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The influence of nonlinear scattering light distributions on the optical limiting properties of carbon nanotubes

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Abstract
The optical limiting (OL) properties of carbon nanotubes (CNTs) with different lengths were investigated using a nanosecond pulse laser. Experimental results showed that the OL behaviour of CNTs dispersion with shorter tube length and smaller bundle size was much better than for those with a longer length and larger bundle size. The nonlinear scattering experiments and numerical modelling results indicated that forward scattering light played an important role in deteriorating the OL property of longer CNTs. By removing parts of the forward scattering light using an aperture placed before the detector, the OL properties of materials could be improved.

Keywords: nonlinear optics, nanotubes, nonlinear scattering

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

1. Introduction

Optical limiting (OL) is a very important nonlinear optical phenomenon in protecting sensitive optical sensors and human eyes. An ideal optical limiter should strongly attenuate intense incident beams and exhibit high transmittance for low intensity light. Much effort has been devoted to the development of OL materials with large nonlinear responses. These materials include fullerenes [1, 2], single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs [3–5]), graphene [6–9], carbon black suspensions [10, 11], porphyrins and phthalocyanines [12–15].

The OL properties of SWNTs and MWNTs have been investigated extensively for over a decade. Previous research results indicated that the mechanism of such OL behaviour is generally attributed to nonlinear scattering (NLS) arising from the formation of solvent micro-bubbles and carbon micro-plasmas [4, 5, 16]. It was found that the OL behaviour of carbon nanotubes (CNTs) could be influenced by many factors, such as bundle size, length, solvent property, wavelength, pulse duration of the incident laser, etc [3, 5, 17–20]. There are two intrinsic parameters affecting OL behaviour: the structure of the CNTs and the thermo-dynamical properties of solvents. Although the structure dependence of the OL performance of CNTs with different sizes has been studied in some previous reports [19], the angular distribution of scattering light in the OL process, especially its influence on the OL performance, has seldom been investigated.

In this paper, we investigated the influence of nonlinear scattering light distributions on the OL properties of carbon nanotubes using a nanosecond pulsed laser. Experimental results show that the OL behaviour of CNTs with a shorter tube length and smaller bundles was much better than those with a longer length and larger bundles. The NLS experiments and numerical modelling results for the CNTs dispersion indicated that the forward scattering light played a key role in deteriorating the OL property of longer CNTs. The OL ability of materials could be improved by using an aperture placed before the detector to remove parts of the forward scattering light.

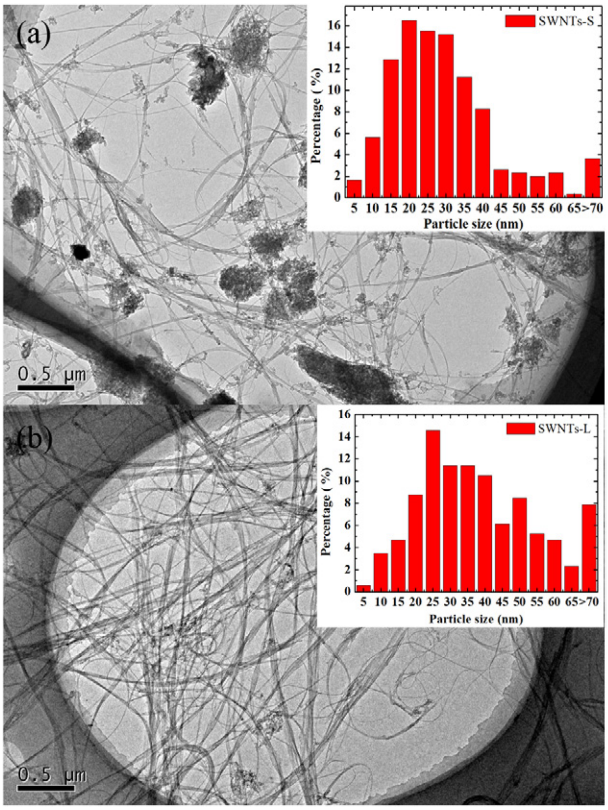

Figure 1. Typical TEM micrographs of SWNTs in ethanol solution: (*a*) SWNTs-S, (*b*) SWNTs-L. The insets of (*a*) and (*b*) show the measured diameter distributions of SWNTs-S and SWNTs-L samples.

2. Experiments

The SWNTs were obtained from Nanjing XFNano Materials Tech Co., Ltd, (Nanjing, China).

