulfoxide, increasing the manipulation and processing of RGO. The nonlinear optical properties of the RGO-ZnPc nanohybrid were investigated by using the Z-scan technique. At a concentration of 0.13 mg/L, the RGO-ZnPc nanohybrid showed much larger nonlinear absorption coefficient β and better optical limiting performance than those of individual GO, ZnPc, and GP-ZnPc nanohybrids, ascribed to a combination of two-photon absorption resulting from the sp^3 domains, saturable absorption from the sp^2 carbon clusters, and excited state absorption from numerous localized sp^2 configurations in RGO moiety, reverse saturable absorption resulting from ZnPc moiety, and the contribution of improved photo-induced electron/energy transfer from ZnPc to RGO. Indeed, an improved photo-induced electron/energy transfer process with more efficient fluorescence quenching and energy release is observed in RGO-ZnPc than that of GO-ZnPc. In addition, the effect of peripheral substituents attached to phthalocyanines on the third-order nonlinear optical properties of graphene oxide-zinc(II) phthalocyanine hybrids, and the effects of central metals on the photophysical and nonlinear optical properties of reduced graphene oxide-metal(II) phthalocyanine hybrids were also reported [34, 35].

3.2. Porphyrin and phthalocyanine covalently functionalized carbon nanotubes

Carbon nanotubes (CNTs) are structures from the fullerene family consisting of a honeycomb nanosheet of sp^2 bonded carbon atoms rolled seamlessly into itself to form a cylinder. Typically, CNTs are divided into two distinct types, both with high structural perfection: single-walled carbon nanotubes (SWCNTs) that are made from one graphene sheet rolled as a tube and multiwalled carbon nanotubes (MWCNTs) that are obtained when several stacked graphitic shells are built to give concentric cylinders or graphene sheets are rolled [36]. CNTs have attractive mechanical, electrical, and thermal properties, which have found many potential applications in the field of nanoscience and nanotechnology. CNTs exhibit remarkable optical limiting properties on intense laser beams with ultrafast recovery time and broad bandwidth operation [37]. The advantage of CNTs-based nanomaterials manifests themselves in tailorable chemical properties by combining functional materials. Most importantly, the one-dimensional nanostructure of CNTs acts a favorable host for functional materials, forming versatile optical limiting nanocomposites [38]. It is therefore that CNTs are becoming a key component toward the development of nonlinear photonic devices. However, a CNTs system alone is not sufficient to fulfill all of the specifications of optical limiting. Indeed, various systems need to be coupled to extend the spectral and temporal ranges of effective optical limiting.

A CNT possesses one of the most extensive delocalized π-electron systems, which has been observed to be effective in optical limiting material and extends outside the range of many other optical limiting materials [39]. Covalently functionalized CNTs with porphyrins naturally pursued. For instance, Liu et al. reported the preparation and optical limiting

performances of three covalently functionalized SWCNTs with porphyrins [40]. The optical limiting properties were determined by Z-scan experiments with linearly polarized 5 ns pulses at 532 nm generated from a frequency doubled Q-switched Nd:YAG laser. The structures of the porphyrin-functionalized SWCNTs are illustrated in **Figure 9**. The optical limiting performances of the three SWCNTs-based nanohybrids are better than not only the individual porphyrins, SWCNTs, and C_{60} but also the blended system of SWCNTs and porphyrins. The optical limiting thresholds approximately 70, 100, and 150 mJ/cm^2 were determined for I, II, and III, respectively, all of which are much smaller than those of C_{60} (300 mJ/cm^2) and SWCNTs (250 mJ/cm^2).

Recently, Liu et al. reported the preparation of tetraphenylporphyrin covalently functionalized MWCNTs (MWCNT-TPP) with diameter ranges of <10, 10–30, and 40–60 nm by the reaction of MWCNTs with *in situ* generated porphyrin diazonium compounds (**Scheme 3**) [41]. A considerable quenching of the fluorescence intensity was found in the photoluminescence spectrum due to the fact that the unique direct linkage mode facilitates the effective photo-induced electron transfer between the excited porphyrin moiety and the extended π-system of MWCNTs. As laser pulse width increased from 5.6 to 11.7 ns, an obvious enhancement in the optical nonlinearities of MWCNT-TPP nanohybrid materials was observed (**Figure 10**), due to the improved efficiency of photo-induced electron transfer from porphyrin to MWCNTs with the increasing of pulse width.

