Influence of structure on the optical limiting properties of nanotubes

N. Izard

Centre Technique d'Arcueil, Délégation Générale pour l'Armement, 94114 Arcueil Cedex, France, and Groupe de Dynamique des Phases Condensées, Université Montpellier II, Montpellier 34095, France

P. Billaud and D. Riehl

Centre Technique d'Arcueil, Délégation Générale pour l'Armement, 94114 Arcueil Cedex, France

E. Anglaret

Groupe de Dynamique des Phases Condensées, Université Montpellier II, Montpellier 34095, France

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We investigate the role of carbon nanotubes structure on their optical limiting properties. Samples of different and well-characterized structural features are studied by optical limiting and pump–probe experiments. The influence of the diameter's size on the nano-object is demonstrated. Indeed, both nucleation and growth of gas bubbles are expected to be sensitive to diameter. © 2005 Optical Society of America

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Several nonlinear optical materials for optical limiting were proposed in the past 15 years; they include reverse saturable absorbers,[1] multiphoton absorbers,[2] and nonlinear scattering systems such as carbon black suspensions[3] and single-wall carbon nanotube (SWNT) suspensions.[4] Indeed, the association of materials with complementary limiting properties, i.e., nonlinear scattering from SWNTs and multiphoton absorption from organic chromophores, was recently shown to be a promising approach to achieving optical limiting systems with broad temporal and spectral ranges of efficiency.[5] The main mechanism for the optical limiting properties of carbon nanotube suspensions is now well known.[4] Heating of the nanotubes leads to formation of solvent bubbles (by heat transfer from the nanotubes to the solvent) and to sublimation of carbon nanotubes, inducing efficient nonlinear scattering of the incident laser beam. Optimization of carbon nanotube suspensions requires a better understanding of the relationship between carbon nanotube structures and the structures' optical limiting properties. Indeed, currently published data are only fragmentary[6–8]: Either the materials studied were not well characterized or the studies treated only a few samples.

In this Letter we report on the optical limiting behavior of model carbon nanotubes of various structures. Samples were purchased from Mer, Inc., from Nanoledge, and Nanolab, Inc. SWNTs were produced by the electric arc process, whereas multiwall carbon nanotube (MWNTs) were produced by chemical-vapor deposition. All samples were extensively characterized by scanning and transmission electron microscopy, x-ray diffraction, and Raman and optical spectroscopy.[9] The mean diameter of a SWNT is 1.35 ± 0.15 nm. They are assembled into crystalline hexagonal bundles with diameters of approximately 10–15 nm. We also worked on MWNT samples ofvarious lengths and diameters, as summarized in Table 1.

We obtained aqueous suspensions of nanotubes from these raw samples in water, using 1 wt. % of sodium dodecylsulfate, which we designate hereafter SWNT-Bundles and MWNT-*X*. A suspension of individual SWNTs was prepared from the suspensions of SWNT bundles, following the procedure described by O'Connel *et al.*[10] and is designated SWNT-Individual. Evidence of SWNT exfoliation was obtained by direct high-resolution transmission electron microscopy observation, fluorescence, and Raman scattering.[11] Finally, we prepared a suspension of SWNTs shortened by an oxidative treatment that we designate SWNT-Short. We verified by electron microscopy that these tubes were significantly shorter (less than 100 nm) than the unshortened tubes (>1 μm) and that the diameter of the bundle was not affected (not shown). Linear optical transmissions of the suspensions were adjusted to 70% at 532 nm in 2-mm-thick cells (the concentration was ~ 10 mg/l). Nonlinear optical transmittance measurements were performed with a *Q*-switched but noninjected frequency-doubled Nd:YAG laser with a pulse duration of 15 ns in an $f/50$ focusing geometry. Pump–probe experiments were performed with a frequency-doubled Nd:YAG pump laser emitting 4-ns pulses at 532 nm and a 633-nm continuous probe.

First we investigated the influence of nanotube

Table 1. Length and Tube Diameter Distributions for MWNT Samples

Sample	Tube Diameter (nm)	Length (μm)
MWNT-1	20–50	5–20
MWNT-2	20–50	1–5
MWNT-3	10–20	5–20
MWNT-4	10–20	1–5
MWNT-5	10–20	<1

