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Letter

Transparent multi-walled carbon nanotube–silica composite prepared by hot-pressed sintering and its nonlinear optical properties

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ABSTRACT

Transparent multi-walled carbon nanotube (MWNT)-fused silica bulk composites were prepared by the hot-pressing technique. The results of transmission electron microscopy (TEM) proved that MWNTs were relatively well dispersed in the fused silica matrix. The linear transmittance of the composites reached 70% in the visible light region and about 76% near 1100 nm. The *z*-scan method was used to investigate the nonlinear optical properties of the composites, which exhibited optical limiting properties at 800 nm at the incident power of 30 mW and 50 mW. The main mechanism of the optical limiting performances of the composites was deduced to be nonlinear absorption. The composites may be a good candidate for optical limiting application.

1. Introduction

Nowadays, laser sources are widely used in the fields of industry, medicine, biology and military. The development of laser has brought us many benefits; however, it has also brought potential hazards for human eyes and optical sensors. Therefore, increasing interests have been inspired in preparing materials with strong optical limiting properties. This kind of material can effectively attenuate intense laser beam and possesses high transmittance of low-intensity ambient light. So, it can not only protect human eyes and optical sensors from the high energy laser beam, but also make sure the reception of normal signals. Different kinds of materials such as fullerenes [1,2], organometallics [3,4], carbon black suspensions (CBS) [5,6], semiconductors and liquid crystals, have been investigated and selected as candidates for good optical limiters in the visible domain for short laser pulse.

Carbon nanotubes (CNTs) have been the focus of extensive physical studies concerning their fascinating electronic, mechanical and other properties [7,8]. Moreover, theoretical calculations [9] have shown that CNTs with large second hyperpolarizabilities γ (also called third-order optical nonlinear coefficient) correlate with the high optical limiting properties. Furthermore, many researchers have observed strong and broad-band optical limiting in single-walled and multi-walled nanotube suspensions [10,11] or solutions [12,13], as well as in organic films [11]. For example, Wang et al. [14] have investigated the optical limiting performances of the aqueous dispersions of multi-walled carbon nanotubols and [C60] fullerols using the *z*-scan measurements at 532. All the carbon nanotube materials, especially multi-walled carbon nanotubols, showed much better optical limiting performances than [C60] fullerols and C60. But most of these investigations were carried out in suspensions or solutions, which brought many difficulties in practical use. Zhan et al. [15,16] prepared MWNT–silica xerogel composite and found its optical limiting properties were better than those of MWNT suspension. However, this xerogel without sintering lacked strength and stability for practical use. Furthermore, it required a long aging procedure of 2 months. Considering the above reasons, it is urgent and also interesting to prepare CNT-ceramic bulk material with improved strength and stability for optical limiter.

An ideal optical limiter should have broad-band optical limiting efficiency over the whole visible spectrum. On the other hand, it should also possess high linear transmittance at low incident energy and neutral colorimetry, to ensure the acceptance of signals for eyes and optical sensors. Silica (SiO_2) is a widely used optical material, which has a high transmittance (more than 90%) and environmental stability (such as resistance to creep, excessive hardness and anti-abrasion properties, high resistance to oxidation and chemical attack). So it is suitable for the matrix of optical limiter. In addition, SiO_2 composites with varied contents of CNTs have been prepared successfully and the composites possess improved

