Solvent Effect on Optical Limiting Properties of Single-Walled Carbon Nanotube Dispersions

Jun Wang* and Werner J. Blau

School of Physics, Trinity College Dublin, Dublin 2, Ireland

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Single-walled carbon nanotubes (SWNTs) were dispersed in *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMA), respectively. The nonlinear optical properties of SWNT dispersions were studied using the open aperture Z-scan technique at 532 nm. The nonlinear extinction coefficients strongly increase with increasing SWNT concentration. In the three dispersions, the DMF dispersions show the strongest nonlinear extinction effect. In conjunction with this, the optical limiting performance is also superior for the DMF dispersions. Compared with DMF and DMA, NMP has a much better debundling effect for SWNTs; however, the optical limiting properties of the NMP dispersions is inferior. The SWNT dispersions seem to attenuate the intense light more effectively, as is shown by the stronger optical limiting response compared to the zinc phthalocyanine solution, at the same concentration. The static light scattering experiment revealed that the DMF dispersions have the largest average bundle size. The main origin of the optical limiting effect of the SWNT dispersions is due to the solvent and/or carbon vapor bubble-induced nonlinear scattering. Our results show that the average bundle size of SWNTs in combination with the physical properties of the solvent dominate the nonlinear extinction and optical limiting properties of SWNT dispersions.

1. Introduction

Following the invention of the laser, it was recognized that intense laser beams can easily damage delicate optical instruments, especially the human eye. Protecting the eyes and instruments from such beams motivates a lot of interest in research in optical limiting materials. An ideal optical limiter should strongly attenuate intense and potentially dangerous laser beams, while exhibiting high transmittance for low intensity ambient light. Up to now, a number of organic materials, including phthalocyanines,[1,2] porphyrins,[3,4] fullerene C_{60},[5,6] and carbon nanotubes,[7−10] have been found to show strong nonlinear extinction (NLE) to high-intensity light and hence could serve as candidates for practical optical limiters.

As one-dimensional nanostructured materials, carbon nanotubes have attractive mechanical, electrical, and thermal properties, which have found many potential applications in the field of nanoscience and nanotechnology. In the past decade, carbon nanotubes have been extensively studied as optical limiting materials.[10] As opposed to phthalocyanines, porphyrins, and fullerene, carbon nanotubes have a significant optical limiting effect, resulting from thermally induced nonlinear scattering, covering a broad wavelength range from the visible to the near-infrared. However, carbon nanotubes tend to aggregate into large bundles because of their relatively high surface energy,[11] which is a serious obstacle when it comes to real-life applications. Recently, many groups have reported that carbon nanotubes can be dispersed in a range of amide solvents.[12−15] In these dispersions, carbon nanotubes can exist stably as individual nanotubes or small bundles for reasonable periods of time. However, to the best of our knowledge, the nonlinear optical and optical limiting properties of these stable dispersions have not been reported yet.

In this paper, we report the NLE and optical limiting properties of single-walled carbon nanotubes (SWNTs) dispersed in three nitrogen-containing solvents: *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMA). The open aperture Z-scan technique was undertaken for the NLE measurements at 532 nm. Very different NLE responses were observed in the three different dispersions. The DMF dispersions show the strongest NLE response, resulting in a lower limiting threshold and a better optical limiting effect; this is in comparison to the NMP dispersions which exhibit inferior NLE and optical limiting abilities. The larger average bundle size, which in combination with the suitable physical properties of DMF determines the superior optical limiting properties, was ascertained in DMF dispersions by a static light scattering experiment. The current optical limiting results are compared with those of the fullerene, zinc phthalocyanine, and its nanoparticles. The primary mechanism for optical limiting is determined to be the solvent and/or the carbon vapor bubble-induced nonlinear scattering.

2. Experimental Section

The nitrogen-containing solvents such as NMP, DMF, and DMA are good dispersants for carbon nanotubes. We largely followed the preparation procedure in our previous work to prepare SWNT dispersions.[15] Purified SWNTs (HiPCO) from Carbon Nanotechnologies, Inc., were used (lot no. 288). Dispersions of SWNTs were prepared in NMP, DMF, and DMA, respectively, at an initial concentration of 5.0×10^{-2} mg/mL. In general, initial dispersions were produced by sonicating for 2 min using a high-power ultrasonic tip processor, model GEX600 (120W, 60 kHz), followed by 4 h in a low-

* Author to whom correspondence should be addressed. Phone: +353-1-8963281; fax: +353-1-6711759; e-mail: jwangsci@gmail.com.

