Optical limiting properties of suspensions of singlewall carbon nanotubes

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Abstract: Suspensions of single wall carbon nanotubes are good candidates for optical limiting. We compare their performances with those of other carbonaceous materials. Z-scan and pump-probe experiments are used to identify and investigate nonlinear scattering as the main origin of optical limiting. In suspensions of SWNT, non linear scattering is due both to heat transfer from particles to solvent, leading to solvent bubble formation, and to sublimation of carbon nanotubes.

INTRODUCTION

The development of high power laser sources has motivated extensive research for the design of auto-activated, so-called optical limiting, systems for eye and sensor protection [1-13]. Optical limiting can be due to several different non linear light-matter interactions, especially nonlinear absorption, refraction and scattering. Non linear absorption leads to optical limiting via reverse saturable absorbption (RSA) [1] or via multi-photon absorption (MPA) [2]. The best materials for RSA are molecules of the phtalocyanines, naphtalocyanines or fullerene families. MPA is observed in some solid semiconductors (GaAs, ZnSe…) or in some organic dyes. Non linear refraction can be due to thermal effects, *i.e.* dilatation of the solvent [3] or to optical Kerr effet (CS_2) [4]. Finally, non linear scattering is observed when a laser beam induces an index mismatch in a biphasic media [5], or a growth of gazeous scattering centers due to heating of absorbing particles [6]. This latter effect is the dominating effect for metallic nanoparticles or carbon black suspensions (CBS). The optical limiting properties of suspensions of carbon nanotubes were demonstrated and investigated since 1998 [7-13]. In this paper, we compare the performances of singlewall carbon nanotube suspensions (SWNT) and other carbonaceous materials. From Z-scan and pump-probe studies of SWNT, we show that nonlinear scattering is responsible for limiting and we discuss the thermodynamical origins of the phenomenon. Finally, we discuss possible routes for improving the optical limiting performances of SWNTS and we show that nanotubes are among the best candidates for efficient protection over broad spectral and temporal ranges.

EXPERIMENTAL

SWNT were prepared by the electric arc discharge and purified in a three-steps procedure [10]. From scanning electron microscopic measurements, we estimate that this purified material contains about 90 vol% of SWNT. Nanotubes suspensions were prepared in water with the help of a surfactant (Triton X100) or in chloroform. The linear transmittance was adjusted to be close to 70%.

The optical limiting curves were measured in a f/30 focusing geometry using a Q-switched Nd:YAG laser generating 5 ns pulses at 532 or 1064 nm and a Titanium:Sapphite laser generating 80 ns pulses at 1000 nm. Pump-probe experiments were carried out using the Nd:YAG laser as the pump beam and the 632.8 nm line of a continuous He-Ne laser as the probe beam.

RESULTS AND DISCUSSION

As underlined above, many carbonaceous materials exhibit optical limiting. Figure 1 compares the performances of C_{60}, C_{70} (in toluene solutions), CBS (in water/surfactant suspensions), multi-wall carbon nanotubes (MWNT) prepared byt he electric arc and SWNT (in water/surfactant suspensions). Both MWNT and SWNT appear to be competitive with respect to other limiters. Below, we will focus only on SWNT. We will especially discuss how their performances can be improved in the future. In this section, we first address the origin of optical limiting in suspensions of SWNT.

