Optical Limiting in Single-walled Carbon Nanotube Suspensions

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Abstract

Optical limiting behaviour of suspensions of single-walled carbon nanotubes in water, ethanol and ethylene glycol is reported. Experiments with 532 nm, 15 nsec duration laser pulses show that optical limiting occurs mainly due to nonlinear scattering. The observed host liquid dependence of optical limiting in different suspensions suggests that the scattering originates from microbubbles formed due to absorption-induced heating.

I. INTRODUCTION

Carbon nanotubes provide a unique class of nanostructured materials. Improved methods of synthesis, purification and functionalization have triggered many experiments exploring basic physics of mesoscopic objects as well as various possible applications [1-4]. Like in C_{60} and other fullerene derivatives, optical limiting is an important application of nanotubes. Optical limiting in liquid suspensions of multi-walled carbon nanotubes (MWNTs) has been reported recently [5,6]. The observed limiting has been compared with that of its well-studied cousin C_{60} fullerene. Whereas optical limiting in C_{60} solution occurs due to the reverse saturable absorption and subsequent nonlinear refraction and scattering [7], optical limiting in MWNT suspension is attributed to the nonlinear scattering arising from expanding microplasmas as in carbon black suspension (CBS) [6]. Optical limiting investigations of carbon nanotubes become even more important since they combine the relative advantages of both CBS and fullerene solutions. As for CBS, the nanotube suspensions consist of relatively large size (length $>$ 100 nm) constituents. However, unlike CBS but like fullerenes, their structure and electronic properties are well characterized and their optical response is susceptible to further improvements by molecular engineering. We have carried out a detailed investigation of the optical limiting of suspensions of well-characterised single-walled carbon nanotubes (SWNTs) in ethanol, water and ethylene glycol by carrying out optical limiting, z-scan and scattering measurements. The results demonstrate that optical limiting in SWNT suspensions occurs mainly due to absorption-induced scattering in the suspension. Furthermore, the limiting strongly depends on the host liquid. While this manuscript was in preparation, optical limiting in a water suspension of SWNTs has been reported by Vivien et al [8]. However, the present report includes studies of three host liquids, an aspect relevant to optical limiting, and the results suggest that the optical limiting is due to nonlinear scattering from absorption-induced microbubbles.