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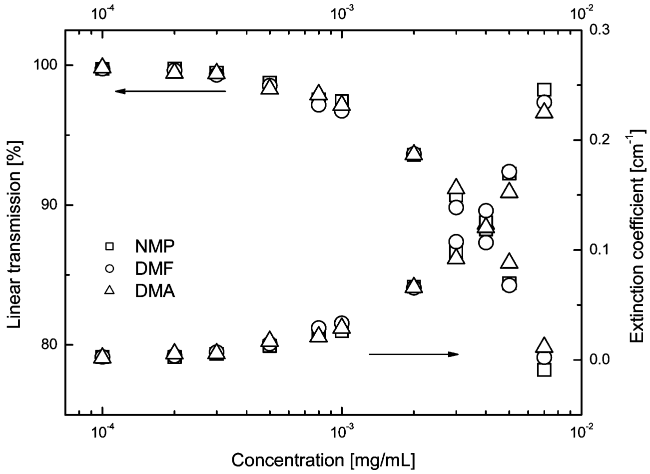

Figure 1. Linear transmission and extinction coefficient as a function of SWNT concentration for NMP (opened square), DMF (opened circle), and DMA (opened triangle) dispersions.

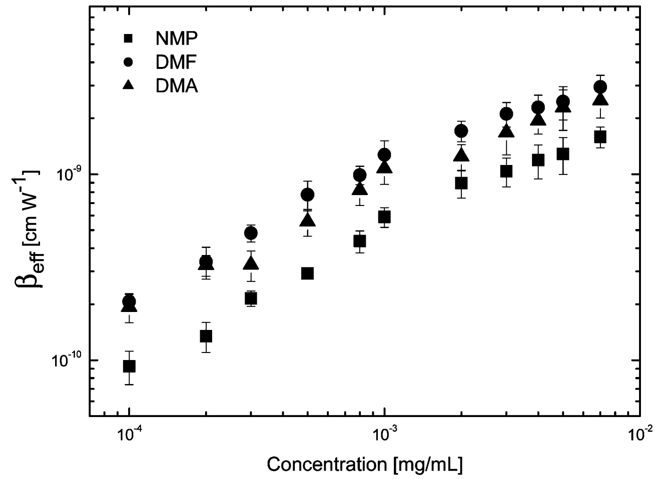

Figure 2. The nonlinear extinction coefficient as a function of SWNT concentration for NMP (square), DMF (circle), and DMA (triangle) dispersions.

power ultrasonic bath (Ney Ultrasonik), and then 1 min with the sonic tip. All dispersions were subsequently centrifuged at 5500 rpm for 90 min to remove any large aggregates. UV−vis absorption measurements were made before and after centrifugation using a Varian Cary 50 UV−vis spectrophotometer. The concentrations of SWNTs after centrifugation were deduced from the absorbance ratios of dispersions before and after centrifugation.[15] The final dispersions were then consecutively diluted to produce a range of dispersions with concentrations from 1.0×10^{-4} to 7.0×10^{-3} mg/mL. All dispersions are stable against sedimentation and no further aggregation for a period of weeks. The detailed study of nature and quality of these nanotube dispersions has been reported in our previous publication.[15]

A standard open aperture Z-scan apparatus was used to measure the NLE coefficients of SWNT dispersions.[1] All experiments described in this study were performed with 6-ns pulses from a Q-switched Nd:YAG laser. The beam was spatially filtered to remove higher-order modes and tightly focused to a 19−26 μm spot for all experiments. The laser was operated at the second harmonic, 532 nm, with a pulse repetition rate of 10 Hz. All SWNT dispersed samples were tested in 1 cm quartz cells. For the static scattering experiments, a focusing lens setup was arranged at 45° to the direct incident beam.

3. Results

The linear extinction coefficient, α_0, as defined by $T = \exp(-\alpha_0 L)$, was measured at 532 nm for each sample, where T defines the ratio of transmitted to incident laser light, and $L = 1.0$ cm is the sample thickness. Figure 1 shows the linear transmission and extinction coefficients for a range of dispersions. The data in Figure 1 were corrected by accounting for the reflection loss of quartz cuvette. It should be noted that the NMP, DMF, and DMA dispersions, with identical linear transmissions, might have different mass concentrations since the particles sizes are different, as what we will show in the scattering experiments. For simplicity, we still use the same concentration in this paper to identify the different dispersions with the similar transmission.

