Size-dependent optical limiting behavior of multi-walled carbon nanotubes

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Abstract

The size-fractionation of multi-walled carbon nanotube (MWNT) in the dimethylformamide (DMF) solution of poly(vinylidene fluoride) (PVDF) has been achieved by controlled sonication–centrifugation cycles. The Z-scan experiments and fluence-dependent transmission measurements with nanosecond laser pulses of 532 nm wavelength show that the optical limiting behavior of MWNTs in PVDF/DMF solution is size-dependent. The tubes of large aspect ratio possess stronger limiting properties. The size-dependent effect is more obvious at low input fluence than at high input fluence.

1. Introduction

Optical limiting is an important property of carbon nanotubes. This property has been observed in various forms of carbon nanotubes, including single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) suspended in liquids or embedded in a solid-state matrix, and SWNTs or MWNTs stabilized by surfactants (or polymers) in solutions [1–10]. The mechanism responsible for such limiting behavior is generally attributed to nonlinear scattering arising from absorption-induced microplasmas or/and bubble formation in surrounding liquids, similar to those in carbon black suspension (CBS) [1]. It was found that the strength of limiting effects in carbon nanotubes depends on many factors. For example, host materials such as liquids [4,5] or solid-state matrix [1] play an important role in the limiting effects. The study of optical limiting properties of fullerene derivatives shows that viscosity may also be a contributing factor [11].

Recently, Riggs et al. [8] reported a study on the optical limiting behavior of normal-length SWNT and shortened SWNT suspensions. They observed that the limiting performance of shortened SWNTs is weaker than that of normal-length SWNTs. Although they measured the limiting effect of shortened MWNTs, they did not compare the limiting effects of MWNTs with different length or radius.

In this study, we report the size-dependent limiting properties of MWNTs in poly(vinylidene fluoride) (PVDF)/dimethylformamide (DMF)
solution. The size-fractionation of MWNTs in PVDF/DMF solution is achieved by controlled sonication–centrifugation cycles. The Z-scan experiments and fluence-dependent transmission measurements with nanosecond laser pulses of 532 nm wavelength show that the optical limiting behavior of MWNTs in PVDF/DMF solution is size-dependent, and the tubes with larger aspect ratios possess stronger limiting properties. This size-dependent effect is more obvious at low input fluence than at high input fluence. The possible mechanism is discussed.

2. Experimental

PVDF (weight-average molecular weight $M_w = 534000$) was purchased from Aldrich and used without further purification. MWNTs were synthesized by arc-discharge method and dried in 80 °C oven overnight. PVDF (0.083 g) and MWNTs (0.15 g, raw material) were dispersed in DMF (35 ml) and sonicated for 2 h. The suspension of MWNT/PVDF in DMF was then centrifuged at 3500 rpm for 10 min. PVDF/DMF solution (same concentration as in the previous step) was added to the above sediment and sonicated again. This procedure was repeated three times to extract most carbon nanotubes from the raw materials. The combined supernatant solution was centrifuged at 7000 rpm for 20 min, producing a MWNT/PVDF/DMF solution (Sample 2) and a sediment. The sediment was sonicated again in the PVDF/DMF solution to produce a stable suspension, labeled as Sample 1. Sample 2 is stable for several months, while Sample 1 remains stable for over one week.

To observe the surface modifying effect of PVDF, TEM (JEOL CX100, 100 kV) and SEM (Philips XL 30) measurements were carried out. A drop of Sample 1 or 2 was placed on the carbon-coated grid for TEM observation. The solution was also placed and evaporated on a small piece of clean silicon wafer for SEM study.

