Investigation of an optical limiting mechanism in multiwalled carbon nanotubes

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We report our investigation of the mechanism that is responsible for the optical limiting behavior in multiwalled carbon nanotubes. We conducted energy-dependent transmission measurements, picosecond time-resolved pump–probe experiment, and nonlinear scattering experiments at 532-nm wavelength on multiwalled carbon nanotube suspension. For comparison, C_{60}–toluene solutions and carbon black suspensions were also studied in the same experiments. The similarities that we observed between the multiwalled carbon nanotubes and carbon black suspension suggest that nonlinear scattering, which is known to be responsible for the limiting action in carbon black suspension, should play an important role in the limiting effect in multiwalled carbon nanotubes. © 2000 Optical Society of America

OCIS codes: 190.0190, 190.4400, 290.5850, 160.4330, 290.5820, 190.5890.

1. Introduction

As a new one-dimensional structure of carbon family,[1] carbon nanotubes have attracted considerable attention because of their unique structure, which may lead to various electronic and optical applications.[2–4] Our previous study showed that multiwalled carbon nanotubes, which consist of multilayers of graphene sheets that can be rolled into the shape of a hollow cylinder, are promising candidates for broadband optical limiting from the visible to the infrared regions.[5,6] The limiting action was also observed in single-walled carbon nanotubes[7] that are made of one layer of a graphene sheet. However, to our knowledge no direct experimental evidence was reported on the physical origin of the limiting behavior in carbon nanotubes. Here we present an experimental investigation into the mechanisms that are responsible for the optical limiting phenomena in multiwalled carbon nanotubes.

The origins of the optical limiting properties of a C_{60} solution and of carbon black suspension (CBS), which are amorphous aggregates of carbon particles, have been studied extensively.[8–17] Two different mechanisms, excited-state absorption and nonlinear scattering, were employed to interpret their respective limiting behavior.[8–17] It is generally accepted that excited-state absorption is dominant for C_{60}, which can be described by a five-level model.[8–13] On the other hand, nonlinear scattering was found to be responsible for the limiting action in CBS. In the nonlinear scattering model, the limiting action is a result of the breakdown of absorbing particles.[14] Because of heating by intense laser pulses, the carbon particles heat up, vaporize, and ionize to form micrometer-sized plasmas. As a consequence, plasma absorption and nonlinear scattering by expansion of the induced microplasmas takes place, which gives rise to the limiting effect. It is also possible that the heat is transferred from the particles to the surrounding liquid and form micrometer-sized bubbles, which subsequently scatter light.[14–17]

To investigate the mechanism for the limiting behavior in the multiwalled carbon nanotube (MWNT) suspension, we performed the following experiments at 532-nm wavelength: (1) energy-dependent transmission measured with picosecond and nanosecond laser pulses; (2) picosecond time-resolved pump–probe experiment; and (3) nonlinear scattering measured with nanosecond pulses. For comparison, a C_{60}–toluene solution and CBS were also studied in the same experiments.

