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2015 Laser Phys. 25 035901

(http://iopscience.iop.org/1555-6611/25/3/035901)

IOP Publishing | Astro Ltd

Laser Physics

Laser Phys. **25** (2015) 035901 (4pp)

doi:10.1088/1054-660X/25/3/035901

Effect of solvent surface tension on optical limiting properties of graphene dispersions

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Received 8 December 2014, revised 15 January 2015
Accepted for publication 18 January 2015
Published 12 February 2015

Abstract

The optical limiting (OL) properties and the mechanisms of graphene dispersions in alcohol aqueous solutions with different concentrations were investigated using a nanosecond pulse laser. With increasing the incident laser influence, optical transmittance of graphene dispersions decreased and the nonlinear scattering (NLS) light intensity increased synchronously, indicating that the NLS effect was mainly responsible for the OL process of graphene dispersions. By changing the alcohol concentration in the solvent and analyzing the relations between the solvent surface tensions and the OL properties of different dispersions, we demonstrated that solvent surface tension played a significant role in the OL performance of graphene dispersions, and a lower surface tension would induce a stronger NLS effect and a lower OL threshold.

Keywords: graphene, optical limiting, nonlinear scattering, surface tension

(Some figures may appear in colour only in the online journal)

1. Introduction

Optical limiting (OL) is a very important nonlinear optical phenomenon for devices for protecting sensitive optical sensors and human eyes. An ideal optical limiter should strongly attenuate intense incident light and exhibit high transmittance for low intensity light. Nonlinear OL processes, such as nonlinear absorption (NLA), nonlinear scattering (NLS) and nonlinear refractive index change, have been studied in various materials [1–4]. Numerous organic and inorganic materials have proved to be good candidates for optical limiters, among which carbon-based materials, such as fullerenes [5], carbon black suspensions (CBS) [6] and carbon nanotubes (CNTs) [7] have exhibited excellent OL performance. Much effort has been devoted to the development of the OL effect with stronger nonlinear responses from carbon-based materials.

With the emergence of graphene material, its excellent electronic, thermal conductivity and optical properties, especially nonlinear optical properties have attracted significant research interest [8, 9]. Since the first report by Wang *et al* [10], more and more scholars have begun to study the OL properties of graphene, graphene oxide [11] and their composites with various molecules [12]. As has been demonstrated in CBS and CNTs suspensions, the main mechanism of the OL process of graphene suspensions was attributed to the NLS process, during which micro-bubbles in solvent were formed at a high input light fluence and caused the decrease of transmittance of the limiter. According to the theoretical investigations by Belousova [13, 14], the OL performance could be greatly influenced by the thermodynamic properties of the dispersion solvents, as the NLS efficiency is greatly dependent on the formation dynamics of the scattering centers. Hence, although graphene materials have been demonstrated to have excellent OL properties, their OL performance could be further improved by selecting solvents with appropriate thermodynamic properties.

In this paper, we investigated the OL properties and mechanisms of graphene dispersion in alcohol aqueous solutions

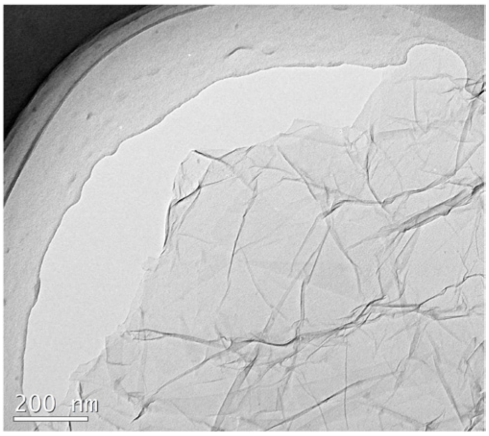

Figure 1. Typical TEM image of graphene.

with different concentrations using a nanosecond pulse laser. The experiment results demonstrated that the optical transmittance of graphene dispersions decreased and the nonlinear scattering (NLS) light intensity increased synchronously with increasing the incident laser fluence, indicating that the NLS effect was mainly responsible to the OL process of graphene dispersion. By changing the alcohol concentration in the dispersion solvents and analyzing the relations between the solvent surface tensions and the OL properties of different dispersions, we demonstrated that solvent surface tensions played an important role in the OL performance of the graphene dispersions. A lower surface tension induced a stronger NLS effect and a lower OL threshold in the graphene dispersion.

2. Experiments and sample preparation

In our experiments, the graphene material (thickness: ~0.8 nm, diameter: 0.5–2 μm, purity: ~99%, single layer ratio: >80%) was obtained from Nanjing XFNano Materials Tech Co, Ltd, (Nanjing, China). The dispersions were prepared by adding 6 mg of graphene in 40 mL of solvents, which were then sonicated for 2 h in an ice bath. All dispersions were subsequently centrifuged at 5000 rpm for 30 min to remove large aggregates. The solvents used in our experiments were alcohol aqueous solutions with different concentrations. All the dispersions were filled in 5 mm thick quartz cells and were stable against sedimentation and with little aggregation occurring in a few days. Using a transmission electron microscopy (TEM, JEOL JEM-2100), we measured the morphology of the dispersed graphene by dropping a few milliliters of sample on copper holey carbon grids. Figure 1 shows the typical TEM image of the graphene sheet. The graphene sample was stretched on copper grids mainly in single-layer form and flakes with multilayer were seldom observed.