The open aperture of the Z-scan technique was employed to probe the NLE response at 532 nm for a variety of SWNT dispersions with high transmissions (>75%). The NLE coefficients, β_{eff}, were estimated from the Z-scan spectra by curve-fitting theory based on an intensity-dependent extinction coefficient.[1] The incident laser pulsed energy, used in Z-scan measurements, was altered from 0.035 to 0.33 mJ. The corresponding on-focus beam intensity was varied from 0.2 to 2.5 GW cm^{-2}. Figure 2 shows the β_{eff} as a function of SWNT concentration in the different solvents. In general, the logarithm of β_{eff} is linearly dependent on the concentration. It can clearly be seen that the DMF dispersions have the larger β_{eff} values in the range of concentrations used. In contrast, the smaller β_{eff} values were observed in the NMP dispersions. The DMA dispersions exhibit a series of midrange β_{eff} values but close to that of DMF dispersions. For example, the β_{eff} is $(2.95 \pm 0.45) \times 10^{-9}$ cm W^{-1} for DMF dispersion of 7×10^{-3} mg/mL. At the same concentration, the β_{eff} values of NMP and DMA dispersions decrease to $(1.59 \pm 0.20) \times 10^{-9}$ and $(2.49 \pm 0.48) \times 10^{-9}$ cm W^{-1}, respectively.

Figure 3, in which the output energy density (J cm^{-2}) was plotted as a function of input energy density, presents the optical limiting behavior of SWNT dispersions at a series of concentrations. The optical limiting curves were directly converted from the Z-scan spectra. The solid lines are intended as a visual guide. It is evident that for all three kinds of dispersions, the optical limiting responses are dramatically improved by increasing the concentration. However, the increased optical limiting responses are inevitably associated with the decrease of linear transmission. This complementary relationship allows one to choose the suitable dispersion for certain laser sources. Figure 4 illustrates the comparison of optical limiting performances for NMP, DMF, and DMA dispersions at the same concentration of 3.0×10^{-3} mg/mL. In agreement with the NLE results in Figure 2, the optical limiting performance of DMF dispersions outperforms those of NMP and DMA dispersions. The NMP dispersions exhibit a lower optical limiting effect than the DMF and DMA dispersions.

In an effort to evaluate the ability of the optical limiting of SWNT dispersions, we carried out the Z-scan measurements for zinc 2,9,16,23-tetra-*tert*-butyl-29*H*,31*H*-phthalocyanine (abbreviated as tBu$_4$PcZn) and fullerene solutions, for comparative purposes. Both zinc phthalocyanine and fullerene are proven to be excellent reverse saturable absorbers for passive optical limiting materials.[1,2,5,6] The tBu$_4$PcZn powders purchased from Sigma-Aldrich Co. were dissolved in toluene at a concentration of 0.5 mg/mL. Subsequently, the solution was diluted to several desired concentrations. All solutions were gently agitated before and after dilution for approximately 1 h in a low power (60 W) sonic bath to ensure a homogeneous solution. The fullerene