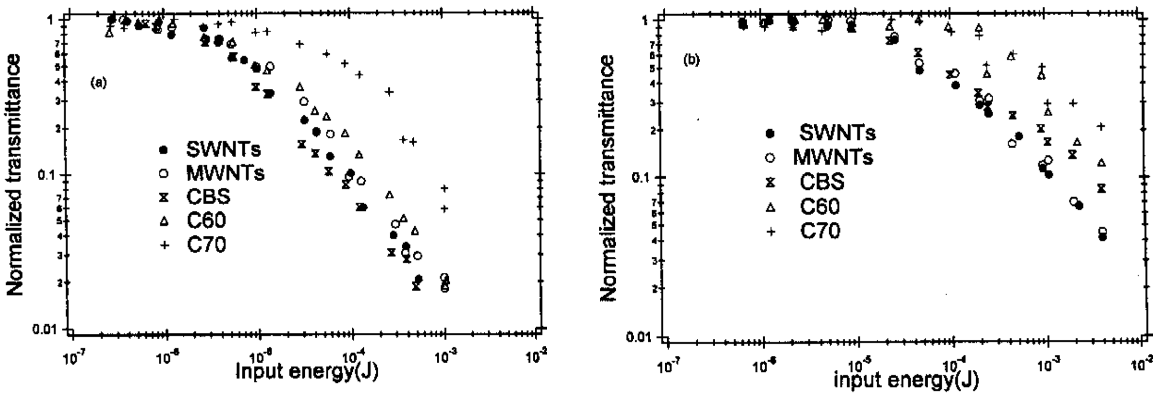

FIGURE 1 : Comparison of optical limiting by solutions of fullerenes in toluene, CBS and suspensions of MWNT or SWNT, for 5 ns pulses, at 532 nm (left) and 1064 nm (right).

First, z-scan experiments were used to identify the phenomenon responsible of limiting in SWNT. In both water and chlorofom, for nanosecond pulses, one observes the signature of an auto-defocalisation effect as well as a very strong non linear scattering [8-9]. The auto-defocalisation effect is associated with a negative nonlinear index, characteristic of a thermal effect related to a heat-induced dilatation of the solvent. A detailed study of the dominating non linear scattering contribution was achieved with the help of pump-probe experiments [10-11]. In such experiments, the non linear effect is excited by a pulsed laser "pump" and studied by measuring the transmittance of a continuous laser "probe". Typical results are presented in figure 2 for 5 ns pump pulses. At low input fluences, the perturbation of the probe beam occurs a few nanoseconds after the pump pulse, both in water (fig. 2a and 2c) and in chlorofom (fig. 2b and 2d), for pump beams at 1064 nm (fig. 2a and 2b) and 532 nm (fig. 2c and 2d). Such a slow process rules out any non linear absorption phenomenon. When the input fluence increases, the perturbation of the probe beam shifts towards small timescales and develops much faster. The optical limiting threshold corresponds roughly to a loss of transmittance of the probe at the top of the pump pulse. This suggests that two different mechanisms are responsible for the probe perturbation. We assign the first (slow) mechanism to the formation of solvent vapor bubbles due to heat transfer from the nanotubes to the surrounding liquid. The second (fast) mechanism occurs at much larger input fluences. We assign it to the sublimation of the nanotubes themselves leading to the formation of carbon vapor bubbles. The thresholds for both mechanisms are much smaller for chloroform than for water. This can be understood easily by considering the thermodynamic properties of the solvents : the heat conductivity, calorific capacity, boiling point and vaporisation energy of chloroform are all much smaller than those of water, which makes much easy both its heating and vaporization. One can also underline that the threshold for mechanism 1 is much smaller for SWNT than for CBS. This may be due to a better heat conductivity of the former and also possibly to a larger specific area. This makes SWNT good candidates for optical limiting for longer pulses. As a matter of fact, we checked that the limiting performances of SWNT suspensions were much better for 80 ns pulses.

