Enhanced nonlinear optical properties of graphene-oligothiophene hybrid material

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Abstract: The nonlinear optical and optical limiting properties of an oligothiophene (6THIOP) covalently functionalized graphene hybrid material (Graphene-6THIOP) were investigated by using Z-scan technique with a 5ns Q-switched pulsed laser at 532 nm. Results show that the hybrid material of Graphene-6THIOP exhibits enhanced nonlinear optical and optical limiting properties in comparison to individual 6THIOP, graphene moiety and C_{60}. The enhanced nonlinear optical properties of Graphene-6THIOP should be attributed to the combination of the observed nonlinear scattering with the possible photoinduced electron or energy transfer mechanism between 6THIOP moiety and graphene.

OCIS codes: (190.0190) Nonlinear optics; (190.4710) Optical nonlinearities in organic materials; (290.5820) Scattering measurements

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References and Links

1. L. W. Tutt, and A. Kost, “Optical limiting performance of C_{60} and C_{70} solutions,” Nature **356**(6366), 225–226 (1992).
2. C. L. Liu, G. Z. Zhao, Q. H. Gong, K. L. Tang, X. L. Jin, P. Cui, and L. Li, “Optical limiting property of molybdenum complex of fullerene C_{70},” Opt. Commun. **184**(1-4), 309–313 (2000).
3. 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).
4. X. Sun, R. Q. Yu, G. Q. Xu, T. S. A. Hor, and W. Ji, “Broadband optical limiting with multiwalled carbon nanotubes,” Appl. Phys. Lett. **73**(25), 3632–3634 (1998).
5. P. Chen, X. Wu, X. Sun, J. Lin, W. Ji, and K. L. Tan, “Electronic structure and optical limiting behavior of carbon nanotubes,” Phys. Rev. Lett. **82**(12), 2548–2551 (1999).
6. L. Vivien, P. Lancon, D. Riehl, F. Hache, and E. Anglaret, “Carbon nanotubes for optical limiting,” Carbon **40**(10), 1789–1797 (2002).
7. Z. X. Jin, X. Sun, G. Q. Xu, S. H. Goh, and W. Ji, “Nonlinear optical properties of some polymer/multi-walled carbon nanotube composites,” Chem. Phys. Lett. **318**(6), 505–510 (2000).
8. J. E. Riggs, D. B. Walker, D. L. Carroll, and Y. P. Sun, “Optical limiting properties of suspended and solubilized carbon nanotubes,” J. Phys. Chem. B **104**(30), 7071–7076 (2000).
9. L. Q. Liu, S. Zhang, T. J. Hu, Z. X. Guo, C. Ye, L. M. Dai, and D. B. Zhu, “Solubilized multi-walled carbon nanotubes with broadband optical limiting effect,” Chem. Phys. Lett. **359**(3-4), 191–195 (2002).
10. D. Li, and R. B. Kaner, “Materials science. Graphene-based materials,” Science **320**(5880), 1170–1171 (2008).
11. D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen, and R. S. Ruoff, “Preparation and characterization of graphene oxide paper,” Nature **448**(7152), 457–460 (2007).
12. J. S. Bunch, A. M. van der Zande, S. S. Verbridge, I. W. Frank, D. M. Tanenbaum, J. M. Parpia, H. G. Craighead, and P. L. McEuen, “Electromechanical resonators from graphene sheets,” Science **315**(5811), 490–493 (2007).
13. A. K. Geim, and K. S. Novoselov, “The rise of graphene,” Nat. Mater. **6**(3), 183–191 (2007).
14. Z. B. Liu, Y. Wang, X. L. Zhang, Y. F. Xu, Y. S. Chen, and J. G. Tian, “Nonlinear optical properties of graphene oxide in nanosecond and picosecond regimes,” Appl. Phys. Lett. **94**(2), 021902 (2009).
15. Y. F. Xu, Z. B. Liu, X. L. Zhang, Y. Wang, J. G. Tian, Y. Huang, Y. F. Ma, X. Y. Zhang, and Y. S. Chen, “A graphene hybrid material covalently functionalized with porphyrin: synthesis and optical limiting property,” Adv. Mater. **21**(12), 1275–1279 (2009).
16. Z. B. Liu, J. G. Tian, Z. Guo, D. M. Ren, F. Du, J. Y. Zheng, and Y. S. Chen, “Enhanced optical limiting effects in porphyrin-covalently functionalized single-walled carbon nanotubes,” Adv. Mater. **20**(3), 511–515 (2008).