The OL behaviors of graphene dispersions were measured using 10 ns laser pulses from a Q-switched Nd^{3+}: YAG laser (Surelite I-10, Continuum) 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 spatially filtered to obtain a neat Gaussian beam profile and then tightly focused with a lens of 30 cm focal length. An open-aperture (OA) Z-scan system was used to study the OL behavior of the dispersions. The linear transmittances of all the samples were adjusted to 60% by changing the graphene concentrations. To clarify the OL mechanisms of the samples, we measured the laser influence 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.

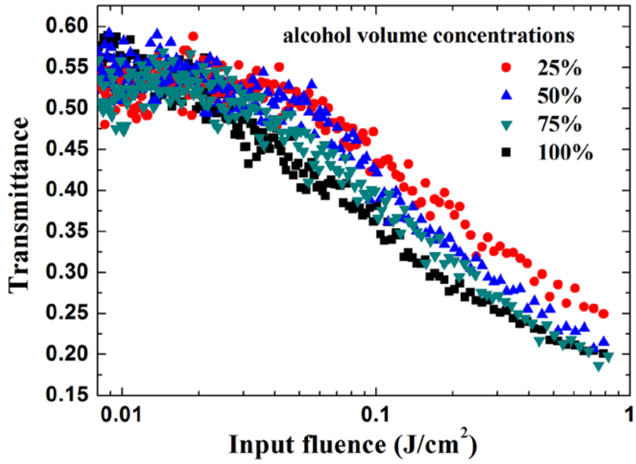

Figure 2. Nonlinear transmittance for graphene dispersed in different alcohol solutions with volume concentrations of 25% (circles), 50% (up triangles), 75% (down triangles) and 100% (squares), respectively.

3. Results and discussions

First, we measured the OL behaviors of the different graphene dispersions. Figure 2 shows the nonlinear transmittance as a function of the input laser fluence of graphene dispersed in different alcohol (ethanol) aqueous solutions. The alcohol volume concentrations in the aqueous solutions were set as 100, 75, 50 and 25%, respectively. From the figure, we can see that the optical transmittance of the dispersions decreased sharply with increasing the input laser fluence, exhibiting an excellent OL property. Among all the dispersions, graphene dispersion in pure alcohol showed the best OL properties. The OL threshold was estimated to be about 0.2 J cm^{-2} (The OL threshold was defined as the energy density, under which the nonlinear transmittance decreased to half of the linear transmittance). The transmittances of the dispersions increased significantly along with the decrease of alcohol concentrations of the solvents, indicating that the solvents played an important role in the OL behavior of the graphene dispersions. It should be noted that there was no variation of the transmittance of alcohol solutions observed at the same input energy density. Hence, the contribution of the solvent itself to the OL behavior was ruled out.

To clarify the OL mechanisms of graphene dispersion, we further measured the NLS effect in different graphene dispersions. A fraction of the scattered light was collected using a convex lens at ~30° in the forward direction and the incident beam was collected using a detector. Figure 3 shows the

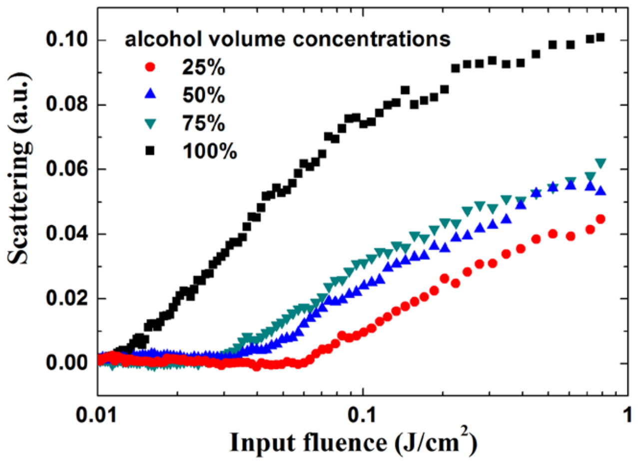

Figure 3. Scattered light intensity for graphene dispersions in different alcohol solutions with volume concentrations of 25% (circles), 50% (up triangles), 75% (down triangles) and 100% (squares), respectively.

scattering intensities as a function of incident pulse energy density for different graphene dispersions. By comparing with the results given in figure 2, we can see that the scattered light intensities increase significantly along with the decrease of nonlinear transmittance and the onset of the growth of scattered signals is synchronous with the onset of the decrease of transmittance for all dispersions. The results indicated that the OL behavior of graphene dispersions in alcohol solutions could be mainly attributed to the NLS effect.

