# Broadband optical limiting with multiwalled carbon nanotubes

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(Received 15 May 1998; accepted for publication 14 October 1998)

Optical limiting effects in multiwalled carbon nanotubes have been observed in the visible and infrared spectral regions with nanosecond laser pulses. The multiwalled carbon nanotubes investigated include those suspended in distilled water and embedded in polymethyl methacrylate films. Among all the samples measured, the limiting performance of the carbon nanotube suspension is the best with the limiting threshold determined to be ~1, 5, and 13 J/cm$^2$ at 532, 700, and 1064 nm, respectively. The possible mechanism for the observed effects is discussed. © *1998 American Institute of Physics.* [S0003-6951(98)02451-6]

In recent years, there has been increasing interest in materials that exhibit strong optical limiting properties.[1] $C_{60}$ in solution has been reported as one of such materials[2] and investigated extensively.[1–5] When irradiated by laser pulses, ground-state absorption in $C_{60}$ promotes electrons to excited states. Then excited-state absorption, that is greater than the ground-state absorption in $C_{60}$, gives rise to the optical limiting effect. Optical limiting has also been observed in carbon black suspension (CBS).[6–8] CBS consists of nanometer-sized carbon particles suspended in liquids and can be made by diluting commercially available black ink (e.g., India ink). Optical limiting in CBS has been attributed to nonlinear scattering process.[6–8] The absorption of strong laser radiation induces heating to the carbon particles, which results in avalanche ionization and formation of microplasmas. And then these plasmas rapidly expand to the surrounding liquid, which in turn strongly scatter the incident laser light. As a consequence, the light energy in the propagation direction is decreased, leading to the limiting behavior. In addition, at incident energies well above a threshold, the strong heating leads to bubble formation and further enhances the scattering process.[6,8]

We note that there exists another interesting member of carbon family, carbon nanotubes.[9] These tubes may be found in two types of structures: single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs). Each SWNT is made of single graphitic cylinder while there are many coaxial graphitic cylinders for each MWNT. Each cylinder may be visualized as the conformal mapping of a two-dimensional honeycomb lattice onto its surface. The fundamental properties of carbon nanotubes, such as electronic structure, electrical conductivity, mechanical and thermal behavior, have been studied (see Refs. 10–12 for recent review). However, investigations on their nonlinear optical properties were mainly theoretical predictions for third-order nonlinearities in SWNTs.[13–15] Here we present the observation of optical limiting with MWNTs in the visible and infrared spectral regions.

We prepared three samples of MWNTs by using an arc discharge method.[16] The preparation and purification were described in detail in our previous report.[17] Sample A was nearly pure MWNTs suspended in distilled water (contained in 1 cm quartz cell). To test whether it is feasible for these MWNTs to be fabricated into solid devices, we also synthesized sample B in which the pure MWNTs are embedded in polymethyl methacrylate (PMMA) film, a widely used host material for optical limiting application.[18] As a comparison, we prepared a PMMA film (sample C) containing a mixture of MWNTs and carbon particles, directly produced by the arc discharge without the purification. The thickness of samples B and C was in the range of 100–250 $\mu$m. The carbon concentrations in the three samples were adjusted so that their linear transmittance (the transmission at very low incident light energy) was about 50% at 532 nm. The transmission electron microscopy (TEM) image in Fig. 1(a) shows that the mixture in sample C consists of 50% MWNTs and 50% carbon particles (in aggregates with sizes ranging from several to ten nanometers). Figure 1(b) displays the MWNTs used in samples A and B, and these tubes range from 10 to 40 nm in diameter and several micrometers in length, with a purity of up to 95%. Because the purification was achieved by treating the arc-produced carbon deposit with a mixed acid ($H_2SO_4$–$HNO_3$, 1:1 v/v), the MWNTs in samples A and B were functionalized with functional groups, such as hydroxyl and carboxyl groups being on the surface of the MWNTs.[17] As a standard sample,[19] a $C_{60}$ solution (50% linear transmittance at 532 nm) was prepared with $C_{60}$ (a purity of 99.5%) purchased from Southern Chemical Group, LLC, USA.

The linear transmission spectra of the samples were recorded on a Hitachi UV-3410 spectrophotometer at room temperature in the 200–1100 nm region, as shown in Fig. 2. The spectra of the MWNTs are nearly flat in the 500–750 nm range, different from the pronounced absorption in the $C_{60}$-toluene solution due to the vibronic transitions from the HUMO derived, $A_g$ symmetry ground state to excitonic states in $C_{60}$.[10] In the infrared spectral part, the linear transmission of samples A, B, and C is ~60% at 1064 nm. In sample A, there is an absorption band centered at 980 nm, caused by the vibronic transitions of the O–H bond in water.[20]

