Optical limiting behavior of nano-gold self-assembled multi-wall carbon nanotube

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The optical limiting behaviors of nano-gold self-assembled multi-wall carbon nanotube (MWNT) were experimentally investigated at 532 and 1064 nm, respectively. The comparison of the limiting performances between carbon nanotube suspension, C_{60} solution, and carbon black suspension (CBS) was performed. The results show that the optical limiting characteristic of nano-gold self-assembled MWNT is better than those of C_{60} and CBS. The mechanisms of the optical limiting for the samples were discussed.

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Recently, the materials with strong optical limiting characteristic have been paid more attention[1−7] since laser source has become an increasing threat in battle field. The optical limiting became an essential measure to protect human eyes and detectors against intense laser radiation, which requires high linear transmittance in weak incident fluence and low transmittance at intense fluence of light. Because of its unique electric and mechanical properties and potential applications, carbon nanotube has become one of the hotspots of research. Meanwhile, the carbon nanotube is a good candidate in optical limiting materials. For the pure multi-wall carbon nanotube (MWNT) and single-wall carbon nanotube (SWNT), their limiting performances have been investigated[2−5]. Heretofore, there are a lot of investigations on limiting performance of C_{60} and other fullerene derivatives, including their limiting origins. The accepted optical limiting of C_{60} originates from reverse saturable absorption. It predicates that the absorption cross section of the excited states is larger than that of the ground state under intense incident light field. The optical limiting of carbon nanotube (whether MWNT or SWNT) is very different from that of C_{60}. It is similar to that of carbon black suspension (CBS), the nonlinear scattering due to micro-bubble generation and plasma formation[5]. The nonlinear scattering of CBS is considered that micro-particles in CBS are heated after absorption of the intense laser radiation, which leads to avalanche ionization and microplasmas formation.

Optical nonlinearity of metal nano-particles is attracting more attention[8,9]. Generally, their nonlinerities are quite different from that of bulk materials because of quantum size effect and surface plasmon resonant influence. The optical limiting of nano-gold particles is believed that the laser radiation interacts with nano-gold particles, which results in resonant absorption and formation of surface plasmon, then produces surface plasmon resonant scattering[10]. Self-assembled materials show wide promise in applications. In this letter we prefabricated the nano-gold MWNTs, and investigated its optical limiting performances.

The MWNTs were produced by chemical vapor deposition (CVD)[11], treated with HCl and HNO_3 in turn during the purification process. Gold nano-particles were prepared according to the Ref. [12]. The MWNTs were placed into the (3-Aminopropyl) trimethoxysilane solution for 30 minutes and rinsed with water, then the MWNTs were placed into the gold colloid solution. Thus the nano-gold MWNT composite was successfully prepared. The transmission electron microscope (TEM) images of the nano-gold MWNT are shown in Fig. 1.

The optical limiting behaviors for a novel nanoparticles, MWNTs decorated by nano-gold particles, are investigated. The linear absorption of the nano-gold MWNTs' suspension was measured by a spectrophotonmeter (UV-3101PC, SHIMADZU Corp.), as shown in Fig. 2. There is a strong absorption of sample suspension in ethanol below 300 nm. The linear transmittances of nano-gold MWNTs suspension are 68% at 532 nm, and 70% at 1064 nm, respectively. For comparison, a solution of C_{60} in toluene and a suspension of CBS in ethanol at same transmission in rough were measured in the experiment.

Nonlinear optical limiting was made by nonlinear transmission method[13]. The experimental setup consists of a Nd:YAG laser with injection seeder (model PL8000, Continuum Corp.) with pulse width of 5 ns at 532 nm and

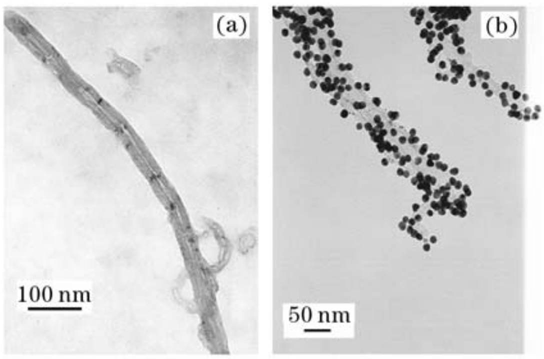

Fig. 1. The TEM photos of the MWNTs (a) and the MWNTs which have absorbed gold nano-particles (b).

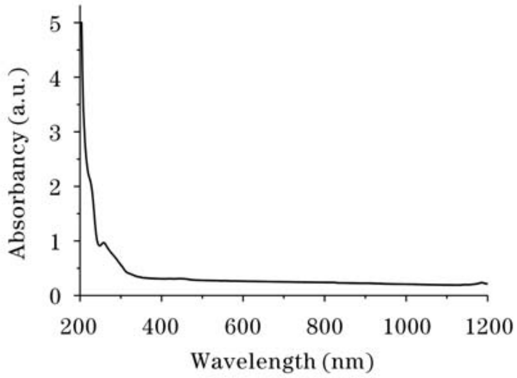

Fig. 2. The linear optical absorption spectrum of nano-gold MWNTs in ethanol.