Nanohybrids MWCNT-TPP and MWCNT-AIBN were prepared by radical polymerization (**Scheme 4**) [42]. The open-aperture Z-scan technique at 532 nm with 4 ns laser pulses was used to investigate the optical limiting performances; the results suggested that these nanohybrids exhibited generically good nonlinear optical properties. Comparison between the optical limiting performances of nanohybrids MWCNT-TPP and MWCNT-AIBN and that of TPP, MWCNTs, and mixture of both was effectuated. All samples displayed that the output fluence increased linearly with increasing input fluence at low laser pulse and deviations from linearity with further increase in input fluence pointed to the occurrence of optical limiting response. The order of the decreases in output fluence was MWCNT-TPP > TPP > MWCNT-AIBN > MWCNTs, implying that the optical limiting effect of MWCNT-TPP was superior to that of the MWCNT-AIBN and to that of the individual porphyrin as well as MWCNTs. As shown in **Figure 11**, at the wavelength used, the mechanism of

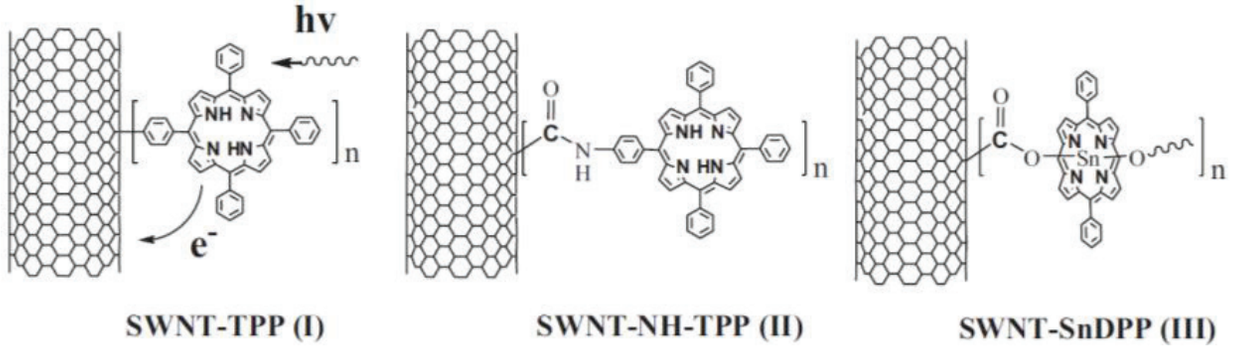


Figure 9. Structures of porphyrins covalently functionalized SWCNTs I, II, and III [40].

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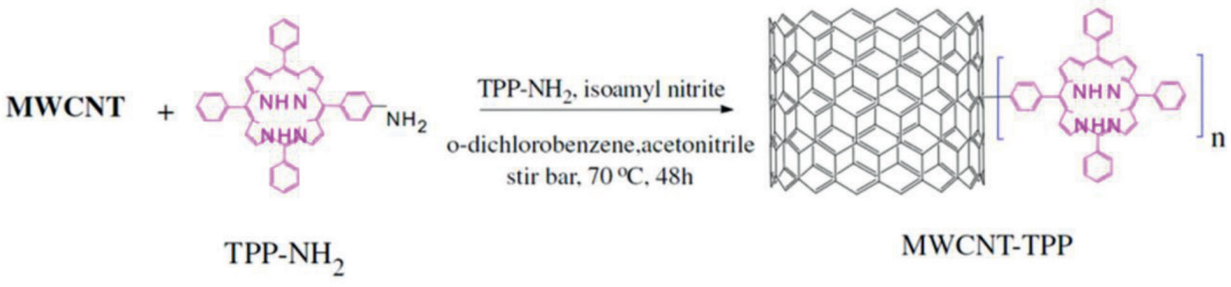


Scheme 3. Synthetic routes of MWCNT-TPP [41].