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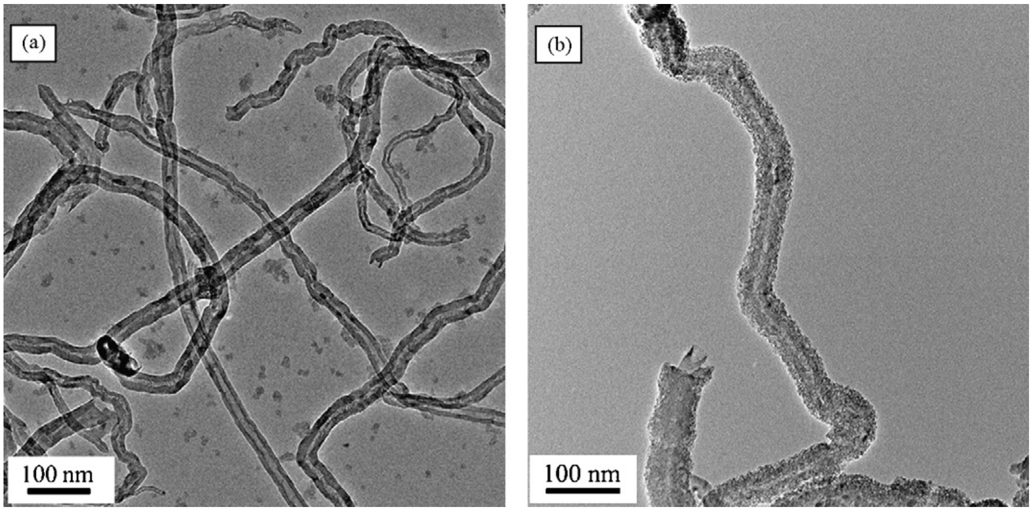

Fig. 1. TEM images of (a) pristine MWNTs and (b) MWNTs coated with SiO_2.

mechanical properties [17,18] and excellent microwave attenuation properties [19]. But to the best of our knowledge, there is still no report about the optical limiting properties of the CNT/SiO_2 composite prepared by hot-pressed sintering.

In this paper, we described the preparation of MWNT/SiO_2 powder and the hot-pressing process of the bulk MWNT/SiO_2 composite, and then discussed the microstructures and optical limiting properties.

2. Experimental procedures

MWNTs with diameters from 20 nm to 40 nm and lengths from 5 μm to 15 μm were provided by Shenzhen NANO Tech. Port. Co. Ltd. of China. In order to achieve better performance of the composite, the received MWNTs were coated with SiO_2 by a sol–gel method as described in Ref. [20]. The modified MWNTs were marked as SiO_2@MWNT. Pure SiO_2 powder was prepared by a rapid sol–gel method. The molar ratio of tetraethyl orthosilicate (TEOS):ethanol:distilled water in the precursor was 1:4:8. The hot-pressed sintering technique was used to obtain bulk material.

The experiments were conducted as follows. The SiO_2@MWNT and the pure SiO_2 powder prepared previously were mixed according to the designed ratio. Then the mixture was ball-milled with absolute alcohol for 12 h, and using agate balls as the grinding media. After been dried and sieved through a screen, the MWNT/SiO_2 powder with a MWNT content of 0.02 wt% was obtained. Finally, the MWNT/SiO_2 powder was added into a graphite die and hot-pressed at 1250 °C under an applied stress of 30 MPa in N_2 atmosphere for 0.5 h. The sintered composites were cut into 30 mm × 20 mm × 0.1 mm, and both sides of the composites were polished to fit for the transmittance and optical limiting properties tests.

Transmission electron microscopy (TEM) (JEOL JEM 2100F FETEM) was used to observe the microstructures of SiO_2@ MWNT powder and the bulk composites. The transmittance test was carried out on a Model U-2800 Spectrophotometer, Hitachi, Japan. The *z*-scan experimental setup was based on a Spectra-Physics mode-locked Ti:sapphire laser which produces laser pulses of about 100 fs duration with 82 MHz repetition rate at 800 nm wavelength. The measurements were performed using TZ-scan [21,22] techniques with a 10 cm focal-length objective lens and the beam waist radius at the focus was about 10 μm.

