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Optical Limiting Properties of Graphene/Polymer Composites

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Graphene oxide (GO) was doped into four polymers films: Poly(methyl methacrylate) (PMMA), polystyrene (PS), polycarbonate (PC), and polyacrylonitrile (PAN). Following that, their optical limiting properties were investigated at 532 nm. In order to make GO hydrophobic, the lipophilic alkyl chains were connected to GO. The results showed that GO/PAN composite possesses better nonlinear response than the other three composites at the same transmission ($T \approx 59\%$). The reason were attributed to the thermal effect coming from high input fluence of laser, which improved the cross link density of PAN and further enhanced the interaction between the GO-ODA and PAN. Meanwhile, GO/PC and GO/PS had similar optical limiting property and GO/PMMA film gave the weakest optical limiting effect in our experiment.

Keywords: Graphene, Optical Limiting, Polymers Films, Nonlinear Response.

1. INTRODUCTION

Recently, considerable progresses have been made in the development of optical limiting devices by using organic conjugated molecules such as porphyrins, phthalocyanines, organometallic compounds, fullerenes, carbon nanotubes, carbon black suspensions and graphene, and so on.[1–14] Among them, graphene is especially attractive because of its stable two-dimensional (2D) hexagonally symmetry which can provide large π–π conjugated electrons and it can be associated with third nonlinear susceptibility.[15] Wang et al. observed a significant nonlinear optical (NLO) response of graphene dispersions to nanosecond laser pulses at 532 and 1064 nm.[16] Liu et al. reported nonlinear optical properties of graphene oxide (GO), a product of graphene oxidation, in nanosecond and picosecond regimens.[17] Husaini reported concentration-dependent NLO properties of graphene-polyvinyl alcohol nanocomposite in the nanosecond and picosecond regimes.[18] These investigations imply that graphene and its derivatives may become excellent optical limiting materials with broadband and multi-time scale. However, it is difficult for practical applications of optical limiter to use only using graphene. This problem can be partly overcome when graphene is doped into a solid substrate with high optical stability and good optical transparency to form composites. Therefore, it is necessary to investigate the optical limiting properties of these composites for practical applications.

In this paper, GO was mixed into several common transparent polymers to form different composites, such as, poly(methyl methacrylate) (PMMA), polystyrene (PS), polycarbonate (PC) and polyacrylonitrile (PAN) to investigate its NLO response at 532 nm. Considering the solubility of polymers in organic solvents, GO with lipophilic alkyl chains (GO-ODA) was synthesized in order to make hydrophilic GO hydrophobic. Our results showed GO-ODA/PAN composite possesses more effective nonlinear response than the other three composites in attenuate the high energy fluence.

2. EXPERIMENTAL DETAILS

2.1. Preparation of GO with Lipophilic Alkyl Chains (GO-ODA)

Graphene oxide (GO) was prepared by a modified Hummers method from natural graphite powder.[19] The obtained GO (30 mg) powders were dispersed into 150 mL

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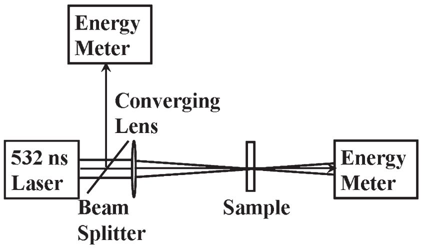

Figure 1. Schematic representation of optical limiting property measurement system.

anhydrous tetrahydrofuran under ultrasonication. After being ultrasonicated for 1 hour, octadecylamine (200 mg) and dicyclohexylcarbodiimide (410 mg) were added to the suspension under nitrogen atmosphere. The mixture were stirred for 20 min at room temperature and then refluxed for 24 h at 90 °C. The precipitate was purified by repeating dispersion in ethanol and filtration through a 0.2 μm polytetrafluoroethene membrane. The filtered product (GO-ODA) was dried in a vacuum drying oven at 60 °C for 12 h.

2.2. Preparation of GO-ODA/Polymer Composites

GO-ODA was dispersed into $CHCl_3$ or DMF with stirring (5 mg/mL). PMMA, PS and PC were dissolved in $CHCl_3$ and PAN was dissolved in DMF (500 mg/mL) with stirring. The suspension of GO-ODA was then added to polymer solution with v/v 0:1, 1:1, 2:1, 3:1, 4:1. Aliquots of mixed solution (40 μL, 80 μL, 120 μL, 160 μL, 200 μL) were dropped onto a glass disk with 12 mm diameter and then dried under vacuum at 60 °C for 12 h.