According to the theoretical prediction for the NLS effect of carbon particle suspensions such as CNTs and graphene materials, when carbon particles were heated by the intense laser pulse, they would transfer thermal energy to the surrounding solvents, and the surrounding solvents would be evaporated resulting in the formation of gas bubbles. The initial bubbles quickly expanded due to the huge pressure differences at the vapor–solvent interface 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 atmospheric pressure and the surface tension of the solvents, as well as the thermal potential energy of the expended bubbles [8, 9]. When the size of the bubbles grew to the magnitude of incident light wavelength, the bubble clouds could effectively scatter the incident light, realizing the reduction of transmission. Effective nonlinear scattering could be achieved in a nanosecond time scale after laser irradiation. In the equilibrium condition, the bubble size could be defined by the following equations [15, 16]:

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

where 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.

According to equation (1), the lower surface tension will result in larger bubble size, hence more effective scattering and optical limiting. Although the boiling points of solvents might influence the buildup time of the initial bubbles, it rarely has an effect on the growth dynamics of gas bubbles, as has been demonstrated by Wang [15]. To investigate the influence of the solvent surface tensions on the OL and NLS effects in graphene dispersions, we plotted the OL thresholds and scattered light intensities as functions of the solvent surface tensions. The results are given in figures 4(*a*) and (*b*), respectively (the surface tensions of solvents are summarized in table 1). The figure indicates that smaller surface tension could result in larger bubble size, more effective scattering effect and lower limiting threshold. The onset of the growth of scattered signals is synchronous with the onset of the decrease of transmittance for all dispersions. This result agreed well with the previous studies reported by Wang *et al* [17]. This indicates that the solvent surface tension has a crucial effect on the OL process of graphene dispersion and the OL effect can be controlled by selecting solvents with appropriate surface tensions.

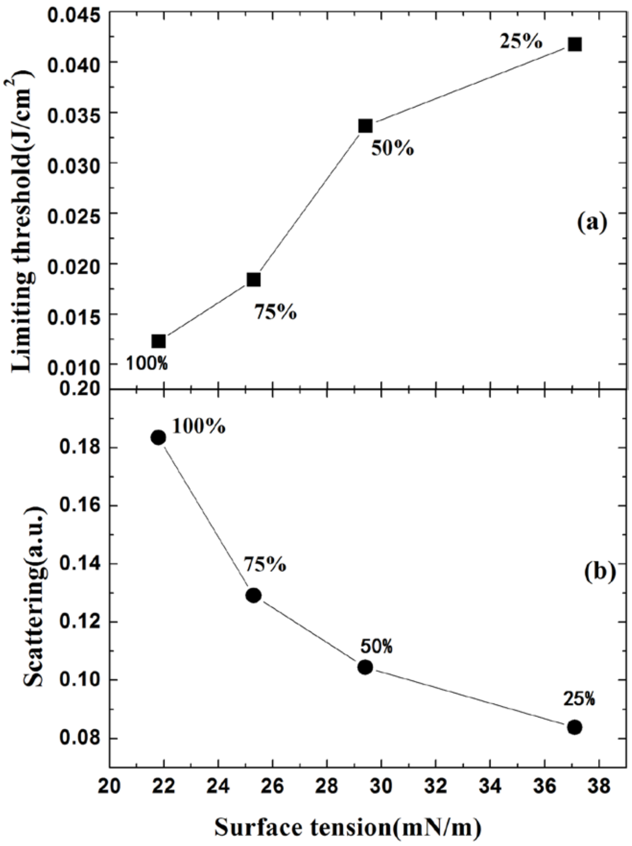

Figure 4. (*a*) OL thresholds and (*b*) scattered light intensities of different graphene dispersions as functions of solvent surface tensions.

Table 1. The surface tensions of alcohol aqueous solutions with different volume concentrations.

Alcohol volume concentration	25%	50%	75%	100%
Surface tension (mN m^{-1})	37.12	29.38	25.25	21.78

4. Conclusions

In conclusion, we studied the OL properties and the mechanism of graphene dispersions in alcohol aqueous solutions with different concentrations using a nanosecond pulse laser. The OL threshold decreased while the NLS light intensity increased with increasing the concentration of solutions and the onset of the growth of scattered signals was synchronous with the onset of the decrease of transmittance. It indicated that the OL behavior of graphene dispersion in alcohol solutions could be mainly attributed to the NLS effect. By analyzing the relations between the solvent surface tensions and the OL properties of different dispersions, we demonstrated that solvent surface tension played a significant role in the OL performance of graphene dispersions and a lower surface tension would induce a stronger NLS effect and a lower OL threshold in the graphene dispersions. The results indicated that the OL effect of graphene dispersions could be controlled by selecting solvents with appropriate surface tensions.

Acknowledgments

This work was supported the by the National Natural Science Foundation of China (NSFC) under Grant Nos. 61235003, 1130424 and 11474078 and the Research Fund for the Doctoral Program of Higher Education under Grant No. 20130201120025. This work was also supported by the Collaborative Innovation Center of Suzhou Nano Ncience and Technology. The TEM work was done at the International Center for Dielectric Research (ICDR), Xi'an Jiaotong University, Xi'an, China. In addition, the authors thank Mr Ma and Ms Lu for their help in using TEM.

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