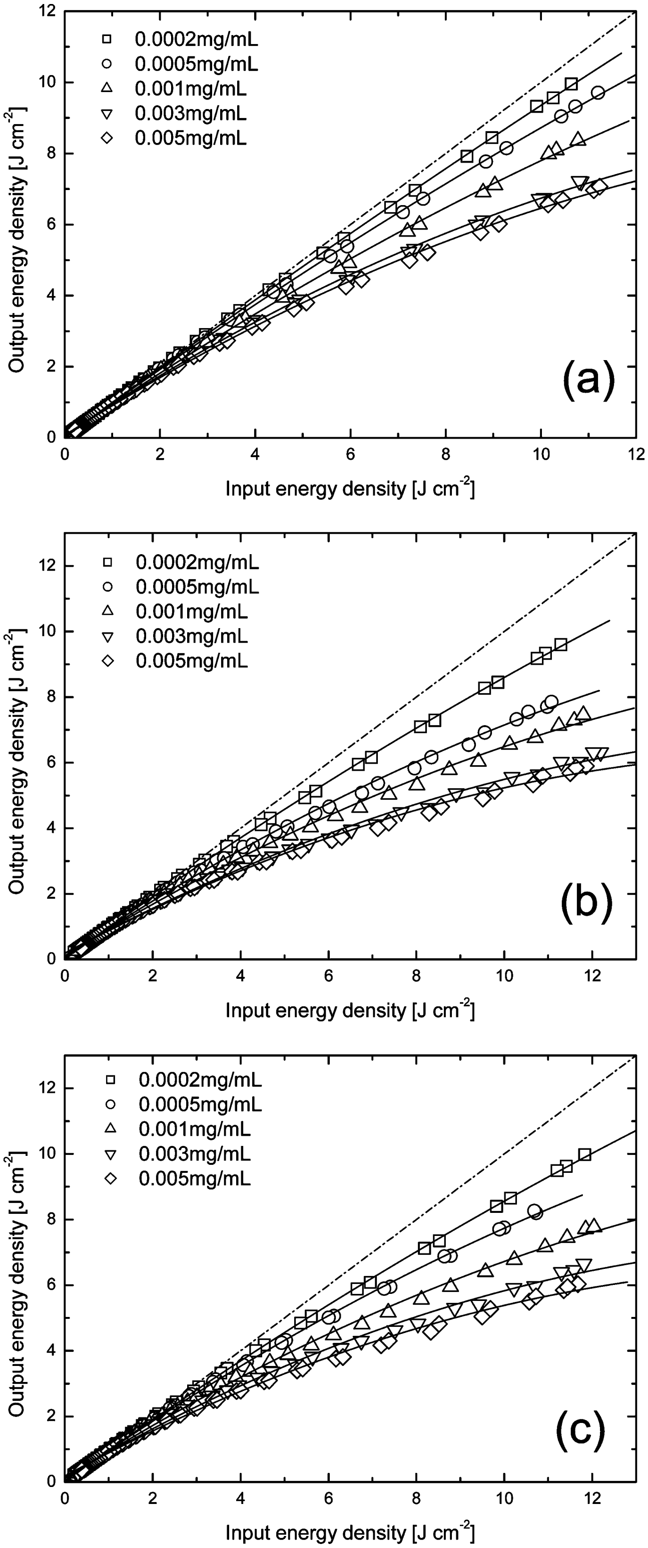

Figure 3. Optical limiting behavior of (a) NMP, (b) DMF, and (c) DMA dispersions at different concentrations. The solid lines are intended as a visual guide. The dash-dotted lines represent the linear transmission.

solutions in toluene were prepared by a similar procedure. The linear and nonlinear properties of the *t*Bu$_4$PcZn and fullerene samples were also measured in 1 cm quartz cells. Table 1 gives out the NLE coefficients for the DMF dispersion of SWNT, *t*Bu$_4$PcZn solution, and fullerene solution. At the same level of transmission, the β_{eff} of *t*Bu$_4$PcZn and fullerene are larger than that of SWNT dispersion by a factor of 2.5 and 1.3, respectively. It is worth noting that the mass concentration of SWNT dispersions is merely 5.0 × 10^{-3} mg/mL, which is much lower than those of *t*Bu$_4$PcZn and fullerene solutions. We also measured the β_{eff} of *t*Bu$_4$PcZn solution at a concentration of 5.0 × 10^{-3} mg/mL. In this case, the β_{eff} of the DMF dispersion exceeds that of *t*Bu$_4$PcZn by a factor of 4.8, as shown in Table 1. Figure 5 depicts the optical limiting behavior of the samples in Table 1. It can be seen that at similar transmissions, both *t*Bu$_4$PcZn and fullerene show better optical limiting effects than the DMF dispersion. Nevertheless, the SWNT dispersion is more effective to attenuate the intense light, as is evidence from the stronger optical limiting response compared with the *t*Bu$_4$PcZn solution at the same concentration.

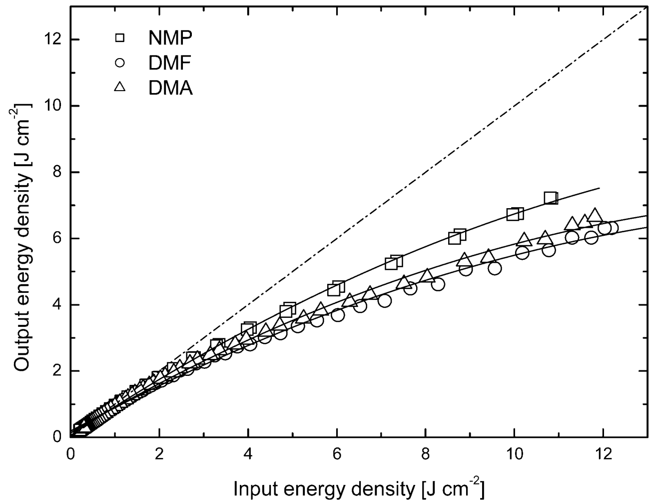

Figure 4. Output energy density (J cm^{-2}) as a function of input energy density for the NMP (opened square), DMF (opened circle), and DMA (opened triangle) dispersions at the same concentration of 3.0 × 10^{-3} mg/mL. The solid lines are intended as a visual guide. The dash-dotted line represents the linear transmission.