2.3. Measurements

Infrared spectra ranged from 400 to 4000 cm^{-1} were obtained on a SHIMADZU FTIR-8400 spectrometer with fresh KBr pellets. Nuclear magnetic resonance (NMR) spectra were performed on a Bruker Advance III NMR spectrometer with $CDCl_3$ as solvent, operating at 400 MHz for the corresponding 1H nuclei. Thermal gravimetric analysis (TGA) was carried out on DSC/TGA 1600 LF, METTLER TOLEDO instrument with a heating rate of 20 °C min^{-1} under nitrogen flow rate of 60 mL min^{-1}. Optical limiting properties were measured at room temperature with the samples mounted in a manual measurement system (Fig. 1). A pulsed Nd:YAG laser equipped with second (532 nm) harmonic generators was used as excitation source, which has pulse duration of 5 ns, and repetition frequency of 100 Hz. The reflected and transmitted pulse energies were measured simultaneously with two energy meter (Ophir). The photo of GO and GO-ODA in solutions were acquired with a digital camera.

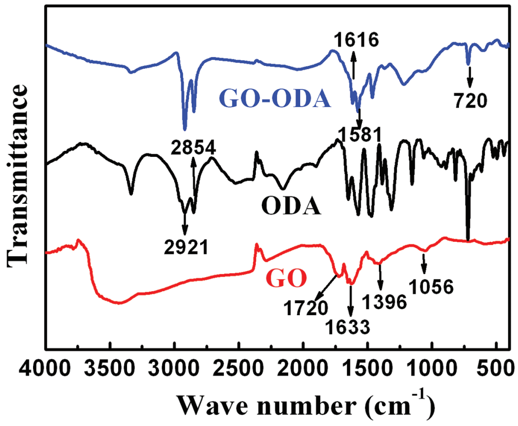

Figure 2. FT-IR spectra of GO, ODA and GO-ODA.

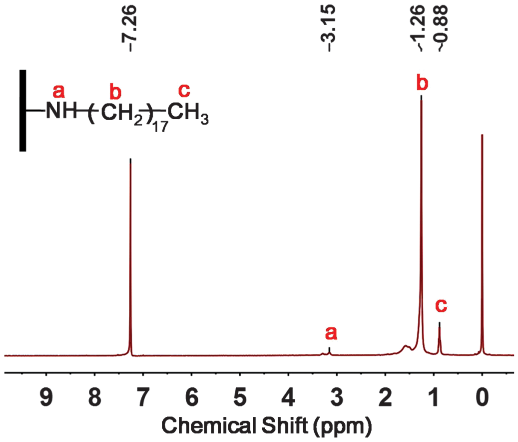

Figure 3. H-NMR spectrum for GO-ODA.

3. RESULTS AND DISCUSSION

Figure 2 shows the FT-IR spectra of GO, ODA and GO-ODA. From the FT-IR spectra, it can be observed that the typical peaks of GO appear at 1720 cm^{-1} (C═O carboxyl stretching vibration), 1633 cm^{-1} (C═C in aromatic ring), 1398 cm^{-1} (C–OH stretching) and 1058 cm^{-1} (C–O–C in epoxide). In the FT-IR spectrum of GO-ODA, the two

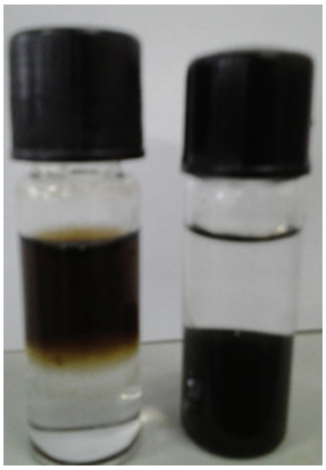

Figure 4. Solubility of GO (left), and GO-ODA (right) in $CHCl_3/H_2O$ (V/V, 1/1) mixture (0.5 mg/mL).