The optical limiting properties of the MWNT/PVDF solutions were investigated by both Z-scan technique and fluence-dependent transmittance measurement. The pulsed radiation of 532 nm wavelength was provided by a frequency-doubled Q-switched Nd:YAG laser. The pulse duration was determined to be $7 \pm 1$ ns (full width at half-maximum) using a photodetector and a Tektronix 7104 oscilloscope. The spatial profile of the pulses was of nearly Gaussian form after employing a spatial filter. The laser pulses were then focused by a focusing mirror with the beam waist of 45 μm at the focal point. In the Z-scan experiment, the sample was moved in the propagation direction of the laser pulses, while the sample was fixed at the focal point in the fluence-dependent transmittance measurement.

3. Results and discussion

3.1. Size-fractionation of MWNTs

We have recently found that PVDF assists in the dispersion of MWNTs in DMF [12], and thus it can facilitate the size-fractionation of MWNTs. Ultracentrifuge is a useful tool for the study of lyophilic colloids and particularly in the study of proteins. Using band sedimentation or boundary sedimentation techniques, viruses with different molecular weight can be separated [13]. The choice of a proper centrifugation speed is critical in size-fractionation. Many factors such as the viscosity of medium, the size, shape and charge of particles, and the centrifugation force influence the sedimentation velocity of particles in a colloid system [13]. Centrifugation was also employed in the size-separation of graphite particles in sodium dodecylsulfate (SDS) solution [14]. It was found that centrifugation at 5000 rpm can remove all graphite particles larger than 500 nm. We found that by centrifugation at 3500 rpm for 10 min, both longer and shorter tubes can be extracted to solution from raw materials, and thus separated from very large tubes and heavy graphite debris as sediment. An additional centrifugation at 7000 rpm for 20 min of the supernatant solution further separate those tubes according to their aspect ratios. The tubes with smaller aspect ratios are stable upon centrifugation at 7000 rpm and remain in the supernatant (Sample 2), whereas the tubes with larger aspect ratios form sediment. This sediment can
be dispersed in PVDF/DMF solution by sonication to produce a meta-stable colloidal system (Sample 1). The aspect ratios for Sample 1 and Sample 2 are around 80 and 30, respectively, as shown in Figs. 1a,b.

Based on five TEM micrographs, the distributions of MWNTs with different aspect ratio in the two samples are summarized in Table 1. For Sample 1, over 60% of the tubes have aspect ratios over 50. On the other hand, the aspect ratios of the tubes in Sample 2 are smaller, with over 80% of the tubes having aspect ratios smaller than 50.

Bonard et al. [14] also demonstrated size selection of MWNTs by centrifugation and filtration. SDS was the stabilizer for carbon nanotubes. They investigated the size-dependent flocculation of droplets in colloidal system. Flocculation was observed when the SDS concentration was 12 times of the critical micelle concentration (cmc) value. The materials remaining in suspension consist of nanoparticles with a few short tubes (<600 nm). This sample was then subjected to two sedimentation runs with the SDS concentration reduced to eight times of cmc and then to six times of cmc. The observed average tube lengths are 1.1 μm (in 8 cmc suspension), 1.3 μm (in 6 cmc suspension) and 1.7 μm (+0.3 μm) (in 6 cmc sediment). The tubes obtained from the suspensions of 8 and 6 cmc are similar to our Sample 1 (using an estimated tube diameter of 25 nm, the aspect ratios of Bonard’s tubes are about 50–70). The 12 cmc sample is similar to our Sample 2. However, the size-separation mechanism in these two cases is different. The separation of their experiment is based on size-dependent flocculation of droplets in emulsions.

### 3.2. Optical limiting properties

The separation of nanotubes based on aspect ratio enabled us to study the size-dependent optical limiting properties of MWNTs. It should be pointed out that the tubes in our samples are similar to those MWNT suspensions in term of their structure because PVDF is nonactive to carbon nanotubes. However, Riggs’ samples contain some functional groups on the surface or tips of the shortened SWNTs and MWNTs [8].

The limiting properties of the two samples were investigated. Fig. 2 shows the Z-scan (open aperture) results of Sample 1 and Sample 2 under different input fluences. The two samples show different limiting performances under low input fluences (<1.2 J/cm²), with the limiting properties of Sample 1 better than those of Sample 2. This difference in the limiting behavior decreases with increasing input fluence. At 4 J/cm², the behavior of both samples is nearly the same.