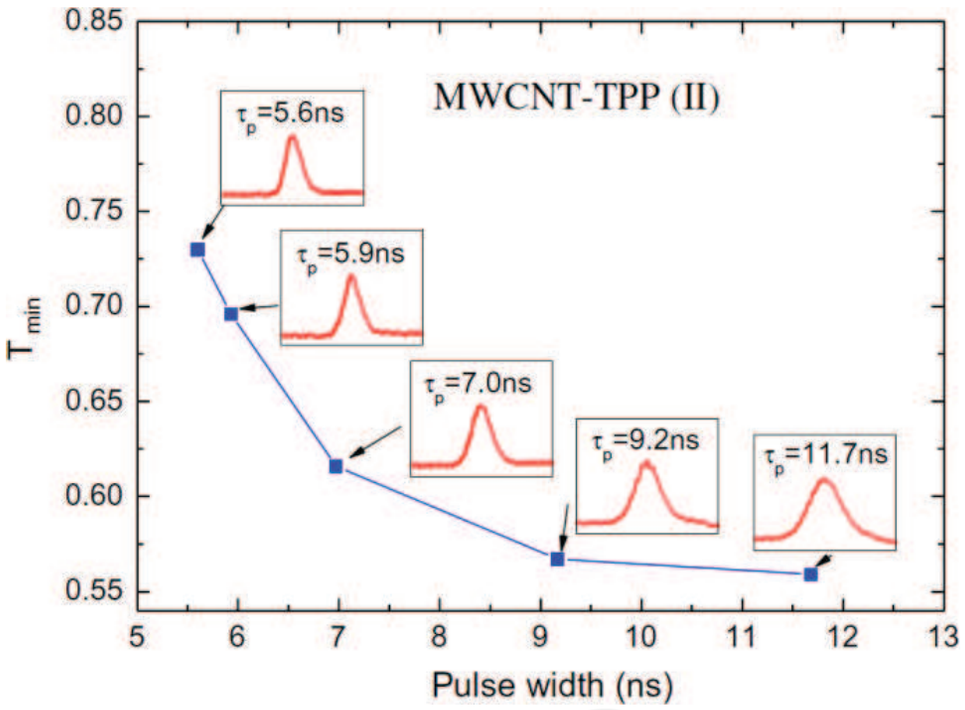
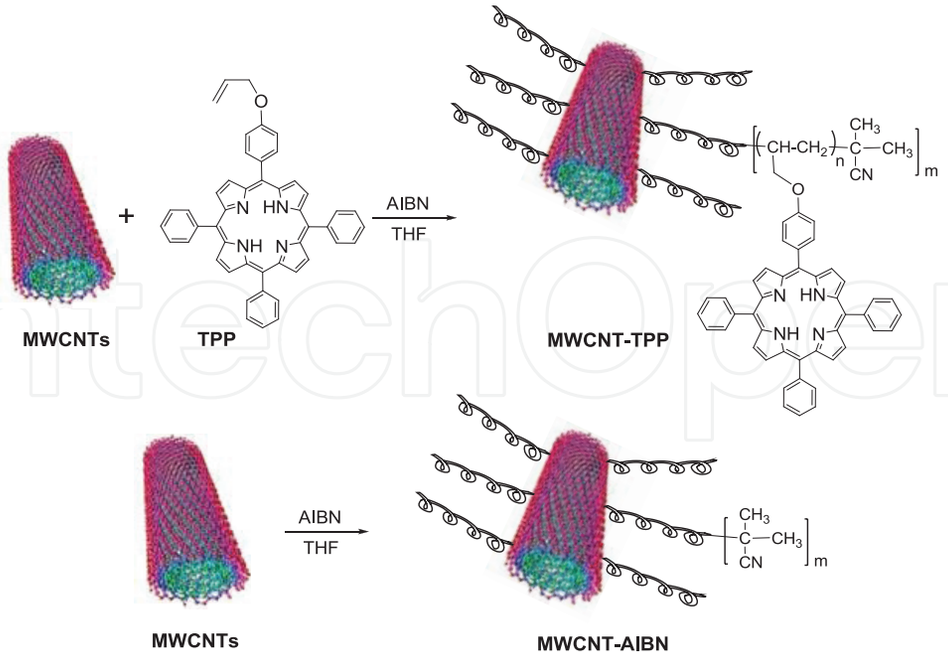