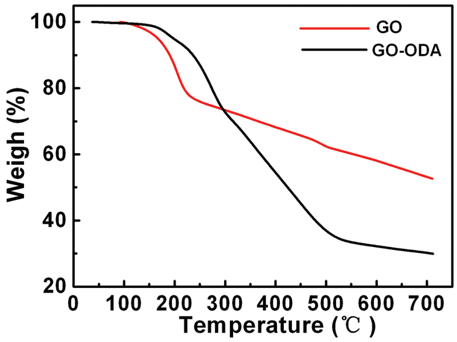

Figure 5. TGA curves of GO and GO-ODA.

peaks at 2921 and 2854 cm^{-1} are assigned to the C–H stretching vibrations of the octadecyl group, and together with the peak at 720 cm^{-1}, support the existence of the octadecyl chain on GO-ODA. The new peak at 1581 cm^{-1} indicates the formation of amide (–C(O)–NH–C–) bonds due to the reaction between the carboxyl group and the amino group, which also supports the presence of lipophilic alkyl groups on the GO derivatives. In order to further confirm the reaction of ODA with GO, the 1H-NMR spectrum of GO-ODA was performed, as shown in Figure 3. The peak at 0.88 ppm and 1.26 ppm are attributed to the CH_3 and CH_2 of octadecyl chain. The peak of amide (–NH) at 3.15 ppm is also observed, which indicates the covalent connection between ODA with GO.

After GO modified by lipophilic alkyl chains, the improved solubility in organic solvents was observed, as shown in Figure 4. From the photo, it can be seen that different solubility of GO and GO-ODA in the mixture of $CHCl_3/H_2O$ (v/v, 1/1) solvents. Since $CHCl_3$ and H_2O are immiscible, there is a phase separation with the $CHCl_3$ phase at the bottom of the glass bottle. GO is completely dispersed in H_2O and GO-ODA is completely dispersed in $CHCl_3$. The good dispersion of GO in organic solvents benefit its processing. Except the transformation of hydrophilic GO to hydrophobic GO, the thermal stability of GO was also changed after alkyl chains covalently bonded onto GO, as shown in Figure 5. The TGA curve of GO powers exhibits two steps of mass loss from 25 to 700 °C. The mass loss of GO between 100–600 °C is attributed to pyrolysis of the oxygen-containing functional groups, hydroxy, carboxyl and group, yielding CO, CO_2 and water vapors.[20] Comparing with the GO powers, the main mass loss of GO-ODA from 160 to 550 °C came from the decomposition of oxygen-containing groups, alkylated chains and bulk of the carbon skeleton. The thermal degradation curve of GO-ODA exhibits more mass loss than that of GO, which also suggests that octadecylamine has been already connect to the GO.

Figure 6 shows the total transmittance through multiple samples as a function of incident laser intensity at 532 nm, presenting the optical limiting property of GO-ODA doped into different polymer films. For all the polymer films without GO-ODA, the nearly 90% linear transmissivity (T) was obtained, without NLO property. For all four kinds of GO/polymer composites, it is clearly seen that the linear transmission decrease along with the increase of GO-ODA concentration with the same input fluence. Meanwhile, the optical limiting responses are improved with the increase