3. Results and discussion

MWNT/SiO_2 composite, which combines MWNT and transparent silica matrix, is expected to have excellent broad-band optical limiting properties. The critical challenge, however, is how to enhance the dispersion and alignment of MWNTs in the matrix. Therefore, it is necessary to coat MWNT with silica, which could eliminate the undesirable attractive interactions between the nanotubes and improve the interfacial bonding with matrix [20]. Fig. 1 shows the TEM images of the MWNTs without modifying and the MWNTs coated with SiO_2. The pristine MWNTs are curved and twisted with each other (Fig. 1(a)). After coating process, MWNTs have been coated with a uniform SiO_2 layer about 5–10 nm (Fig. 1(b)), which is confirmed as amorphous in the XRD analysis (not shown).

In an ideal optical limiter, the linear transmittance at low incident energy must be reasonable, at least of 70% [23]. Fused SiO_2 has high linear transmittance, but many researches show that, crystallization in fused SiO_2 will ruin the transparency and other properties. SiO_2 powders obtained from melted quartz may retain some crystalline structures as nucleation centers, which is beneficial for crystallization. So it is unsuitable for the preparation of the transparent material. The number of the O–H groups in sol–gel SiO_2 powders is greater than that of in SiO_2 powders obtained by other methods. The O–H groups could effectively depress the crystallization of SiO_2 during the hot-pressed sintering [24], and then benefit of the high linear transmittance of the material. Furthermore, the diameters of the sol–gel SiO_2 powders are around nanometer, which would help to reduce the sintering temperature. Another challenge comes from the contamination of the graphite die. Under higher temperature, more carbon atoms in the graphite die are intent to diffuse into the composite during the sintering procedure. For the above reasons, we chose the sol–gel SiO_2 powder for sintering. The composite was sintered at 1250 °C, which was 50 °C lower than the sintering temperature we usually used [17,19]. Finally, we got the transparent bulk material of MWNT/SiO_2

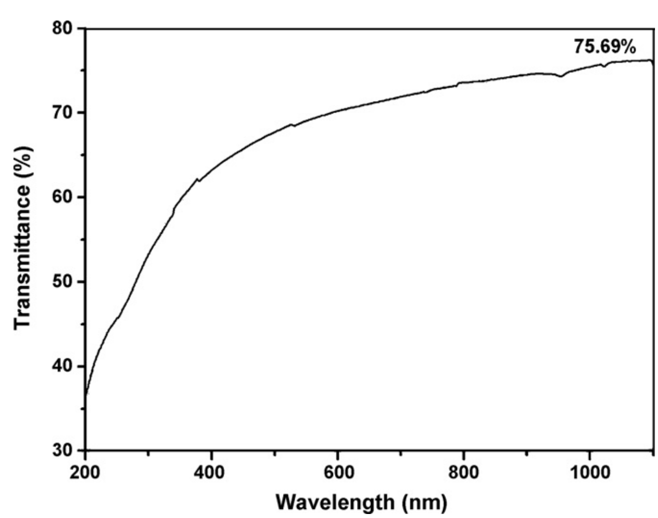

Fig. 2. Optical transmission spectrum of the MWNTs/SiO_2 composite.

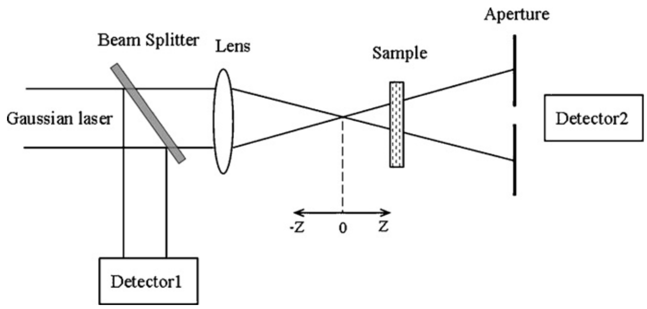

Fig. 3. The *z*-scan experimental apparatus in which the ratio D2/D1 is recorded as a function of the sample position *z*.

by the hot-pressing method. Fig. 2 shows the optical transmission spectrum of the composite from 200 nm to 1100 nm. The transmittance reaches 70% in the visible light region and about 76% near 1100 nm. The linear optical transmittance of the composite meets the requirement of an ideal optical limiter, which ensures the quality of observation/detection. And its transmittance is much better than the previous reported MWNT-silica xerogel composite [15], which is 55% at 532 nm and about 60% at 800 nm.