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17. W. S. Li, Y. Yamamoto, T. Fukushima, A. Saeki, S. Seki, S. Tagawa, H. Masunaga, S. Sasaki, M. Takata, and T. Aida, "Amphiphilic molecular design as a rational strategy for tailoring bicontinuous electron donor and acceptor arrays: photoconductive liquid crystalline oligothiophene--C_{60} dyads," J. Am. Chem. Soc. **130**(28), 8886–8887 (2008).
18. R. Yamada, H. Kumazawa, T. Noutoshi, S. Tanaka, and H. Tada, "Electrical conductance of oligothiophene molecular wires," Nano Lett. **8**(4), 1237–1240 (2008).
19. K. Schulze, C. Uhrich, R. Schüppel, K. Leo, M. Pfeiffer, E. Brier, E. Reinold, and P. Bäuerle, "Efficient vacuum-deposited organic solar cells based on a new low-bandgap oligothiophene and fullerene C_{60}," Adv. Mater. **18**(21), 2872–2875 (2006).
20. Y. S. Liu, J. Y. Zhou, X. L. Zhang, Z. B. Liu, X. J. Wan, J. G. Tian, T. Wang, and Y. S. Chen, "Synthesis, characterization and optical limiting property of covalently oligothiophene-functionalized graphene material," Carbon **47**(13), 3113–3121 (2009).
21. H. A. Becerril, J. Mao, Z. F. Liu, R. M. Stoltenberg, Z. N. Bao, and Y. S. Chen, "Evaluation of solution-processed reduced graphene oxide films as transparent conductors," ACS Nano **2**(3), 463–470 (2008).
22. N. Venkatram, D. N. Rao, and M. A. Akundi, "Nonlinear absorption, scattering and optical limiting studies of CdS nanoparticles," Opt. Express **13**(3), 867–872 (2005).
23. M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Van Stryland, "Sensitive measurement of optical nonlinearities using a single beam," IEEE J. Quantum Electron. **26**(4), 760–769 (1990).
24. W. Wu, S. Zhang, Y. Li, J. X. Li, L. Q. Liu, Y. J. Qin, Z. X. Guo, L. M. Dai, C. Ye, and D. B. Zhu, "PVK-modified single-walled carbon nanotubes with effective photoinduced electron transfer," Macromolecules **36**(17), 6286–6288 (2003).
25. Z. B. Liu, Y. L. Liu, B. Zhang, W. Y. Zhou, J. G. Tian, W. P. Zang, and C. P. Zhang, "Nonlinear absorption and optical limiting properties of carbon disulfide in a short-wavelength region," J. Opt. Soc. Am. B **24**(5), 1101–1104 (2007).
26. R. L. Sutherland, *Handbook of Nonlinear Optics (Second Edition)*; Chapter 9, (Marcel Dekker: New York, **2003**).
27. D. Vincent, "Optical limiting threshold in carbon suspensions and reverse saturable absorber materials," Appl. Opt. **40**(36), 6646–6653 (2001).