We measured the nonlinear (energy-dependent) trans-

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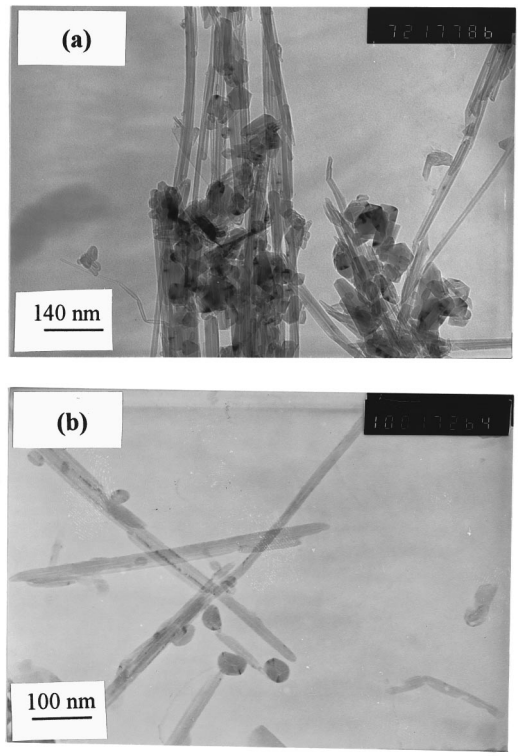


FIG. 1. Micrographs of (a) mixture of MWNTs and carbon nanoparticles and (b) purified MWNTs, obtained with a JEOL-100 CXII transmission electron microscope (TEM) at 100 kV accelerating voltage.

mission of the samples with 7 ns pulses generated from a *Q*-switched Nd:YAG laser or a dye laser pumped by it. To produce 532 nm pulses or to pump the dye laser, a second-harmonic crystal was used. The spatial profiles of the pulses were nearly of Gaussian form. The pulses were split into two parts: the reflected was used as reference, and the transmitted was focused onto the sample using a focusing geometry ($f/65$). The sample was placed where the spot radii of the pulses at the focus were of $30\pm5$, $46\pm5$, and $73\pm5$ $\mu$m for 532, 700, and 1064 nm, respectively, measured by *Z*-scan method.[21] To assess the application potential, we also set up a tightly focusing geometry ($f/3$) with a spot radius of $\sim7$ $\mu$m at the focus, as required by real applications.[22] In our experiments, the maximum incident fluence at the sample was set at 15 J/cm$^2$, and the relative error in the measured fluences was $\sim50\%$, mainly due to the uncertainty in determining the spot sizes. The laser pulses were produced at single shots or 10 Hz repetition rate.

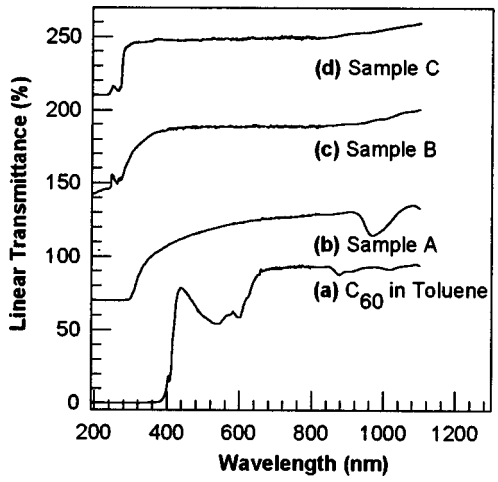


FIG. 2. Linear transmission spectra of the samples studied. For presentation, spectra (b), (c), and (d) are shifted vertically by 70%, 140%, and 210%, respectively.

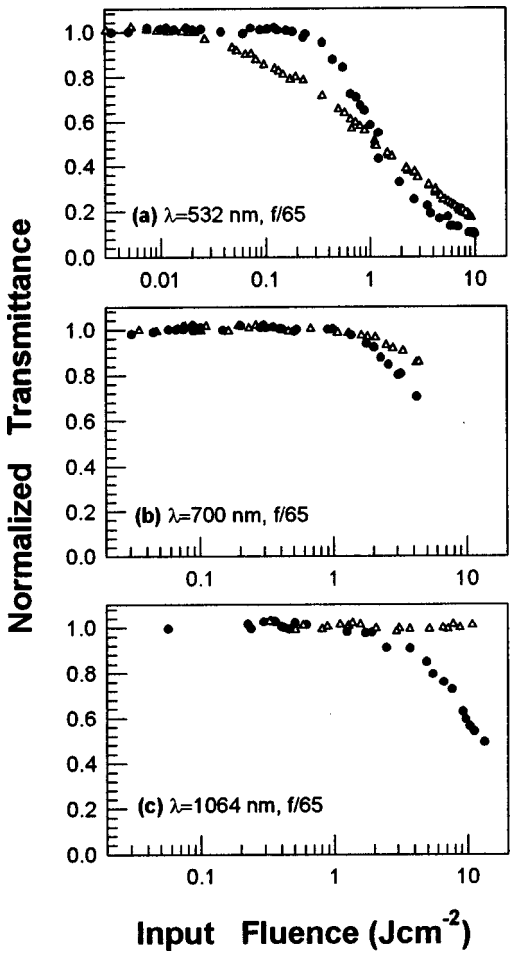


FIG. 3. Nonlinear transmission of sample A (filled circles) and the $C_{60}$-toluene solution (open triangles) at (a) 532 nm, (b) 700 nm, and (c) 1064 nm measured in the $f/65$ focusing setup with the nanosecond laser pulses.