Figure 10. Transmittance valleys (T_{min}) of Z-scan curves of MWCNT-TPP (II) with different pulse width of 5.6, 5.9, 7.0, 9.2, and 11.7 ns [41].

increased optical limiting may be ascribed to reverse saturable absorption, nonlinear scattering, and photo-induced electron/energy transfer between the MWCNTs and the porphyrin moieties. The covalent attachment of porphyrins onto the surfaces of MWCNTs is expected to facilitate the fabrication of devices requiring the use of CNTs in optical limiting applications.

Two porphyrin covalently functionalized MWCNTs nanohybrids, MWCNT-ZnTPP and MWCNT-TPP, have been prepared directly from pristine MWCNTs through 1,3-dipolar cycloaddition reactions (**Scheme 5**), and the respective optical limiting properties of the materials were compared to those of zinc and free-base meso-tetraphenylporphyrins (ZnTPP and TPP) [43]. The nanohybrids displayed improved optical limiting ability. At the highest



Scheme 4. Synthetic routes of MWCNT-TPP and MWCNT-AIBN [42].

input fluence used in the experiments (1.65 J/cm^2), the output fluences were determined to be 0.90, 0.83, 0.75, 0.40, and 0.27 J/cm^2 for TPP, ZnTPP, MWCNTs, MWCNT-ZnTPP, and MWCNT-TPP, respectively. This clearly suggested that MWCNT-ZnTPP and MWCNT-TPP possessed the best optical limiting effect. In addition, the closed-aperture Z-scan measurements were also performed at 532 nm with both nanosecond and picosecond pulses for TPP, ZnTPP, MWCNT-TPP, and MWCNT-ZnTPP. As shown in **Figure 12**, all samples exhibit a self-defocusing effect, corresponding to a negative nonlinearity as revealed by the peak-valley signature, and the differences between the normalized transmittance values and

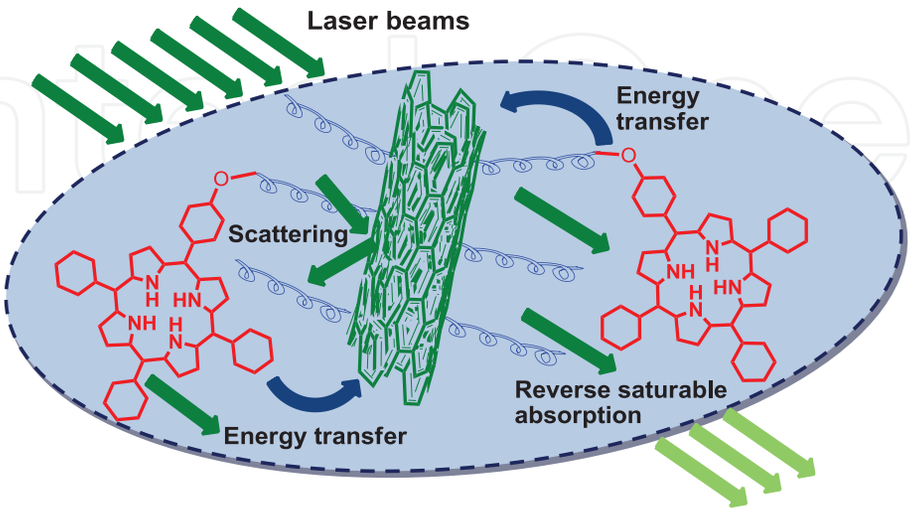


Figure 11. Possible mechanisms for the enhanced optical limiting effect of MWCNT-TPP [42].