1. Introduction

The development of high-power laser sources has motivated an extensive research for designs of optical limiting systems for eye and sensor protection. Among widely investigated materials for optical limiting, some carbon-based materials have been shown to be good candidates. Fullerenes and their derivatives have shown excellent optical limiting arising from their larger excited-state absorption [1,2]. Carbon black suspensions (CBS) can undergo dramatic changes in transmittance because of nonlinear scattering [3]. Both single-walled carbon nanotube (SWNT) and multiwalled carbon nanotube (MWNT) suspensions have been reported to have strong optical limiting effects due to strong nonlinear scattering [4–6], similar to CBS, while some soluble carbon nanotubes have shown relatively weak optical limiting properties because of a proposed nonlinear absorption mechanism [7–9]. As another carbon allotropic forms, graphene has been a very recent rising star in material science, which is atomically thin and exhibits remarkable electronic and mechanical properties [10–13]. We have observed nonlinear optical properties in graphene oxide (GO) [14] and much stronger optical limiting effects in graphene-porphyrin hybrid material than in GO [15]. The enhanced optical limiting performance was believed to arise from a combination of nonlinear mechanisms with the photoinduced electron or energy transfer from the electron donor porphyrin moiety to the electron-acceptor graphene, similar results have also been observed in the hybrid materials of SWNT-Porphyrin [16].

Polythiophenes and Oligothiophenes possess extensive π-electron delocalization along the molecular backbone and are well known as high hole mobility materials, which makes them interesting for various optoelectronic applications [17–19]. In this paper, we report the nonlinear optical and optical limiting properties of oligothiophene (6THIOP)-covalently functionalized graphene hybrid material (Graphene-6THIOP) at 532nm. Results show that although 6THIOP shows no obvious nonlinear optical properties, the covalent attachment of 6THIOP to graphene makes Graphene-6THIOP exhibit enhanced nonlinear optical and optical limiting properties compared with individual 6THIOP, graphene moiety and C_{60} due to the observed nonlinear scattering behavior and the possible photoinduced electron or energy transfer mechanism.

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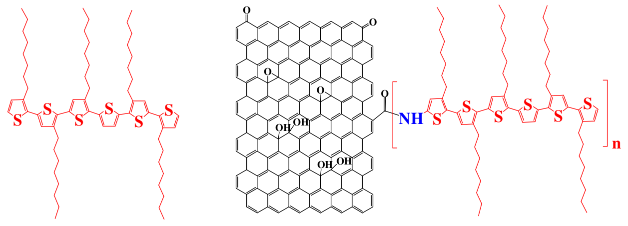
2. Experimental section

The synthesis of the graphene-oligothiophene nanohybrid was carried out using an amine functionalized oligothiophene (6THIOP-NH_2) and graphene oxide in o-dichlorobenzene (ODCB) [20]. The oligothiophene and graphene in the nanohybrid act as a donor and acceptor, respectively. Large scale and water soluble graphene oxide was prepared by the modified Hummers method [21]. The covalent functionalization of graphene oxide with oligothiophenes changes graphene oxide from hydrophilic to hydrophobic and the hybrid can be dissolved in organic solvents such as ODCB. This makes it possible that this graphene hybrid can be homogeneously dispersed (together with other organic materials) in organic solvents needed for various organic electronic applications. Based on elemental analysis, it was estimated that there is one 6THIOP unit for every 108 graphene carbons in the hybrid. Figure 1 gives the structure of 6THIOP and Graphene-6THIOP.