II. EXPERIMENTAL

SWNTs were produced by the dc arc discharge method using a composite graphite rod containing Y_2O_3 (1 at.%) and Ni (4.2 at.%) as anode and a graphite rod as cathode under a helium pressure of 660 torr with a current of 100 A and 30 V [9]. The web produced from the arc-discharge contained SWNT bundles, amorphous carbon along with metal encapsulated carbon particles as seen from the high resolution electron microscope (HREM) image. It was heated in air at 300°C for about 24 hours to remove the amorphous carbonaceous materials. The heat-treated material was stirred with concentrated nitric acid at 50°C for about 12 h and washed with distilled water to remove the dissolved metal particles. The SWNT material so obtained was suspended in ethanol by using an ultrasonicator and filtered through a micropore filter paper (0.3 μm) from Millipore to remove polyhedral carbon nanoparticles present. The product was then dried at 50°C for about 12 h. The SWNT content of the product was found to be 80% by thermogravimetric analysis. High-resolution electron microscopic examination (HREM) showed that the SWNTs with an average diameter of 1.4 nm were present as bundles of 10-50 nanotubes. About 5-10 mg of the purified SWNT was dispersed in 15 ml of water/ethanol by ultrasound sonication for 30 minutes. This dispersion was used for our study. All suspensions were stable for several hours after ultrasonication. Optical transmission spectra were found to remain unchanged during the experiment. Dynamic light scattering measurements were performed on the suspensions to characterise the average size of the scatterers. The light scattering experiments were done using λ = 647.1nm radiation from a Kr^+ ion laser, a home-made spectrometer and a correlator (Malvern 7132CE 64 channel model). Fig. 1 shows the plot of the normalised intensity autocorrelation function $g_2(t) - 1 = \langle I(0)\, I(t)\rangle / \langle I(0)\rangle^2 - 1$ versus time for different scattering angles θ, which have been fitted to $g_2(t) - 1 = A \exp(-\Gamma\, t)$, where $\Gamma = 2Dq^2$, $q = \frac{4\pi n}{\lambda} \sin\frac{\theta}{2}$ is the wavevector transfer, n = 1.33 is the refractive index of the solvent and D is the diffusion coefficient of the scatterer (nanotube). The inset of Fig. 1 shows a plot of Γ versus q^2, and a linear fit gives $D = 1.49 * 10^{-8}$ cm^2s^{-1}. Taking the average diameter of the nanotube bundles to be 40nm as suggested by electron microscopy and using the equations $D = k_BT\, [6 - 0.5(\gamma_{\parallel} + \gamma_{\perp})]/3\pi\eta_{\circ}L$, $\gamma_{\parallel} = 1.27 - 7.4(\frac{1}{\delta} - 0.34)^2$, $\gamma_{\perp} = 0.19 - 4.2(\frac{1}{\delta} - 0.39)^2$ and $\delta = \ln \frac{2L}{d}$ [10], where L and d are the length and diameter of the cylindrical rods and $\eta_{\circ}$ is the solvent viscosity, we obtain an average value for L $\sim$ 25μm. Experiments were performed using a frequency doubled Nd:YAG laser giving 532 nm, 15 ns laser pulses with pulse repetition every $\sim$3 seconds. The laser emission was focussed using a 50 cm lens such that $1/e^2$ radius of the focussed beam was $\sim$ 50 μm at the focus. For optical limiting measurements the nanotubes sample was kept at the focus and the transmitted emission was passed through an aperture with $\sim$ 95% transmission at low fluences. Thus the aperture would block off-axis scattered emission, if any, from the sample at high fluences. The input energy was measured by taking a fraction of the input beam on a calibrated biplanar photodiode and output energy was measured by a calibrated PIN-photodiode kept after the aperture. The input and output fluences were estimated by measuring input and output energy and beam size at the sample position.