We performed a *z*-scan experiment to determine the optical limiting properties of the sample. The *z*-scan technique is a sensitive and simple characterization method of the intensity-dependent optical properties of materials. When the measurement begins, a sample is moved along the axis of propagation (*z*) of a focused Gaussian beam through its focal plane. The input and output energies are simultaneously measured by two high sensitive detector (D1 and D2) for each *z* position. When all the transmitted light is detected, open-aperture *z*-scan provides information about the nonlinear absorption of the sample. The detailed experiment set-up is shown in Fig. 3.

Fig. 4 displays the open-aperture *z*-scan results, using the 100 fs, 800 nm laser pulses. The laser beam waist radius at the focus is about 10 μm. The hollow circle and filled circle are the data measured at incident power of 30 mW and 50 mW, respectively. The corresponding incident laser intensities at the focus are about 0.88 GW/cm^2 and 1.47 GW/cm^2. As the sample moves toward the focus, the normalized transmittance decreases from 100% to 83% and 73%, respectively. The pronounced valleys of transmission curves around $Z = 0$ are the signatures of either nonlinear absorption or nonlinear scattering. Nonlinear refraction is excluded, because there is no pronounced signal in the close-aperture *z*-scan experiments. Furthermore, it is regarded that the dominant contribution to the observed transmission valley in Fig. 4 is from nonlinear absorption because there is no light emitted from the sample during the measured process. Moreover, the 50 mW curve has deeper valley than 30 mW, which indicates that MWNTs have stronger nonlinear effect under higher incident intensity. In fact, it has been previously reported that optical limiting behavior in the MWNT suspension was attributed to the nonlinear scattering arising from expanding microplasmas as in the carbon black suspension [25]. And contributions from other mechanisms such as self-defocusing and thermal lensing effect have also been suggested [10]. According to our work, it seems that the optical limiting mechanism of MWNT in the solid is different from that of MWNT in the suspension, which is consistent with Ref. [15]. Further research will be necessary to identify all the physical mechanisms involved in the optical limiting properties of the composite.

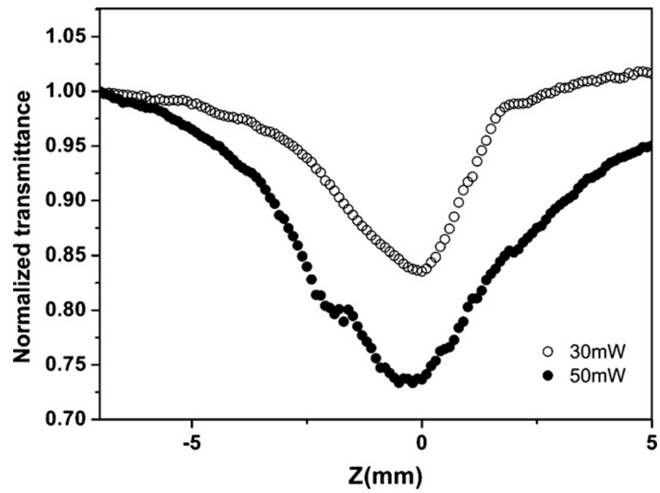

Fig. 4. Open-aperture *z*-scan measurement on the MWNTs/SiO_2 composite, by using the 100 fs, 800 nm laser pulses, with a power: (a) 30 mW and (b) 50 mW.

