Optical limiting properties and mechanisms of single-layer graphene dispersions in heavy-atom solvents

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Abstract: The optical limiting (OL) properties of single-layer graphene dispersions in different solvents were studied using a nanosecond pulse laser. The graphene dispersions, especially in heavy-atom solvents, showed much better OL properties compared with referenced C_{60}-toluene solution. The dependences of OL thresholds and nonlinear scattering (NLS) intensities on the solvent surface tensions indicated that, NLS effect played an important role in the OL process of graphene dispersions, while nonlinear absorption (NLA) effect might also contribute in solvents with heavy atoms. The NLA measurements further demonstrated the contribution of NLA effect to the excellent OL property of graphene dispersions in heavy-atom solvents.

OCIS codes: (190.0190) Nonlinear optics; (160.4330) Nonlinear optical materials; (230.4320) Nonlinear optical devices; (190.4400) Nonlinear optics, materials.

References and links

1. P. C. Haripadmam, M. K. Kavitha, H. John, B. Krishnan, and P. Gopinath, "Optical limiting studies of ZnO nanotops and its polymer nanocomposite films," Appl. Phys. Lett. **101**(7), 071103 (2012).
2. J. Yang, Y. Song, W. Zhu, X. Su, and H. Xu, "Investigation of optical nonlinearities and transient dynamics in a stilbenzene derivative," J. Phys. Chem. B **116**(4), 1221–1225 (2012).
3. Y. Gao, Y. Wang, Y. Song, Y. Li, S. Qu, H. Liu, B. Dong, and J. Zu, "Strong optical limiting property of a novel silver nanoparticle containing C_{60} derivative," Opt. Commun. **223**(1-3), 103–108 (2003).
4. Y. P. Sun and J. E. Riggs, "Organic and inorganic optical limiting materials. From fullerenes to nanoparticles," Int. Rev. Phys. Chem. **18**(1), 43–90 (1999).
5. K. Mansour, M. J. Soileau, and E. W. Van Stryland, "Nonlinear optical properties of carbon-black suspensions (ink)," J. Opt. Soc. Am. B **9**(7), 1100–1109 (1992).
6. L. Vivien, P. Lancon, D. Riehl, F. Hache, and E. Anglaret, "Carbon nanotubes for optical limiting," Carbon **40**(10), 1789–1797 (2002).
7. D. Tan, Y. Yamada, S. Zhou, Y. Shimotsuma, K. Miura, and J. Qiu, "Carbon nanodots with strong nonlinear optical response," Carbon **69**, 638–640 (2014).
8. F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, "Graphene photonics and optoelectronics," Nat. Photonics **4**(9), 611–622 (2010).
9. J. M. Dawlaty, S. Shivaraman, M. Chandrashekhar, F. Rana, and M. G. Spencer, "Measurement of ultrafast carrier dynamics in epitaxial graphene," Appl. Phys. Lett. **92**(4), 042116 (2008).
10. Y. W. Song, S. Y. Jang, W. S. Han, and M. K. Bae, "Graphene mode-lockers for fiber lasers functioned with evanescent field interaction," Appl. Phys. Lett. **96**(5), 051122 (2010).
11. J. Wang, Y. Hernandez, M. Lotya, J. N. Coleman, and W. J. Blau, "Broadband Nonlinear Optical Response of Graphene Dispersions," Adv. Mater. **21**(23), 2430–2435 (2009).
12. M. Feng, H. B. Zhan, and Y. Chen, "Nonlinear optical and optical limiting properties of graphene families," Appl. Phys. Lett. **96**(3), 033107 (2010).
13. M. Krishna, V. P. Kumar, N. Venkatramaiah, R. Venkatesan, and D. N. Rao, "Nonlinear optical properties of covalently linked graphene-metal porphyrin composite materials," Appl. Phys. Lett. **98**(8), 081106 (2011).
14. G. K. Lim, Z. L. Chen, J. Clark, R. Goh, W. H. Ng, H. W. Tan, R. H. Friend, P. Ho, and L. L. Chua, "Giant broadband nonlinear optical absorption response in dispersed graphene single sheets," Nat. Photonics **5**(9), 554–560 (2011).
15. N. Karousis, A. Sandanayaka, T. Hasobe, S. P. Economopoulos, E. Sarantopoulou, and N. Tagmatarchis, "Graphene oxide with covalently linked porphyrin antennae: Synthesis, characterization and photophysical properties," J. Mater. Chem. **21**(1), 109–117 (2010).