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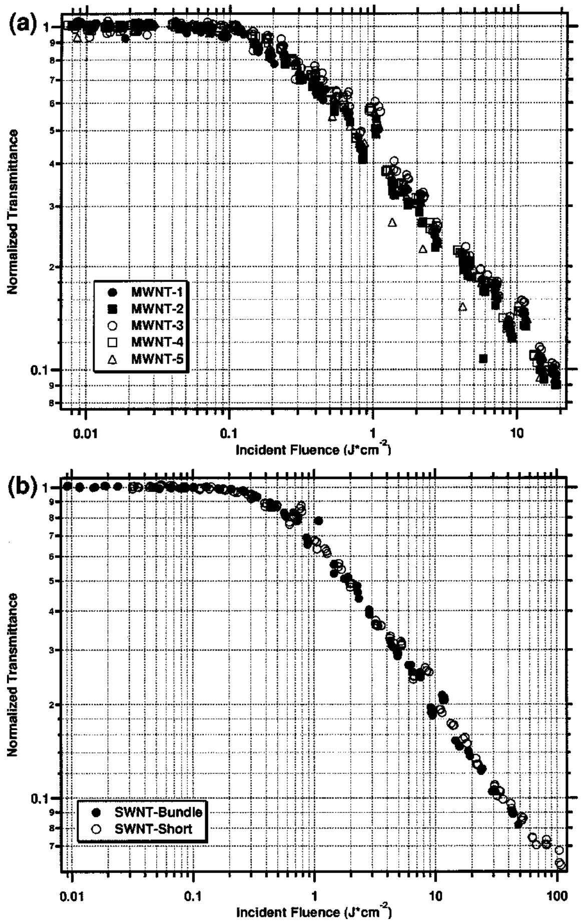

Fig. 1. Normalized transmittance measurements with 15-ns pulses at 532 nm for (a) MWNT-1–MWNT-5 suspensions and (b) SWNT-Bundle and SWNT-Short suspensions.

length. Optical limiting measurements of suspensions MWNT-1–5 are shown in Fig. 1(a). Optical limiting performance was comparable for all samples, despite the strong variation in nanotube length (there was a factor-of-5 difference between the longest and the shortest tubes). This result clearly shows that length is not a structural parameter that influences the optical limiting properties of a nanotube. No diameter influence was observed either, but here the diameter variation is small (a factor of 2 at most). The optical limiting properties of suspensions SWNT-Bundle and SWNT-Short, which contain nanotubes of the same diameter, are shown in Fig. 1(b). These data confirm the irrelevance of the length. Note that Riggs *et al.*[12] reported slightly weaker optical limiting performances for shortened nanotubes, but their data do not demonstrate a length effect: Such behavior could also be due to a slight unbundling of the nanotubes following shortening, and the lack of preprocessing and postprocessing characterization of nanotube diameter and length does not permit a choice between the two hypotheses.

We also studied the influence of diameter on nanotubes. Figure 2 shows transmittance measurements for suspensions of individual SWNTs, bundled SWNTs, and MWNTs. The diameter of a MWNT (20–50 nm) is larger than the diameter of bundled SWNTs (10–15 nm), which is larger than the diameter of an individual SWNT (1.4 nm). The optical limitation thresholds obtained with MWNTs, bundled SWNTs, and individual SWNT suspensions are approximately 100, 200, and 400 mJ cm^{-2}, respectively. The dependence of the optical limiting properties on the nano-object's diameter is thus clearly demonstrated. Better efficiency and a lower optical limiting threshold are achieved for the nano-object with the largest diameter.

To get a better insight into the effect of diameter, we carried out pump–probe experiments with SWNT suspensions in bundles [Fig. 3(a)] and individually [Fig. 3(b)]. At low fluence, 52 mJ cm^{-2} for a SWNT-Bundle suspension, the probe is not perturbated by the pump.

The fluence of 150 mJ cm^{-2} corresponds roughly to the limitation threshold: The probe is perturbed (i.e., bubbles are created) just at the end of the pump pulse. This threshold value is the limiting threshold, which is comparable to the value determined from Fig. 2, although the pulse is shorter. Finally, for higher pump energy, 540 mJ cm^{-2}, the transmission of the probe falls at the beginning of the pump pulse: The transferred energy is sufficient to sublimate nanotubes and to create bubbles that are effective for optical limiting. The behavior is dramatically different for SWNT individual suspensions. Indeed, at 150 mJ cm^{-2} the probe transmission decreases only slightly, more than 10 ns after passage of the pump beam. This means that some bubbles are nucleated inside the suspension by the pump, but they are too small to be effective for limiting. Fluence must increase to 540 mJ cm^{-2} to reach the limitation threshold. At 4500 mJ cm^{-2}, efficient optical limiting of the pump beam is observed. This value is more than eight times larger for individual tubes than for bundles.