TABLE 1: Linear and Nonlinear Extinction Coefficients for the DMF Dispersion of SWNT, *t*Bu$_4$PcZn Solutions, and Fullerene Solution

sample	concentration [mg/mL]	α_0 [cm^{-1}]	transmission [%]	β_{eff} [cm W^{-1}]
DMF dispersion	0.005	0.17	84.3	(2.46 ± 0.50) × 10^{-9}
*t*Bu$_4$PcZn	0.17	0.19	82.9	(6.07 ± 1.20) × 10^{-9}
*t*Bu$_4$PcZn	0.005	0.04	96.2	(5.09 ± 0.59) × 10^{-10}
C_{60}	0.11	0.16	84.9	(3.28 ± 0.51) × 10^{-9}

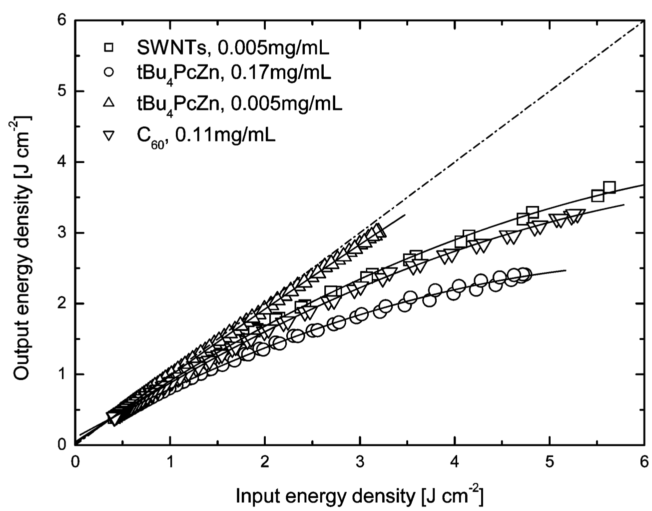

Figure 5. Optical limiting behavior of the samples in Table 1. The solid lines are intended as a visual guide. The dash-dotted line represents the linear transmission.

TABLE 2: Linear and Nonlinear Extinction Coefficients for SWNT Dispersion, *t*Bu$_4$PcZn Nanoparticle Dispersion,[16] and *t*Bu$_4$PcZn Solution[16]

sample	concn [mg/mL]	α_0 [cm^{-1}]	β_{eff} [cm W^{-1}]
DMF dispersion	0.007	0.23	$(2.95 \pm 0.45) \times 10^{-9}$
*t*Bu$_4$PcZn nanoparticles[16]	0.007	0.095	$(1.6 \pm 0.3) \times 10^{-9}$
*t*Bu$_4$PcZn solution[16]	0.007	0.10	$(4.9 \pm 1.0) \times 10^{-10}$

It is also interesting to compare the SWNT dispersions in DMF to our previous results on the *t*Bu$_4$PcZn nanoparticle dispersions in DMF.[16] Table 2 summarizes the linear and NLE coefficients for SWNT dispersion, *t*Bu$_4$PcZn nanoparticle dispersion, and *t*Bu$_4$PcZn solution. At the same concentration of 7.0×10^{-3} mg/mL, the *t*Bu$_4$PcZn nanoparticle dispersion exhibits $\beta_{eff} = (1.6 \pm 0.3) \times 10^{-9}$ cm W^{-1}, while the SWNT dispersion exhibits a β_{eff} coefficient approximately 1.8 times larger. The *t*Bu$_4$PcZn solution shows the smallest value of $\beta_{eff} = (4.9 \pm 1.0) \times 10^{-10}$ cm W^{-1}. It should be noted that the origin of the optical nonlinearities exhibited by the SWNT and *t*Bu$_4$PcZn nanoparticle dispersions is mostly attributed to the nonlinear scattering. In contrast, the optical nonlinearities of *t*Bu$_4$PcZn and fullerene solutions are clearly due to the nonlinear absorption.

