Optical limiting phenomena of carbon nanoparticles prepared by laser ablation in liquids

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Abstract. We report optical limiting properties of carbon nanoparticles, which were made in liquids by laser ablation of a bulk carbon target. The carbon nanoparticles were analyzed with micro-Raman spectroscopy, UV-Vis spectroscopy and Electron microscopy. Optical limiting responses towards 532-nm wavelength were measured with a 7-ns Nd:YAG laser. Nanoparticle size and laser pulse repetition rate effects on optical limiting behaviour were studied. A model was proposed to explain the physical origin of this nonlinear optical process. This work can provide useful information for designing carbon nanoparticle based optical limiters.

1. Introduction
Optical limiting phenomena have attracted much research effort during recent decades for promising applications in a broad range of areas such as safety protection from intense laser light and nonlinear optical devices for optical processing [1]. Particularly, the development of high-power lasers has motivated extensive research for the production of optical limiting materials to minimize the potential hazard to eyes and optical sensitive devices due to the high energy density (fluence) of narrow-divergence laser beam. Among different optical limiting materials, colloids of carbon-based nanomaterials ranging from carbon blacks to carbon nanotubes were demonstrated as excellent candidates for optical limiting [2]. They can provide wide band limiting responses over visible and near infrared wavelengths towards intense laser irradiation. Optical limiting is a nonlinear optical process, and its origin was proposed to be related to photo-thermal induced micro-plasma screening and micro-bubble scattering. Previous studies indicated that nanomaterial size, solvent and laser parameters can influence the limiting behaviour. However, carbon blacks usually have a large size distribution up to 200 nm [2], while carbon nanotubes involve antennae effect due to large aspect ratios [3]. All of these effects may affect the limiting performances. To study the optical limiting properties of carbon nanomaterials with simple structure and narrow size distribution, we made carbon nanoparticles in liquids by laser ablation of a submerged bulk carbon target. This novel method has advantages of fast preparation speed, low cost and nearly no chemical contamination [4, 5]. Morphology, bonding property, linear transmittance and optical limiting effect of carbon nanoparticles were studied using associated techniques.
2. Experimental
The fabrication method of carbon nanoparticles by laser ablation in liquids can be found elsewhere [6]. In brief, a pure glassy carbon plate was cleaned and immersed in different liquids (deionized water and tetrahydrofuran) with a depth around 5 mm during laser ablation. An Nd:YAG laser with a pulse duration of 7 ns was used as light source. It is well known that polyynes can be formed at high laser power by ablating the high-concentration carbon materials dispersed in solutions [7-9]. To minimize the formation of this by-product, we conducted the experiments at the wavelength of 532 nm, the repetition rate of 10 Hz and the laser fluence around 1 J/cm². After 30 min, the solution containing carbon nanoparticles were vibrated in an ultrasonic cleaner before sampled for further examination.

The prepared carbon nanoparticles were studied with TEM, micro-Raman spectroscopy and UV-Vis spectroscopy. The optical limiting properties were measured using a standard setup with a Q-switched Nd:YAG laser (Spectra Physics DCR3) as light source [10]. The wavelength is 532 nm at second harmonic output. The spatial profile of laser pulses is nearly Gaussian and pulse duration is 7 ns. The laser beam was focused into the sample by a focusing mirror with a focus length of 25 cm. The optical path length of samples was fixed at 1.0 cm. Both the incident and transmitted laser energies were measured simultaneously by two energy detectors (Laser Precision RjP-735). Transmission properties were determined by the ratio between laser energies before and after passing through the sample. As the transmission depends on the input laser energy, optical limiting behavior of samples can be illustrated by the trends of transmission with the increase of laser energies.

3. Results and discussion
3.1 Preparation of carbon nanoparticles in different liquids
The produced carbon nanoparticles were self-stabilized with quite a narrow size distribution without the addition of any surfactant. Especially, carbon nanoparticles obtained in tetrahydrofuran can stand stable over a year without any precipitation or flocculation formed. TEM study indicates that the nanoparticles fabricated in water (with an average size around 15 nm) are larger than that made in tetrahydrofuran (with an average size around 6 nm). It demonstrates that tetrahydrofuran helps to produce smaller particles than that of water. As the growth of nanoparticles is a dynamic formation process that the ablated carbon species strongly interact with surrounding liquids, there are two factors that may give rise to this size difference. The first one is the difference of vaporizing temperatures between water (100°C) and tetrahydrofuran (66°C). During laser ablation, faster vaporization of the solution adjacent to the target surface may occur in tetrahydrofuran than in water. As the strong interaction of the evaporated carbon with solution vapour contributes much to the formation of nanoparticles, the lower vaporizing temperature of tetrahydrofuran may bring about the difference in size. The second factor is from the chemical properties of tetrahydrofuran, which tends to polymerize through a ring-opening process at high enough temperature. This polymerizing condition can be easily provided by laser ablation. It suggests that the growth of carbon nanoparticles in tetrahydrofuran is terminated by a protecting polymerization process that is different from water [11].