(a) 6THIOP

(b) Graphene-6THIOP

Fig. 1. Structure of 6THIOP and Graphene-6THIOP

The Z-scan and optical limiting experiments were preformed with linearly polarized 5 ns pulsed laser at 532 nm generated from a frequency doubled Q-switched Nd:YAG laser. The pulsed laser was set at a repetition rate of 10Hz. The spatial profile of the pulsed beam was of nearly Gaussian form after spatial filtering. The pulsed beam was split into two parts: the reflected part was used as reference, and the transmitted part was focused onto samples by using a 25-cm focal length lens. Sample was placed at the focus where the focused spot radius was about 23 μm ($1/e^2$). The reflected and transmitted pulses energies were measured simultaneously by using two energy detectors (Molectron J3S-10). C_{60} toluene solution was employed as a reference. The measurements of nonlinear optical properties were carried by Open-aperture Z-scan, where a lens was used to collect the transmitted energy, but scattering lights at large angle to z axial were not collected. For nonlinear scattering measurements, the experimental setup was the same as that in Ref [22], and a small area lens was placed at a certain angle with *z* axial to collect the scattered signal. All the samples were adjusted to have the same concentration of 0.2mg/mL for the measurements of nonlinear optical and scattering properties. For the measurements of optical limiting, an 8 mm aperture was placed between the detector and the sample where all the transmitted energy just can go through it when the sample is far away from the focus. All the energy through the aperture was focused into the detector by a lens between the aperture and detector. The samples were adjusted to have the same linear transmittance of 65% at 532 nm. All the samples were contained in 1-mm-thick quartz cell. No nonlinear response and damage of the quartz cell were observed at the fluence used in our experiments.

3. Results and discussion

3.1 Absorption and fluorescence spectra

Figure 2a gives UV-Visible absorption spectra of Graphene-6THIOP (in ODCB), 6THIOP (in ODCB), the blend sample of GO and 6THIOP (with a mass ratio of 1:1) in mixed solvent of ODCB and N, N-dimethylformamide (DMF), and GO (in DMF). GO shows a broad absorption continuously decreasing to 800 nm. The 6THIOP shows a strong broad π-π* absorption band around 411 nm. The blend sample also shows a strong broad π-π* absorption

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band with 6nm blue-shift relative to 6THIOP. Graphene-6THIOP shows a broad absorption band around 412 nm, derived from the 6THIOP group, which suggests a charge-transfer interaction between the 6THIOP and graphene units.

Figure 2b gives the fluorescence spectra of Graphene-6THIOP and 6THIOP in ODCB. Upon excitation at 411 nm, the solution of Graphene-6THIOP exhibits about 98% quenching of the fluorescence emission bands at 522 nm, as compared to that of 6THIOP at a matching absorption (0.21). The almost complete luminescence quenching observed in Graphene-6THIOP indicates that there is a strong interaction between the excited state of 6THIOP and graphene moieties in the hybrid.

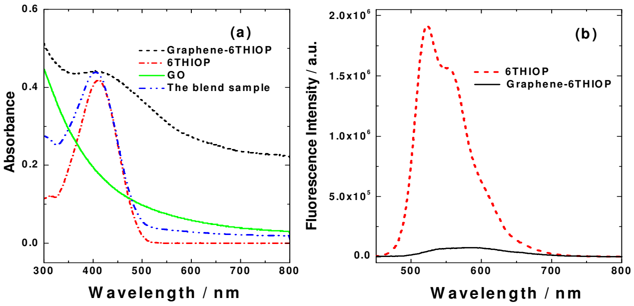

Fig. 2. (a) Absorption spectra of Graphene-6THIOP (in ODCB), 6THIOP (in ODCB), GO (in DMF), the blend sample of 6THIOP and GO (in mixed solvent of ODCB and DMF). (b) Fluorescence spectra of Graphene-6THIOP and 6THIOP in ODCB.