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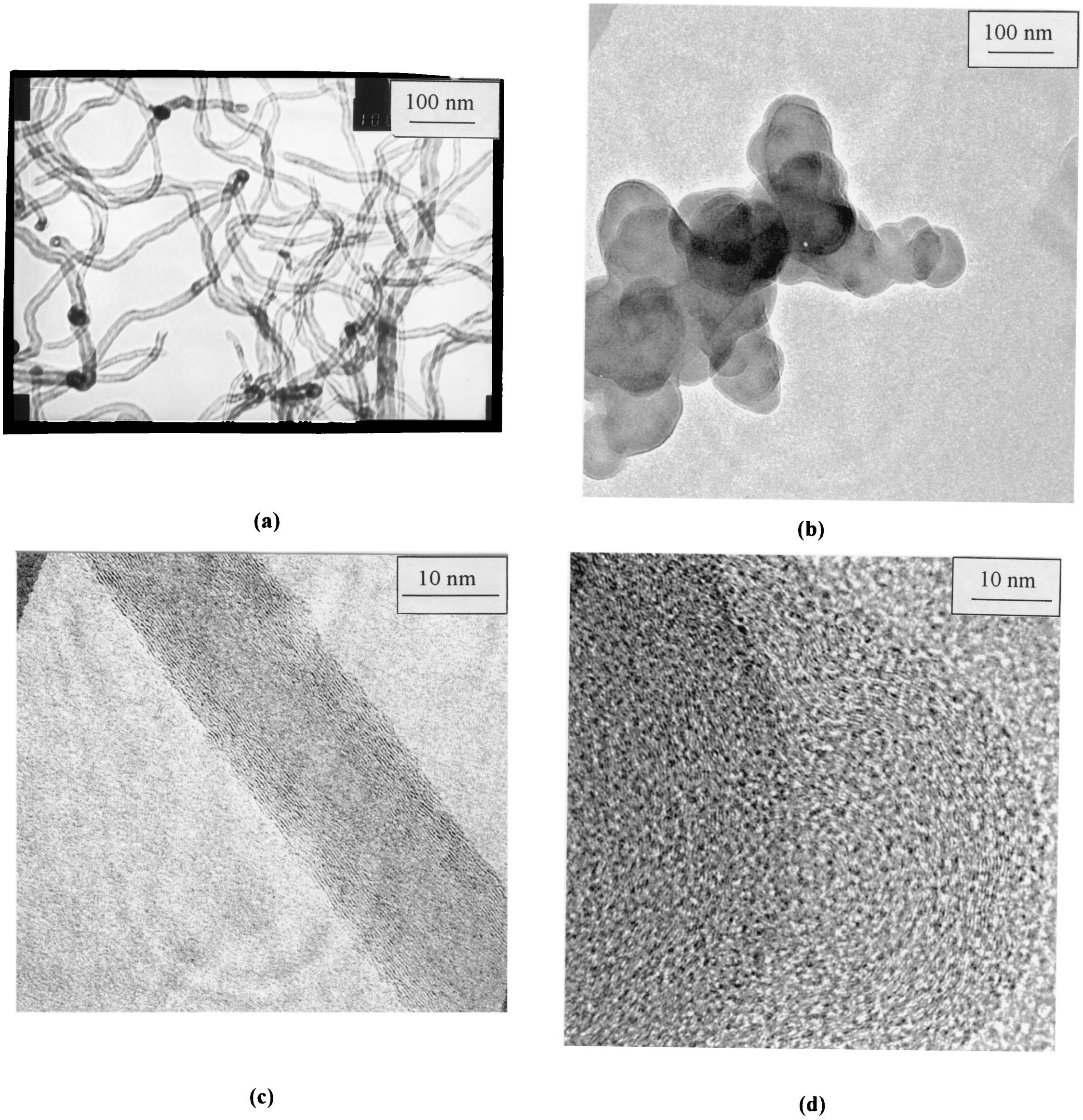
Received 27 July 1999; revised manuscript received 22 October 1999.

0003-6935/00/121998-04$15.00/0



(a) (b) (c) (d)

Fig. 1. Transmitted electron microscope images of (a) the MWNT's (low resolution), (b) carbon particles in the CBS (low resolution), (c) the MWNT's (high resolution), (d) carbon particles in the CBS (high resolution).

2. Materials

The MWNT's in this investigation were prepared by catalytic CO disproportionation, which has been developed to produce highly (>95%) purified tubes in desired sizes under control, as described in Ref. 18. The MWNT's were suspended in ethanol for measurements. The C_{60} solution was prepared with C_{60} (a purity of 99.5%) purchased from Southern Chemical Group, LLC. We prepared the CBS by grinding a carbon ink stick (made in Wuhan, China, and commonly used in traditional Chinese calligraphy) with distilled water. Both the MWNT's and the carbon particles in the CBS were characterized by transmitted electron microscopy (Philips FEG CM300 electron microscope). The images in Fig. 1 show more than 90% tubes that range from 10 to 20 nm in diameter in the MWNT sample. The CBS consists of carbon amorphous aggregates, and the average diameter of the carbon particles in the aggregates is approximately 50 nm. For comparison, the concentrations of the MWNT's, C_{60}, and carbon particles in the three samples were adjusted to have the same linear transmittance of approximately 50%.