Figure 1 shows the micro-Raman spectra of carbon nanoparticles produced in water and tetrahydrofuran with carbon target as reference. The significant peak (D band) near 1350 cm⁻¹ refers to disordered carbon, while the major peak (G band) around 1580 cm⁻¹ attributes to graphitic carbon. Compared to carbon target, the D band for carbon nanoparticles is slightly shifted upward to around 1400 cm⁻¹, while the G band remains near 1580 cm⁻¹. It indicates that bonding structures were further disordered during the formation of carbon nanoparticles. Furthermore, the full-width half maximum (FWHM) of the D band in Raman spectra of carbon nanoparticles was broadened. The upshifting and broadening in D band reveal an increased disordered level and shrank graphitic domains [12]. This result shows that the carbon nanoparticles are amorphous in carbon bondings. In addition, the Raman spectra of carbon nanoparticles made in tetrahydrofuran have a strong photoluminescence background, which comes from the high hydrogen content [13]. It demonstrates the presence of polymerization during nanoparticle formation in tetrahydrofuran.

Figure 2 presents the UV-Vis transmission spectra of carbon nanoparticles prepared in water and
tetrahydrofuran. The transmittances show that a great amount of carbon nanoparticles were produced in the solution. The high transmittance from UV to visible wavelengths implies that carbon nanoparticles have potential of being used as broad band optical limiting materials. We measured transmission spectra before and after optical limiting test. There is no severe damage of the samples during optical limiting measurement, showing high photo-stability of the samples.

**Figure 1** Raman spectra of carbon nanoparticles and carbon target.

**Figure 2** UV-Vis transmission spectra of carbon nanoparticles in water and tetrahydrofuran.

**Figure 3** Size effect on optical limiting performance of carbon nanoparticles towards 532 nm laser light.

**Figure 4** Repetition rate effect on optical limiting performance of carbon nanoparticles in tetrahydrofuran.

3.2 Influencing factors on optical limiting properties of carbon nanoparticles

3.2.1 nanoparticle size effect. Optical limiting behaviors of carbon nanoparticles in water and tetrahydrofuran are shown in Figure 3. The transmittance begins to decrease at laser fluence around 0.3 J/cm² and reaches nearly 1/3 of initial transmittance at 10 J/cm² for carbon nanoparticles in tetrahydrofuran and 1/4 for that in water. The size of carbon nanoparticles plays a key role on the difference of limiting performances between carbon nanoparticles in tetrahydrofuran and water. To study the size effect, carbon nanoparticles made in tetrahydrofuran were further pulverized using high power laser ablation. The nanoparticle size should be less than 3.5 nm since we could not determine them using a field emission SEM with resolution of 3.5 nm. The optical limiting responses were
greatly decreased as shown in Figure 3. There is no obvious limiting even with incident laser fluence up to 10 J/cm².

3.2.2 Laser repetition rate effect. The repetition rate of incident laser pulses is another important factor that may influence the optical limiting behavior. We studied the repetition rate effect on optical limiting performance of carbon nanoparticles in tetrahydrofuran as displayed in figure 4. A stronger limiting performance at a low repetition rate of 1 Hz was observed. When the repetition rate was increased to 10 Hz, the limiting performance became relatively weak. It indicates that fully recovering the limiting ability needs a time longer than 100 ms.

3.3 Physical model of optical limiting responses of carbon nanoparticles

The physical origin of optical limiting of carbon nanoparticles can be understood by investigating the temporal output of an Nd:YAG laser pulse. In this study, the output of laser pulses is in the form of temporal Gaussian distribution that the evolution of laser energy with time is composed with an increasing leading edge and a decreasing ending edge. At the beginning of a laser pulse, the leading edge helps heat carbon nanoparticles to form solvent nanobubbles. The nanobubbles bring about intense scattering to dissipate the laser light in the periods of ending edges, which gives rise to optical limiting. As the input fluence is further increased, micrometer-sized plasma may occur to provide stronger optical limiting responses. This is a high order nonlinear dynamic process that needs further physical and mathematical elucidation.

Bigger nanoparticles have larger absorption cross section, which absorb more heat in comparison with smaller ones. It leads to faster growth of solvent nanobubbles and micro-plasmas, giving rise to stronger optical limiting responses than smaller nanoparticles.

Under intense laser irradiation, the explosive growth and final collapse of nanobubbles can cause turbulence in liquid. Thus, the uniform distribution of carbon nanoparticles is broken. It needs time to recover the solution for the optical limiting of the coming laser pulses. But at high repetition rate, the balance of the system cannot be restored in time. It finally gives rise to a relative weak limiting performance.

4. Conclusions

In summary, we prepared carbon nanoparticles in different solutions using laser ablation technique. Carbon nanoparticles made in water are a bit larger than those made in tetrahydrofuran due to different growth models. Carbon nanoparticles fabricated in both liquids are in amorphous phase and cover a broad range of wavelengths with high transmittance. The samples behave unique optical limiting properties, which are stronger with larger nanoparticle size and lower laser pulse repetition rate. This study may contribute to the understanding of the physics behind the optical limiting phenomena of carbon nanoparticles and to the design of carbon nanoparticle based nonlinear optical devices.

5. References

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