After the *z*-scan measurement, the composite was characterized by TEM to confirm whether MWNTs were damaged or not. Fig. 5 displays the TEM image of MWNTs in the fused SiO_2 matrix, (a) and (b) are low-magnification image and high-resolution image, respectively. It is found that MWNTs are maintained after sintering and *z*-scan experiment. We can clearly see the layers of MWNTs from Fig. 5(b), which proves that the laser beam irradiation in the *z*-scan

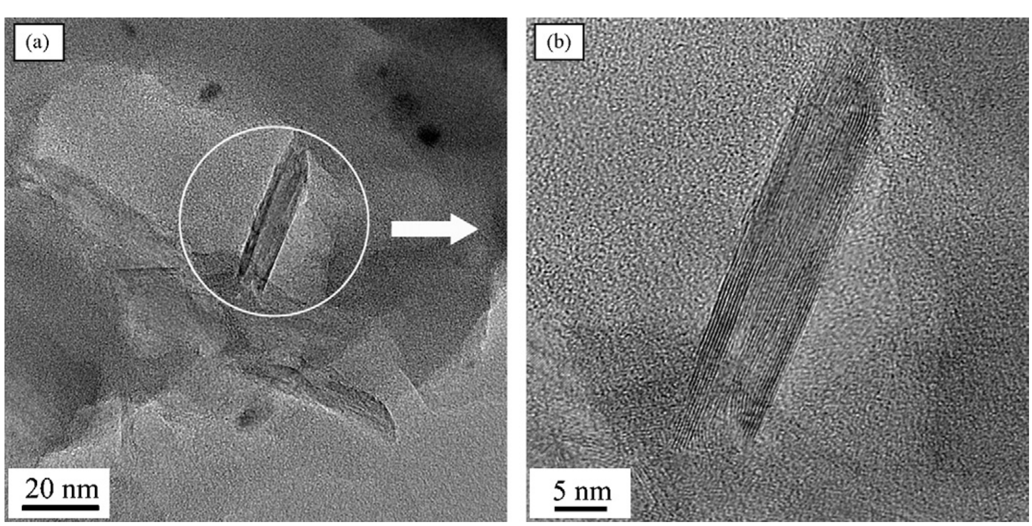

Fig. 5. TEM images of MWNTs in the silica matrix after laser beam irradiation: (a) low-magnification image and (b) high-resolution image.

experiment did not destroy the structure of MWNTs. The result confirms the previously deduction of nonlinear absorption mechanism, because nonlinear scattering in the suspension will lead to sublimation of carbon nanotubes. The nondestructive nonlinear absorption mechanism of the MWNTs/SiO_2 bulk material makes it recyclable, and this turns out to be an advantage for practical use.

As an optical limiter, the material should have not only optical limiting properties and high linear transmittance, but also environmental stability, especially under severe conditions. When the laser beam is induced, energy absorbed by CNT will transform into heat energy, leading to a high temperature in the matrix. The CNT suspension is not stable, and polymer matrix cannot withstand the high temperature of the incident laser. Silica is a ceramic material, with good room and high temperature mechanical strength and resistance to creep, excessive hardness and anti-abrasion properties, high resistance to oxidation and chemical attack, etc. All of these factors make it suitable as the matrix for optical limiter. Therefore, MWNT/SiO_2 bulk materials prepared by hot-pressed sintering might be a competitive candidate for practical use of optical limiting.

4. Conclusions

MWNT/SiO_2 bulk materials were prepared by hot-pressing method and its optical limiting properties were investigated. The transmittance of the composite reached 70% in the visible light region and about 76% near 1100 nm, which met the requirements of an ideal optical limiter (>70%). In the *z*-scan experiments, the composite showed optical limiting properties in different incident intensity, and the main mechanism was deduced to be nonlinear absorption. TEM proved that the hot-pressed sintering and the laser beam irradiation did not destroy the MWNTs in the matrix. The nondestructive nonlinear absorption mechanism of the MWNTs/SiO_2 bulk material makes it recyclable, and this turns out to be an advantage for practical use. Further work will be focused on the improvement of MWNT dispersion and the resultant optical limiting properties of the composites.

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