The SWNTs with a long tube length (SWNTs-L) were prepared using methane as a carbon source with a cobalt catalyst system and then the SWNTs were oxidized in air to get rid of activated carbon. The outside diameters of the SWNTs were 1–2 nm. The SWNTs with a short tube length (SWNTs-S) were prepared by mechanically cutting the prepared SWNTs-L. The SWNT-S and SWNT-L were separately dispersed in N-methyl-2-pyrrolidinone (NMP). Both of the dispersions were prepared by adding 6 mg of material in 40 mL of solvent and they were then sonicated for 2 h in an ice bath. All dispersions were subsequently centrifuged at 5000 rpm for 30 min to remove any large aggregates. The samples were stable against sedimentation and with little aggregation occurring in a few weeks. The morphology of the dispersed SWNTs was observed using transmission electron microscopy (TEM, JEOL JEM-2100).

The TEM samples were prepared by dropping a few milliliters of each dispersion on copper holey carbon grids. Figures 1(*a*) and (*b*) show the TEM images of SWNTs-S and SWNTs-L, respectively. The insets in figure 1(*a*) and (*b*) show the measured diameter distributions of SWNTs-S and SWNTs-L samples, respectively. The figures indicate that, the diameter of the SWNTs-L bundles was measured to be approximately 10–60 nm, while that of the SWNTs-S bundles was approximately 10–40 nm. Due to the unbundling of the nanotubes following shortening, the averaged bundle sizes of the SWNTs-S were obviously smaller than those of the SWNTs-L sample. The length and bundle diameters of the SWNTs are summarized in table 1.

Table 1. Length and bundle diameters for SWNTs samples.

Sample	Bundle diameters (nm)	Length (μm)
SWNTs-S	10–40	1–3
SWNTs-L	10–60	5–20

The OL performance of the CNTs dispersions was measured using 10 ns pulses from a Q-switched Nd^{3+}: YAG laser. The laser source was spatially filtered to remove the higher-order modes and obtain a neat Gaussian beam profile and then tightly focused with a lens of 20 cm focal length. The laser was operated at the second harmonic of 532 nm, with a pulse repetition rate of 10 Hz. An open-aperture Z-scan measurement system was used in our experiments and the OL behavior was calculated from the open-aperture Z-scan data. To investigate the angular dependence of the scattering light intensity, a diode was used to collect the scattering light at different azimuth angles. All the dispersions were filled in 5 mm thick quartz cells and the linear transmittances of the samples were adjusted to 70%.

3. Results and discussion

Firstly, we measured the OL properties of SWNTs-S dispersion and SWNTs-L dispersion using 532 nm laser pulses. The OL curves are plotted and shown in figure 2 for SWNTs-S and SWNTs-L dispersions. It can clearly be seen that the transmittance of these dispersions decreased with increasing input fluence, exhibiting promising OL behaviour. For these samples, the energy transmittance remained constant at a light fluence less than 0.02 J cm^{-2}, while the transmittance decreased when the incident fluence increased. The OL threshold (F_{th}) is defined as the input fluence at which the transmittance falls to 50% of the linear transmittance. The F_{th} value of SWNTs-S and SWNTs-L dispersions were estimated to be about 0.4 and 0.6 J cm^{-2}, respectively. CNTs with a short tube length showed a slightly better OL performance than those with longer tube length.

It has been reported by many researchers that the NLS effect is responsible for the principle mechanism of the OL phenomenon in dispersions of nanotubes [4, 17, 21]. In such a NLS process, the nanotubes absorb light from the laser and convert it into heat. The thermal energy is then transferred into the solvent, which induces a high temperature of the solvent and results in the formation and growth of solvent bubbles, as well as the formation and expansion of carbon microplasmas due to the ionization of nanotubes. The formation and rapid expansion of these microplasmas and bubbles in turn give rise to an increase in the scattering and OL occurs.

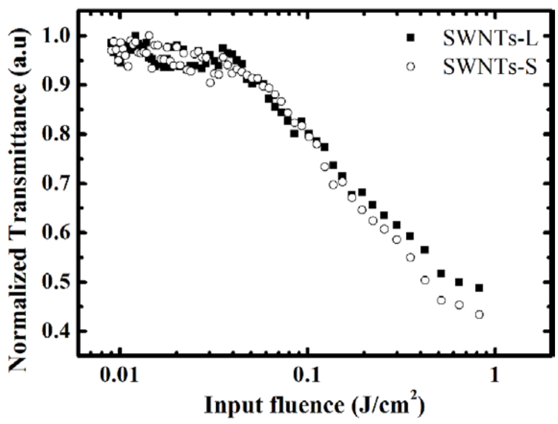

Figure 2. Transmittance as a function of the incident pulse energy density for SWNTs-S (◯) and SWNTs-L (■) dispersions.