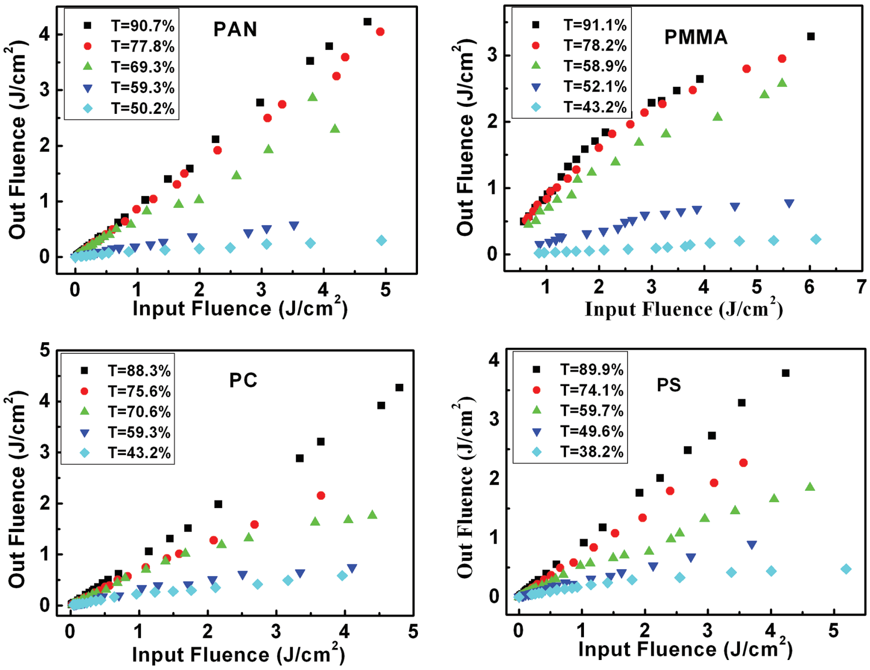

Figure 6. Nonlinear transmission for GO-ODA in four polymers composite as a function of incident laser intensity at 532 nm: GO-ODA/PAN, GO-ODA/PMMA, GO-ODA/PC, GO-ODA/PS.

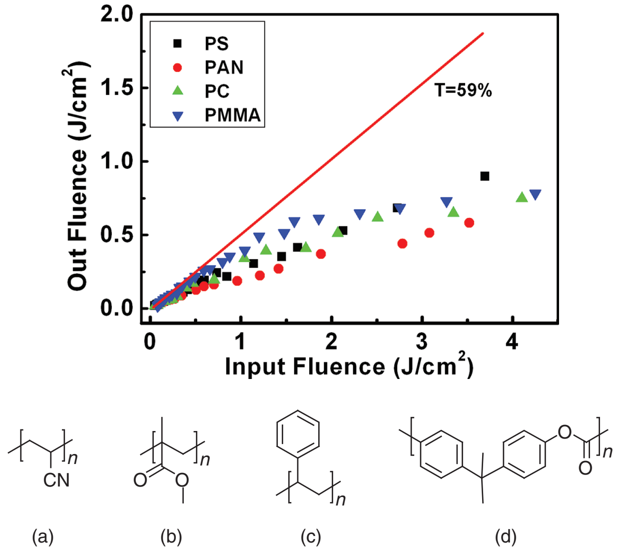

Figure 7. Output fluence as a function of input fluence for the GO-ODA/PAN, GO-ODA/PC, GO-ODA/PS, GO-ODA/PMMA at the same transmission ($T \approx 59\%$) and molecular structure of (a) PAN (b) PMMA (c) PS (d) PC.

of GO-ODA concentration. This relationship means a suitable concentration is necessary for practical application. Figure 7 illustrates the comparison of optical limiting performance for PMMA, PS, PC and PAN composites film for $T \approx 59\%$. The chemical structures of these four polymers are also given. From the figure, it can be seen that GO/PAN exhibits the best optical limiting effect. It is well known that PAN is a normal carbon fiber with heat stabilization and can be converted into cross-linked PAN under irradiation.[21] Recently, PAN was used as a precursor to produce graphene.[22] In our experiment we suggest that the high input fluence of the laser induced crosslinking of PAN and then the interaction between the GO-ODA and PAN was enhanced. Therefore, the output fluence decreases with the increase of input fluence. GO-ODA/PC and GO-ODA/PS have similar optical limiting property in the $T \approx 59\%$ in our experiment. This may due to the formation of π–π stacking between benzene ring and graphene.[23] The large π system is beneficial for the optical limiting. The GO-ODA in PMMA film gives the weakest optical limiting effect. The weak NLO response may attributed to the relatively low thermal stability and molecular structure.

4. CONCLUSIONS

In conclusion, GO-ODA was firstly synthesized to make hydrophilic GO hydrophobic, and then it was doped into several kinds of transparent polymer hosts, such as poly(methyl methacrylate) (PMMA), polystyrene (PS), polycarbonate (PC) and polyacrylonitrile (PAN), to investigate its nonlinear optical properties. The optical limiting properties were observed in all these composites for ns laser pulses at 532 nm. Among them, GO-ODA/PAN composite showed the best nonlinear property in attenuating the high energy fluence. This work is useful for developing graphene/solid substrate composite materials with high thermal stability for practical applications.

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