We attribute this result to the effect of diameter on nucleation and growth of bubbles. Indeed, it is reasonable to assume that the size of the scattering center created by the nano-object is a function of the object's diameter. Consequently, individual nanotubes are expected to nucleate smaller bubbles than bundled nanotubes. This observation leads to two consequences: From the Laplace law (here given below for a sphere),

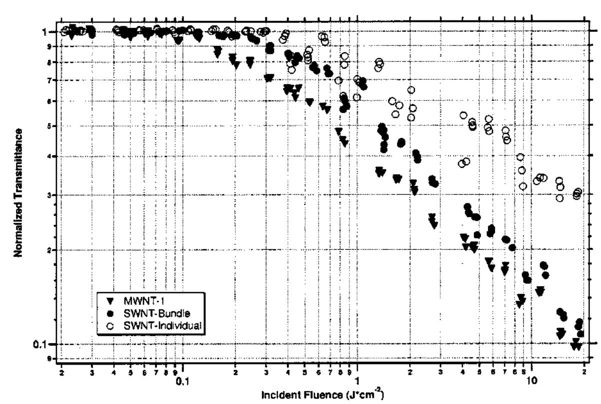

Fig. 2. Normalized transmittance measurements with 15-ns pulses at 532 nm for SWNT-Individual, SWNT-Bundle, and MWNT-1 suspensions.

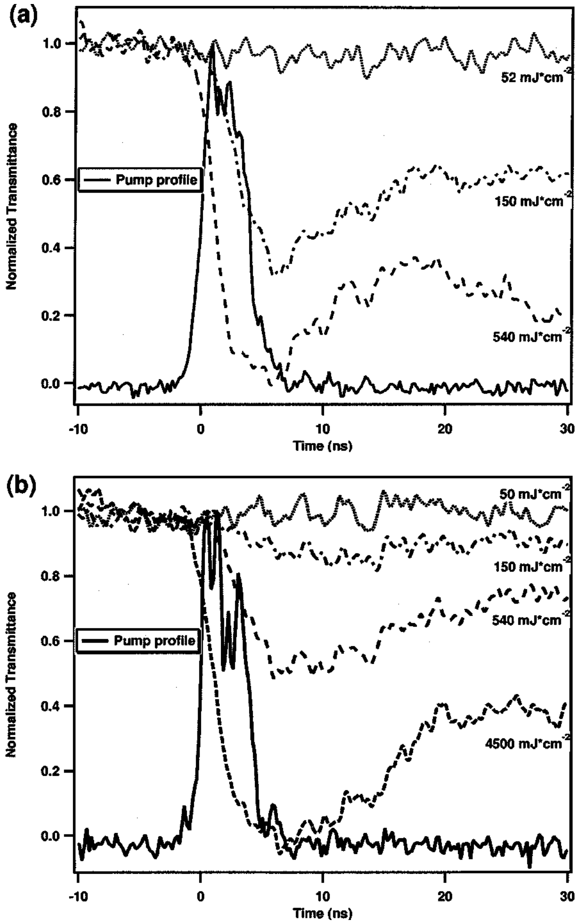

Fig. 3. Pump–probe experiments for (a) SWNT-Bundle and (b) SWNT-Individual suspensions. In each case the pump profile (532 nm, 4 ns) is represented by a solid curve and the probe profile (633 nm) is represented by dashed curves for several pump energies.

$$P_{\text{ext}} = P + (2\gamma/R), \tag{1}$$

where P is the pressure of a gas bubble, P_{ext} is the pressure of the surrounding fluid, γ is the tensile liquid–gas surface, and R is the radius of a bubble, the surpression needed to nucleate a bubble in a liquid increases when the bubble's diameter decreases. So, more energy is involved in the nucleation of bubbles in individual tube suspensions than for bundled tube suspensions; i.e., a bundled tube will create bubbles at lower incident fluence than individual tubes. Furthermore, once a bubble is nucleated, its diameter is much smaller than the laser wavelength, so bubbles will scarcely scatter the incident laser beam. They have to grow until they reach a critical (efficient for scattering) size to allow for efficient scattering of light. The time of this growth depends strongly on the liquid–gas tensile surface and other thermodynamic parameters[13] but also on the initial bubble size. Thus a small bubble will take a longer time to reach the critical size than a larger bubble. Therefore suspensions of individual nanotubes will exhibit poorer optical limiting efficiency than suspensions of bundled nanotubes.

Finally, it cannot be ruled out that nanotubes in bundles will heat faster than individual tubes, if the heat capacity for bundles is smaller than that for individual tubes or if the absorption cross section per unit of mass is larger for bundles than for individual tubes. Data on nanotube thermal properties are scarce, and no distinction has been made between tubes in bundles and individual tubes. Meanwhile, plasmons are mainly responsible for absorption in carbon nanotubes, and their properties are expected to be sensitive to the environment (including bundling). To go further in our interpretation, plasmon coupling between carbon nanotubes inside bundles may induce significant absorption enhancement.

In summary, we have reported the influence of the diameters of nanotubes on the optical limiting properties of the tubes. A twofold interpretation was proposed. First, a larger nanotube size involves a larger nucleation center and a faster growth and thus improves optical limiting efficiency. Second, the absorption cross section might be larger for bundled nanotubes, owing to changes in plasmon properties. In conclusion, increasing nanotubes' diameters will help to improve the optical limiting properties of suspensions. However, the increase in size must be limited to preserve the stability of suspensions and to prevent light scattering at low fluences.

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