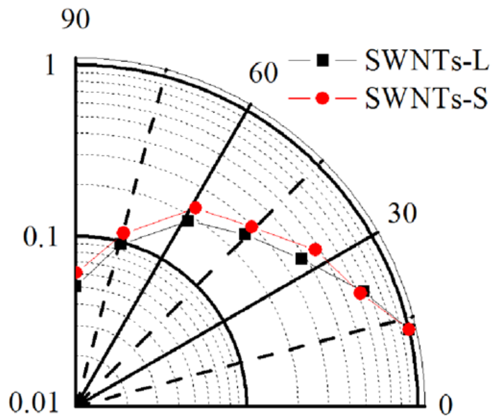

Figure 3. Angular dependence of the scattering light for the SWNTs-S and SWNTs-L dispersions under an incident intensity of 0.8 J cm^{-2} at 532 nm.

As demonstrated by Izard *et al*, the bundle sizes of nanotubes played an important role in the OL properties of nanotubes, as a larger nanotube size would induce a larger nucleation centre and a larger absorption cross section resulting in a stronger NLS effect [19]. In our experiments, however, the SWNTs-S showed a slightly better OL property than SWNTs-L dispersion, although the bundle diameter of the SWNTs-L was larger than that of SWNTs-S. We speculated that the nonlinear scattering light distributions influenced the OL properties of CNTs, as the azimuth distribution of the scattering light is strongly dependent on the size of the scattering centres, according to Mie's scattering theory [22]. Because the forward scattering light increases with an increasing size of the scattering centers, when CNTs with a longer tube length and larger bundle size are used in the OL measurements, more scattering light might incident into the detector along with the transmitted light, deteriorating the OL property of the dispersions.

To study the influence of the forward scattering light on the OL properties of different nanotubes, we measured the azimuth distribution of the scattering light intensity of different samples from 14° to 90°. Figure 3 shows the scattering signals at different angles with respect to the transmitted laser beam for SWNTs-S and SWNTs-L dispersions at an incident intensity of 0.8 J cm^{-2} for 532 nm laser pulses. We can see that the scattering signals for SWNTs-S dispersions are stronger than those for SWNTs-L dispersions at large azimuth angles, although the nonlinear transmittance of the SWNTs-S dispersion is higher than that of SWNTs-L dispersion. When the angle became smaller, the difference of NLS signals for both samples decreased, while the signal intensity was measured to be the same at about 20 degrees. Limited by the active area of the detector however, the NLS signals at angles smaller than 14 degrees could not be precisely measured due to the receipt of the transmitted light.

To measure the angular dependence of the NLS signals at small angles in the OL process, we put a whiteboard with a pinhole on the beam propagation direction behind the sample. To precisely record the intensity distribution of the scattering light, the transmitted laser was allowed to pass through the pinhole and a CCD camera was used to photograph the scattering light intensity on the board. Figure 4(*a*) and figure 4(*b*) show the scattering light intensity of SWNTs-S and SWNTs-L dispersions, respectively. A common colour bar has been assigned for showing the increase of scattering light from blue to red. We can see that the scattering light intensity increased with a decreasing distance from the centre of the pinhole, indicating that the scattering light intensity increased with decreasing the azimuth angle for both samples. The red and black lines in figure 4(*c*) show the integrated scattering intensity for the SWNTs-S and SWNTs-L dispersions as functions of the radius calculated from figure 4(*a*) and figure 4(*b*). From the figure, we can see clearly that the scattering intensity of SWNTs-L dispersion was stronger than that of SWNTs-S dispersion at a small angle, but it is the opposite in the case with a much larger angle, which agreed well with the results shown in figure 3.

According to Mie's scattering theory, the size of the scattering particles will decide their anisotropy parameters and this will influence the direction of the scattering light [23, 24]. Larger scattering centres will cause more forward scattering light. In our experiments, CNTs with longer tube length and larger bundle size might cause larger scattering centres than those with shorter ones, as larger micro-bubbles might be induced surrounding the bundles in the NLS process. To confirm our predictions, we simulated the azimuth distribution of the scattering light by 3 μm and 15 μm particles and the results are shown in figure 5. For 3 μm particles, the angular distribution of scattering photons is relatively homogeneous versus the scattering angle. But with increasing scattering particle size to 15 μm, the angular distribution of scattering signals exhibits a strong forward scattering peak, especially when the angle is smaller than 10°.