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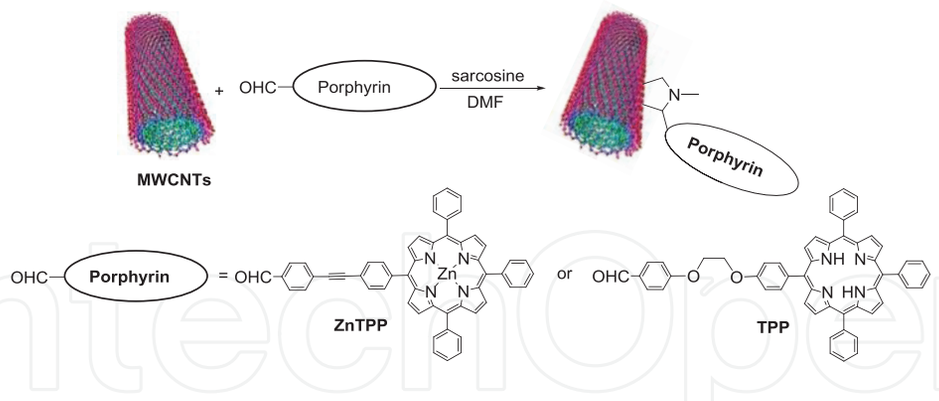


Scheme 5. Preparation of MWCNT-ZnTPP and MWCNT-TPP hybrid materials through a 1,3-dipolar cycloaddition reaction [43].

valley positions for MWCNT-TPP and MWCNT-ZnTPP are larger than those for the other compounds in this study. This clearly indicated that the porphyrin-functionalized MWCNT nanohybrids possess larger nonlinear refraction coefficients than the individual components, presumably originating from their covalent linkage.

Wang et al. synthesized axially coordinated metal-porphyrin-functionalized multiwalled carbon nanotubes nanohybrids via two different synthetic approaches (**Scheme 6**, a one-pot 1,3-dipolar cycloaddition reaction and a stepwise approach that involved 1,3-dipolar cycloaddition followed by nucleophilic substitution) [44], namely MWCNT-SnTPP 1 and MWCNT-SnTPP 2. The attachment of the tin porphyrin as an electron-donor onto the surface of the MWCNTs resulted in an increased electron absorption than its parent compound in the whole spectral region and an efficient fluorescence quenching. The resultant materials exhibit significant reverse saturable absorption or saturable absorption when nanosecond or picosecond pulses, respectively, are employed. A combination of the outstanding properties of MWCNTs and the chemically attached metal-porphyrins should be responsible for the improvement in the nanosecond