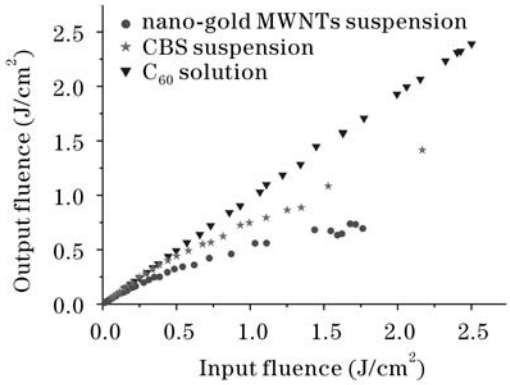

Fig. 4. The output fluence as a function of the input fluence at 1064 nm with the pulse width of 8 ns.

8 ns at 1064 nm, respectively, the repetition rate is 10 Hz. The energy detectors were made by Newport Corp., the 1-mm-thick sample was placed in quartz cell. Optical system with $f/57$ focuses the laser beam on the sample. Measured data from transmitting and reference beams were acquired by a digital meter, and then sent to a computer via general purpose interface bus (GPIB bus). The whole experiment was controlled in the program, and the data acquisition was obtained by a computer.

Figures 3 and 4 show the results measured at 532 and 1064 nm in experiment, respectively. For quantitative description of the optical limiting behavior, we used a thresholed so-called "optical limiting threshold", which was

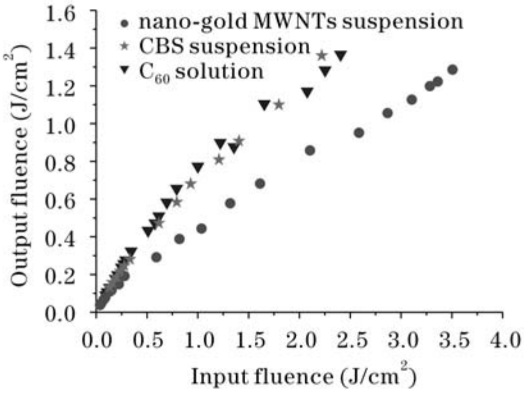

Fig. 3. The output fluence as a function of the input fluence at 532 nm with the pulse width of 5 ns.

defined as the input energy fluence when linear transmittance fell a half[5].

The nonlinear scattering of nano-gold MWNTs starts from the fluence of 0.022 J/cm^2 at 1064 nm, much less than that of CBS, its nonlinear optical limiting threshold was one time less than that of CBS. For the results at 532 nm, the differences between their nonlinear behaviors were more obvious. The nonlinear scattering of the nano-gold MWNTs starts at less than 0.038 J/cm^2 at 532 nm, which is much less than those of CBS and C_{60}, while the nonlinear limiting threshold of the nano-gold MWNTs is as 50% of CBS and 25% of C_{60}, respectively. The results showed that the optical limiting behaviors of the nano-gold MWNTs were better than those of CBS and C_{60}. Meanwhile, the nonlinear absorption of C_{60} disappeared at 1064 nm, which was consistent with the published result[4]. This also validates that the nonlinear absorption of C_{60} differs from other samples in the limiting mechanism. The limiting results also showed that the optical limiting behavior of nano-gold MWNTs was better than that of pure MWNTs[4,5]. Pure MWNTs are usually of no absorption at 532 and 1064 nm, but the surface plasmon absorption is related to the wavelength. The nano-gold particles absorption peaks are just located above 450 nm. The number and intensity of the peaks depend on the aspect ratio of the nano-gold particles[10]. The result indicates that the nano-gold particles also contribute to

Table 1. Nonlinear Thresholds (F_{th}) of Different Samples Measured with Nanosecond Laser Pulses

λ (nm)	Samples	Nonlinear Scattering/Absorption Starting Value (J/cm^2)	F_{th} (J/cm^2)	Solvent
532	Nano-Gold MWNTs	< 0.038	0.28	Ethanol
	CBS	0.16	0.48	Ethanol
	C_{60}	0.13	0.88	Toluene
	Pure MWNT[4,5]	0.06	1	Ethanol
1064	Nano-Gold MWNTs	0.022	0.37	Ethanol
	CBS	0.244	0.63	Ethanol
	C_{60}	—	—	Toluene
	Pure MWNT[4,5]	1.0	13	Ethanol

the optical limiting. This is the reason why the limiting behavior of nano-gold MWNTs differs highly from that of pure MWNTs[4,5]. The limiting performance of nano-gold MWNTs is considered that its optical scattering comes from the corporate interactions of nonlinear scattering of MWNT and the influence of surface plasmon of nano-gold particles. The limiting property of nano-gold MWNTs is better than that of CBS in that the former has a larger special surface-volume ratio. The nonlinear thresholds of different samples are listed in Table 1 for comparison.

From the above results, it is clear that the optical limiting performance of nano-gold MWNTs at 532 nm is much better than that at 1064 nm.

The bubble formation from the nano-gold MWNTs suspension was also observed when the incident laser radiation was beyond some threshold value in the experiment, which will be discussed elsewhere.

In summary, the optical limiting behaviors of nano-gold MWNTs was investigated with nanosecond laser pulse via nonlinear transmission method at 532 and 1064 nm, respectively. The optical limiting performances of nano-gold MWNTs, CBS, and C_{60} were compared. It was found that the optical limiting properties depend on the input fluence. The limiting characteristics of the nano-gold particles MWNTs are better than those of pure MWNTs, C_{60}, and CBS. The experimental results show that nano-gold MWNT is a good candidate for the wide-band optical limiting material.

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