The comparison of optical limiting responses of SWNT suspensions and fullerene solutions have also been investigated by some research groups,[7,17] but the results appear to be inconsistent. For example, L. Vivien et al. demonstrated that the SWNT suspensions in water/surfactant have better optical limiting responses than those of fullerene solutions.[17] Meanwhile, S.R. Mishra et al. observed the superior optical limiting responses from fullerene solutions rather than those from SWNT suspensions in water.[7] The above-mentioned results reveal that the nonlinear optical limiting properties of carbon nanotubes can be influenced by many effects, such as bundle size,[9] solvent property,[7] wavelength, and pulse width of incident laser,[18] etc. These effects, as well as the mechanism leading to the distinguishing optical limiting performances for different dispersions in our experiments, will be discussed in the next section.

On the other hand, the static light scattering experiments were performed to monitor the relative particle size of SWNTs in the three solvents. The scattered signal was collected at 45° to the incident irradiation direction. The path length of the cylindrical cell used for light scattering is 1.5 cm. The repetition rate of incident pulses was set to be 1 Hz to avoid the uncontrollable heating effect. Figure 6 shows the scattered intensity as a function of SWNT concentration. At the same level of linear transmission, the scattered intensity from DMF dispersions is larger than that from both DMA and NMP dispersions. The difference between the scattered signals implies that the SWNT particle sizes, especially the bundle diameters, have an appreciable difference in the solvents used. DMF dispersions have the largest average bundle size, while the bundle diameter is smaller in NMP dispersions because of its superior debundling effect. For NMP dispersions, the percentage of the individual nanotubes is expected to be more than 70% when the concentration is diluted to less than 4.0×10^{-3} mg/mL.[15] The maximum scattered intensity for DMF dispersions occurred at around 2.0×10^{-3} mg/mL, which shifted to around 3.0×10^{-3} mg/mL for NMP dispersions. At the lower concentration region, the increase of particle density enhances the scattered signal. In contrast, the scattered intensity gradually decreases at the higher concentration region because of the strong extinction of SWNTs.

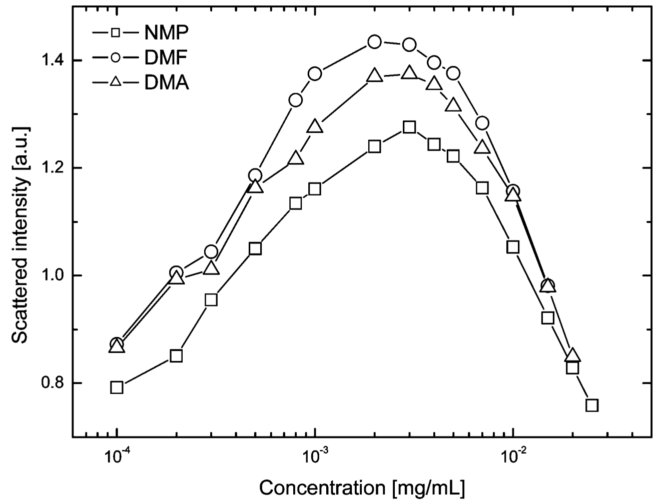

Figure 6. Scattered intensity as a function of SWNT concentration for the NMP (opened square), DMF (opened circle), and DMA (opened triangle) dispersions.

4. Discussion

The mechanism leading to optical limiting effect in carbon nanotubes has been studied by many researchers.[7−10,19,20] Nonlinear scattering is regarded as the principal mechanism for optical limiting. The induced scattering centers consist of two origins: (1) the formation and expansion of solvent bubbles, which is due to the thermal energy transfer from nanotubes to solvent; (2) the formation and growth of carbon vapor bubbles, which is due to the sublimation of nanotubes. The former takes place at the lower incident energy fluence, while the latter takes place at the higher energy fluence. Many other factors, which could influence the optical limiting property of carbon nanotubes, have also been discovered.[7−10,18,21] Regardless of the effect of the incident laser beam, i.e., the pulse width and wavelength,[18] there exists two intrinsic effects on the optical limiting of nanotubes: (1) the structure of nanotubes; (2) the properties of the solvent used to disperse the nanotubes. The optical limiting property is very sensitive to the bundle diameters of carbon nanotubes. The nanotubes with the largest bundle size have the biggest initial scattering center size, more effective heat transfer from nanotubes to solvents, and hence the fastest solvent bubble growth, resulting in the lowest limiting threshold and the best limiting efficiency.[9] In contrast, the length of carbon nanotubes has been proven to have less of an effect on the optical limiting property.[9] Moreover, it is difficult to strictly conclude which is the best material for an optical limiter: SWNTs or multiwalled carbon nanotubes (MWNTs). For both the MWNTs and SWNT bundles, the crucial effect for optical limiting is still the diameter size, rather than their specific structures.[9] In addition, the physical properties of the host solvents also have contribution significantly to the limiting performance of nanotube suspensions. For instance, the carbon nanotubes, dispersed in the solvent with the lower boiling point, show a lower limiting threshold and a better limiting effect.[7] The heat-induced solvent bubbles grow much faster in the solvent with the lower liquid−gas tensile surface; thus, the bubbles can reach the critical size in a shorter time for effective scattering, resulting in the faster limiting response.[9,20] Henceforth, we will discuss the potential reasons for the difference of optical limiting effects observed from the three dispersions.