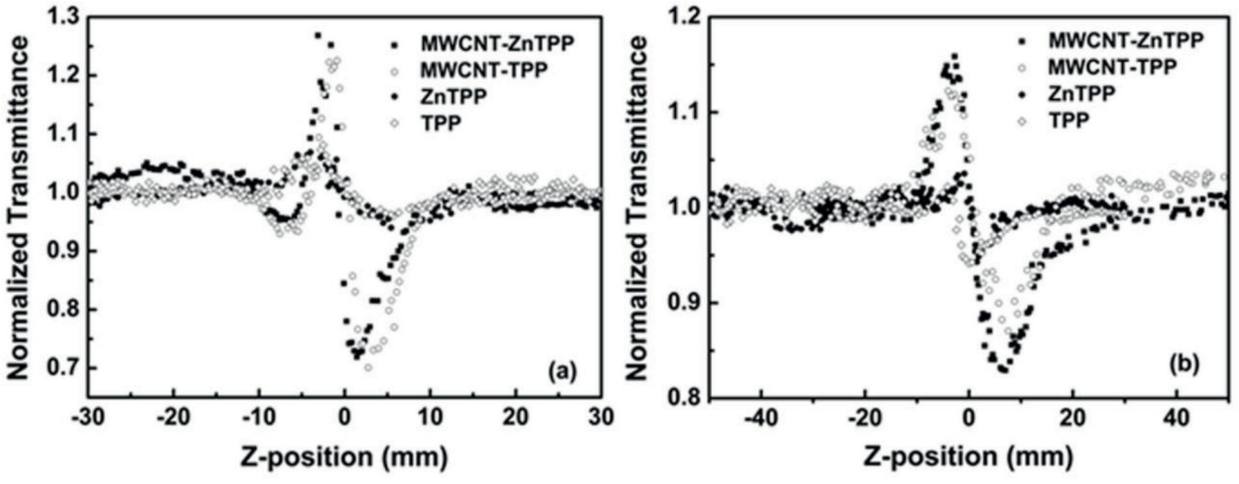
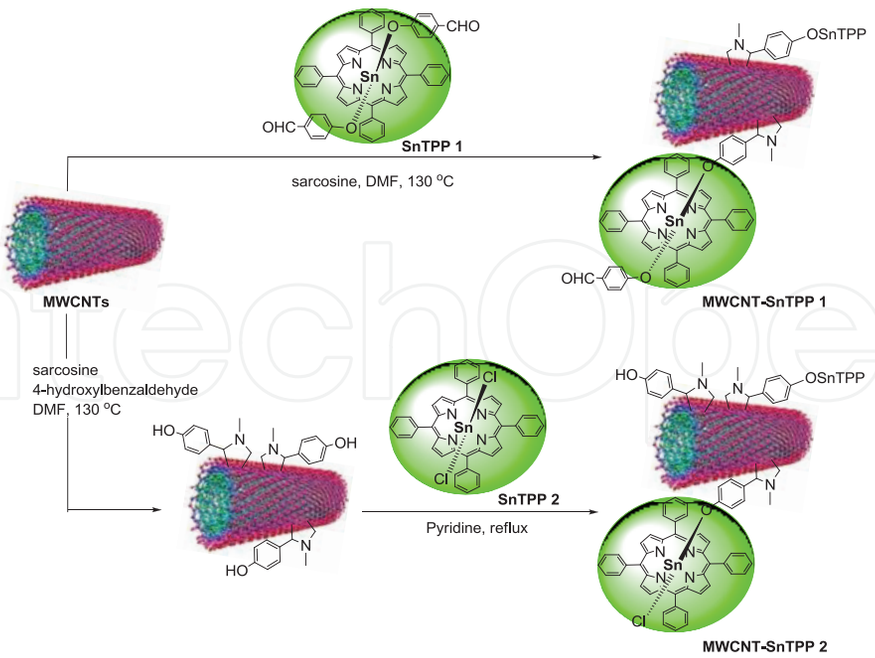


Figure 12. Normalized closed-aperture Z-scan curves of TPP, ZnTPP, MWCNT-TPP, and MWCNT-ZnTPP in N,N-dimethylformamide (DMF) with (a) 4 ns and (b) 21 ps pulse durations [43].



Scheme 6. Preparation of MWCNT-SnTPP 1 and MWCNT-SnTPP 2 [44].

regime nonlinear absorption. It is well-known that nonlinear absorption performance is strongly affected by the pulse width. Indeed, the behaviors of MWCNT-SnTPP 1 and MWCNT-SnTPP 2 were quite different at the ns and ps time scales. Both nanohybrids exhibit saturable absorption performance in the ps regime, while reverse saturable absorption was observed in the ns regime. This change was ascribed to the result of transitions from the first excited state to higher excited states arising from the temporally longer pulse width under ns conditions.