III. RESULTS AND DISCUSSION

Fig. 2 shows the observed variation of output fluence with input fluence for a SWNTs suspension in water and a C_{60} -toluene solution . The transmission spectrum of SWNT sample is shown in the inset. Both absorption and scattering may contribute to the loss in transmitted intensity. The SWNTs and C_{60} samples were kept in two identical cuvettes and concentrations were adjusted so that the low fluence transmission through the cuvette was the same ($\sim$ 55 %) for both the samples. It is evident from the figure that optical limiting in C_{60} solution is stronger than that in SWNTs suspension in water. On the other hand, stronger limiting in MWNTs suspension in ethanol than that in C_{60} solution in toluene has been earlier reported by Chen et al [6]. To know the contribution of nonlinear refraction to the observed optical limiting in nanotubes suspension, we performed z-scan measurements [11]. In these measurements the aperture used in the limiting geometry was moved to the far-field region with $\sim$ 16% transmission without the nanotubes sample in the beam path. Fig. 3 shows the z-scan results. The transmission shown in this figure is the ratio of the aperture transmission measured with the sample in the beam path to that measured without the sample. Thus at large z values the transmission corresponds to the low intensity transmission through the sample. At smaller z values (i.e higher fluences) transmission reduces and reaches its minimum near z=0 . The absence of any peak in the z-scan data in Fig. 3 indicates that nonlinear scattering is much stronger than nonlinear refraction. The observed pronounced valley shown in this figure can occur due to nonlinear scattering as well as nonlinear absorption. We believe that the dominant contribution to the observed transmission valley in Fig. 3 is from nonlinear scattering because the optical limiting was found to be very sensitive to the size of the aperture. We note that optical limiting in multi-walled carbon nanotubes suspensions has also been attributed to absorption induced scattering in the suspensions [6]. Z-scan measurement of SWNT suspension in water by Vivien et al [8] showed negative lensing corresponding to thermally induced nonlinear refraction, in apparent variance with our observations. The difference could be due to much higher intensities and much smaller aperture transmission used by them. On the other hand, Chen et al [6] found stronger optical limiting in MWNT suspension in ethanol compared to C_{60} solution in toluene. Similarly, Vivien et al [8] also reported stronger optical limiting in SWNT suspension in water compared to C_{60} solution in toluene. We note that optical limiting due to nonlinear refraction of thermal origin would be stronger for longer pulses used in our experiments. This mechanism is expected to be more important in C_{60} solution than in SWNT suspensions. To understand the nature of scattering, we measured the scattered light at different angles from the sample cell. Fig. 4 shows the results for an angle $\sim 0.8^\circ$ from the beam axis. For these measurements, the energy of scattered light passing through a suitably positioned 3 mm diameter aperture was measured using a PIN photodiode in integrating mode. The y-axis in Fig. 4 shows the ratio of the signal from this PIN photodiode to the signal from another photodiode monitoring the input pulse energy. For linear scattering this ratio is expected to be constant for all values of the input fluence. The data in Fig. 4 clearly shows evidence of nonlinear scattering. The ratio initially rises and then falls as input fluence is increased which appears to be due to a change in angular distribution of scattered light. We have also measured optical limiting in nanotubes suspended in different liquids viz. ethylene glycol, water and ethanol. For this purpose, identical 10 mm path length cuvettes were used and low fluence transmission was kept at $\sim 42\%$. During measurements with the three samples, all the cells containing SWNTs suspension were accurately positioned at the same place and other experimental set-up was unaltered. Fig. 5 shows the observed limiting data for different suspensions. It is evident that optical limiting in ethanol suspension was strongest among the three suspensions. The threshold fluence (defined as the fluence at which the transmission reduces to half of its low fluence value) in different liquids was also different. As estimated from Fig. 5, the lowest value was ~ 1.0 J/cm^2 for ethanol suspension. These observations suggest that the extent of nonlinear scattering depends on the liquid host. The nonlinear scattering from suspensions of absorbing particles in liquids can result from several mechanisms . The scattering centres can be expanding microplasmas generated by vaporization of the particles [12], bubbles formed by vaporization of the liquid [13] or transient refractive index inhomogeneities resulting from localised heating around absorbing particles [7]. Our observation of strong solvent dependence of optical limiting rules out plasma formation as being an important mechanism. The change in refractive index of a liquid depends on its thermal figure of merit $\mathrm{F} = \frac{1}{c\rho}\frac{dn}{dT}$ (where c is the specific heat, ρ is the density and $\frac{dn}{dT}$ is the thermo-optic coefficient). The values of F are 7.5, 8.0 and 1.0 $10^{-4}\mathrm{cm}^3\mathrm{calK}^{-1}$ for ethylene glycol, ethanol and water , respectively. We note that although ethylene glycol has much larger F, optical limiting in glycol suspension was much weaker than that in water suspension. This implies that absorption induced refractive index inhomogeneities did not make significant contribution to the nonlinear scattering. We thus believe that the observed nonlinear scattering in our experiments is mainly from microbubbles formed in the suspension. The strongest optical limiting in ethanol suspension is qualitatively consistent with its lowest boiling point of ~ 78 °C among the three liquids. This conclusion also agrees with the recent pump-probe investigation of CBS by Durand et al [14] using 30 ps laser pulses. These authors found that while for the first few nanosecond after the pump pulse, probe attenuation was solvent independent suggesting scattering from microplasma, for larger delays the probe transmission showed strong solvent dependence implying scattering from bubbles or thermo-optic effects. In conclusion, we report optical limiting of visible ns laser pulses in suspensions of single-walled carbon nanotubes. The dominant mechanism for the observed limiting has been found to be absorption induced nonlinear scattering. Optical limiting has been found to be significantly different for different liquids indicating that scattering is probably due to bubble formation in the suspension, although other causes like sublimation of particles cannot be ruled out at present.

IV. ACKNOWLEDGEMENTS

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V. REFERENCES

[1] S. Ijima, Nature 354, 56 (1991).