Generally speaking, the NLS both in SWNTs-L and SWNTs-S dispersions increased with a decreasing azimuth angle and the NLS intensity in SWNTs-L dispersions increased more sharply than in SWNTs-S dispersions. In other words, the forward scattering light in SWNTs-L dispersions was stronger than in SWNTs-S dispersions. In the OL process, forward scattering light would deteriorate the OL property, as it might be collected by the detector along with the transmitted light. Hence, a stronger forward scattering light would result in a higher nonlinear transmittance and a poorer OL property of the sample.

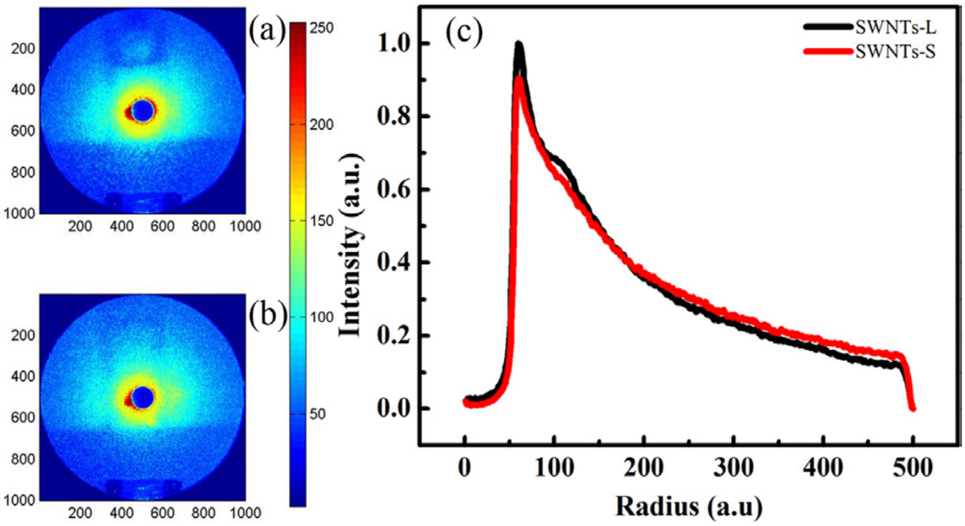

Figure 4. The scattering light photograph on whiteboard for SWNTs-S (*a*) and SWNTs-L (*b*) dispersions; (*c*) the scattering intensity as a function of the azimuth angle.

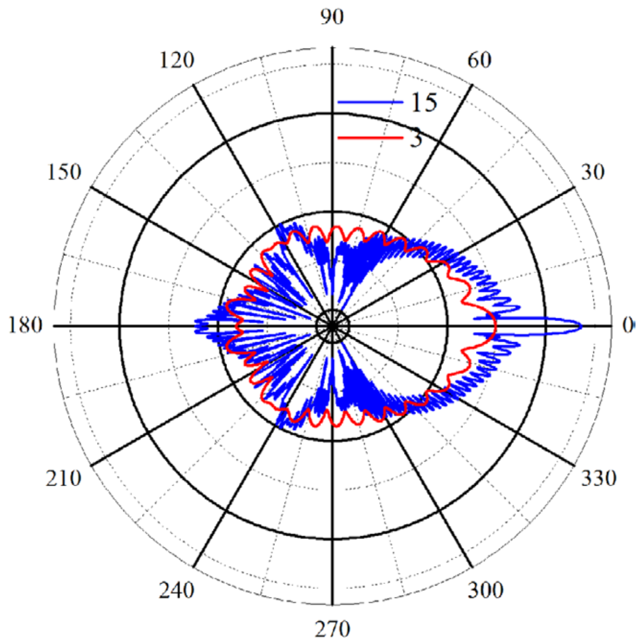

Figure 5. The scattering signal intensity as a function of angle by numerical analysis.

To control the influence of the forward scattering light on the OL property of the materials, we used an aperture to block parts of the scattering light in the optical path of the transmitted light before the detector, and measured the OL properties of the two SWNTs dispersions. Figure 6 shows the transmittance as a function of the incident pulse energy density for SWNTs. Contrary to the results in figure 2, the nonlinear transmittance of the SWNTs-L dispersions was much lower than that of the SWNTs-S dispersions, indicating that the forward scattering light was partly blocked by the aperture. Because the nanotubes with a longer length and larger bundle size supplied larger initial scattering centres [19], more effective heat transferred from nanotubes to solvents and induced larger microbubbles, resulting in a lower limiting threshold and better OL properties.