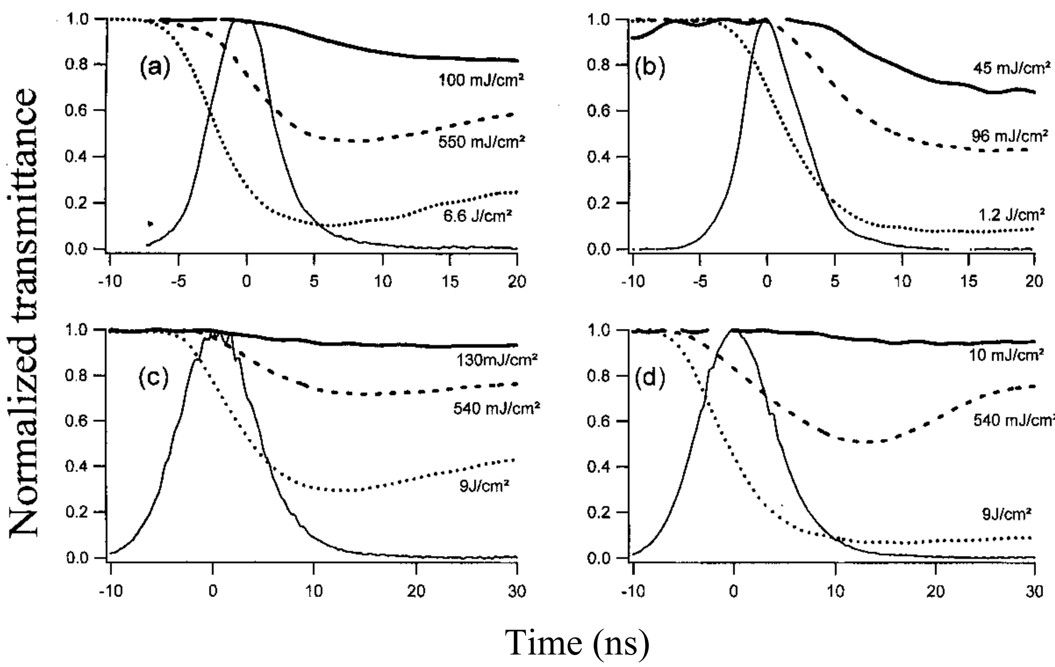

FIGURE 2 : Pump-probe results for SWNT suspensions in water (left) and in chloroform (right), for 5 ns pulses at 1064 nm (top) and 532 nm (bottom). The peak in solid line corresponds to the pump pulse.

Figure 3 compares typical limiting curves for pulses of 5 and 80 ns, for water and chloroform suspensions. The limiting threshold is significantly smaller at 80 ns for water and much smaller for chloroform. In addition, one can distinguish two regimes of limiting for long pulses and only a single one for short pulses (indicated by straight lines in figure 3). We assign the first regime to scattering by solvent vapor bubbles and the second one to scattering by both solvent and carbon bubbles. As stated by the pump-probe measurements, only this second mechanism can be effective for short pulses. The optical limiting performances were measured for various wavelengths (from 430 nm to 1064 nm) and pulse durations (from 2 ns to 100 ns) [11]. Limiting is effective all over these broad ranges, with better performances for shorter wavelengths, as expected for a scattering process.

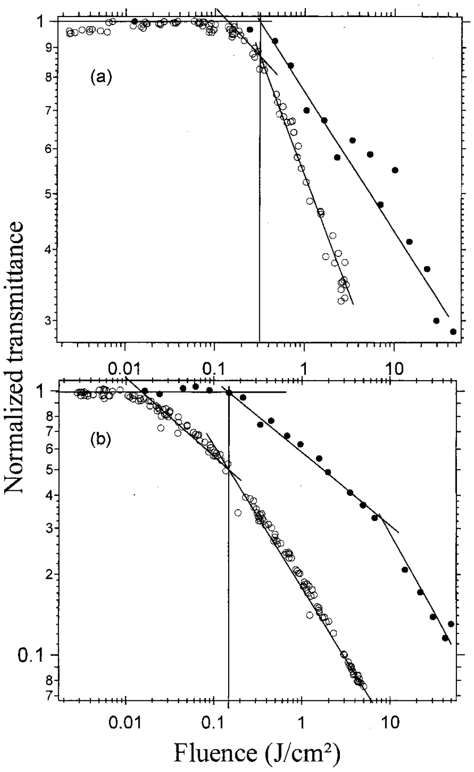

FIGURE 3 : Comparison of optical limiting by suspensions of SWNT, for 5 ns pulses at 1064 nm (full circles) and 80 ns pulses at 1000 nm (open circles) for SWNT suspensions in water (top) and in chloroform (bottom).

CONCLUSIONS AND PERSPECTIVES

Carbon nanotubes are broadband optical limiters from visible to near infrared and for pulse durations from a few nanoseconds. Limiting is due to a strong nonlinear scattering, due to formation of solvent and carbon bubbles. The performances strongly depend on the thermodynamical properties of the solvent and possibly on the structure/specific area of tubes and bundles. In the future, the availability of nanotubes of different structure [13] and the development of chemical modifications through functionalization will probably open many routes to improve the performances of SWNT-based limiters.

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