[2] T. W. Ebbesen, "Synthesis and Characterization of Carbon Nanotubes" in Physics and Chemistry of Fullerenes, Ed., K. Prassides (Kluwer Academic Publishers, Netherlands, 1994), T. W. Ebbesen, "Carbon Nanotubes", Physics Today (June 1996, p-26).
[3] C.N.R.Rao, A. Govindaraj, R.Sen and B. Satishkumar, Mater. Res. Innovat 2, 128 (1998) and references therein.
[4] R. Saito, G. Dresselhaus and M. S. Dresselhaus, "Physical Properties of Carbon Nanotubes" (Imperial College Press, London, 1998)
[5] X. Sun, R. Q. Yu, G. Q. Xu, T. S. A. Hor and W.Ji , Appl. Phys. Lett. 73, 3632 (1998).
[6] P. Chen, X. Wu, X. Sun, J. Lin, W. Ji and K. L. Tan, Phys. Rev. Lett. 82, 2548 (1999).
[7] S. R. Mishra, H. S. Rawat, M.P. Joshi and S. C. Mehendale, J. Phys. B 27, L157 (1994).
[8] L. Vivien, E. Anglaret, D. Riehl, F. Bacou, C. Journet, C. Goze, M. Andrieux, M. Brunet, F. Lafonta, P. Bernier, F. Hache, Chem. Phys. Lett. 307, 317 (1999).
[9] Journet, C., Maser, W. K., Bernier, P., Loiseau, A., Lamy de la Chapelle, M., Lefrant, S., Denierd, P., Lee, R. and Fischer, J. E., Nature, 1997, 388, 756.
[10] S. Broersma, J. Chem. Phys. 32, 1626 (1960).
[11] M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagen and E. W. Van Stryland, IEEE J.Quant. Electr. 26, 760 (1990).
[12] K. Mansour, M. J. Soilcau and E. W. Van Stryland, J.Opt. Soc. Am. B 9, 1100 (1992).
[13] T. F. Bogges, G. R. Allan, D. R. Labergerie, C. H. Venzke, A. L Smirl, L. W. Tutt, A. R. Kost, S. W. McCahahon, M. B. Klein, Opt. Engg. 32(5), 1063 (1993)
[14] O. Durand, V. Grolier-Mazza and R. Frey, Opt. Lett. 23, 1471 (1998).

VI. FIGURE CAPTIONS

Fig. 1. Intensity autocorrelation functions measured at different scattering angles in dynamic light scattering experiments with SWNT suspension in water. The inset shows the linear fit to the plot of Γ versus q^2.

Fig. 2. Optical limiting in SWNTs - water suspension and C_{60}-toluene solution. Circles show output with SWNTs-water suspension and triangles show output with C_{60} solution. The inset shows transmission loss spectrum of SWNTs-water suspension.

Fig. 3. Variation of transmission with z in a close-aperture z-scan measurements on SWNTs-water suspension.

Fig. 4. Measured variation of ratio of the scattered energy to the input fluence with input fluence at an angle of $\sim 0.8^\circ$ in the forward direction from the beam axis.

Fig. 5. Measured variation of output fluence with input fluence in SWNTs suspensions in different solvents. Crosses, circles and triangles show output from SWNTs suspension in ethanol, water and ethylene glycol respectively.