The different mechanisms for optical limiting, for example nonlinear scattering and reverse saturable absorption (RSA), can be revealed by the variation of normalized transmission as a

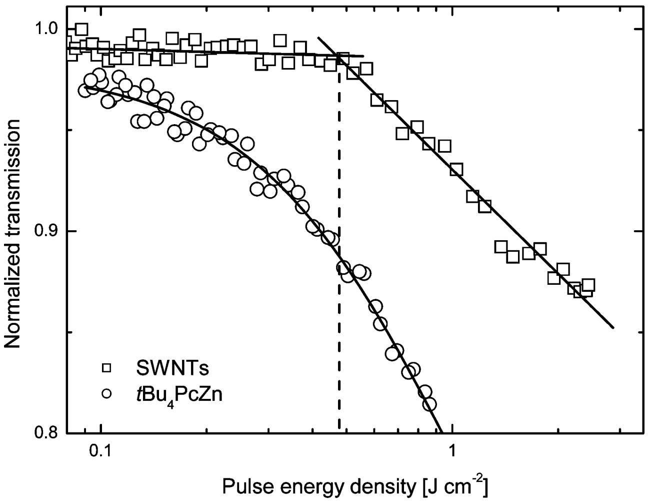

Figure 7. Normalized transmission as a function of the incident pulse energy density for the SWNT dispersion in DMF (3.0×10^{-3} mg/mL) and tBu$_4$PcZn solution (9.0×10^{-2} mg/mL) with the similar linear transmission. The solid lines are intended as a visual guide. The dashed line indicates the limiting threshold.

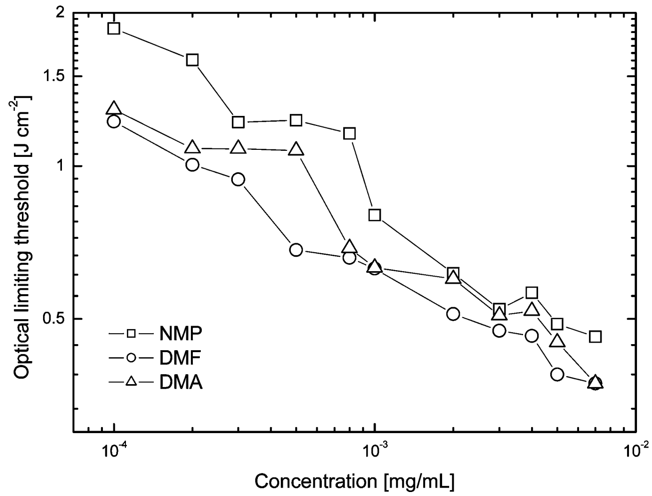

Figure 8. Limiting threshold as a function of concentration of SWNTs in dispersions of NMP (opened square), DMF (opened circle), and DMA (opened triangle).