Figure 3 displays the measurements for sample A (the

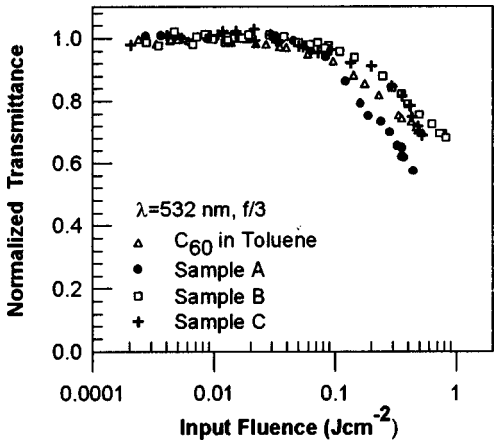


FIG. 4. Nonlinear transmission of sample A (MWNTs in water, filled circles), sample B (MWNTs in PMMA film, open squares), sample C (MWNTs and carbon particles in PMMA film, crosses) and the $C_{60}$-toluene solution (open triangles), measured in the $f/3$ focusing geometry with the nanosecond laser pulses of 532 nm wavelength.

TABLE I. Limiting thresholds, $F_{th}$(J cm$^{-2}$), measured with nanosecond laser pulses.

| Sample | Compound | $F_{th}$ at 532 nm $f/3$ | $f/65$ | $F_{th}$ at 700 nm $f/65$ | $F_{th}$ at 1064 nm $f/65$ |
|---|---|---|---|---|---|
| A | MWNTs suspened in water | 0.9 | 1.0 | 5.5 | 13 |
| B | MWNTs in PMMA | 2.6 | 3.1 | 4.1 | $\sim 8$[a] |
| C | MWNTs and carbon particles in PMMA | 2.5 | 3.0 | 4.4 | $\sim 8$[a] |
| | $C_{60}$ in toluene | 1.1 | 1.1 | 11 | $>15$ |

[a]These numbers are the damage thresholds.

MWNT suspension) with the $f/65$ focusing geometry. Results of the $C_{60}$-toluene solution recorded under the same conditions are also included in Fig. 3. For the 532 nm pulses, the nonlinear transmission of sample A occurs at 0.2 J/cm$^2$, ten times greater than that of the $C_{60}$ solution. However, the limiting performance in sample A is better than the $C_{60}$ solution at fluences in excess of 1 J/cm$^2$. Figure 3 demonstrates that sample A is a broadband limiter with wavelengths of up to 1064 nm. But the limiting phenomena in the $C_{60}$ solution diminish at 700 nm and completely disappear at 1064 nm, in agreement with both published findings[4,5] and excited-state absorption model.[1–5] Figure 4 shows the measurements obtained with the $f/3$ focusing setup at 532 nm. The nonlinear transmission of sample A starts at 0.07 J/cm$^2$, better than the other samples and the $C_{60}$ solution.

To quantitatively describe the limiting behavior, we define a limiting threshold as the input fluence at which the transmittance falls to 50% of the linear transmittance. Table I summarizes the measured limiting thresholds. At 1064 nm, the films were damaged by the laser pulses at 8 J/cm$^2$ before the transmittance fell to 50%, and hence, the damage thresholds were listed instead of the limiting thresholds. Note that in sample C the half carbon composition is the MWNTs and the rest is the carbon particles. Thermally initiated nonlinear scattering has been observed as a cause for optical limiting in carbon particles.[6–8] The similarity between samples B and C in Table I implies that thermally induced nonlinear scattering should also play an important role in the MWNTs. It is further supported by the evidence, shown in Table I, that the limiting effects in the films are inferior to the suspension. This should be expected because the expansion of the microplasmas is easier in solution than in solid host. In addition, the better limiting action in the $f/3$ setup than in the $f/65$ setup is another indicator of thermal origin. Thermal effects should take a time to manifest themselves and this time is proportional to the spot size of the focused laser beam.[22] The spot size is smaller in the $f/3$ geometry, and hence, thermal effects occur earlier during the pulsed radiation, which enhances the limiting response.

In conclusion, the broadband limiting responses of MWNTs suspended in water or embedded in PMMA films have been observed with nanosecond laser pulses. A possible nonlinear scattering mechanism has also been discussed qualitatively. The quantitative investigation of the nonlinear scattering is already under the way. Note that large quantity MWNTs are easily attainable.[10–12] These show that MWNTs are a promising candidate for limiting applications, particularly in the infrared spectral region.


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