In addition, a CBS was also studied for comparison purpose. The CBS was the soot during
arc-discharge and was suspended in the same PVDF/DMF solution. The Z-scan (open aperture) data of the three samples are shown in Fig. 3. Sample 1 gives the strongest limiting effect, whereas CBS is slightly weaker and Sample 2 is the weakest. Fig. 4 shows the optical limiting results for the three samples. Similarly to the Z-scan results, Sample 1 shows a stronger limiting response than Sample 2, while CBS is similar to Sample 1. We also conducted the same experiments on PVDF/DMF solution and found no limiting effect. Therefore the observed limiting effect in the MWNT/PVDF/DMF solutions represents the intrinsic property of carbon nanotubes.

All our experiments demonstrate that Sample 1 shows a stronger limiting effect than Sample 2 at low fluences (<1 J/cm²). This indicates that longer tubes (or tubes of smaller radius) have a stronger limiting effect than the shorter tubes (or tubes of larger radius), similar to Riggs’ report [8]. This is also consistent with the nonlinear scattering model as discussed in the following. The light absorption
by carbon nanotubes induces a very high temperature rise in the tubes, which leads to the formation of microsized plasmas. The formation and rapid expansion of these microplasmas in turn give rise to increases in the absorption and scattering, and hence optical limiting occurs. For shorter tubes or tubes of larger radius, there is less bundling of the tubes and hence less scattering, which results in a weaker scattering. At higher fluences (>1 J/cm²), the heat in the microplasmas is quickly transferred to the surrounding liquid and form bubbles. We believe that the scattering of these bubbles in the surrounding liquid dominates the limiting behavior, which leads to a similar limiting performance, regardless the size of the tubes anymore.

We also investigated the photostability of Sample 1 and Sample 2. At room temperature and exposure to normal daylight, Sample 2 is more stable than Sample 1 due to their smaller size. We observed that there was no change in color and linear transmittance of Sample 2 for more than 3 months. However, Sample 2 became unstable after exposure to several hundreds of the laser pulses as shown by the appearance of flocculation, while Sample 1 showed no change compared to a fresh solution which was not exposed to laser radiation. A similar phenomenon was also reported by Francois et al. [15], who studied optical limiting induced by nonlinear scattering in gold particles. They observed that for larger gold particles, there was a loss of limiting efficiency for the first few pulses, but after 20 pulses the sample’s response became stable and the limiting effect was constant (two times lower than for the first pulse). On the contrary, the limiting response of smaller particles was completely degraded after 10 pulses, and the sample was even slightly bleached. They attributed it to fragmentation of the particles under the laser fluence. The fragmentation is more efficient for smaller particles than for larger particles. We believe that a similar fragmentation occurs in our tubes.

It should be noted that the limiting mechanisms in both carbon nanotubes and gold nanoparticles are the same, assuming to be a nonlinear scattering process. In the gold particle case, Francois et al. [15] reported that gold clusters of 2.5 nm radius were unable to limit light transmission even at very high fluence of nanosecond laser pulses, while gold clusters of 15 nm radius can produce limiting performance at fluences of 0.1 J/cm² or higher. This is consistent with our study in MWNTs and Riggs’ results in SWNTs [5], in which large-size tubes (or long tubes) possess stronger limiting effects. All these experimental evidences show that good optical limiting induced by nonlinear scat-
tering can be achieved by using scattering centers of relatively large sizes. In spherical structures such as carbon particles (CBS) and gold particles, the radius should be ranged between 10 and 100 nm, and in carbon nanotube structures, the aspect ratio should be greater than 50.

In conclusion, we have shown that MWNTs with large aspect ratio in PVDF/DMF solution possess stronger optical limiting properties and are more stable to nanosecond pulsed laser radiation.

References