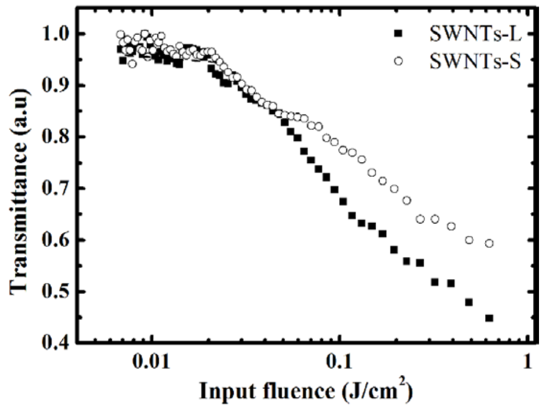

Figure 6. Transmittance as a function of the incident pulse energy density for SWNTs-S (○) and SWNTs-L (■) dispersions using an aperture, blocking parts of the forward scattering light.

4. Conclusions

In summary, we studied the influence of nonlinear scattering light distributions on the optical limiting properties of CNTs. The results clearly indicated that the OL property of SWNTs dispersion with shorter tube length and smaller bundle size was much better than those with longer length and larger bundles. The NLS experiments and numerical modelling results indicated that the forward scattering light played an important role in deteriorating the OL property of longer SWNTs. By blocking parts of the forward scattering light using an aperture placed before the detector, the influence of the forward scattering light on the OL abilities of materials could be controlled.

Acknowledgments

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References

[1] Tutt L W and Boggess T F 1993 *Prog. Quantum. Electron.* **17** 299–38
[2] Song Y, Fang G, Wang Y, Liu S, Li C, Song L, Zhu Y and Hu Q 1999 *Appl. Phys. Lett.* **74** 332–34
[3] Jin Z, Huang L, Hong Goh S, Xu G and Ji W 2002 *Chem. Phys. Lett.* **352** 328–33
[4] Vivien L, Lancon P, Riehl D, Hache F and Anglaret E 2002 *Carbon* **40** 1789–97
[5] Wang J and Blau W J 2008 *J. Phys. Chem.* C **112** 2298–303
[6] Wang J, Hernandez Y, Lotya M, Coleman J N and Blau W J 2009 *Adv. Mater.* **21** 2430–35
[7] Lim G, Chen Z, Clark J, Goh R G, Ng W, Tan H, Friend R H, Ho P K and Chua L 2011 *Nat. Photon.* **5** 554–60
[8] Xiong Y, Yan L, Si J, Yi W, Ding W, Tan W, Liu X, Chen F and Hou X 2014 *J. Appl. Phys.* **115** 83111
[9] Bludov Y V, Vasilevskiy M I and Peres N M 2012 *J. Appl. Phys.* **112** 84320
[10] Nashold K M and Walter D P 1995 *J. Opt. Soc. Am.* B **12** 1228–37
[11] Vincent D, Petit S and Chin S L 2002 *Appl. Opt.* **41** 2944–46
[12] Calvete M, Yang G Y and Hanack M 2004 *Synth. Met.* **141** 231–43
[13] Perry J W, Mansour K, Lee I, Wu X, Bedworth P V, Chen C, Ng D, Marder S R, Miles P and Wada T 1996 *Science* **273** 1533–36
[14] Senge M O, Fazekas M, Notaras E G, Blau W J, Zawadzka M, Locos O B and Ni Mhuircheartaigh E M 2007 *Adv. Mater.* **19** 2737–74
[15] Krishna M, Kumar V P, Venkatramaiah N, Venkatesan R and Rao D N 2011 *Appl. Phys. Lett.* **98** 81106
[16] Wang J and Blau W J 2008 *Appl. Phys.* B **91** 521–24
[17] Sun X, Xiong Y, Chen P, Lin J, Ji W, Lim J H, Yang S S, Hagan D J and Van Stryland E W 2000 *Appl. Opt.* **39** 1998
[18] Riggs J E, Walker D B, Carroll D L and Sun Y 2000 *J. Phys. Chem.* B **104** 7071–76
[19] Izard N, Billaud P, Riehl D and Anglaret E 2005 *Opt. Lett.* **30** 1509–11
[20] Wang J, Früchtl D and Blau W J 2010 *Opt. Commun.* **283** 464–68
[21] Vivien L, Riehl D, Delouis J F, Delaire J A, Hache F and Anglaret E 2002 *J. Opt. Soc. Am.* B **19** 208–14
[22] Mie G 1908 *Ann. Phys.* **25** 377–45
[23] Sedarsky D, Berrocal E and Linne M 2011 *Opt. Express* **19** 1866–83
[24] Zhan P, Si J, Tan W, Liu X, Wu B, Xu S, Chen F and Hou X 2014 *Laser Phys.* **24** 15401