FIGURES

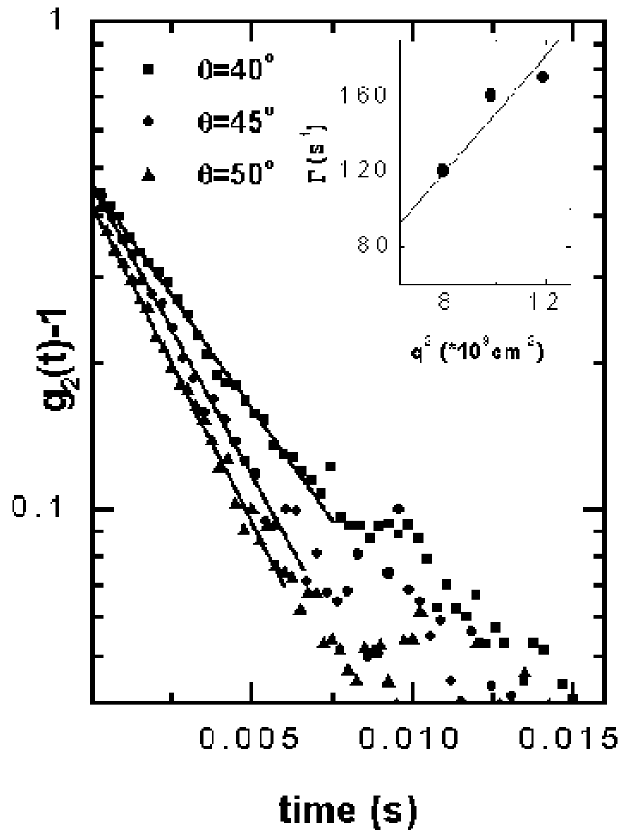
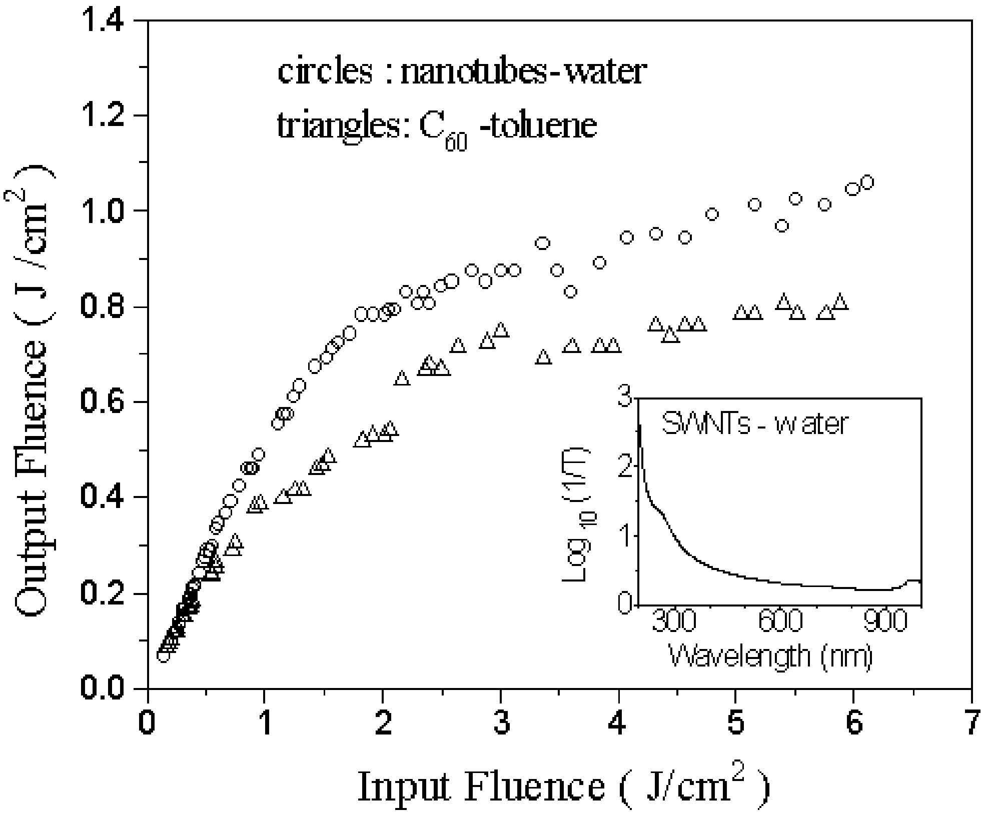


Fig. 1



circles : nanotubes-water
triangles: C60 -toluene
Output Fluence (J /cm2)
Input Fluence (J/cm2)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
1
2
3
4
5
6
7
SWNTs - water
Log10 (1/T)
Wavelength (nm)
300
600
900