3. Nonlinear Optical Measurements

We measured the nonlinear (energy-dependent) transmission of each sample at 532 nm with 7-ns and 35-ps (FWHM) pulses generated from a frequency-doubled Q-switched Nd:YAG laser and a mode-locked Nd:YAG laser, respectively. The spatial profiles of the pulses were of nearly Gaussian form. The pulses were split into two parts: the reflected pulse was used as reference, and we focused the transmitted pulse onto the sample by using a 25-cm focal length lens. The sample was placed at the focus where the spot radii of the pulses were 30 ± 5 and

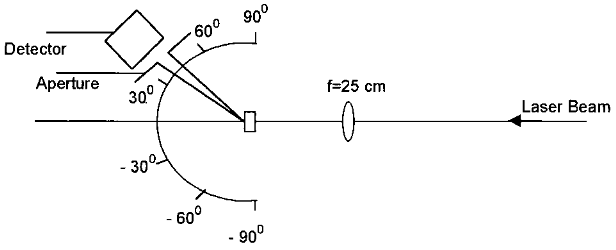


Fig. 2. Experimental setup for nonlinear scattering measurements with 7-ns laser pulses at 532 nm.

28 ± 5 μm for nanosecond and picosecond laser pulses, respectively, measured by the Z-scan method. In the experiments, the maximum incident fluence at the sample was set at 10 J/cm^2. The laser systems were operated at single shots.

We conducted the pump–probe experiment by using the second harmonic of a Nd:YAG mode-locked laser with a pulse width of 28 ps (FWHM) at 532 nm, in which a strong pump pulse was used to induce a change in the sample transmission and a weak probe pulse was used to monitor the change in the sample transmission at various delay times. The pump and probe beams were focused into the sample to radii of 100 and 20 μm by use of 100- and 20-cm focal length lenses, respectively. The experimental setup is described in detail in Ref. 14.

The experimental setup of the nonlinear scattering measurements is shown in Fig. 2. When we irradiated the sample by using the 7-ns laser pulses of p polarization at normal incidence, the forward-scattered energy was recorded at angles from −80° to 80° in steps of 10° with an ~0.02-rad solid angle.

4. Results and Discussion

The energy-dependent transmission results of the samples with 7-ns and 35-ps are displayed in Fig. 3, which shows that the limiting performance of the MWNT sample is close to those of both C_{60} and CBS samples for nanosecond pulses, whereas the response of the MWNT suspension for picosecond pulses is similar to that of the CBS but differs from the behavior of the C_{60} solution. The similarity between the limiting action of the MWNT suspension and CBS suggests that nonlinear scattering, which is known to be responsible for the limiting action in CBS, may play an important role in MWNT suspension.

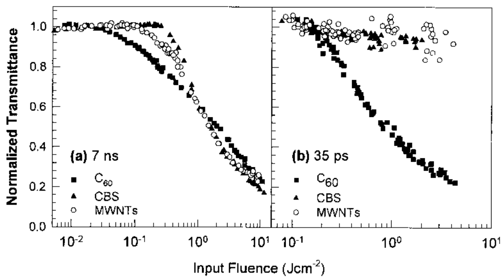


Fig. 3. Nonlinear transmittance of the C_{60} solution (squares), CBS (triangles), and MWNT suspension (open circles) measured at 532 nm with (a) 7-ns and (b) 35-ps laser pulses.

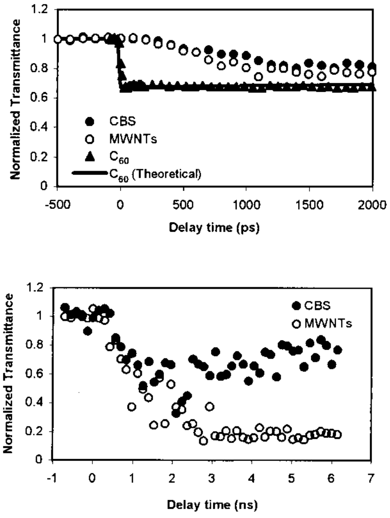


Fig. 4. Probe transmittance versus delay time recorded with the maximum delay of (a) 2 ns and (b) 7 ns. The solid circles, open circles, and solid triangles represent the data for the CBS, MWNT suspension, and C_{60} solution, respectively. The solid line represents the theoretical fit for C_{60}.