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16. T. C. He, W. Wei, L. Ma, R. Chen, S. X. Wu, H. Zhang, Y. H. Yang, J. Ma, L. Huang, G. G. Gurzadyan, and H. D. Sun, "Mechanism Studies on the Superior Optical Limiting Observed in Graphene Oxide Covalently Functionalized with Upconversion $NaYF_4$:Yb^{3+}/Er^{3+} Nanoparticles," Small **8**(14), 2163–2168 (2012).
17. Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Y. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari, and J. N. Coleman, "High-yield production of graphene by liquid-phase exfoliation of graphite," Nat. Nanotechnol. **3**(9), 563–568 (2008).
18. R. C. Hollins, "Materials for optical limiters," Curr. Opin. Solid State Mater. Sci. **4**(2), 189–196 (1999).
19. I. M. Belousova, N. G. Mironova, A. G. Scobelev, and M. S. Yur'ev, "The investigation of nonlinear optical limiting by aqueous suspensions of carbon nanoparticles," Opt. Commun. **235**(4-6), 445–452 (2004).
20. I. M. Belousova, N. G. Mironova, and M. S. Yur'Ev, "Theoretical investigation of nonlinear limiting of laser radiation power by suspensions of carbon particles," Opt **94**(Spec.), 86–91 (2003).
21. J. Wang, D. Fruchtl, Z. Y. Sun, J. N. Coleman, and W. J. Blau, "Control of Optical Limiting of Carbon Nanotube Dispersions by Changing Solvent Parameters," J. Phys. Chem. C **114**(13), 6148–6156 (2010).
22. X. Cheng, N. N. Dong, B. Li, X. Y. Zhang, S. F. Zhang, J. Jiao, W. J. Blau, L. Zhang, and J. Wang, "Controllable broadband nonlinear optical response of graphene dispersions by tuning vacuum pressure," Opt. Express **21**(14), 16486–16493 (2013).
23. Q. Y. Ouyang, H. L. Yu, Z. Xu, Y. Zhang, C. Y. Li, L. H. Qi, and Y. J. Chen, "Synthesis and enhanced nonlinear optical properties of graphene/CdS organic glass," Appl Phys Lett, **102**, 19123–1-3 (2013).
24. Q. Y. Ouyang, Z. Xu, Z. Y. Lei, H. W. Dong, H. L. Yu, L. H. Qi, C. Y. Li, and Y. J. Chen, "Enhanced nonlinear optical and optical limiting properties of graphene/ZnO hybrid organic glasses," Carbon **67**, 214–220 (2014).

1. Introduction

With the increasing utilization of high power laser sources, great challenges have been posed to design efficient optical limiting (OL) materials to protect human eyes and delicate detecting devices from optical damage [1–3]. Nonlinear OL processes, such as nonlinear scattering (NLS), nonlinear absorption (NLA), refractive index change, have been studied in various materials. Numerous organic and inorganic materials have been proved to be good candidates for optical limiters, among which carbon-based materials, such as fullerenes [4], carbon black suspensions (CBS) [5], carbon nanotubes (CNTs) [6], and carbon nanodots (C-Dots) [7], have exhibited excellent OL performance.

With the emergence of graphene, its excellent electronic, thermal conductivity, optical properties, especially nonlinear optical properties have attracted significant research interests [8–10]. Since the first report by J. Wang etc [11], much work has been done to study the OL properties and mechanisms of graphene, graphene oxide [12], and their composites with various molecules [13]. As has been demonstrated in CBS and CNTs, one of the main OL mechanisms of graphene suspensions was attributed to NLS process, in which solvent microbubbles and/or microplasmas would be formed at a high input light fluence, inducing the decrease of transmittance of the limiter. In 2011, G. Lim and associates demonstrated the giant broadband nonlinear optical absorption effect in graphene dispersed sheets, when they studied the OL response of the materials [14]. It was claimed that, when single-layer graphene sheets were dispersed as single sheets in appropriate solvents or film matrices, the initially delocalized electron–hole gas would localize at high excitation densities in the presence of heavy atoms, to give strongly absorbing excitons. The resultant excited state absorption mechanism could be very effective, causing apparent nonlinear OL behavior of the material. Moreover, some graphene composites have been reported to be of effective OL properties due to strong NLA effects [15, 16]. Now that both NLS and NLA effects could attribute to the OL behavior of graphene materials, to investigate the different OL mechanisms of graphene dispersions in different solvents make much sense to design efficient OL materials and devices based on graphene.