Fig. 2

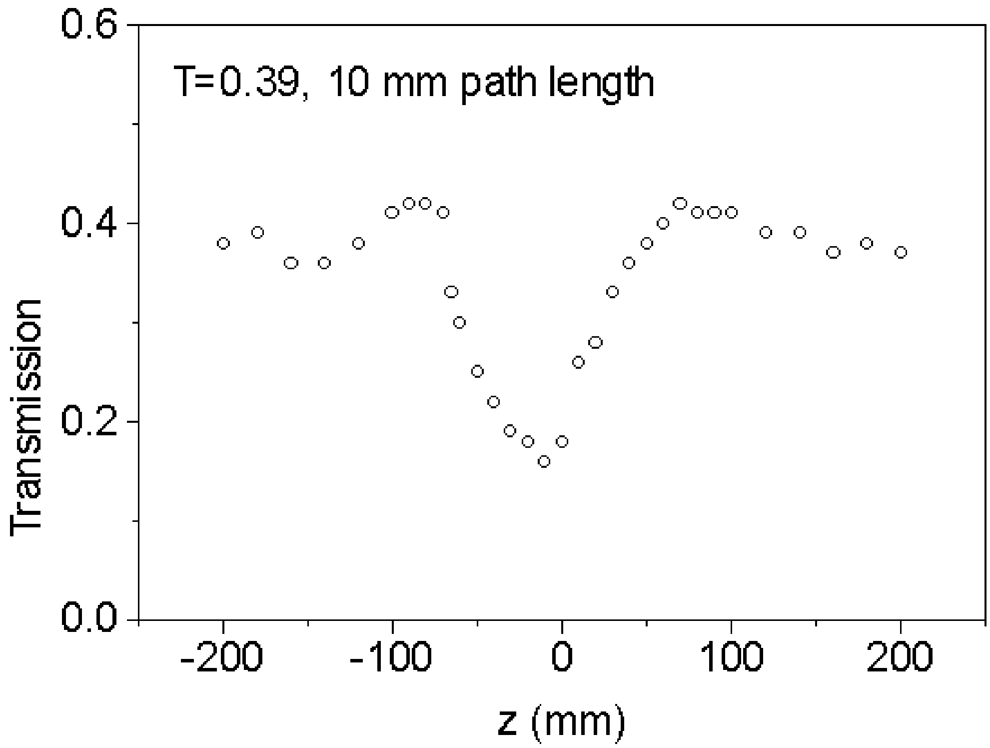

T=0.39, 10 mm path length
Transmission
0.0
0.2
0.4
0.6
-200
-100
0
100
200
z (mm)