To investigate this further, we conducted the pump–probe experiment. Figure 4(a) shows that the change in the transmission of the C_{60} solution is induced immediately by the pump pulse and shows only a small amount of decay up to the maximum measured delay of 2 ns. The results are in good agreement with a five-level model with the excited-state absorption cross sections and lifetimes obtained from Ref. 11. However, for both the MWNT suspension and the CBS, Fig. 4(a) shows that it takes more than 1-ns delay to reach the maximum change in the transmittance. The similarity between the MWNT suspension and CBS in Fig. 4, along with the results of the energy-dependent transmission measurements enables us to conclude that the limiting mechanism in the MWNT suspension is a nonlinear scattering process similar to that which occurs in CBS.

In the detailed comparison between the MWNT sample and the CBS, we found that the change in the probe transmission is nearly the same for both samples to within a delay time of 1.2 ns. But at delay times greater than 1.2 ns, there is a difference between the MWNT sample and the CBS [Fig. 4(b)]. This difference is expected because the two samples have different structures and surrounding liquids.[11] We believe that the difference is a result of the different sizes of the carbon materials. The particle size of the carbon particles in the CBS is five times greater than the diameter of the MWNT's. To absorb the same amount of light energy, the smaller the size, the higher the temperature rise, which leads to stronger nonlinear absorption and scattering. Such a size effect was observed in CBS and carbon black deposited upon glass as discussed in Ref. 15. Our experiments on MWNT's with larger diameters also

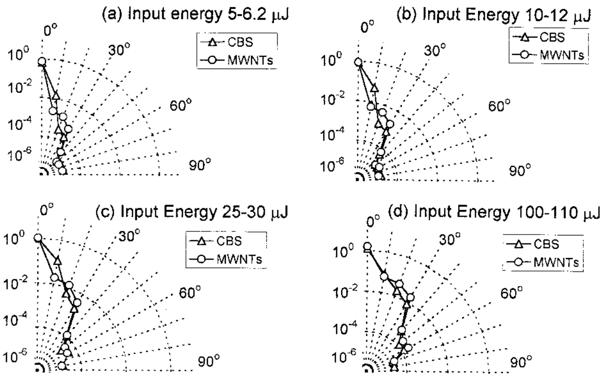


Fig. 5. Energy dependence of the scattered light in the MWNT sample and the CBS as measured with 532-nm, 7-ns laser pulses at a variety of input energies.

confirmed that they possess smaller changes in the probe transmission, although the data are not shown here.

To obtain direct evidence of the occurrence of nonlinear scattering in the MWNT sample, we measured the energy dependence of the scattered light as a function of scattering angle. Our measurements showed that the scattering behavior was symmetric about the propagation direction of the incident pulses and dominated in the forward direction. Measurements with positive angles from 0° to 80° at different input energies are presented in Fig. 5, showing that the scattered light in the CBS between angles of 10° and 40° increased significantly when the input laser energy increased. These results are consistent with previously reported findings for CBS.[14,15] The scattering behavior of the MWNT sample was similar to that seen in the CBS. This again reenforces the nonlinear scattering model for the limiting mechanism in the MWNT suspension.

5. Conclusion

In summary, we investigated the optical limiting performance and its mechanism of a novel material, carbon nanotubes, by using nanosecond and picosecond laser pulses. The energy-dependent transmission of the MWNT suspension showed strong limiting action on the nanosecond time scales but there was no limiting behavior in the picosecond regime even with an input fluence as high as 3 J/cm^2. This differs from the behavior of C_{60} but is similar to that of CBS. The pump–probe experiments indicate that it takes approximately 0.5 ns for the nonlinear transmission to take place for both the MWNT suspension and the CBS. In addition, the pump–probe experiments show that the smaller the external diameters of the MWNT suspension, the faster and larger are the changes of the transmission. To confirm that nonlinear scattering exists in the MWNT suspension, we measured the energy dependence of the scattered light and found that it is similar to that seen with CBS. Thus, all our experiments show that the limiting action in the MWNT suspension originates from a mechanism similar to that in CBS.

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