In this paper, we investigated the OL behaviors of single-layer graphene dispersions in different solvents using a nanosecond pulse laser. The graphene dispersions exhibited much lower OL thresholds compared with the reference sample of C_{60} solution in toluene. The dependences of the OL property and the NLS intensity of the samples on the surface tensions of the solvents indicated that, NLS effect played an important role in the OL behavior of graphene dispersions, while NLA effect might contribute when the material was dispersed in solvents with heavy atoms. The NLA measurements were conducted to further demonstrate the contribution of NLA effect to the excellent OL property of graphene dispersions in heavy-atom solvents.

2. Experiments and sample preparation

In our experiments, the single-layer graphene (thickness: ~0.8 nm, diameter: 0.5-2 μm, single layer ratio: >80%) was obtained from Nanjing XFNano Materials Tech Co., Ltd., (Nanjing, China). The dispersions were prepared by adding 6 mg graphene in 40 mL solvents, and then sonicated for 2 h in an ice bath. All dispersions were subsequently centrifuged at 5000 rpm for 30 min to remove large aggregates. According to the previous reports, solvents with surface tensions in the region of 40-50 dyn/cm were most suitable to be used as the dispersion solvents, due to the minimal energy cost of overcoming the van der Waals forces between two graphene sheets [17]. Hence, we selected solvents with surface tensions in and near this region, including toluene (TOL), N,N-dimethyl-formamide (DMF), N-methyl-2-pyrrolidinone (NMP), chlorobenzene (CB), 1,2-Dichlorobenzene (2CB), and bromobenzene (BB). Single-layer graphene dispersions in the last three solvents (CB, 2CB, and BB) have been demonstrated to be of strong NLA effect due to their heavy-atom effect, but the NLS effect was not discussed [14]. All the dispersions were stable against sedimentation and with little aggregation occurring in a few days.

The OL behaviors of graphene dispersions were measured using 10 ns laser pulses from a Q-switched Nd^{3+}: YAG laser with a harmonic generator. The laser was operated at the second harmonic of 532 nm with a pulse repetition rate of 10 Hz. The laser source was focused with a lens of 30 cm focal length. An open-aperture (OA) Z-scan system is used to study the OL behavior of the dispersions. All the dispersions were filled in a 5 mm thick quartz cells, and the linear transmittances of all the samples were adjusted to 60% by changing the solute concentrations. As a reference, OL behavior of the C_{60} solution in toluene was also measured. To clarify the OL mechanisms of the samples, we measured the pulse energy dependence of the scattered light intensity for different samples. A fraction of the scattered light was collected using a convex lens at ~30° in the forward direction from the beam axis, and then detected by a photodiode.

3. Results and discussions

Firstly, we measured the OL behaviors of the graphene dispersions and C_{60}-toluene solution. Figure 1(a) shows the nonlinear transmittances as functions of the input energy intensity for single-layer graphene dispersed in TOL (red circles), NMP (cyan diamonds), DMF (blue triangles), and CB (black squares), respectively. The solid squares indicate the nonlinear transmittance for reference sample of C_{60}-TOL solution. From the figure we can see that, the OL response of the dispersions increased across solvent series from NMP, DMF, TOL, and CB, and all the graphene dispersions showed better OL performance than C_{60} solution. The OL threshold in CB was estimated to be about 0.07 J/cm^2 (where transmittance fell to 50% of linear transmittance), which was similar as that of the graphene dispersions has been reported by G. Lim et al [14].

Figure 1(b) shows the input energy intensity dependence of scattered light intensity for graphene dispersions and C_{60} solution. As has been demonstrated in the previous reports, very little scattered light was detected in C_{60} solution as the OL behavior of the sample was mainly originated from NLA effect [2, 18]. For graphene dispersions, the onset of the growth of scattered signals was synchronous with the onset of the decrease of transmission for dispersions in TOL, NMP and DMF. What was extraordinary was that, graphene dispersion in CB showed a superior OL property than that in TOL, but the scattered signal intensity was lower than the latter one. The contribution of the solvents themselves to the OL behavior was ruled out, as no transmittance change of the solvents was observed at the same input fluence. Hence, we speculated that some other nonlinear effects besides NLS could also contribute to the OL process of graphene dispersion in CB.