Fig. 3

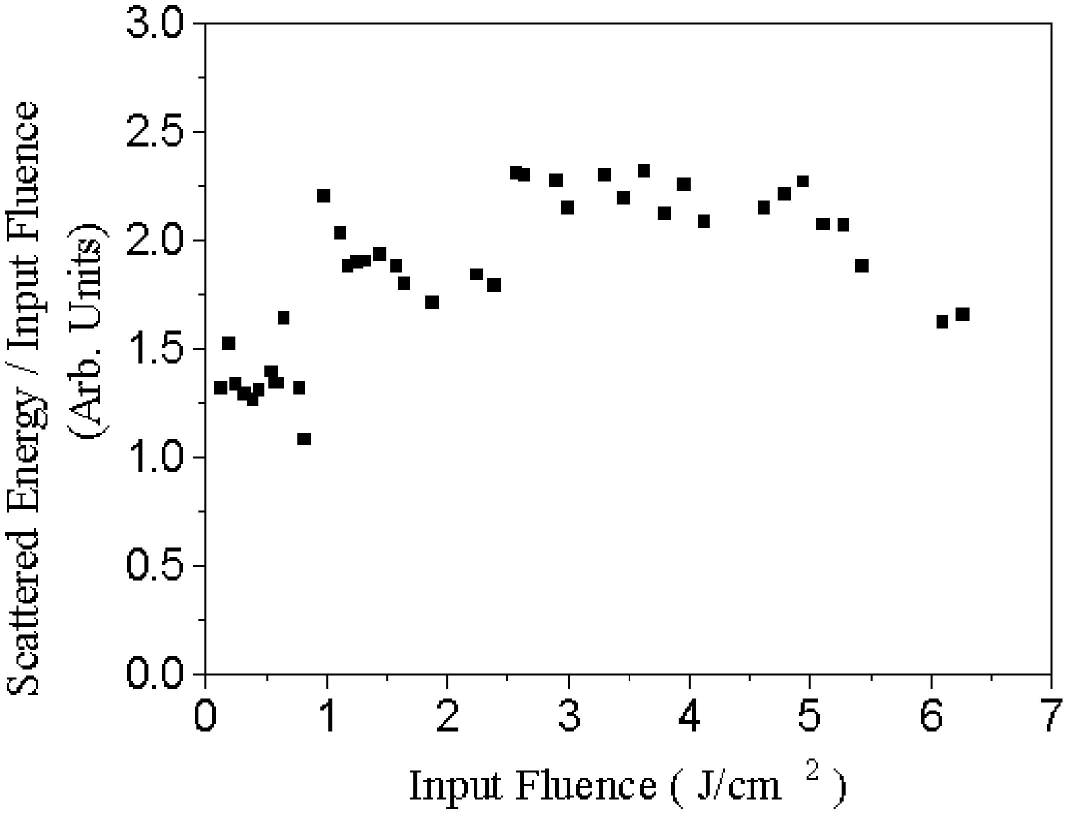
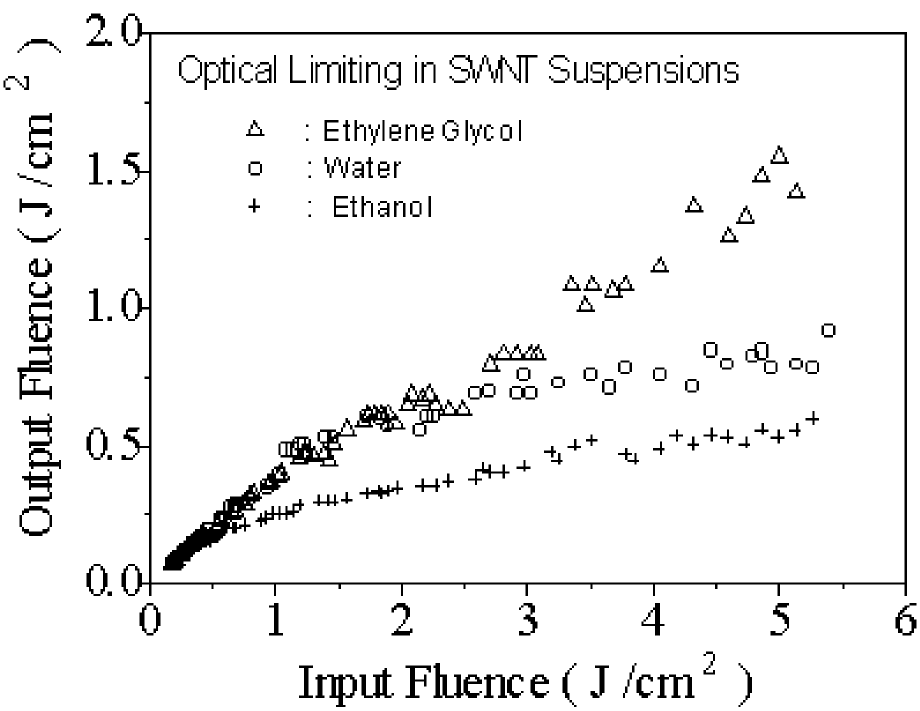

3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
Scattered Energy / Input Fluence
(Arb. Units)
Input Fluence (J/cm 2)

Fig. 4



Optical Limiting in SWNT Suspensions
: Ethylene Glycol
: Water
: Ethanol
Output Fluence (J /cm 2)
Input Fluence (J /cm 2)
0.0
0.5
1.0
1.5
2.0
0
1
2
3
4
5
6

Fig. 5