3.2 Nonlinear optical properties

The nonlinear optical properties of these materials were measured by Z-scan technique [23] at 532 nm with 5-ns pulses. Figure 3 shows Open-aperture Z-scan curves of Graphene-6THIOP (in ODCB), 6THIOP (in ODCB), GO (in DMF), the blend sample of 6THIOP and GO with a mass ratio of 1:1 (in mixed solvent of ODCB and DMF, because of the poor solubility of GO in ODCB), and C_{60} (in toluene).The linear transmittance of Graphene-6THIOP, 6THIOP, GO, the blend sample and C_{60} were 45%, 98%, 84%, 91%, 95%, respectively. The nonlinear absorption of C_{60} is attributed to the well known reverse saturable absorption (RSA). The normalized transmittance of GO and 6THIOP exhibit negligible decrease at the focus as shown in Fig. 3, indicating that there are weak nonlinear absorption/nonlinear scattering. For GO, we have observed nonlinear optical properties at high concentration [14]. Here the weak nonlinear optical response of GO should be attributed to the low concentration used in this experiment. The blend sample shows stronger nonlinear absorption/nonlinear scattering than the individual components (Go and 6THIOP) but weaker than Graphene-6THIOP and C_{60}. The Graphene-6THIOP has the largest dip among the Z-scan curves of these materials, indicating that it should have the largest nonlinear absorption/nonlinear scattering. So the covalent hybrid material of Graphene-6THIOP exhibits enhanced nonlinear optical properties compared with the individual components and the blend sample.

The enhanced nonlinear optical properties can arise from the combination of nonlinear absorption and nonlinear scattering, and photoinduced electron transfer between GO and 6THIOP. It is known that the photoinduced electron transfer can result in an enhanced nonlinear optical performance, as observed in the PVK-modified SWNTs system [24] and SWNT-Porphyrin [16]. Strong fluorescence quenching in Graphene-6THIOP indicates strong interaction and photoinduced electron transfer between GO and 6THIOP in this hybrid. We believe that photoinduced electron or energy transfer from electron donor 6THIOP moiety to acceptor Graphene may also have important contribution to the enhanced nonlinear optical properties of Graphene-6THIOP. Furthermore, the linear absorption of Graphene-6THIOP hybrid material at 532nm is significantly enhanced and it has stable solution forms in ODCB.

Just as some soluble carbon nanotubes [7–9], it is reasonable to believe that the nonlinear absorption of Graphene-6THIOP may exist.

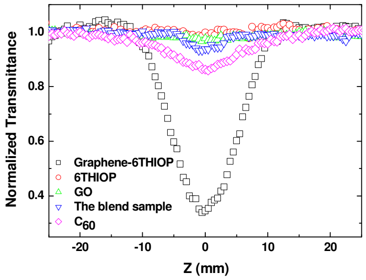

Fig. 3. Open-aperture Z-scan curves of Graphene-6THIOP, 6THIOP, GO, the blend sample and C_{60}.

The enhanced nonlinear scattering behavior was observed for Graphene-6THIOP. Figure 4a shows the scattered light signal versus the sample position, where C_{60} toluene solution was used as a reference. Result shows that a peak appears as the sample of Graphene-6THIOP moved to the focus, which means that the scattered light increases with input fluence. There is also a similar peak for the blend sample, but it is much weaker and only emerges at higher fluence, indicating that a weaker scattering exists. For 6THIOP, GO and C_{60}, there are no such obvious peaks in the scattering curves, so there are no nonlinear scattering for them in our experiments. Comparing Fig. 3 and Fig. 4a, Graphene-6THIOP have the largest dip of transmittance and the largest scattered intensity signal when the cell is placed at the focus, so nonlinear scattering plays an important role in the enhancement of optical nonlinear properties of Graphene-6THIOP.

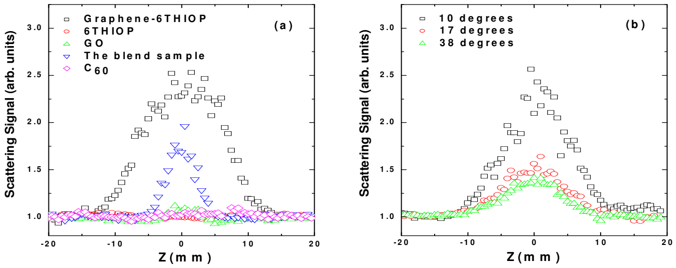

Fig. 4. (a) Scattering of Graphene-6THIOP, 6THIOP, GO, the blend sample and C_{60} with fluence (Z position) at an angle of 7 degrees. (b) Scattering of Graphene-6THIOP at three different forward angles with fluence (Z-position).