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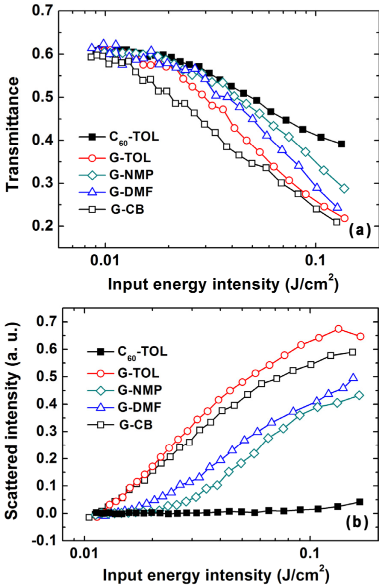

Fig. 1. Input energy intensity dependence of (a) nonlinear transmittance and (b) nonlinear scattered light intensity for single-layer graphene dispersed in TOL (red circles), NMP (cyan diamonds), DMF (blue triangles), and CB (black squares), respectively. The solid squares in (a) and (b) indicate the nonlinear transmittance and scattered light intensity for C_{60}-toluene solution.

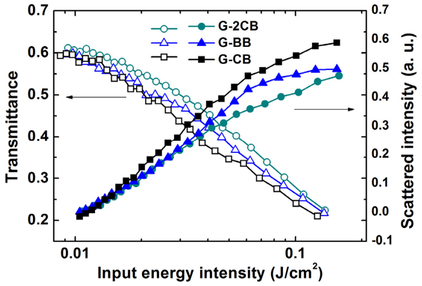

Fig. 2. Nonlinear transmittance and scattered light intensity for single-layer graphene dispersed in CB (squares), BB (triangles), and 2CB (circles), respectively.

To clarify the OL mechanisms of graphene dispersions in CB, we further measured the OL behavior of dispersions in CB, 2CB, and BB solvents. Compared with TOL, NMP and DMF, these three solvents were characteristic of marked heavy-atom effect. Figure 2 show the nonlinear transmittance and scattered light intensity of graphene dispersed in CB (squares), BB (triangles), and 2CB (circles), respectively. From the figure we can see that, the OL response of graphene dispersion in CB outperformed those in BB and 2CB, while the BB dispersion exhibited a stronger OL effect than 2CB dispersion, and the scattering intensity decreased in the same order.

According to the theoretical prediction for the NLS effect of carbon particles suspensions, when carbon particles were heated by the intense light, they would transfer thermal energy to the surrounding solvents, and the surrounding solvents would be evaporated resulting in the formation of gas bubbles. The high pressure in the initial bubbles would cause the fast expansion of the bubbles, and finally the thermal energy transferred from the carbon particles to the liquid would be converted into the work of the expansion of the initial bubbles overcoming the atmosphere pressure and the surface tension of the solvents, as well as the thermal potential energy of the expended bubbles [19, 20]. In the equilibrium condition, the bubble size could be defined by the following equations [11]:

$$2\gamma=\frac{3nRT}{4\pi r_B^2}-p_\infty r_B \tag{1}$$

Here, γ is the surface tension, n is the number of moles of gas, R is the universal gas constant, T is the absolute temperature in the bubble. r_B is the bubble size and P_∞ is the pressure far from the bubble. When the initial bubbles expanded to the magnitude of incident light wavelength, they would induce the scattering of the incident light, causing the reduction of transmittance. According to Eq. (1), the lower the surface tension γ is, the more quickly the initial micro-bubbles expand, resulting in efficient scattering to the incident beam, and hence more reduction of transmission. We plotted the scattered light intensity as a function of the surface tension of solvents as shown by the squares in Fig. 3(a). It can be seen clearly that, the lower surface tension resulted in larger bubble size and stronger NLS effect. It should be pointed out that, although the NLS intensity of the dispersions could also be influenced by the ratio of refractive indices inside and outside of the scattered centers, the refractive indices of the solvents showed less of an effect on the NLS intensity by plotting the dependence of the NLS intensity on the solvents refractive indices. These results agreed well with the previous studies reported by J. Wang et. al [11, 21, 22], as well as the theoretic predictions above.