function of the incident pulse energy density. Figure 7 shows the normalized transmission against incident energy for the SWNT dispersion in DMF (3.0×10^{-3} mg/mL) and tBu$_4$PcZn solution (9.0×10^{-2} mg/mL) with similar linear transmissions. It is apparent that the nonlinear transmission of SWNT dispersion has a distinct discontinuity, corresponding to the limiting threshold. The transmission is roughly constant when the energy fluence is below the threshold. When the incident fluence exceeds the threshold, the transmission decreases significantly. The limiting threshold implies that the nanotubes transfer enough heat energy to the surrounding solvent to cause the solvent to vaporize and grow to the critical size, in order to effectively scatter the incident beam. In contrast, the transmission of the reverse saturable absorber tBu$_4$PcZn decreases with increasing incident energy. We did not observe any evidence of the limiting threshold for tBu$_4$PcZn in the experiments. As shown in Figure 7, the nonlinear transmission of SWNT dispersions obtained from the Z-scan technique is very similar to that from the *f*/30 focusing geometry.[8] At present, the main mechanism of optical limiting of SWNT dispersions is attributed to the nonlinear scattering. The larger average bundle size ascertained by light scattering in DMF dispersions is the straightforward reason for its superior optical limiting performance. However, it is quite difficult to confirm which constitutes the majority of scattering centers, the solvent bubbles or the carbon vapor bubbles. We did not clearly observe the second discontinuity, which corresponds to the formation of carbon vapor in the higher energy fluence region, as described by L. Vivien et al.[8] However, the energy fluence corresponding to the sublimation of carbon in ref 8 is even lower than the limiting thresholds in our work (see Figure 8). On the basis of the above-mentioned analysis, we believe that the main mechanism for optical limiting of SWNT dispersions is the solvent and/or carbon vapor bubble-induced nonlinear scattering.

Figure 8 presents the limiting thresholds of SWNT dispersions in different solvents. The thresholds were determined as illustrated in Figure 7. It is clear that the thresholds dramatically decrease as the concentration is increased, which is attributed to the increase of both particle density and bundle sizes. DMF dispersions exhibit the lowest limiting thresholds due to the presence of larger bundles, which in combination with the other physical properties of DMF, produce the most effective scattering in the dispersions. The effect of solvent properties on optical limiting will be discussed below. Due to the superior debundling effect, the average bundle size of SWNTs in NMP is smaller, resulting in higher limiting thresholds.

In addition to the bundle size, the physical properties of the solvents also contribute to a certain extent to the optical limiting. The boiling points, surface tensions, and viscosities of NMP, DMF, and DMA are quoted in Table S1 in the Supporting Information. The lower boiling point and surface tension of DMF imply that the vapor bubbles can be formed at the lower energy fluence and reach the larger size within the laser pulse duration (a few nanoseconds). In conjunction with the more effective heat transfer, resulting from the larger bundle sizes, the optical limiting effect of the DMF samples are the best of the three dispersions. In contrast, the higher boiling point and surface tension, as well as the smaller bundle sizes of NMP dispersions, lead to inferior optical limiting performances. On the other hand, the low viscosity of DMF can increase the diffusion rate of SWNT bundles and hence avoid the serious depletion of SWNTs, which may improve the operation lifetime and make the dispersions undergo much higher incident fluence.[22]

The solvent effect is also shown by the waist radius of the focused incident laser beam. Figure S1 in the Supporting Information shows the variation of the waist radii in the three dispersions. The waist radii were directly deduced from the Z-scan spectra. In general, the radii slightly increase as the concentrations are increased. However, a significant difference between the waist radii for the three dispersions is observed at the same concentration. The DMF dispersions have the larger waist radius, which implies that they have a more effective defocusing effect than the NMP and DMA dispersions. The improved defocusing of the beam is important, and desirable in practical optical limiters, as it helps to spatially disperse the incident pulse, further reducing the energy density.[1]

5. Conclusion

The nonlinear optical and optical limiting properties of SWNTs were studied by the Z-scan method in NMP, DMF, and DMA dispersions, respectively. The NLE coefficients increase strongly as the SWNT concentration is increased. The DMF dispersions show a larger NLE coefficient, a lower limiting threshold, and superior optical limiting effects. At the same concentration, SWNT dispersions have better optical limiting properties in comparison with the RSA material *t*Bu_4PcZn. The origin of optical limiting of SWNT dispersions is proposed to be the solvent and/or carbon vapor bubble-induced nonlinear scattering. The static light scattering experiments revealed that the DMF dispersions have the larger average bundle size, which in combination with the lower boiling point and surface tension of DMF, results in the superior optical limiting performance of SWNT dispersions in DMF. Our results extend the understanding of SWNTs as optical limiting materials. However, the carbon nanotubes as optical limiting materials still have room for improvement. We expect the carbon nanotube-based complex multicomponent materials to realize the applicable optical limiting devices.

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Supporting Information Available: Physical properties of NMP, DMF, and DMA. Variation of waist radii of incident beam with SWNT concentration in NMP, DMF, and DMA dispersions. This information is available free of charge via the Internet at http://pubs.acs.org.

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