CNTs in combination with Pcs were also investigated as optical limiting materials. Several reports appeared on the preparation and nonlinear optical properties of covalently functionalized CNTs with Pcs. For instance, the nonlinear optical properties of a novel unsymmetrically substituted metal-free phthalocyanine covalently functionalized MWCNTs nanohybrid (PcH_2-MWCNTs) were investigated by using the Z-scan technique at 532 nm in the ns time scale [45]. Strong nonlinear scattering was observed for this material at higher intensities, which evidently comes from the MWCNTs moiety. However, no obvious nonlinear scattering was observed from the pristine PcH_2 solution, indicating that the optical limiting effect totally originates from reverse saturable absorption. The nonlinear optical response of PcH_2 is ascribed to reverse saturable absorption, while that of PcH_2-MWCNTs is due to both reverse saturable absorption and nonlinear scattering. Both nonlinear mechanisms may be conflicting for optical limiting, suppressing the whole nonlinear response of PcH_2-MWCNTs. However, an improved nonlinear absorption was observed for indium phthalocyanine-SWCNTs composite in DMSO, when compared to the nonlinked phthalocyanine counterpart [46]. The optical properties of this composite were found to display high sensitivity toward the change of solvent matrix. Due to quenching by the counterionic DMF species, the triplet quantum yield values of the materials in DMF were found to be lower than those of their values in DMSO. In other words, solvents that can generate resonance-stabilized counterions as shown for DMF may tend to lower the inherent optical limiting effect of materials. However, the longest-lived triplet lifetimes with a

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highest triplet quantum yield was observed for the nanocomposite in DMSO, and thus the best optical limiting properties can be expected when compared to the other systems investigated.

4. Summary and outlook

Many functional materials have been widely investigated with the view to realize practical passive optical limiting application. However, preparation of the required nonlinear optical active materials for optical limiters still presents a significant chemical challenge. As we mentioned above, the excellent chemical activity of graphene and CNTs provides a broad platform for various functional counterparts, forming multi-component, multifunctional hybrid composites with wider spatial and temporal responses for optical limiting, which are suitable candidates to satisfy the requirements for the next generation of photonic components. The porphyrins and phthalocyanines covalently functionalized graphene and carbon nanotubes nanohybrids described in this work are the product of recent efforts spent in designing effective nanomaterial structures for optical limiting applications. The nanohybrids exhibited a strong optical limiting behavior, and the incorporation of porphyrins and phthalocyanines significantly increased the nonlinear optical performances of graphene and CNTs. The nonlinear optical mechanisms observed in inorganic-organic nanohybrids, i.e., nonlinear scattering, nonlinear absorption, nonlinear refraction, and others, are discussed in conjunction with the influence of the materials properties and the laser source on the optical limiting performances.

Generally speaking, covalent functionalization of graphene and CNTs materials results in better optical limiting effect than noncovalent functionalization. This is because the covalent link can more effectively improve photo-induced energy or electron transfer from the functional moiety to the graphene and CNTs. In most of such nanohybrids, it is being attached importance to the photo-induced energy or electron transfer from functional moieties to graphene or CNTs, which is considered playing an important role on improving optical limiting performance. However, the data are very fragmentary, a detailed understanding of the factors affecting the nonlinear response is still necessary, and further work should be devoted to this objective. Multifunctional optical limiters are expected to have broad application range for various laser sources. The plasticity and flexibility of graphene and CNTs allow one to design and fabricate a range of structures to meet different demands. Graphene- and CNTs-based nanomaterials are still in their infancy, current demonstrations only show modest results, and while the very high third-order susceptibility combined with the fast optical response is promising, significant developments will need to be made before optical limiting by graphene- and CNTs-based nanomaterials can become a reality in a realistic commercial application. Looking toward the future use of graphene- and CNTs-based nanomaterials, it may be that in expanding on the already studied synthetic procedures lies a key to unlock a realm of opportunities for these materials. From a practical application of view, many efforts have been currently invested into the research of graphene- and CNTs-based nanocomposites in an attempt to allow for the fabrication of solid-state films or embedded solid-state thin films, which is very significant but challenging, and will undoubtly open a way to design and fabricate the industrially applicable optical limiters.

Acknowledgements

This research was supported financially by the National Natural Science Foundation of China (51506077, 51602130), the Natural Science Foundation of Jiangsu Province (BK20150488), the Natural Science Foundation of Jiangsu High School (15KJB430007, 15KJB610003), the China Postdoctoral Foundation (2016M601733), and Research Foundation of Jiangsu University (13JDG066, 15JDG156).

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