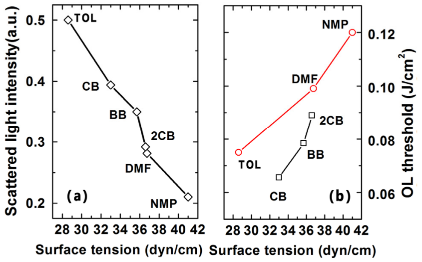

Fig. 3. Scattered light intensity (a) and OL threshold (b) of different graphene dispersions as functions of the surface tensions of solvents.

Figure 3(b) shows the OL thresholds for different graphene dispersions as a function of the surface tension of the solvents. The red circles in the figure indicate the OL thresholds of graphene dispersions in TOL, DMF, and NMP. For comparison, OL thresholds of graphene dispersions in CB, BB and 2CB solvents were plotted using black squares. The OL thresholds of different dispersions decreased roughly with the decrease of surface tension, indicating that the NLS effect played an important role in the OL behaviors of all the dispersions. For dispersions in CB, BB and 2CB with strong heavy-atom effect, however, the OL thresholds were obviously lower than those in other solvents with similar surface tensions. Hence, we speculated that NLA effect could also contribute to the OL process besides nonlinear scattering effect.

In order to directly observe the contribution of NLA effect to OL behaviors of graphene dispersions in heavy-atom solvents, we conducted NLA measurements in different graphene dispersions. In the experiments, the output light of optical limiter was divided into two parts using a beam splitter. One part of the light only including the transmitted light was detected by a detector (D1) since an aperture was used to block the scattered light, and the other part including amounts of scattered light was collected by lens and detected by another detector (D2). The detailed optical scheme was similar with that described in the reference [23, 24]. In this case, D1 recorded the transmittance changes caused by NLS and NLA, while D2 recorded the transmittance changes mainly induced by NLA.

Figures 4(a) and (b) represent the measured output energy intensities as functions of the input energy intensity in different dispersions detected by D1 and D2, respectively. From Fig. 4(a) we can see that, when both NLS and NLA effects contributed, graphene dispersions in

BB and TOL showed the similar OL behavior, which were much better than that in NMP. This result agreed well with that shown in Fig. 1-3. As shown by Fig. 4(b), when parts of the scattered light was collected into the detector, the OL behaviors of graphene in NMP and TOL were obviously deteriorated, indicating that NLS effect played the main role in the OL behavior for NMP and TOL dispersions. For BB dispersion, however, the input-output relations still showed a strong OL behavior. This result indicated that NLA effect also contributed to the OL process of dispersions in heavy-atom solvents. The strong NLA effect could be attributed to strongly absorbing excitons induced by the initially delocalized electron–hole gas localizes at high excitation densities in the presence of heavy atoms, as demonstrated by G. Lim. Because of the co-contributions of NLA and NLS effects, single-layer graphene dispersions in heavy-atom solvents showed more excellent OL property compared with those in solvents without heavy atoms.

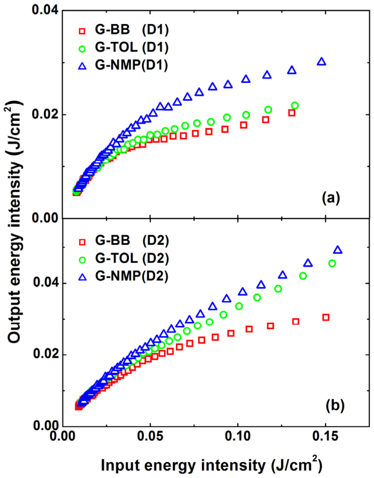

Fig. 4. Input energy intensity dependence of the output energy intensity detected by (a) D1 with an aperture blocking the NLS light, and (b) D2 with a lens collecting mounts of the NLS light into the detector, respectively.

4. Conclusions

In summary, we investigated the OL behaviors and mechanisms of single-layer graphene dispersions in different solvents. The graphene dispersions exhibited very excellent OL properties, especially when they were dispersed in heavy-atom solvents. The NLS measurements of the materials indicated that, NLS effect played an important role in the OL behavior of graphene dispersions, while NLA effect might contribute when the materials were dispersed in solvents with heavy atoms. The NLA measurements were conducted to further verify the contribution of NLA effect to the excellent OL property of graphene dispersions in heavy-atom solvents. Due to the co-contributions of NLA and NLS effects, graphene dispersions showed more excellent OL property in heavy-atom solvents.

Acknowledgments

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