To get a better understanding of the nonlinear scattering behavior of Graphene-6THIOP, we measured the nonlinear scattering signals of Graphene-6THIOP as a function of the input fluence (Z-position) at three different forward scattering angles with respect to the beam propagation direction. As shown in Fig. 4b, the scattering signal increases with the input fluence for each angles, and the scattering signal is stronger for smaller angle, similar to the behavior observed in CdS nanoparticles [22].

Figure 5 gives the Open-aperture Z-scan curves of Graphene-6THIOP for different input fluence. Using the Crank–Nicolson finite-difference method, we fitted the Z-scan curves numerically (the solid lines) and obtained the values of effective nonlinear absorption coefficient β [25], as shown in Fig. 5. In general, the value of β will decrease as input fluence increases for RSA process because of the saturation of RSA [26], but it will keep unchanged for two-photon absorption process. However, the increase of β with input fluence implies the

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existence of nonlinear scattering in high-fluence regime. Therefore, Graphene-6THIOP can serve as a good scatterer and an effective optical limiter at high fluence.

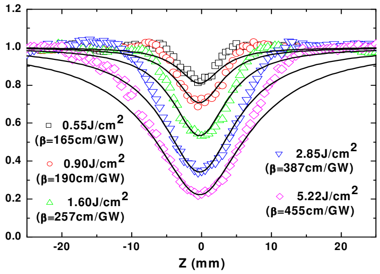

Fig. 5. Open-aperture Z-scan curves of Graphene-6THIOP for different input fluence.

Figure 6a and Fig. 6b give the Open-aperture Z-scan curves and the optical limiting of Graphene-6THIOP, GO, and C_{60}, respectively. For comparison, all of the sample concentrations were adjusted to have same linear transmittance of 65% at 532 nm. Graphene-6THIOP showed strong nonlinear scattering, while GO and C_{60} did not exhibit nonlinear scattering during the experiments, which is similar to Fig. 4a. From Fig. 6a and Fig. 6b, it can be seen that the optical limiting effect of Graphene-6THIOP is much better than GO and C_{60}. For example, at the highest input fluence (7.22 J/cm^2) used in our experiments, the output fluence are 3.58, 1.68, 1.01 J/cm^2, and the limiting thresholds of optical limiting are about 1.15, 0.06, 0.15 J/cm^2 for GO, C_{60}, and Graphene-6THIOP, respectively. Graphene-6THIOP exhibits a higher limiting threshold compared with that of optimized CBS suspensions which is near 0.03 J/cm^2 [27]. However, it should be noted that we used a different experimental geometry from Ref [27].

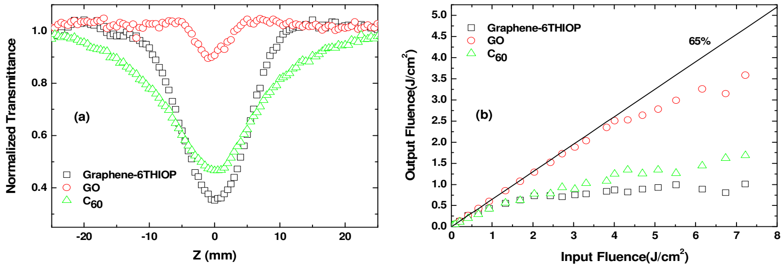

Fig. 6. (a) Open-aperture Z-scan curves and (b) the optical limiting of Graphene-6THIOP, GO, and C_{60}.

4. Conclusions

The nonlinear optical properties of Graphene-6THIOP hybrid material have been studied, and results show that Graphene-6THIOP exhibits enhanced nonlinear optical and optical limiting properties compared with the individual components(GO and 6THIOP) and C_{60}. The enhanced nonlinear scattering exists in Graphene-6THIOP, and photoinduced electron or energy transfer mechanism is proposed.

Acknowledgments

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